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RESEARCH ARTICLE
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Key Points:
- Ambient CFCs and HCFC-22 concurrently measured at 84 sites in the PRD region
- Sources of CFCs and HCFC-22 were apportioned by PMF
- Emissions of CFCs and HCFC-22 in the PRD were estimated by CO-ratio method

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Ambient CFCs and HCFC-22 observed concurrently at 84 sites in the Pearl River Delta region during the 2008–2009 grid studies

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Abstract Air samples were collected concurrently at 05:00 A.M. and 10:00 A.M. local Beijing time (geomagnetic time + 8) at 84 sites during two grid-study campaigns on 29 September 2008 and 1 March 2009 in the Pearl River Delta region, in order to offer snapshots of ambient CFCs and hydrochlorofluorocarbons (HCFCs) in different seasons and to indicate the presence of local emission sources. Compared to the subtropical northern hemisphere background levels, mean mixing ratios of CFC-11, CFC-12, CFC-113, CFC-114, and HCFC-22 were enhanced by 7%–11%, 8%–11%, 5%–6%, 8%–9%, and 71%–135%, respectively. When data from this tudy were pooled together with previous observations in the region, ambient CFC-11, CFC-12, and CFC-113 unambiguously showed declines in mixing ratios, while HCFC-22 showed an increase. Spatial variations revealed potential emission hot spots in the region, and levels of CFCs and HCFC-22 were higher in September than in March due to many more refrigeration and air-conditioning activities during summer. Source apportioning by positive matrix factorization revealed that new input of CFCs and HCFC-22 into the ambient air was largely attributed to emission from air-conditioning and refrigerating activities instead of industry activities. Average emissions in the region estimated by the CO-tracer method were 0.8 ± 0.2, 1.4 ± 0.6, 0.2 ± 0.1, 0.1 ± 0.02, and 4.4 ± 1.0 Gg/yr for CFC-11, CFC-12, CFC-113, CFC-114, and HCFC-22, respectively, and they accounted for 5.5%–25.5% of the total estimated CFC and HCFC-22 emissions in China.

1. Introduction

Chlorofluorocarbons (CFCs) are man-made chemicals with no known natural sources. They were introduced in the 1930s as nontoxic and nonflammable refrigerants [*Midgley*, 1937; *McCulloch et al*., 2003]. They were used extensively in many commercial and industrial applications including refrigeration, air-conditioning, foam blowing, solvents, and propellants particularly before 1990s [*Intergovernmental Panel on Climate Change* (*IPCC*), 2005]. The production, consumption, and emission of these stable chemicals had once made them accumulate rapidly in the atmosphere, and their potential to deplete stratospheric ozone was first recognized in 1974 [*Molina and Rowland*, 1974]. Due to their major contribution to seasonal ozone depletion over the Antarctic continent [*Manzer*, 1990], they increasingly attracted regulatory concerns worldwide. The 1987 Montreal Protocol and its Amendments (MPA) lay out schedules to ultimately cease the production and consumption of these ozone layer depleting substances (ODS). According to the MPA, CFCs were to be phased out at the end of 1995 in developed countries and by 2010 in developing countries [*United Nations Environment Programme* (*UNEP*), 2003]. Under worldwide regulations, significant decreases were observed in atmospheric concentrations of CFC-11, CFC-113, and several other ODS [*Clerbaux et al*., 2007; *Montzka et al*., 2011] due to the reduction in their production, use, and emissions [*Solomon*, 2004; *UNEP*, 2005; *Rowland*, 2006], and there has been emerging evidence for a gradual recovery of stratospheric ozone [*Newchurch et al*., 2003; *Reinsel et al*., 2005]. The global and northern hemisphere (NH) surface trends revealed mean decline rates of 0.78–0.88%/yr for CFC-11 during 2001–2009 and 0.2%/yr during 2001–2008 for CFC-12 [*Montzka et al*., 2011]. For the first-generation CFC-replacement products, hydrochlorofluorocarbons (HCFCs), a less stringent phase out is in force under MPA, with a stepwise consumption and production reduction between

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2013 and 2040 for "Article 5" countries, including China. HCFC-22, the most abundant HCFC, became a significant new refrigerant in the 1960s, and its global emission has grown since then [*Midgley and Fisher*, 1993; *McCulloch et al*., 2003]. Contrary to the declining trends of CFCs, HCFC-22 increased at a rate of about 8 parts per trillion (ppt)/yr (or 4.3%/yr) during 2007–2008 [*Montzka et al*., 2011]. In addition to their roles as ODS, many halocarbons also have relatively high global warming potentials [*United Nations Framework Convention on Climate Change*, 2005; *IPCC*, 2005] and therefore are also important greenhouse gases [*Fisher et al*., 1990; *Solomon and Daniel*, 1996; *Wigley*, 1998a, 1998b] that contribute to the radiative forcing of the atmosphere [*IPCC*, 2005; *Velders et al*., 2007].

As an "Article 5 party" country, by 1995, China became the world's largest producer and consumer of ODS [*Hu et al*., 2005], and the emissions and ambient concentrations of ODS in China have attracted extensive attention worldwide. However, a few studies of ambient halocarbon mixing ratios in China were available before 2000 [*Wang and Tang*, 1993; *Wang et al*., 1998, 2000]. In the past decade, a number of studies of ambient halocarbon mixing ratios have been carried out in China, for example, Shandianzi and Beijing [*Wang and Tang*, 1993; *Xiu et al*., 2005; *Qin*, 2007; *Vollmer et al*., 2009; *F. Zhang et al*., 2010; *Yao et al*., 2012], Shanghai [*Sun et al*., 2003], the Pearl River Delta region [*Guo et al*., 2004, 2009; *Chan et al*., 2006; *Zhang et al*., 2006, 2007a, 2007b; *Chan and Chu*, 2007; *Chang et al*., 2008; *Y. L. Zhang et al*., 2010; *Shao et al*., 2011], and Taiwan [*Chang et al*., 2001; *Lee and Chiou*, 2007, 2008]. *Barletta et al*. [2006] reported the spatial distributions of halocarbons based on grab air samples collected in 45 Chinese cities in January–February 2001, and a vertical profile of halocarbon mixing ratios in the lower troposphere was obtained from an intensive aircraft study over northeast China in summer 2007 [*Xue et al*., 2011]. *Streets et al*. [2003] developed an inventory of anthropogenic air pollutant emissions in Asia in 2000 during the Transport and Chemical Evolution over the Pacific and Aerosol Characterization Experiment-Asia. *Blake et al*. [2003] and *Palmer et al*. [2003] derived the emission of halocarbons from eastern Asia (China, Japan, and Korea) from aircraft observations of halocarbon/CO enhancement ratios in Asian continental outflow; *Vollmer et al*. [2009] estimated the Chinese emissions of ozone-depleting halocarbons by inverse modeling of the first quasi-continuous high-precision measurements at a Global Atmosphere Watch (GAW) station in northern China; *Wan et al*. [2009] estimated and forecasted the emissions of halocarbons from China for 1995–2024 based on historical consumption, the country program for compliance with the MPA, and sector plans for phasing out halocarbons; and *Li et al*. [2011] and *Kim et al*. [2010] estimated the halocarbon emission from China based on the observations at Gosan, South Korea, from November 2007 to December 2008.

The Pearl River Delta (PRD) region, as one of the most densely populated and highly industrialized regions in China, along with its ~10% share in China's national gross domestic product (GDP), is expected to be a hot spot for the emission of ozone-depleting halocarbons. At present, only two studies are available in which the emissions of major halocarbons in the PRD region are estimated by the CO ratio method [*Guo et al*., 2009; *Shao et al*., 2011], which is based on the incremental slopes of halocarbon concentrations against that of the CO and the known emissions of CO. Their estimates however were based on the field measurements of ambient halocarbon levels at one or two sites in the region. *Guo et al*. [2009] estimated the emissions of CFC-12, CFC-113, and HCFC-22 at 1.0 ± 0.3, 0.9 ± 0.3, and 2.2 ± 1.2, respectively, in the PRD region in 2002, while *Shao et al*. [2011] reported 0.4 ± 0.2, 0, and 3.5 ± 2.2 Gg/yr, respectively, in the PRD region in 2004. In the present study, two grid-study campaigns were carried out on 29 September 2008 and 1 March 2009 to measure the major ozone-depleting halocarbons using grab air samples. The purpose was to measure the ambient mixing ratios as well as spatiotemporal variations for a number of CFCs and HCFC-22 in the PRD region. Emissions of CFCs and HCFC-22 in the PRD region were estimated using the enhancement ratio method with CO as a tracer, using the ambient CO and halocarbon levels measured concurrently at 84 sites during the grid studies. Although those campaigns are at a limited time interval, this is the first time that whole air samples were collected concurrently at 84 sites in the PRD region. This unique data set can therefore help to get a better understanding of halocarbon emissions in the PRD region and contribute to the development of a more reliable national and global emission inventories for these gases.

2. Experiment

2.1. Sampling Sites

The PRD region in south China consists of nine cities within Guangdong Province, namely, Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Jiangmen, Huizhou, and Zhaoqing, plus Hong Kong and

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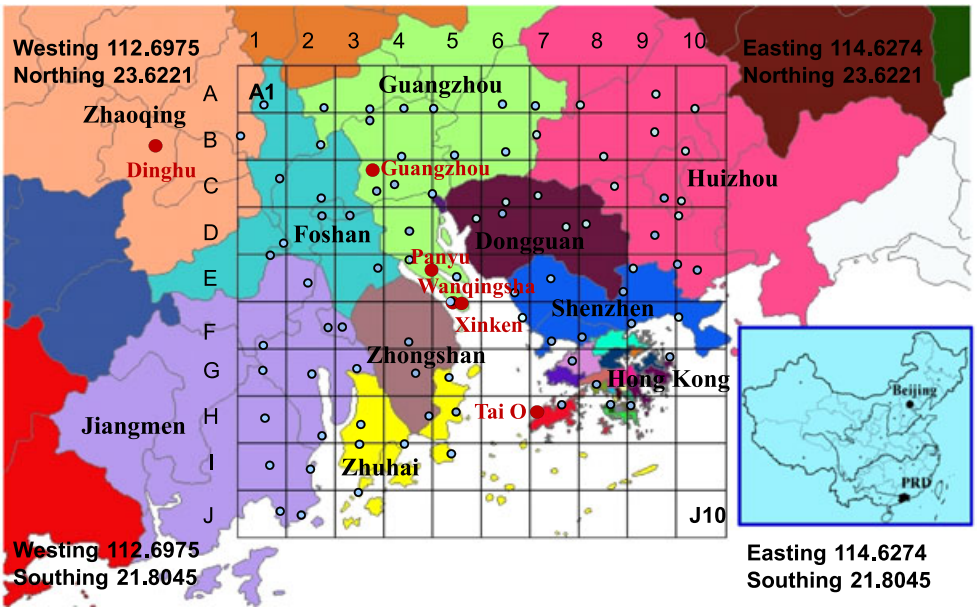

Figure 1. Sampling locations for the grid study in the Pearl River Delta region (grid size is approximately 200km × 200 km; individual grid cell is 20 km × 20 km). Blue dots: grid-study sampling sites. Red dots: sampling sites of previous studies in the PRD region.

