Estimates of major anthropogenic halocarbon emissions from China based on interspecies correlations

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HIGHLIGHTS

▶ HCFC-22 is better as a reference tracer than CO derived from comparisons.
▶ The estimated emissions agree well with other estimates within uncertainties.
▶ HCFC emissions from China contributed more than CFC/HFC emissions to global totals.
▶ CFC emissions are decreasing evidently and HCFC emissions are increasing during 2001−2009.
▶ HCFCs are being accumulated in banking time usages in China.

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ABSTRACT

Halocarbon emissions from China are of great interest to both policy makers and academia. To estimate halocarbon emissions with interspecies correlation methods, previous studies adopted CO, HCFC-22 or other species as reference tracers. However, few of these studies compared the results using different reference tracers. In this study, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and carbon monoxide (CO) concentrations were measured at a monitoring site in northern China in 2009/2010, and halocarbon emissions were estimated using an interspecies correlation method. A comparison was performed of the correlations between estimated halocarbon emissions and two reference tracers, CO and HCFC-22. The results show that both species are significantly correlated with most of the target species ($P < 0.01$), whereas HCFC-22 shows better correlations than does CO. Our estimated halocarbon emissions for 2009 agree within uncertainties with results obtained with other approaches, including inverse modeling and interspecies correlation methods. The emissions for 2001−2009 estimated in different studies (all using top−down approaches) show a clear decrease in the emissions of CFC-11 and CFC-12 and an increase in the emissions of HCFC-22, HCFC-141b and HCFC-142b in China. Moreover, the combined Ozone Depletion Potential weighted emissions of CFCs are much greater than the reported consumption, whereas the emissions of HCFC counterparts are not more than one-half of the reported consumption. This result suggests that HCFCs are being accumulated in banks and that these banks will sustain elevated in China.

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1. Introduction

Halocarbons, including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), are of great concern because their properties imply stratospheric ozone depletion potentials (ODPs) or global warming potentials (GWPs) (IPCC/TEAP, 2005). For this reason, these halocarbons are regulated

under the Montreal Protocol (MP) or the Kyoto Protocol (KP). Many emission inventories at global, national or even regional scales have been established to help determine the annual emissions of halocarbons and the changes occurring during the phase-out process (AFEAS, 2010; McCulloch et al., 2003; Wan et al., 2009). This information is helpful in multi-scale environmental studies and policy making.

Most emission inventories use a bottom−up approach based on considerations of production or consumption data and emission functions in different sectors. However, uncertainties arise if the production data do not cover all the manufactures or if the

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allocation among different end-use sectors is in error (Shao et al., 2011), or if information about the waste/recycling system (Yokouchi et al., 2005), leakage from existing stockpiles and unreported production (Palmer et al., 2003b) is not clearly determined. Due to these uncertainties, emissions estimated by this approach are not always reliable. To obtain more reliable estimates, top–down approaches using observation results or other databases are also used. These approaches can be applied to estimate global emissions (using simple box models or three-dimensional models) or regional emissions (using modeling back-attribution techniques). Intercomparisons between the inventoried emissions and the modeled emissions serve to verify the estimated emissions.

Estimating emissions based on interspecies correlations is one of the top–down approaches. Briefly, the emissions of the target species are quantified by scaling the known emissions of a reference tracer with halocarbon/reference tracer enhancement ratios. This approach is based on several assumptions: (a) the annual emissions of reference tracers are known; (b) there is no significant removal or de novo creation of the target species and the reference tracers in the atmosphere after the initial emissions; and (c) the air mass arriving at the monitoring site represents the regional average of the emission ratios (Shao et al., 2011; Yokouchi et al., 2005). Several studies have been performed using this approach (e.g., Blake et al., 2003; Kim et al., 2010; Li et al., 2011; Millet et al., 2009; Shao et al., 2011; Yokouchi et al., 2005, 2006).

Halocarbon emissions in China attract extensive attention because they are expected to be a significant contributor to global total and East Asian emissions (Li et al., 2011). China is in the process of rapid urbanization, industrialization and mobilization. The emissions of CFCs, HCFCs, and HFCs in metric tons from East Asia in 2008 were estimated to represent 15%, 29%, and 16% of the global totals, respectively. For most halocarbons, China was estimated to contribute more than 80% of the East Asian emissions (Li et al., 2011). Moreover, China's emission patterns are expected to change substantially during the phase-out process. China belongs to the "Article 5 countries" in the MP. The consumption of CFCs in China was banned in mid-2007 (SEPA, 2004), and the consumption of HCFCs, the replacements for CFCs, will be frozen in 2013 at the baseline of an average of the 2009–2010 level and reduced by 10% in 2015 and by 35% in 2020 under the adjustments stipulated by the MP (UNEP, 2009).

Chinese emissions of halocarbons estimated using interspecies correlation approaches are determined primarily from Jeju Island, Korea (126.17°E, 33.28°N) (for example, Kim et al. (2010)) or Hateruma Island, Japan (139.28°E, 35.04°N) (for example, Yokouchi et al. (2006)). In this study, we estimated the Chinese halocarbon emissions using observations from a monitoring site located in northern China. We discussed the selection of CO and HCFC-22 as reference tracers, validated our estimates by conducting comparisons with the results of other studies, explored the Chinese contributions to global total emissions and finally summarized the emission trends during 2001–2009 based on the results of studies that applied the top–down approach.

2. Methods

2.1. Measurement and data selection

Our observations were performed at a campus station at the Peking University (40.00°N, 116.30°E, PKU) in Beijing, China. The whole air samples were collected with canisters every two hours on the roof of a 30 m building. The measurements of halocarbons were conducted with a gas chromatography–mass selective detector (GC–MSD, Varian Saturn 2100, Varian Co., California, USA) coupled with a cryogenic pre-concentration system (Entech 7100A, Entech Instruments Inc., California, USA). Detailed descriptions of the chemical analysis, calibration method, measurement precision/accuracy, and the quality control/assurance are given by Fang et al. (2012). Briefly, the following procedures were used. Before the analysis of the samples each day, the analytical system was challenged with humidified zero air to ensure its cleanliness. Dynamically diluted middle-concentration standard gas was then used to check the performance of the system. All target compounds were quantified using a multipoint external calibration method. In our chemical analysis, the precision of the halocarbon measurements varied compound-by-compound. This precision was 3% for CFCs and 6% for HCFCs and HFCs. The measurement accuracy of the method was 2% for CFCs and 6% for HCFCs and HFCs. The atmospheric concentrations of CO were in-situ measured at an integration time of 1 min by Gas Filter Correlation CO Analyzer of Model 48i Trace Level-Enhanced, Thermo Electron Corporation.

The air masses from northwestern or southeastern continents pass over northern or southern China, respectively, carrying the pollution signals of halocarbon emissions to PKU (see Supplementary Information (SI) Figure S1). The background air is brought from Siberia through northern China (for example SI Figure S1(a)) and from the Pacific through southeastern China (for example SI Figure S1(b)). The measured concentrations of the air masses that previously crossed Korea or Japan were excluded prior to further processing to prevent the confusion of emissions from more than one country. To estimate the annual emissions, observation days were selected in every season (16–18 Apr., 4, 11 and 12 Aug., 24 Oct. 2009, and 11 and 19 Jan. 2010, representing spring, summer, fall and winter in China, respectively). Previous studies showed that the interspecies correlations among these halocarbons from China are virtually consistent for all seasons (Kim et al., 2010). Therefore, the heterogeneous distribution of our sampling times is not expected to strongly influence the estimates of emissions obtained by this study.

2.2. Emission estimates by interspecies correlation

Prior to the estimation of halocarbon emissions, the background halocarbon concentrations should be subtracted from the measured data to obtain the enhanced halocarbon values resulting from pollution. If the data were collected within a short period (for example, two months in Shao et al. (2011)), the background concentrations would not change significantly. In this case, the subtraction of the baseline values would be not necessary. However, most studies are performed over a longer period, and the subtraction of the background is necessary (e.g., Kim et al., 2010; Li et al., 2011; Millet et al., 2009; Yokouchi et al., 2006). In this study, because the observation period was approximately one year, the baseline concentrations were subtracted from the measurements. The background values that we used were derived from the Advanced Global Atmospheric Gases Experiment (AGAGE) and are shown in SI Table S1. Before the subtraction of the baseline values, the time series of the concentration data were treated by removing outliers (residuals larger than 3σ).

According to the assumption that the ratio of the concentration enhancements of two trace gases represents the ratio of the corresponding emissions, the target emissions can be calculated as follows:

$$E_x = E_r \times S \times M_x/M_r, \tag{1}$$

where E_x and E_r represent the emissions of halocarbon X and the reference tracer (CO or HCFC-22 or others), respectively; M_x and M_r represent the molecular weights of halocarbon X and the reference tracer, respectively; and S represents the slopes of the correlation

determined with an orthogonal distance regression method. If CO is chosen as the reference tracer (concentrations expressed in ppmv), the equation should be multiplied by 10^{-6} to derive the E_x. Error propagation was used to estimate the uncertainty of E_x because the target emissions variable is associated with the uncertainties in the regression slopes and in the reference tracer emissions.

$$\sigma_{E_x} = \sqrt{\sigma_{E_r}^2 \times S^2 + E_r^2 \times \sigma_S^2} \times M_x/M_r, \qquad (2)$$

where σ_{E_x}, σ_{E_r} and σ_S are the uncertainties of emissions of halocarbon X, reference tracer and the regression slope, respectively.