Macau special administrative regions. For the grid-study air sampling, the PRD region was delimited by a square of approximately 200 km × 200 km, which was further divided into 100 20 km × 20 km grid cells (Figure 1). Majority of the sampling sites are among the ambient air quality monitoring stations established by the provincial and local governments representative of spatial areas and population density. Sampling sites were chosen based on a field survey in each of the 84 land grids, including 78 sampling sites in inland PRD and 6 sites in Hong Kong. General information of the sampling sites is presented in Table 1. All the sites were located at least 50 m away from major local air pollution sources, such as highways, roads, and industries.

2.2. Field Sampling

Ambient air samples were collected on 29 September 2008 and 1 March 2009 using cleaned and evacuated 2 L electropolished stainless steel canisters. Students from Jinan University and engineers from the Guangdong Provincial Monitoring Center were sent to the 84 sampling sites. Air samples were collected at 05:00 A.M. and 10:00 A.M. local Beijing time (geomagnetic time + 8) at all the sampling sites to capture the prerush and postrush hour activities. These samples were sent to the Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences, for analysis. Duplicate samples were taken at 4 randomly selected sampling sites at both 5:00 A.M. and 10:00 A.M. at each grid study. These duplicate samples were sent to the Rowland/Blake laboratory at the University of California, Irvine (UCI), for comparison and as independent checks.

2.3. Laboratory Analysis of VOCs and Carbon Monoxide (CO)

The determination of VOC mixing ratios by the Rowland/Blake group at UCI has been described elsewhere [*Colman et al.*, 2001; *Simpson et al.*, 2010]. In GIG, air samples were analyzed using a model 7100 preconcentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas chromatography–mass spectrometer detector/flame ionization detector/electron capture detector (GC-MSD/FID/ECD, Agilent Technologies, USA). Detailed cryogenic concentration steps are described elsewhere [*Y. L. Zhang et al.*, 2010]. Briefly, the VOCs inside the canister were first concentrated in a liquid-nitrogen cryogenic trap at −160°C. The trapped VOCs were then transferred by pure helium to a secondary trap at −40°C with Tenax-TA as an adsorbent. In addition to the removal of nitrogen and oxygen, the majority of H_2O and CO_2 were removed during these two steps. The secondary trap was then heated in order to transfer target VOCs by helium to a third cryo-focus trap at −170°C. After the focusing step, the trap was rapidly heated,

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Table 1. Description of the 84 Sampling Sites for the Grid-Study Campaigns

Cell	City	Long.[a]	Lat.[b]	Area Type	Cell	City	Long.[a]	Lat.[b]	Area Type	Cell	City	Long.[a]	Lat.[b]	Area Type
A1	Zhaoqing	112.81	23.49	Rural	C9	Huizhou	114.41	23.08	Urban	F7	Shenzhen	113.92	22.53	Urban
A2	Guangzhou	113.05	23.45	Rural	C10	Huizhou	114.44	23.09	Urban	F8	Shenzhen	114.10	22.55	Urban
A3	Guangzhou	113.22	23.43	Rural	D1	Foshan	112.88	22.90	Urban	F9	Shenzhen	114.26	22.59	Suburban
A4	Guangzhou	113.37	23.42	Suburban	D2	Foshan	113.05	23.02	Urban	F10	Shenzhen	114.47	22.60	Rural
A5	Guangzhou	113.49	23.45	Suburban	D3	Foshan	113.11	23.00	Urban	G1	Jiangmen	112.77	22.45	Suburban
A6	Guangzhou	113.77	23.49	Suburban	D4	Guangzhou	113.35	22.95	Suburban	G2	Jiangmen	113.00	22.43	Suburban
A7	Guangzhou	113.89	23.44	Rural	D5	Dongguan	113.66	22.95	Urban	G3	Jiangmen	113.16	22.46	Urban
A8	Huizhou	114.01	23.46	Suburban	D6	Dongguan	113.74	23.03	Urban	G4	Zhongshan	113.40	22.50	Urban
A9	Huizhou	114.39	23.55	Rural	D7	Dongguan	114.01	22.97	Suburban	G5	Zhongshan	113.52	22.45	Rural
A10	Huizhou	114.50	23.44	Rural	D8	Dongguan	114.10	23.02	Urban	G7	Hong Kong	114.02	22.45	Urban
B1	Zhaoqing	112.72	23.32	Urban	D9	Huizhou	114.38	22.94	Rural	G8	Hong Kong	114.11	22.37	Urban
B2	Foshan	112.97	23.27	Suburban	D10	Huizhou	114.48	22.90	Rural	G9	Hong Kong	114.36	22.47	Rural
B3	Guangzhou	113.21	23.39	urban	E1	Foshan	112.85	22.89	Urban	H1	Jiangmen	112.79	22.25	Urban
B4	Guanghzou	113.31	23.21	Suburban	E2	Jiangmen	112.95	22.77	Urban	H2	Jiangmen	113.08	22.20	Urban
B5	Guangzhou	113.55	23.27	Rural	E3	Foshan	113.27	22.82	Urban	H3	Zhuhai	113.19	22.23	Suburban
B6	Guangzhou	113.74	23.28	Rural	E4	Guangzhou	113.34	22.84	Suburban	H4	Zhongshan	113.46	22.26	Suburban
B7	Huizhou	113.91	23.28	Rural	E5	Guangzhou	113.56	22.80	Suburban	H5	Zhuhai	113.56	22.35	Rural
B8	Huizhou	114.12	23.25	Rural	E6	Shenzhen	113.80	22.74	Suburban	H7	Hong Kong	113.94	22.29	Suburban
B9	Huizhou	114.36	23.38	Rural	E7	Shenzhen	113.94	22.77	Suburban	H8	Hong Kong	114.14	22.29	Urban
B10	Huizhou	114.47	23.30	Rural	E8	Shenzhen	114.24	22.73	Urban	H9	Hong Kong	114.22	22.28	Urban
C1	Foshan	112.89	23.17	Urban	E9	Shenzhen	114.25	22.72	Urban	I1	Jiangmen	112.83	22.07	Rural
C2	Foshan	113.02	23.14	Suburban	E10	Huizhou	114.46	22.78	Suburban	I2	Jiangmen	112.95	22.09	Rural
C3	Guangzhou	113.26	23.13	Urban	F1	Jiangmen	112.78	22.52	Suburban	I3	Zhuhai	113.18	22.18	Rural
C4	Guangzhou	113.28	23.16	Urban	F2	Jiangmen	113.08	22.59	Urban	I4	Zhuhai	113.35	22.15	Rural
C5	Guangzhou	113.45	23.11	Urban	F3	Jiangmen	113.10	22.61	Urban	I5	Zhuhai	113.54	22.11	Suburban
C6	Dongguan	113.78	23.08	Urban	F4	Zhongshan	113.37	22.55	Urban	J1	Jiangmen	112.88	21.89	Rural
C7	Dongguan	113.90	23.10	Suburban	F5	Guangzhou	113.55	22.71	Rural	J2	Jiangmen	112.93	21.87	Rural
C8	Huizhou	114.21	23.16	Rural	F6	Shenzhen	113.85	22.59	Rural	J3	Zhuhai	113.2	21.98	Rural

[a]Long.: longitude.
[b]Lat.: latitude.

and the VOCs were transferred to the GC-MSD/FID/ECD system. The mixture was first separated by an HP-1 capillary column (60 m × 0.32 mm × 1.0 μm, Agilent Technologies, USA) with helium as a carrier gas and then split into three paths controlled by a three-way splitter: the first stream was directed into a 50 cm × 0.10 mm ID stainless steel line followed by MSD detection, the second into a PLOT-Q column (30 m × 0.32 mm × 2.0 μm, Agilent Technologies, USA) followed by FID detection, and the third into a 35 cm × 0.10 mm I.D. stainless steel line followed by ECD detection. The GC oven temperature was programmed to be initially at −50°C, holding for 3 min; increasing to 10°C at 15°C min^{-1}, then to 120°C at 5°C min^{-1}; and finally to 250°C at 10°C min^{-1} and holding for 10 min. The MSD was used in selected ion monitoring mode, and the ionization method was electron impact. In this study CFCs and HCFC-22 were determined based on MSD signals with target ions of *m/z* 103/101, 85, 135/85, 151/101, and 51 for CFC-11, CFC-12, CFC-113, CFC-114 (CFC-114a, if exists, would coelute), and HCFC-22, respectively. Carbon monoxide levels in the air samples were analyzed by an Agilent 6890 gas chromatograph equipped with an FID and a packed column (5A molecular sieve 60/80 mesh, 3 m × 1/8 inch). CO was first converted by a Ni-based catalyst to CH_4 and was then detected by FID after separation by the packed column.

2.4. Quality Control and Quality Assurance

All canisters were pumped and flushed and free of any contaminants before sampling. Before use, each canister was subjected to at least five evacuation/pressurization cycles using humidified zero air. To check if there was any contamination in the canisters, each canister was again pressurized with humidified zero air at the end of the evacuation/pressurization cycles and stored in the laboratory for at least 24 h and then analyzed the same way as air samples. A canister was certificated as clean if all the target compounds were not detected or were below method detection limits (MDLs). After leak checking and flushing, the canisters were reevacuated to <0.05 mm Hg and remained in this condition until field use.