Several studies selected HCFC-22 as a reference tracer (Kim et al., 2010; Li et al., 2011; Yokouchi et al., 2005), and several others selected CO (Blake et al., 2003; Dunse et al., 2005; Millet et al., 2009; Yokouchi et al., 2006). However, few studies have compared the performance of HCFC-22 and CO as reference tracers. In this study, both HCFC-22 and CO were selected as reference tracers for comparative analysis.

The emissions of HCFC-22 from China in 2009, estimated with bottom–up approaches, were 90.6 kt, with an average growth rate of 15.9% (2006–2009) (Wan et al., 2009). In addition, the HCFC-22 emissions in 2008, estimated with top–down approaches, were 83 (64–109) kt (Kim et al., 2010) and 65.5 ± 6.6 kt (Stohl et al., 2010). These values were extrapolated to 2009 with the 15.9% growth rate cited above. Based on these results, the best estimate of the HCFC-22 emissions from China in 2009 is 87.6 (77.2–98.0) kt. The anthropogenic CO emissions from China in 2001 were estimated to be 141,700 ± 97,000 kt (Streets et al., 2006), 168,000 ± 5000 kt (Palmer et al., 2003a) and 145,000 ± 32,000 kt (Allen et al., 2004) (including emissions from fossil fuels and biofuels). These values were extrapolated to 2009 with the annual growth rate derived from the 2001–2006 emissions (Zhang et al., 2009). Approximately 60% of the anthropogenic CO emissions are produced by fossil fuels (Streets et al., 2003). Fossil fuel-related CO is primarily emitted in urban/industrial areas, where most anthropogenic halocarbons are also emitted. However, the biofuel-related CO is primarily emitted in rural areas. The contribution of this CO source to $\triangle$CO (during pollution events involving anthropogenic halocarbons) is considered to be much lower than the ratio of biofuel-related CO to the national total CO emissions (Yokouchi et al., 2006). Therefore, the fossil fuel-related CO emissions, not total emissions, are used to calculate the emissions of the reference tracer CO. Given that the possible range of the percentage of the anthropogenic CO emissions represented by fossil fuels is 45%–75% (Yokouchi et al., 2006), the estimated Chinese CO emissions from fossil fuel were 118,404 ± 39,732 kt in 2009. The emission values of HCFC-22 and CO estimated above will be used in Eqs. (1) and (2) to calculate the emissions of the target species.

3. Results and discussion

3.1. Interspecies correlations of halocarbons vs. CO or HCFC-22

The results of the interspecies correlations of halocarbons vs. CO or HCFC-22 are shown in Table 1. CFC-113 and CFC-114 show poor correlations with the reference tracers (an exception is that CFC-113 is correlated with CO, $P < 0.01$). The lack of a significant correlation has several possible explanations. For example, the emissions of the target species may be minimal (Kim et al., 2010) or the sources of the target species and the tracer are not co-located (Bakwin et al., 1997). The emissions of CFC-114 from China were estimated as 1.3 kt in 2008, a value much smaller than the emissions of other species (Li et al., 2011). The emissions of CFC-114 are expected to decrease substantially in 2009 due to the rapid phase-out of CFCs at

Table 1
The Pearson correlation coefficient (R) and regression slope (S) between target species and reference tracers, with 95% confidence intervals (pptv/ppmv for CO reference, and pptv/pptv for HCFC-22 reference).

Species	CO			HCFC-22		
	R	S		R	S	
CFC-11	0.434(**)	13.5	8.8–18.2	0.799(**)	0.072	0.064–0.080
CFC-12	0.511(**)	13.8	9.8–17.9	0.739(**)	0.059	0.052–0.066
CFC-113	0.490(**)	4.0	2.9–5.1	−0.043	0.001	−0.001 to 0.003
CFC-114	0.053	0.0	−0.3 to 0.3	−0.235(*)	−0.001	−0.002 to 0
HCFC-22	0.404(**)	223.8	161.7–285.9	–	–	–
HCFC-141b	0.516(**)	34.3	30–38.7	0.633(**)	0.073	0.062–0.083
HCFC-142b	0.273(**)	17.5	9.6–25.5	0.770(**)	0.101	0.090–0.112
HFC-134a	0.426(**)	14.7	9.8–19.5	0.647(**)	0.055	0.048–0.062

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

the end of the 2000–2010 decade in China. The emissions of CFC-113 were estimated as 3.2 kt for 2008 (Li et al., 2011); nevertheless, CFC-113 is used primarily as a solvent and process agent in the commercial and industrial sectors in China (Wan et al., 2009), and its sources are less spatially uniform than those of CO and HCFC-22. These characteristics may explain the poor interspecies correlations. The emissions of CFC-113 and CFC-114 were calculated despite the relatively poor interspecies correlations and show large uncertainties due to the weakness of these correlations.