Target compounds were identified based on their retention times and mass spectra and were quantified by an external calibration method. For the CFC analysis, the calibration standards were prepared by dynamically

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diluting 100 ppb TO-14 standard mixtures (Spectra Gases Inc., NJ, USA) to 50, 100, 250, 500, and 1000 ppt. For HCFC-22, a standard of 100 ppb was first prepared by static dilution of pure HCFC-22 and then dynamically diluted the same way as the CFCs for calibration. The calibration curves were obtained by running the five diluted standards plus humidified zero air the same way as the field samples. The analytical system was checked daily with a working standard before running air samples. If the response was beyond ±2% of the determined values by UCI, recalibration was required. The working standard was prepared in a cylinder with pressurized ambient air from White Mountain, California. Before transported to China, the standard was daily checked in UCI laboratory for about 2 months until determined VOCs including halocarbons were stable. Labeled mixing ratios (mean ± standard deviation) were 534 ± 2 ppt, 249.7 ± 0.5 ppt, 80.4 ± 0.3 ppt, 16.5 ± 0.2 ppt, and 222.4 ± 2 ppt for CFC-12, CFC-11, CFC-113, CFC-114, and HCFC-22, respectively. By repeatedly running the working standard 7 times, we obtained relative standard deviation (rsd) within 1% for all the target CFCs and HCFC-22. The limits of detection for the CFCs and HCFC-22 in present study were all below 1 ppt. The relative measurement deviations between UCI and GIG for duplicate samples were within 2% for CFCs and 5% for HCFC-22. The comparison of the global background mole fractions of CFCs and HCFC-22 were made between UCI laboratory and at the National Oceanic and Atmospheric Administration (NOAA) and agreed with each other very well. The relative deviations between the UCI laboratory and the NOAA laboratory were 0.2%, 0.5%, 0.7%, 1.4%, and 1.3% for CFC-11, CFC-12, CFC-113, CFC-114, and HCFC-22 [*Montzka et al*., 2011]. The estimated deviations between GIG and NOAA were therefore within 4% for CFCs and 6% for HCFC-22. A 1 ppm carbon monoxide standard gas (Spectra Gases Inc., NJ, USA) was used to quantify CO in the whole air samples.

Field blank canisters were refilled with zero air in the laboratory and then analyzed the same way as the ambient air samples after at least 24 h storage. All the target compounds in the field blank samples were below their MDLs.

2.5. Positive Matrix Factorization

Positive matrix factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices, factor contributions and factor profiles, which then need to be interpreted by an analyst as to what source types are represented using the measured source profile information, wind direction analysis, and emission inventories. The method is reviewed briefly here and described in greater detail elsewhere [*Paatero and Tapper*, 1994; *Paatero*, 1997].

An ambient data set can be viewed as a data matrix X of i (number of samples) by j (number of chemical species) dimensions. The goal of multivariate receptor modeling is to identify a number of sources p that best characterize the VOC compositions at a site, with the species profile f of each source, and the amount of mass g contributed by each source to each individual sample, plus the residuals e:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

Results are constrained by a penalty function so that no sample can have a negative source contribution and no species can have a negative concentration in any source profile. Another strength of PMF is that it can individually weigh each data point. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. By individually weighing the data, samples with some species missing or below the detection limit do not need to be excluded as a whole; rather, the analyst can adjust the uncertainty so that these missing or below-detection-limit species have little or no impact on the final solution. For a data set with m chemical species in n samples, the PMF solution with p independent sources minimizes the object function Q, based on these uncertainties (u):

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \tag{2}$$

The United States Environmental Protection Agency PMF 3.0 model was applied to explore the sources of observed nonmethane hydrocarbons (NMHCs). The approaches for replacing and developing uncertainty values for missing and below-detection-limit data were drawn from previous works [*Poirot et al*., 2001; *Hopke et al*., 2003]. Briefly, data values below the method detection limit (MDL) were substituted with MDL/2; missing data values were substituted with median concentrations. Uncertainties were treated the same way as *Polissar et al*. [1998]

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Table 2. Mixing Ratios of CFCs, HCFC-22 (ppt), and CO (ppb) in the PRD Region, Together With Their 95% Confidence Intervals (95% CI) and Ranges

Campaign	Time		CFC-11	CFC-12	CFC-113	CFC-114	HCFC-22	CO
Sep 2008	05:00 A.M.	Mean (95% CI)	271(3)	591(9)	83.0(0.9)	17.6(0.3)	414(34)	448(38)
		Range	255–293	545–699	77.8–91.4	15.6–21.2	264–1043	221–1129
	10:00 A.M.	Mean (95% CI)	272(3)	593(8)	82.7(0.8)	17.6(0.2)	472(32)	483(33)
		Range	251–299	549–687	77.5–91.5	15.5–20.2	258–1198	238–1091
Mar 2009	05:00 A.M.	Mean (95% CI)	263(2)	575(8)	82.2(0.7)	17.7(0.3)	352(24)	682(39)
		Range	248–284	540–688	77.6–89.7	15.6–20.3	234–889	248–1394
	10:00 A.M.	Mean (95% CI)	267(3)	580(9)	82.9(0.8)	17.6(0.3)	360(22)	781(53)
		Range	246–292	540–699	77.8–90.5	15.6–20.2	242–799	295–1973
Subtropical NH background (Sep 2008)			245.6(0.2)[a]	536.0(0.5)[a]	78.0(0.1)[a]	16.4(0.2)[b]	201.5(0.6)[a]	
Subtropical NH background (Mar 2009)			244.6(0.1)[a]	534.5(0.3)[a]	77.8(0.1)[a]	16.4(0.2)[b]	206.1(0.9)[a]	
Lifetime (year)[c]			45	100	85	190	11.9	
ODP[c]			1.0	0.82	0.85	1.0	0.055	

[a]North hemisphere monthly mean values with standard derivation on September 2008 and March 2009 from the NOAA/ESRL halocarbon in situ program [http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats_conc.html].
[b]Calculated global surface mixing ratios (ppt) in the Ab baseline scenario by *Montzka and Fraser* [2003].
[c]*Montzka et al*. [2011].

and *Reff et al*. [2007]. If the concentration is less than or equal to the MDL provided, the uncertainty is calculated using the following equation, Unc = 5/6 × MDL. If the concentration is greater than the MDL provided, the calculation is Unc = [(error fraction × mixing ratios)^2 + (MDL)^2]$^{1/2}$. The number of factors in the PMF model was chosen based on the result from a principal component analysis/absolute principal component score model [*Anderson et al*., 2001].

2.6. Emission Estimation

On a global scale, emissions can be determined from measured atmospheric concentrations using box models [*Montzka et al*., 2009] or three-dimensional models [*Prinn et al*., 2000]. On a regional scale, emissions can also be derived from the enhancement ratio of a halocarbon concentration to that of a substance (often CO) with known emission fluxes [*Bakwin et al*., 1997; *Biraud et al*., 2000; *Palmer et al*., 2003; *Dunse et al*., 2005; *Guo et al*., 2009; *Shao et al*., 2011] or by inverse modeling [*Vollmer et al*., 2009; *Stohl et al*., 2010]. In the present study, CO was used as a tracer. We obtained halocarbon and CO enhancements above background levels, Δhalocarbon and ΔCO, by subtracting off the background values, defined here as the lowest 25th percentile of data [*Palmer et al*., 2003], and calculating the slope of the linear relationship between them. Regional halocarbon emissions thus were estimated as

$$E_x = E_{CO} \times S \times (M_x/M_{CO}) \times 10^{-3} \quad \text{(halocarbons in ppt and CO in ppb)} \tag{3}$$

where $\boldsymbol{E}_x$ and $\boldsymbol{E}_{CO}$ (Gg/yr) are the emission of the target halocarbon x and CO, respectively; S is the slope (ppt/ppb) of the linear correlation between Δhalocarbon and ΔCO; and M_x and M_{CO} are the molecular weights of the target halocarbon species x and CO, respectively.

The uncertainties of CFCs and HCFC-22 emissions were calculated using linear least squares fitting method [*Cantrell*, 2008]. The uncertainty calculation formula showed as

$$\sigma_x = \left[(\sigma_{ECO})^2 \times S^2 + (ECO)^2 \times \left(\sigma_{X/CO}\right)^2\right]^{1/2} \times (M_x/M_{CO}) \times 10^{-3} \quad \text{(halocarbons in ppt and CO in ppb)} \tag{4}$$

where σ_x is the uncertainty for the estimated emission of halocarbon species x and σ_{ECO} and $\sigma_{X/CO}$ are the uncertainties of E_{CO} and the X/CO slope, respectively.

3. Results and Discussion

3.1. Ambient Levels of CFCs and HCFC-22

The mean ambient mixing ratios of CFCs, HCFC-22, and CO at 84 sampling sites during two grid-study campaigns in September 2008 and March 2009 in the PRD region, together with their ranges and 95% confidence intervals

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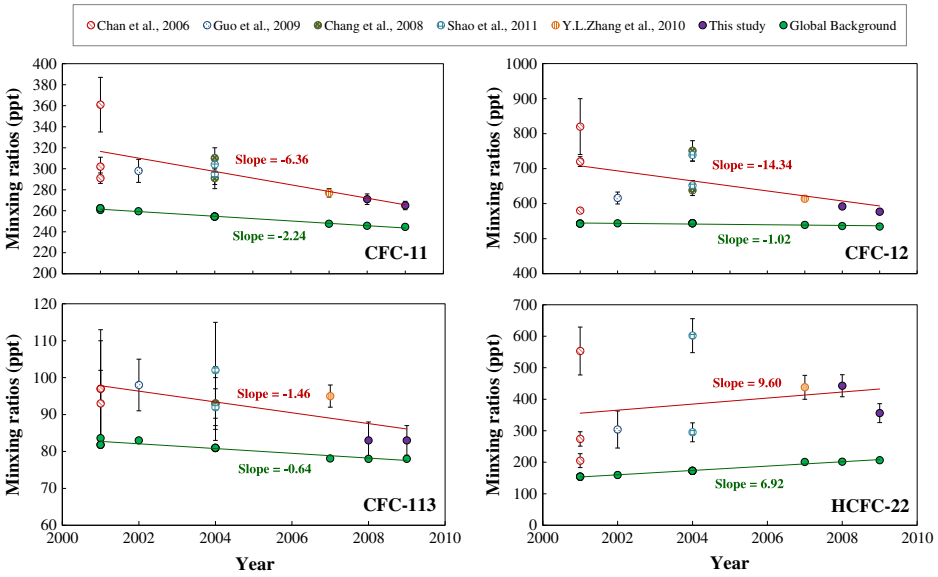

Figure 2. Comparison of CFCs and HCFC-22 with those previously reported in the PRD region. (Global background: Northern hemisphere monthly mean values with standard derivations from the NOAA/ESRL (Earth System Research Laboratory) halocarbon in situ program [http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats_conc.html]).

(95% CI), are shown in Table 2. A comparison of these levels with those previously reported in the PRD region is presented in Figure 2. When compared to the subtropical northern hemisphere (NH) background levels [http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats_conc.html] observed in the same months as when our field campaigns were carried out, the mean mixing ratios of CFC-11, CFC-12, CFC-113, CFC-114, and HCFC-22 from the two campaigns were enhanced by 7%–11%, 8%–11%, 5%–6%, 8%–9%, and 71%–135%, respectively. The 5%–11% enhancement for the long-lived CFCs in the PRD region, though relatively small, suggests the presence of local emission sources for these CFCs. Particularly for the two most abundant CFCs, CFC-11, and CFC-12, there were obvious differences between their levels in the PRD region compared to those in the NH background (Table 2). In China, CFC-11 was historically mainly used in closed cell foam blowing [*Yu et al*., 2000] and CFC-12 as a refrigerant gas. As an Article 5 party country, China was required a full phase out of both production and consumption of CFCs by January 2010. In reality, China began to reduce the production of CFCs in 1999 [*State Environmental Protection Administration* (*SEPA*), 2004]. Nevertheless, even if these long-lived CFCs were not used anymore in industrial processes so that direct emission from industrial processes was quite limited, CFCs that remained in products or were stored in old refrigerant equipment would leak in the service life of products/equipment, and therefore, this steady emission could be an important CFC source leading to enhanced ambient mixing ratios [*Chan and Chu*, 2007; *Y. L. Zhang et al*., 2010]. For HCFC-22, a major substitute of CFC-12, an enhancement of more than 75% was measured in the PRD region as compared to its subtropical NH background levels, suggesting its substantial emission in the region.

In this study, the average mixing ratios of CFC-11, CFC-12, and HCFC-22 in September 2008 were 271 ± 2, 592 ± 6, and 443 ± 24 ppt, which were significantly higher ($p < 0.001$) than those of 265 ± 2, 577 ± 6, and 356 ± 16 ppt in March 2009. Previous observations of ambient halocarbons were conducted mostly in 2001 and 2004 (Figure 2) in urban/suburban/rural areas of Guangzhou. Average halocarbon mixing ratios measured in Guangzhou and Xinken during October–November by the two groups were quite similar [*Chang et al*., 2008; *Shao et al*., 2011], even though their sampling locations and designs were not the same (Figure 2). The three sampling sites, Panyu, where *Chan et al*. [2006] collected samples in 2001; Xinken in Nansha district, where *Chang et al*. [2008] and *Shao et al*. [2011] collected their samples in 2004; and Wanqingsha (WQS), where *Y. L. Zhang et al*. [2010] collected their samples in 2007, are within 10 km of each other in rural/semiurban areas in the south of Guangzhou. The three groups collected air samples at air quality monitoring stations during September–November, so the results can be compared with each other without concern about seasonal effects, and the results can be compared with those collected in September 2008 during this grid study in Panyu, Nansha (Xinken), and WQS, the same site as *Y. L. Zhang et al*. [2010]. Based on the average

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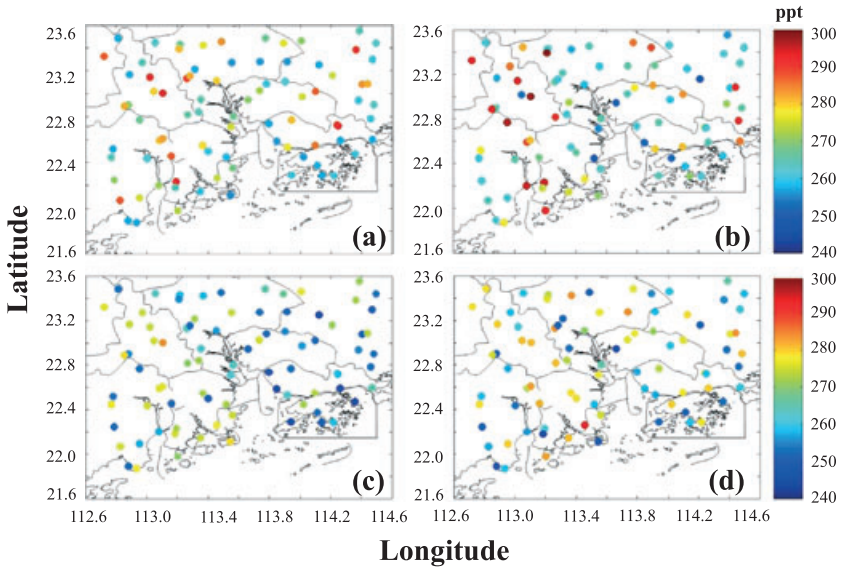

Figure 3. Spatial variations of CFC-11 in the PRD region: (a) 29 September 2008 05:00 A.M., (b) 29 September 2008 10:00 A.M., (c) 1 March 2009 05:00 A.M., and (d) 1 March 2009 10:00 A.M.

mixing ratios at Panyu/Nansha/WQS in September–December during 2001, 2004, 2007, and 2008, HCFC-22 was found to increase steadily in rural/semiurban Guangzhou at an average rate of 15.2 ± 12.3 ppt/yr ($r^2 = 0.43$), while CFC-11, CFC-12, and CFC-113 showed steady decreases of −4.2 ± 0.6 ppt/yr ($r^2 = 0.96$), −34.2 ± 6.9 ppt/yr ($r^2 = 0.95$), and −2.0 ± 1.6 ppt/yr ($r^2 = 0.45$), respectively. Similarly, the decreasing trends of CFC-11, CFC-12, and CFC-113 were confirmed in urban Guangzhou by comparing our September results at two urban sites with those in urban Guangzhou in 2004 as measured by *Chang et al.* [2008] and *Shao et al.* [2011], with average decrease rates of −6.1, −25.8, and −2.4 ppt/yr for CFC-11, CFC-12, and CFC-113, respectively. The reason for faster decreasing of CFC-12 than CFC-11 is probably that CFC-12, as widely used refrigerant in refrigeration and air-conditioning sector, was banned in China on the production of residential refrigerators and freezers since 2006, on the production of industrial and commercial refrigerating equipments since 2005, and on the production of mobile air conditioners in 2002. These CFC-11 decrease rates were faster than that of −2.0 ppt/yr observed at a semirural site Shangdianzi in Beijing from 2006 to 2009 [*F. Zhang et al.*, 2010] or global decrease rate of −2.0 ± 0.1 ppt/yr from 2000 to 2004 [*Montzka et al.*, 2011]. Also, the CFC-12 decrease rates from this study were much larger than that of −2.5 ppt/yr observed at Shangdianzi [*F. Zhang et al.*, 2010] or its global decrease rates of −7.1 ± 0.2 ppt/yr from 2000 to 2004, −1.4 ppt/yr from 2004 to 2007, and −2.2 ppt/yr from 2007 to 2008 [*Montzka et al.*, 2011]. The decrease rates for CFC-113 from this study were higher than that of −0.7 parts per trillion by volume (pptv)/yr from 2006 to 2009 observed at Shangdianzi [*F. Zhang et al.*, 2010] or −0.6~−0.7 pptv/yr global decrease rate from 2004 to 2008 [*Montzka et al.*, 2011]. The HCFC-22 increase rate of 15.2 ± 12.3 ppt/yr in Guangzhou was substantially faster than the global increase rate of 6.73 ppt/yr during 2004–2007 and 8.5 ppt/yr during 2007–2008 [*Montzka et al.*, 2011]. From the grid study in the whole PRD region on 1 March 2009, the average mixing ratios of 265 ± 4, 577 ± 7, and 83 ± 4 ppt were obtained for CFC-11, CFC-12, and CFC-113, respectively; these values were lower when compared to those of 291 ± 5, 580 ± 3, and 93 ± 9 ppt (Figure 2) observed at the background forest site Dinghu in March 2001 [*Chan et al.*, 2006], suggesting a decline of these two CFCs in ambient air in the whole region.

3.2. Spatiotemporal Variations of CFCs and HCFC-22

The two grid-study campaigns offer snapshots of ambient halocarbons in the PRD region. If there were no local emissions of the CFCs and HCFC-22, very uniform mixing ratios with very small spatial variations would be expected. As showed in Figure 2, mixing ratios of CFCs at 84 sites in each grid-study campaign had relative standard deviations (rsd) of less than 7%, while mixing ratios of HCFC-22 had rsd over 30%. This contrast of spatial variations between CFC-11, CFC-12, and HCFC-22 is also illustrated in Figures 3–5. For HCFC-22, its large spatial variation is consistent with its ubiquitous use as an alternative to CFCs in the region [*Chan and Chu*, 2007;

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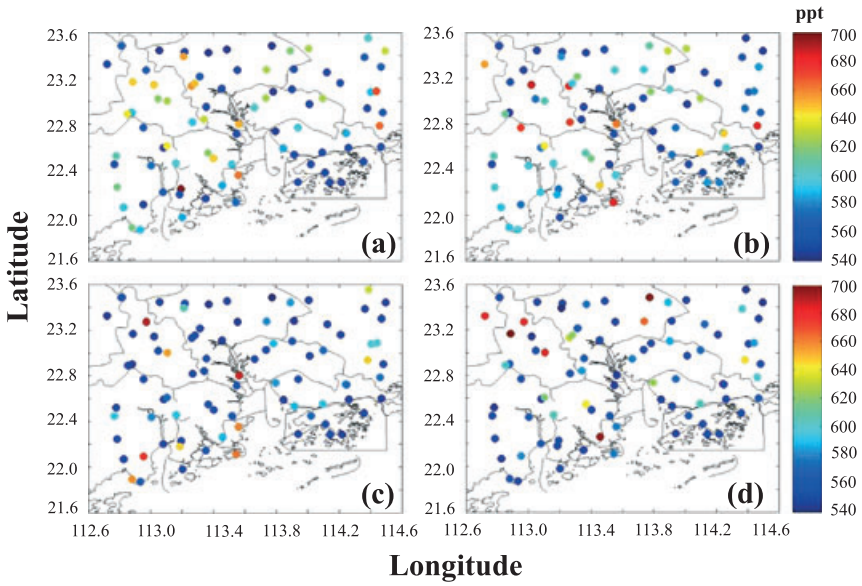

Figure 4. Spatial variations of CFC-12 in the PRD region: (a) 29 September 2008 05:00 A.M., (b) 29 September 2008 10:00 A.M., (c) 1 March 2009 05:00 A.M., and (d) 1 March 2009 10:00 A.M.