The criteria for a good reference tracer include a statistically significant correlation with the target species and a high emission rate with low uncertainties (Li et al., 2011). Table 1 shows that both HCFC-22 and CO are significantly correlated with other target species ($P < 0.01$). HCFC-22 is used primarily in household air conditioners, industrial/commercial refrigerators and freezers, and extruded polystyrene foams (Chan et al., 2006; McCulloch et al., 2003). These varied uses produce a widespread distribution of HCFC-22 sources. The emissions of HCFC-22 in China were estimated to be 83 (64–109) kt in 2008 (Li et al., 2011), the greatest component of Chinese anthropogenic halocarbon emissions. The sources of CO are also widely distributed. CO emissions are of the order of millions of tons, as discussed in Section 2.2. The large amounts of emissions, as well as the significant correlations with the target species, allow both HCFC-22 and CO to be suitable for use as reference tracers. However, the target species are better correlated with HCFC-22 than with CO (Table 1). The reason for this difference may be that HCFC-22 and these halocarbons have similar applications (they are used primarily as refrigerants and blowing agents) and are emitted primarily in urban/industrial areas. In contrast, a substantial proportion of the CO emissions originate from rural areas. Due to their similar uses, HCFC-22 and the target halocarbons are suitably collocated. For this reason, HCFC-22 is more suitable as a reference tracer than CO.

3.2. Estimation and comparison of halocarbons emissions

The estimated regression slopes for the target species and the accompanying 95% confidence intervals are shown in Table 1. Note that the regression slopes for a particular species may differ for data collected at different sites in China. Observation programs were conducted at different sites during 2009–2011. These sites included Beijing (PKU), Guangzhou, Hangzhou and Lanzhou, located in northern, southern, eastern and midwestern China, respectively (see SI Figure S2). Among the regression slopes calculated for these observation sites, the slopes for the PKU dataset tended to show intermediate values (see SI Table S2). Therefore, the PKU dataset was considered to be representative of the entire country and was used to estimate Chinese halocarbon emissions. The Chinese

emissions of halocarbons and the uncertainties in these values were calculated from the regression slopes, the emissions of the reference tracers and Eqs. (1) and (2).

The estimated halocarbon emissions from China in 2009 are shown in Table 2. The estimated emissions of HCFC-22, based on CO, were 81.8 (46.2–117.5) kt, near the 87.6 (77.2–98.0) kt estimated in Section 2.2. The estimates based on CO and those based on HCFC-22 were comparable in most cases. However, discrepancies were also found. The emissions of HCFC-141b, based on CO, were estimated to be 17.0 (10.9–23.1) kt, which are two times of the estimates based on HCFC-22. Previous studies have estimated HCFC-141b emissions of more than 12 kt in China (Li et al., 2011; Stohl et al., 2010), and HCFC-141b emissions are expected to increase due to the growth of HCFC consumption. For this reason, the estimate of the HCFC-141b emission value based on CO appears more reasonable than the estimate based on HCFC-22. Further studies are needed to determine the reasons that the use of HCFC-22 as a reference tracer produced underestimates. The emissions of CFC-113 were estimated to be 3.2 (1.8–4.5) and 0.2 (−0.3 to 0.6) kt based on CO and HCFC-22, respectively. It is possible that this discrepancy is due to the difference between the correlation of CFC-113 with HCFC-22 and the correlation with CO.

The most recent estimates based on interspecies correlations for Chinese halocarbon emissions were obtained for 2008 (Li et al., 2011). A comparison of the results of that study with the results of our study is shown in Fig. 1. The emissions for all species ranged from 0 to 115 kt. This range of values clearly indicates that the emissions (consumption) for different species are of different magnitudes in China. The linear relationship between the estimated emissions found in our study (y) and the estimated emissions found by Li et al. (2011) (x) was estimated to be $y = 1.0357 x = 1.4633$, $R = 0.998$. This result shows that our estimates agree well with those from the previous study. It is possible that the discrepancies between the two sets of estimates result from the different target years examined by the two studies. For small emissions, such as those of CFC-113, relatively large discrepancies are found between the two studies. Most CFC-113 is emitted promptly at the time that it is consumed (Wan et al., 2009), and it is possible that the rapid phase-out of CFC-113 in China induced the substantial decrease in the emissions of this species from 2008 to 2009. In summary, the emissions estimates from these two studies were of similar magnitude for most halocarbons.