Chang et al., 2008]. The highest mixing ratio of 1198 ppt for HCFC-22, nearly 6 times its NH background level (201.5 ± 0.6 ppt), was observed in Zhongshan city at 10:00 A.M. on 29 September 2008. In 2008, the productions of HCFC-22 in China accounted for 59% of the global total HCFC-22 production [*Technology and Economic Assessment Panel*, 2011]. Estimated emission of HCFC-22 in China [*Wan et al*., 2009] increased from 1.78 Gg in 1995 to 79.27 Gg in 2008 and further to 90.63 Gg in 2009 with an annual increase rate of nearly 15%. As confirmed by our tests of coolants sold in 12 markets in Guangzhou and of coolants used in servicing air conditioners, HCFC-22 was coolants used for residential and industrial refrigeration and air-conditioning, while HFC-134a was used in mobile air conditioners. According to *Wan et al*. [2009], projected emissions of HCFC-22 in China peak in 2020 and are about twice that in 2008. Therefore, continuing increase of ambient HCFC-22 would be expected in the PRD region or in China in the next decade.

Although the spatial variations of the CFCs were much smaller in amplitude, 84 sampling sites had mixing ratios statistically larger than the background baseline, indicating continuing emission hot spots in the region for these compounds. From Figure 3, Foshan was the CFC-11 hot spot with an average mixing ratio of 275 ppt, which was higher than the mean levels in the whole PRD region (Table 2). High levels of CFC-12 were observed in Foshan, Guangzhou, Zhongshan, and Zhuhai (Figure 4). The levels of CFC-113 and CFC-114 showed no significant difference among those cities (not shown here), with variability 2%–5% and 0.4%–1.8%. As CFCs substitute, HCFC-22 showed hot spots in Foshan, Jiangmen, Hong Kong, and Zhuhai (Figure 5). The production of CFCs in China had already ceased in mid-2007, which was 2.5 year ahead of the Montreal Protocol schedule [*Wan et al*., 2009]. Despite the current tight control of these species in the PRD region as well as throughout China, a large reservoir of CFCs still remains in older air-conditioning and refrigeration units or foam products, and therefore would inevitably lead to their emission, as indicated by *Wan et al*. [2009], until about 2020 from operation/service of residential, industrial, and mobile CFC refrigerators/air conditioners in stock, from residual CFCs in retired CFC refrigerators/air conditioners and from residuals from foam products. As a result, higher mixing ratios typically occurred in highly industrialized and densely populated areas in the present study (Figures 3 and 4), due largely to emission of HCFC-22 and CFCs from industry activities or storage leaks [*Chan and Chu*, 2007]. In particular, Foshan is an important manufacturing base for refrigerators, air conditioners, and other electronic appliance in China. Emission would also occur from initial charge of coolants during the manufacture of these refrigerators or air conditioners. The average mixing ratio of HCFC-22 at the sites in Foshan during the September 2008 campaign, for example, was about 32% higher than the average at all the 84 sites.

If emissions of a pollutant, like CO, were nearly constant in March and in September in the region, more favorable dispersion conditions and greater advection/mixing in September than in March would result in its

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lower ambient levels in September. Better dispersion condition on 29 September 2008 than on 1 March 2009 was indicated by the bigger wind speed on 29 September 2008 (4.8 ± 0.5 m/s) than that on 1 March 2009 (3.3 ± 0.3 m/s) [http://www.ncdc.noaa.gov/cdo-web/search]. As shown in Table 2, unlike CFCs and HCFC-22, CO levels in March 2009 were significantly higher than those in September 2008, as expected from its normal seasonal variations. There are two major reasons for higher CFC and HCFC levels in September. First, the average ambient air temperature in the subtropical PRD region was much higher in September 2008 (26.4–31.0°C) than in March 2009 (15.5–18.5°C). As most refrigerators would be operating all throughout the year, while air conditioners would only be used in the hot seasons, much more frequent use of air conditioners in industries, offices, and residential buildings in September would lead to more emission of the refrigerant gases HCFC-22 and CFCs. Additionally, the higher temperature would induce more evaporative emission or storage leakage of these gases in old products or in industrial activities. It should be noted that 1 March 2009 was Sunday and might be expected to have lower emissions. However, in the PRD region, a so-called "world factory" industrial activities do not exhibit as much weekdays/weekends difference, since workers normally have holidays by turns instead of in weekends so that factories can maintain a constant supply of goods and products.

Since people in the PRD region typically start work after 08:00 A.M., industrial and human activities at 05:00 A.M. were limited compared to 10:00 A.M. when normal daytime activities were fully established, and thus, comparing mixing ratios at 05:00 A.M. and 10:00 A.M. can indicate the influence of human activities. However, as the long-lived CFCs and HCFC-22 had accumulated in the ambient as a large background "pool," if emission is not strong enough in a region, it would not cause significant changes in the mixing ratios even under the influence of the mixing layer height. In September 2008, significantly higher ($p < 0.05$) ambient mean mixing ratios of HCFC-22 were observed at 10:00 A.M. (472 ± 32 ppt) than at 05:00 A.M. (414 ± 34 ppt) (Table 2), suggesting that the human activities in the PRD region significantly affected the emission of HCFC-22 in the PRD region. On 1 March 2009, however, the average mixing ratio of HCFC-22 at 10:00 A.M. (360 ± 22 ppt) was similar to that at 05:00 A.M. (352 ± 24 ppt), although mixing layer height at 05:00 A.M. was about half of that at 10:00 A.M. [http://envf.ust.hk/dataview/satellite/current/]. The relatively steady levels could be attributed to less use of cooling appliances and air conditioners during the cool season [*Guo et al.*, 2009; *F. Zhang et al.*, 2010]. Accordingly, CFC-11 and CFC-12 had only a little bit higher average levels at 10:00 A.M. than at 05:00 A.M. during both grid-study campaigns (Table 2), indicating that their emission amplitudes were smaller compared to that of the HCFC-22 or their emissions were more likely to be induced by storage loss than direct emission from ongoing industrial or human activities. CFC-113 and CFC-114 showed relatively constant levels with relative standard deviations (rsd) of 4.1%–4.7% and 6.5%–7.1% at 05:00 A.M., respectively, and 4.2%–4.5% and 5.4%–6.8% at 10:00 A.M., respectively, in both campaigns.

3.3. Source Apportioning of CFCs and HCFC-22 by PMF

The receptor model—positive matrix factorization (PMF)—was adopted to identify the source profiles and source contributions of CFCs and HCFC-22 in the PRD region based on the two grid studies' field data. In order to get better attribution of sources, typical nonmethane hydrocarbons (NMHCs) like benzene and toluene, and halocarbon species like trichloroethene (C_2HCl_3, TrCE) and tetrachloroethene (C_2Cl_4, TeCE), were also included in the PMF model. The PMF reconstructed mass matched the observed mass very well, with slopes (reconstructed to observed) of 0.88–0.98 and r^2 of 0.77–0.99 for the data set of these two campaigns. As illustrated in Figure 6, four major sources were resolved at 05:00 A.M. and 10:00 A.M. in 2008 and 2009, respectively. Source 1 was abundant with typical industry solvents like TrCE, n-hexane, and toluene [*Chan et al.*, 2006; *Guo et al.*, 2009; *Y. L. Zhang et al.*, 2010, 2012], and it also included refrigerants species (like CFCs and HCFC-22) emitted during air-conditioning and refrigerating, during the manufacturing of refrigerant products and as residues in foams. So this source was termed as industry activities. The second source was traffic related and characterized by a significant amount of n-pentane, i-pentane, benzene, and toluene, C_8-aromatic hydrocarbons [*Watson et al.*, 2001; *Guo et al.*, 2007; *Zhang et al.*, 2012, 2013]. The CFCs/HCFC-22 from this source is related to mobile air-conditioning. The third source was related to n-propane, n-butane, and n-pentane, which are major species from domestic liquified petroleum gas usage [*Blake and Rowland*, 1995] and also related to toluene, C_8-aromatic hydrocarbons, which are major species from painting [*Chan et al.*, 2006; *Zheng et al.*, 2009]. This source also had considerable amounts of CFCs and HCFC-22, which here were probably related to leakage from air-conditioning systems and refrigeration units used in residential or office buildings during their servicing period [*Aucott et al.*, 1999; *Chan and Chu*, 2007; *Guo et al.*, 2009]. So

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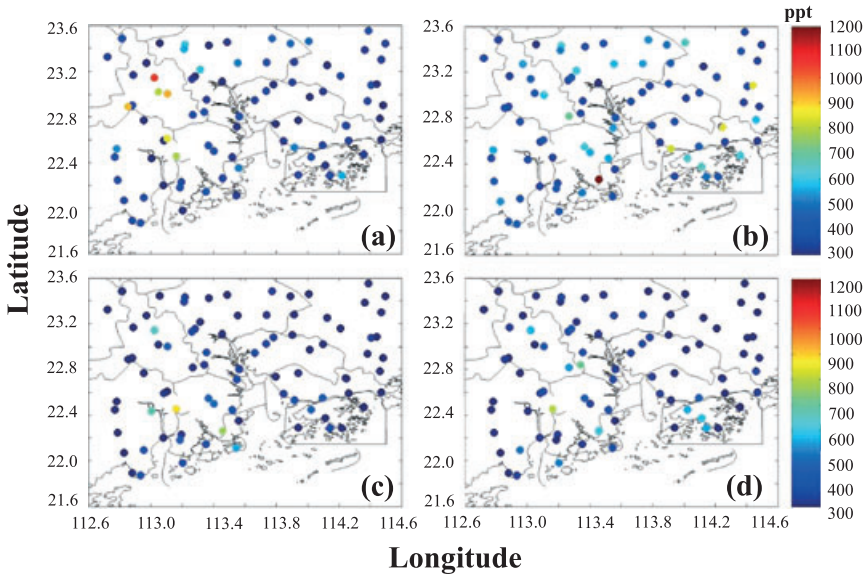

Figure 5. Spatial variations of HCFC-22 in the PRD region: (a) 29 September 2008 05:00 A.M., (b) 29 September 2008 10:00 A.M., (c) 1 March 2009 05:00 A.M., and (d) 1 March 2009 10:00 A.M.

this source can be recognized as cooling/refrigerating in residential and commercial buildings. The fourth source is rich in CFCs and HCFC-22 and low in hydrocarbons and shorter-lived halocarbons. This source represented the background of these halocarbon species that have relatively longer lifetimes and thus accumulated in the air from historical emission.

Based on the PMF approach, the average source contributions in percentages for each CFC species and HCFC-22 at 05:00 A.M. and 10:00 A.M. in 2008 and 2009 are illustrated in Figure 7. The background CFCs shared the largest parts of CFC-11, CFC-12, CFC-113, and CFC-114 in both years, with percentage ranges of 41.8–74.1%, 41.3–72.3%, 42.1–55.6%, and 43.1–66.7%, respectively. As shown in Figure 6, this source contribution became distinctively smaller in the warm season (September 2008) due to much more newly released CFCs from air-conditioning and refrigerating activities. Another major source, residential/commercial refrigerants, accounted for 15.6–36.6%, 14.4–38.2%, 14.6–36.5%, and 24.2–37.8% of CFC-11, CFC-12, CFC-113, and CFC-114, respectively. Largely due to the seasonal difference in air-conditioning activities, contributions from this source in September 2008 (warm season) were over 30%, much higher than that of ~15% in March 2009 (cold season). Refrigerants used in the mobile air-conditioning can be released to the atmosphere and contribute to CFCs from old automobiles [*Wan et al.*, 2009]. In the present study mobile air-conditioning shared 1.9–18.5%, 4.3–17.6%, 13.5–19.5%, and 4.5–18.4% of CFC-11, CFC-12, CFC-113, and CFC-114, respectively. CFC-11, CFC-12, and HCFC-22, as widely used refrigerants in the past, also showed much higher contributions from mobile air-conditioning during warm September 2008. Industry activities had minor contributions to CFCs and only accounted for 0.9–7.5%, 4.6–9.7%, 4.9–16.3%, and 2.3–7.1% for CFC-11, CFC-12, CFC-113, and CFC-114, respectively.

Since HCFC-22 is a much more widely used CFC replacement coolant/refrigerant in the region, the contrast of the source contributions for HCFC-22 between warm and cold seasons should be more distinctive. As shown in Figure 6, the release of HCFC-22 from residential/commercial air-conditioning or refrigerating shared the largest parts (54.2% and 49.0% at 05:00 A.M. and 10:00 A.M., respectively) in September 2008 (warm season), which were nearly 5 times that in March 2009 (11.8% and 10.6% at 05:00 A.M. and 10:00 A.M.f, respectively). These seasonal differences were much larger when compared to that of CFCs, consistent with their varied enhancement of mixing ratios in September. Additionally, in September 2008, HCFC-22 had much higher contribution from residential/commercial air-conditioning or refrigerating at 10:00 A.M. than at 05:00 A.M., also implying that HCFC-22 was strongly related to air-conditioning activities. In March 2009 (cold season), the background HCFC-22 became dominant and shared a fraction of 68.4% and 75.3% at 05:00 A.M. and 10:00 A.M., respectively. Similar to CFCs, the contributions of HCFC-22 in percentages from mobile air-conditioning in September 2008 was significantly elevated when compared to that in March 2009. Industry

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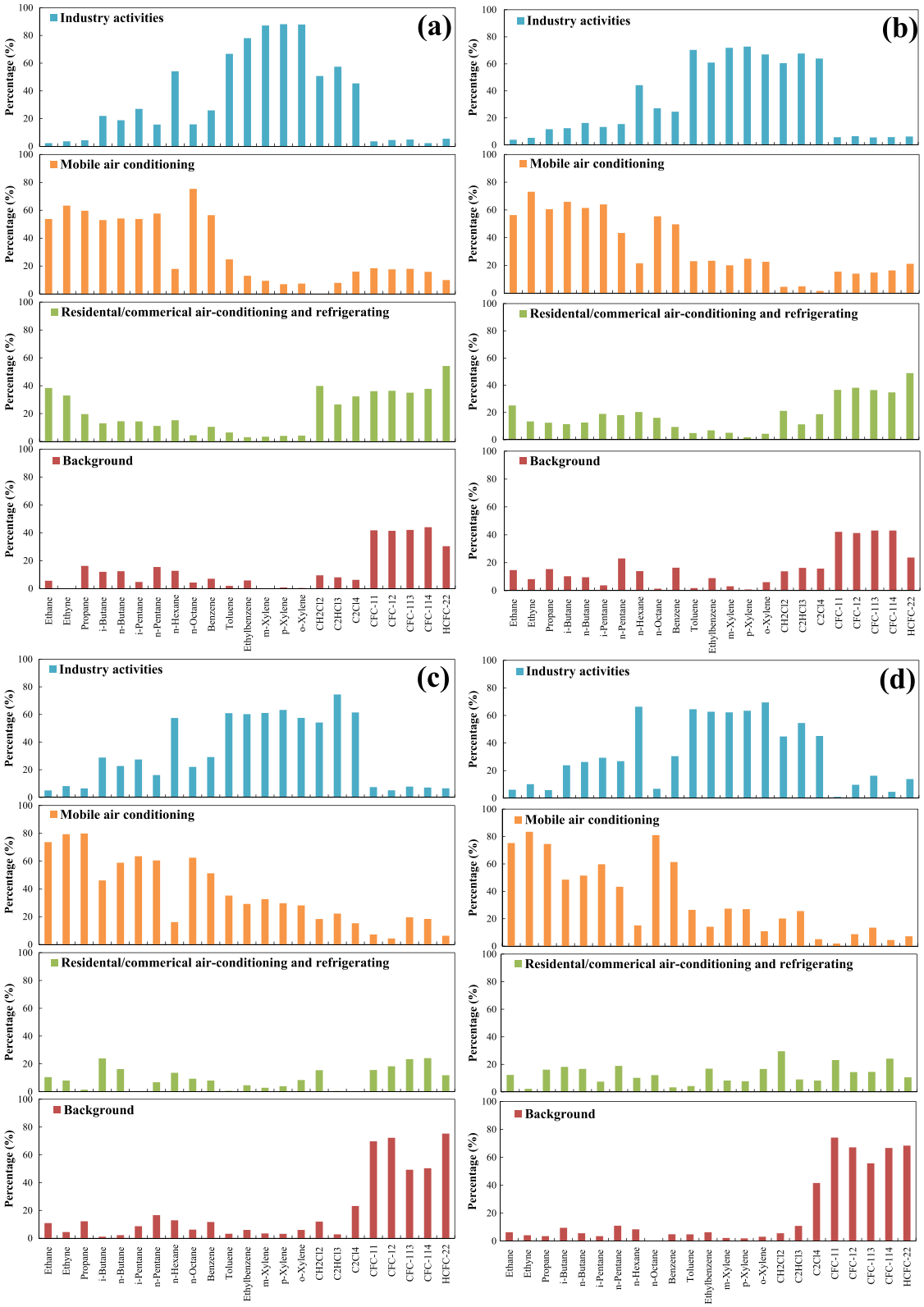

Figure 6. Factor profiles (percentage of species) of VOCs (halogenated hydrocarbons and NMHCs) at (a) 05:00 A.M. and (b) 10:00 A.M. on September 2008 and at (c) 05:00 A.M. and (d) 10:00 A.M. on March 2009.

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Table 3. Estimated Emissions of CFCs and HCFC-22 (Gg/yr) in the PRD Region as Compared With Those in the Same Region as Well as Those in China and the Whole Global From Previous Studies

	Sampling Time	Method	CFC-11	CFC-12	CFC-113	CFC-114	HCFC-22
PRD[a]	Sep 2008	CO ratio	1.0 ± 0.2	1.6 ± 0.5	0.3 ± 0.1	0.1 ± 0.02	6.3 ± 1.2
	Mar 2009	CO ratio	0.5 ± 0.1	1.2 ± 0.3	0.2 ± 0.04	0.1 ± 0.01	2.5 ± 0.7
PRD[b]	Nov 2002	CO ratio	1.0 ± 0.3	1.6 ± 0.4	0.9 ± 0.3	not applicable (NA)	2.3 ± 1.2
PRD[c]	Oct–Nov 2004	CO ratio	0.4 ± 0.2	1.6 ± 1.0	0	0	3.5 ± 2.2
China[d]	Feb–Apr 2001	Top-down	23 ± 6	30 ± 7	NA	NA	51 ± 32
China[e]	Oct 2006–Mar 2008	Inverse model	33 (26–43)	14 (9–19)	0.8(0.4–1.7)	NA	162 (140–213)
China[f]	Nov 2007–Dec 2008	Interspecies correlations	11 (9–15)	6.1 (4.4–8.5)	3.2(2.5–3.8)	1.3(0.9–1.8)	83 (64–109)
China[g]	2008	Bottom-up	14	4	0	NA	79
China[h]	2008	Inverse model	NA	NA	NA	NA	63.5 ± 6.6
China[g]	2009	Bottom-up	13	3	0	NA	91
Global[i]	2007	Top-down	82 ± 30	79 ± 40	<10	NA	330 ± 25
Global[j]	2007	Bottom-up	NA	NA	NA	NA	376
Global[j]	2008	Bottom-up	NA	NA	NA	NA	404
Global[k]	2008	Top-down	80 ± 30	65 ± 40	<10	NA	338 ± 25
Global[j]	2009	Bottom-up	NA	NA	NA	NA	437

[a]This study.
[b]*Guo et al.* [2009].
[c]*Shao et al.* [2011].
[d]*Blake et al.* [2003] and *Palmer et al.* [2003].
[e]*Vollmer et al.* [2009].
[f]*Li et al.* [2011] and *Kim et al.* [2010].
[g]*Wan et al.* [2009].
[h]*Stohl et al.* [2010].
[i]*Clerbaux et al.* [2007].
[j]*Saikawa et al.* [2012].
[k]*Montzka et al.* [2011].

activities accounted for 5.5–13.8% of HCFC-22. In industry sectors, air-conditioning and refrigerating are not so necessary at working hours (10:00 A.M.) during March (cold season) as during September (hot season). Therefore, the contribution from industry activities at 10:00 A.M. was quite near than that at 05:00 A.M. (non working hour) in March 2009 and instead about twice than that at 05:00 A.M. in September 2008 (Figure 6).

3.4. Emission Estimates for CFCs and HCFC-22 by CO-Tracer Method

Although halocarbons and CO do not necessarily come from the same individual sources, the method is valid because their sources are colocated in this densely populated and highly industrialized region. Furthermore, there are no other species in the region with their bottom-up emission inventories compiled as well as CO. To estimate the emissions of CFCs and HCFC-22 using the CO-ratio method, we need the Δhalocarbon/ΔCO slopes and the CO emission in the region. The CO emission inventory has previously been estimated for Guangdong province and the PRD region [*Palmer et al.*, 2003; *Streets et al.*, 2003, 2006; *Zhang et al.*, 2009; *Zheng et al.*, 2009], though not for 2008 and 2009. According to a newly resolved CO emission inventory for the PRD region for 2006 by *Zheng et al.* [2009], on-road mobile sources and industry accounted for 67.2% and 27.1% of the CO emission, respectively. Since CO emissions are predominantly from fossil fuel combustion in the transport and industrial sectors, we can roughly estimate CO emissions in 2008 and 2009 assuming that CO emission is proportional to the fossil fuel consumption from 2006 to 2009. In this way, average CO emissions of 4.4×10^3 Gg/yr are estimated for both 2008 and 2009 based on the fossil fuel (coal and oil) consumption data [*Guangdong Provincial Bureau of Statistics*, 2010; *Hong Kong Environmental Protection Department*, 2009] and the estimation of CO emissions of $(3.8 \pm 1.1) \times 10^3$ Gg in the PRD region in 2006 [*Zheng et al.*, 2009]. Uncertainty in estimating halocarbon emissions by the CO-tracer method depends on the uncertainties of the Δhalocarbon/ΔCO slopes and CO emissions [*Dunse et al.*, 2005]. In fact, differences in the results exist among estimates by *Guo et al.* [2009], by *Shao et al.* [2011], and from this study (Table 3). The varied Δhalocarbon/ΔCO slopes due to different sampling design is a major reason for the varied estimates. Accurate CO emission estimates in the region are another obstacle for sound halocarbon estimates using the

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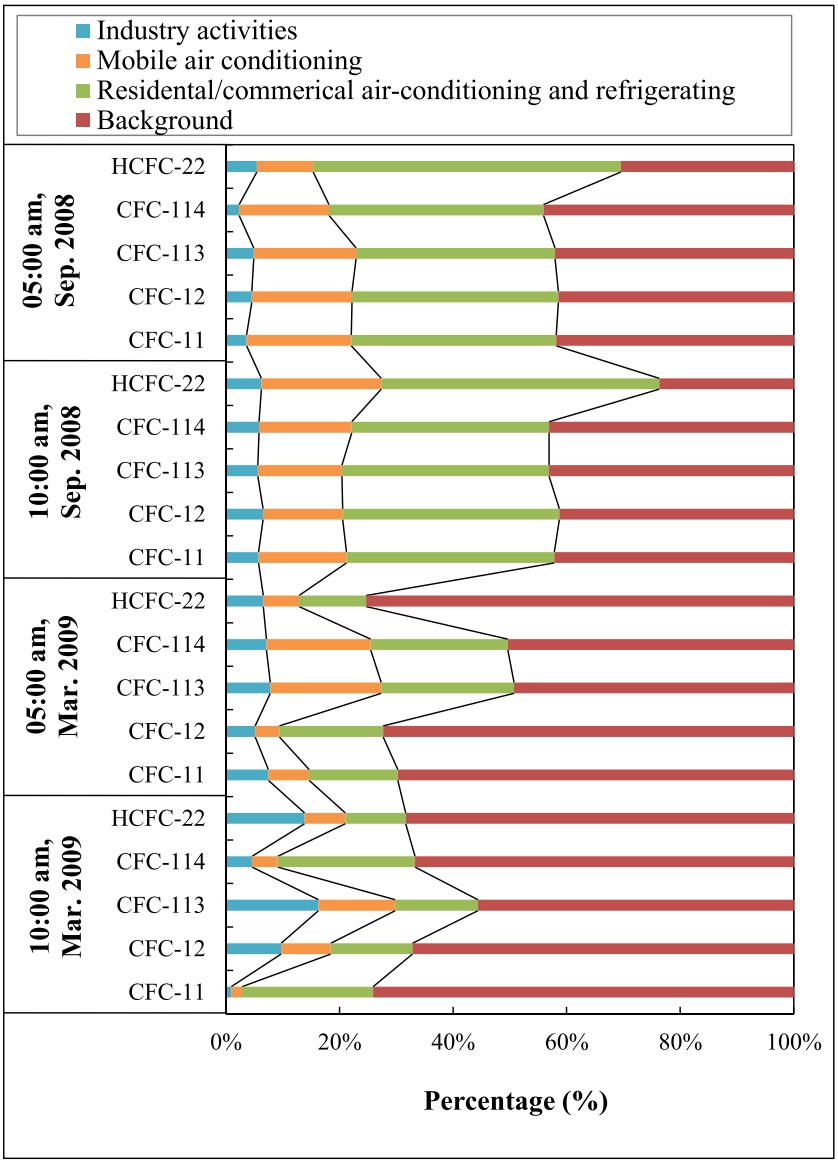

Figure 7. Source contributions of CFCs and HCFC-22 in percentages by PMF.

CO-tracer method. CO emission estimates from China or the PRD region still have large uncertainties. As examples, the CO emission in Guangdong Province was estimated to be 5.9×10^3 Gg in 2000 with an uncertainty of ± 156% (±95% confidence interval) and 8.7×10^3 Gg in 2001 with an uncertainty of ±68% [*Streets et al.*, 2006]. *Zhang et al.* [2009] estimated a CO emission of 8.69×10^3 Gg with an uncertainty of ±70% in Guangdong Province in 2006. In this study, we used the CO emission of 4.4×10^3 Gg/yr in the PRD region and assumed a 100% uncertainty of the CO emission in equation (2) to calculate uncertainties of the estimated halocarbon emissions.

As on-road mobile sources and industry together contributed nearly 95% of the CO emission in the PRD region [*Zheng et al.*, 2009] and there is a very few heating even in winter in this tropical/subtropical region, so CO emission was nearly constant throughout the year in this region. We exclude the data at 05:00 A.M. for estimation by the CO-ratio method since there were very few on-road vehicles and industrial activities in the early morning. Using the 10:00 A.M. data, the correlations between Δhalocarbon and ΔCO from the two grid campaigns, together with their linear regression slopes and Pearson's correlation coefficients, are shown in Figure 8 and Table 4. Relatively significant correlations ($p < 0.01$) between Δhalocarbon and ΔCO are

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Table 4. CFCs and HCFC-22 Versus CO Relationships, Uncertainties, and Their Estimated Emissions[a]

Halocarbons	Campaign	*X*/CO[b] (Forced Through the Origin)[c]	Uncertainty[d]	*r*[e]	Mw (g/mol)	Emission (Gg/yr)	Uncertainty (Gg/yr)
CFC-11	Sep 2008	0.0449(0.0677)	0.0080	0.53[f]	137.37	1.0	0.2
	Mar 2009	0.0215(0.0405)	0.0046	0.46[f]		0.5	0.1
CFC-12	Sep 2008	0.0862(0.1697)	0.0254	0.35[f]	120.91	1.6	0.5
	Mar 2009	0.0651(0.0945)	0.0165	0.43[f]		1.2	0.3
CFC-113	Sep 2008	0.0088(0.0162)	0.0023	0.39[f]	187.38	0.3	0.1
	Mar 2009	0.0062(0.0117)	0.0015	0.43[f]		0.2	0.04
CFC-114	Sep 2008	0.0025(0.0046)	0.0006	0.40[f]	170.92	0.1	0.02
	Mar 2009	0.0024(0.0041)	0.0005	0.53[f]		0.1	0.01
HCFC-22	Sep 2008	0.4654(0.6088)	0.0899	0.50[f]	86.47	6.3	1.2
	Mar 2009	0.1844(0.2707)	0.0415	0.46[f]		2.5	0.8

[a]Based on CO emission of 4.4×10^3 Gg/yr in the PRD region with an uncertainty of 100%.
[b]Slopes of the regressions of Δhalocarbons against ΔCO.
[c]Slopes of the regressions that are forced through the origin (0,0).
[d]Uncertainty of the slopes of Δhalocarbons against ΔCO.
[e]*r*, Pearson's correlation (two-tailed) coefficient of *X*/CO.
[f]Significance level $p < 0.01$.

observed for the 10:00 A.M. data sets. Linear regressions forced through the origin were also indicated in Figure 8 and Table 4. The slopes from forced regressions were found to be 1.31–197 times than that from unforced regressions. This means that forced regression would result in estimated halocarbon emissions about 30–100% higher than those from unforced regressions. Unless specified, the estimated emissions below are based on the slopes from unforced regressions.

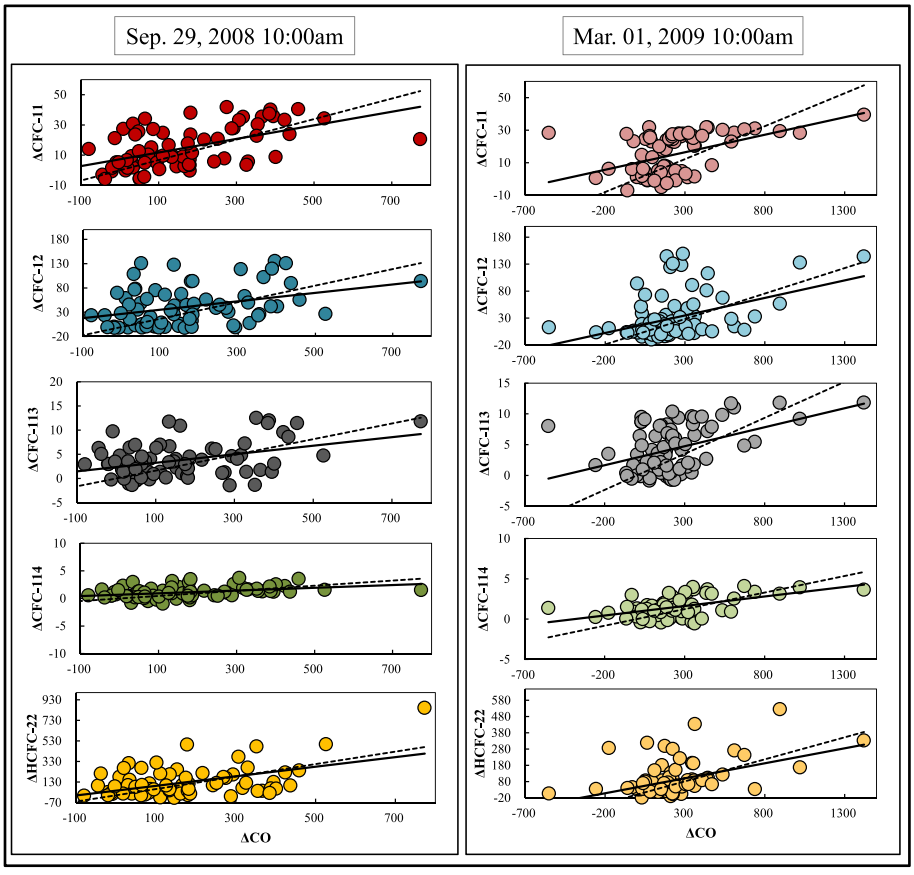

Figure 8. Correlations of Δhalocarbon to ΔCO in 2008 and 2009. The dashed lines are regressions forced through the origin (0,0), while the solid lines denote the unforced regressions.

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CFC-11, CFC-12, and HCFC-22 emission estimates based on the data in March 2009 were 0.5 ± 0.1 (mean ± 95% CI), 1.2 ± 0.3, and 2.5 ± 0.7 Gg/yr, while those based on the data in September 2008 were 1.0 ± 0.2, 1.6 ± 0.5, and 6.3 ± 1.2 Gg/yr, respectively (Table 3). Consistent with the observed mixing ratios and the above PMF results, HCFC-22 emissions in September were more than double than those in March probably due to greater refrigeration and air-conditioning activities during summer. CFC-11 and CFC-12 emissions were also elevated in September when compared to March, particularly for CFC-11. The smaller increase of CFC-12 in September compared to HCFC-22 and CFC-11 was probably due to its decreasing usage as a refrigerant in the region, such that leakage from old products was its major pathway of emission. As discussed before, due to differences in air temperature and in the use of refrigerating and air-conditioning equipment/systems, we expect the emissions based on the March data to be near the lower limit of seasonal emissions, while the September data likely represent the upper limit of seasonal emissions. If we take their averages to roughly represent annual emission estimates for CFCs and HCFC-22, the annual emissions of 0.8 ± 0.2, 1.4 ± 0.6, and 4.4 ± 1.0 Gg/yr are obtained during 2008–2009 for CFC-11, CFC-12, and HCFC-22, respectively. CFC-113 and CFC-114 showed lower average emissions of 0.2 ± 0.1 and 0.1 ± 0.02 Gg/yr in the region, respectively, and CFC-114 showed similar emissions in September (0.1 ± 0.02 Gg/yr) and in March (0.1 ± 0.01 Gg/yr).

As shown in Table 3, the estimated average CFC-11 emission of 0.8 Gg/yr in the present study was lower than the 1.0 Gg/yr calculated by *Guo et al.* [2009] based on November 2002 data but higher than the 0.4 Gg/yr by *Shao et al.* [2011] based on the October–November 2004 data. It seems unlikely that CFC-11 emission in the PRD region dropped sharply from 1.0 Gg/yr by *Guo et al.* [2009] in 2002 to 0.4 Gg/yr by *Shao et al.* [2011] in 2004. Because based on their measurement data, the ambient CFC-11 levels in the region indicate a steady decrease. The difference among the estimates might originate from different data sets from field campaigns with varied time spans or at different sites in the PRD region. Thus, further extensive field works and modeling studies are required to narrow the gaps among the estimates. The average estimated CFC-12 emission in this study was similar to those by *Guo et al.* [2009] and *Shao et al.* [2011]. For HCFC-22, the estimates from *Guo et al.* [2009], *Shao et al.* [2011], and this study reveal increasing HCFC-22 emission in the PRD region. Using the estimates from autumn data in a previous study by *Guo et al.* [2009] and this study, a roughly annual growth rate of 0.7 ± 0.3 Gg/yr is obtained for HCFC-22 in the PRD region. While the study by *Shao et al.* [2011] did not detect CFC-113 and CFC-114 emission in the PRD region, the study by *Guo et al.* [2009] revealed a substantial CFC-113 emission of 0.9 ± 0.3 Gg/yr, which is much larger than the average CFC-113 emission of 0.2 ± 0.1 Gg/yr from this study (Table 3), and also much larger than average CFC-113 emission of about 0.4 Gg/yr if the even higher slopes from forced regressions were adopted. Since the historical production and consumption of CFC-113 in China were much lower than that of the CFC-11 and CFC-12 [*SEPA*, 1999], our estimate of the CFC-113 emission in the PRD region seems to be more plausible than that by *Guo et al.* [2009]. The CFC-113 emission projected by *Wan et al.* [2009] was zero in China after 2008. However, there were quite a few hot spots in the PRD region, suggesting possible emission sources in the region.

For the estimations of halocarbons emission in China, large differences have also been observed [*Blake et al.*, 2003; *Palmer et al.*, 2003; *Vollmer et al.*, 2009; *Wan et al.*, 2009; *Kim et al.*, 2010; *Stohl et al.*, 2010; *Li et al.*, 2011]. Available top-down studies [*Kim et al.*, 2010; *Stohl et al.*, 2010; *Li et al.*, 2011] sample China mostly in winter season and in northern China, these emissions calculated for China may be biased too low due to a significant variation in seasonal emissions. For example, HCFC-22's seasonality at GAW regional background station Shangdianzi in northern China exhibited a summer/autumn maximum and a winter minimum [*Yao et al.*, 2012]. Without considering the large uncertainties, the averaged emissions of halocarbons in China in the year of 2006 to 2008 [*Vollmer et al.*, 2009; *Wan et al.*, 2009; *Kim et al.*, 2010; *Stohl et al.*, 2010; *Li et al.*, 2011] accounted for about 12% (CFC-12), 24% (CFC-11), and 26% (HCFC-22) of the global emission in 2008 [*Montzka et al.*, 2011; *Saikawa et al.*, 2012]. Based on the estimated total emissions from China by *Kim et al.* [2010] and *Li et al.* [2011] (Table 3), the PRD region accounted for 6–26% of CFC and HCFC-22 emissions in China, matching its share of ~10% in China's GDP but contrasting with its share of 0.4% of China's land area. Based on the estimates from this study, the PRD region, with about 0.03% of the world's land area, contributed about 0.94%, 2.2%, 2.5%, and 1.3% to global emission of CFC-11, CFC-12, CFC-113, and HCFC-22, respectively [*Montzka et al.*, 2011]. It is worth noting that if the emission estimates are made based on the slopes from forced regression (Figure 7), the PRD region would account for 10–40% of CFCs and HCFC-22 emissions in China. Despite the large uncertainties in both the CO emission inventories and the halo-CO slopes, the CO

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ratio method has been the only approach used to estimate the emissions of halocarbons in the PRD region [*Guo et al*., 2009; *Shao et al*., 2011]. Until now, this might be the best available method that can be used to roughly estimate the local emissions of halocarbons based on ambient air samples. To narrow the uncertainty of halocarbon emission estimates using the CO-tracer method, both halocarbons and CO observational data and CO emission inventories should be updated with sound spatiotemporal resolutions. Nevertheless, mass concurrent sampling in the present study would potentially be a good way to test the dispersion models and inversion technique.

4. Conclusions

As one of the most industrialized and densely populated city clusters in China, the PRD region bears a considerable portion in the production, consumption, and emission of CFCs and HCFCs in China, and therefore, study of ambient halocarbons in the region may help with ODSs control in China. The production of CFCs in China ceased in mid-2007, and consumption of CFC-11, CFC-12, and CFC-113 in industrial sectors including the foam blowing, solvent, tobacco, aerosol, and chemical industry also stopped in China since the start of 2008. It is necessary to trace the changes in ambient levels following these emission control measures. In the present study, we concurrently collected air samples in 84 grids within the PRD region in 2008 and 2009 to identify CFCs and HCFCs emission hot spots. Compared to the subtropical NH background levels, the observed CFC mixing ratios showed average enhancements of 5%–10%, while HCFC-22 was enhanced by over 75%. The study reconfirmed the decreasing trends for ambient CFC-11, CFC-12, and CFC-113 levels in the region and an increasing trend for HCFC-22, a CFC replacement. Higher halocarbon levels in September than March suggested that their emission was largely related to more refrigerating and air-conditioning activities in hot seasons in the subtropical PRD region. Comparing the mean mixing ratios at 10:00 A.M. with those at 05:00 A.M. also indicated the influence of ongoing human activities on their emission. We found that the levels of CFCs and HCFC-22 were elevated at 10:00 A.M. compared to 05:00 A.M. and that HCFC-22 levels were significantly higher ($p < 0.05$) at 10:00 A.M. than at 05:00 A.M. in September.

Emission sources of CFCs and HCFC-22 were resolved with a PMF technique. The contributions in percentages from air-conditioning and refrigerating activities were found to be significantly higher in warmer September 2009. Industry activities were found to be minor when compared to that from residential/commercial air-conditioning/refrigerating and mobile air-conditioning. The emission of CFCs and HCFC-22 in the region were also estimated by the CO-tracer method based on the data from the two grid-study campaigns. Estimated emissions were 0.8 ± 0.2, 1.4 ± 0.6, 0.2 ± 0.1, 0.1 ± 0.02, and 4.4 ± 1.0 Gg/yr, respectively, for CFC-11, CFC-12, CFC-113, CFC-114, and HCFC-22. The emissions of CFCs and HCFC-22 in the PRD region accounted for 5.5%–25.5% of their estimated total emissions in China.

Acknowledgments

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