If possible, comparisons were also made with other estimates obtained by Wan et al. (2009) for 2009 using bottom–up methods and obtained by Stohl et al. (2010) for 2008 and Vollmer et al. (2009) for 2007 using top–down inverse modeling methods (see Table 2). The estimated emissions of halocarbons from China for 2009 based on top–down studies have not yet been reported. For
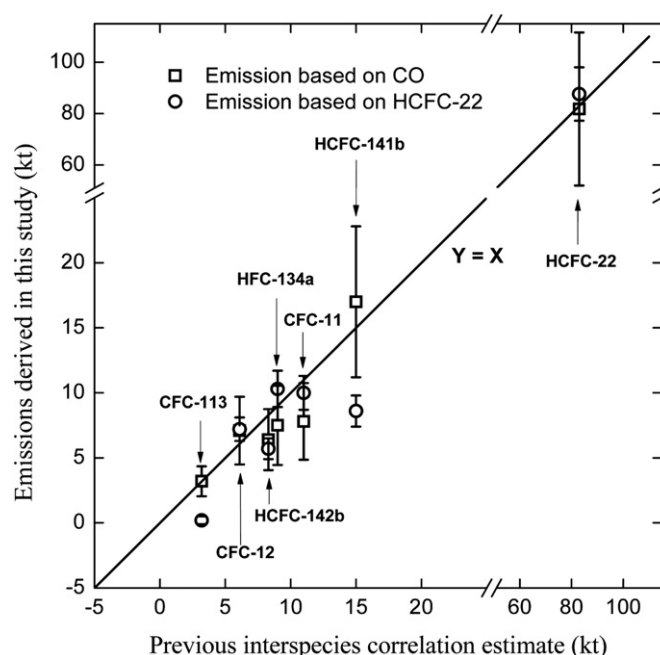

Fig. 1. Comparison between results of the interspecies correlation method for major Chinese halocarbon emissions estimated for 2009 (this study) and for 2008 (Li et al., 2011).

this reason, the results of the two top–down studies cited above were extrapolated to 2009 for comparative purposes by multiplying the original estimates of the emissions by the estimated annual rates of change (see Fig. 2). This comparison shows that within the uncertainty in the estimated values, our estimates agree well with those from Stohl et al. (2010) and Li et al. (2011). However, our estimates of the emissions of several species are lower than those obtained by Wan et al. (2009). For example, the estimates of emissions based on CO are 5.1 kt lower for CFC-11 and 8.8 kt lower for HCFC-22 than those estimated by Wan et al. (2009). Discrepancies in the emissions of CFCs, HCFC-22 and HCFC-142b were found between Vollmer et al. (2009) and the other studies cited above. It is possible that Vollmer et al. (2009) overestimated the values of the emissions. This possible conclusion is consistent with the results of the analysis by Kim et al. (2010) and Stohl et al. (2010). The emissions estimated for these species by our study are comparable, overall, with the corresponding values from other studies, including both bottom–up and top–down approaches. This outcome lends substantial credibility to the method used in our study and to our results.

Table 2
Emissions of anthropogenic halocarbons from China estimated in this study and previously reported values for Chinese and global emissions (kt a^{-1}, "−"means no reported data).

Species	Emissions based on CO		Emissions based on HCFC-22		(Wan et al., 2009) for 2009	(Li et al., 2011) for 2008	(Stohl et al., 2010) for 2008	(Vollmer et al., 2009) for 2007	Global top–down emissions for 2009[a]
CFC-11	7.8	4–11.6	10.0	8.4–11.7	12.9	11 (9–15)	–	33 (26–43)	74
CFC-12	7.1	3.9–10.2	7.2	6–8.4	3.1	6.1 (4.4–8.5)	–	14 (9–19)	63
CFC-113	3.2	1.8–4.5	0.2	−0.3 to 0.6	0	3.2 (2.5–3.8)	–	0.8 (0.4–1.7)	5
CFC-114	0.0	−0.2 to 0.2	0.0	−0.1 to 0.1	–	1.3 (0.9–1.8)	–	–	–
HCFC-22	81.8	46.2–117.5	87.6[b]	77.2–98.0[b]	90.6	83 (64–109)	65.3 ± 6.6	165 (140–213)	420
HCFC-141b	17.0	10.9–23.1	8.6	7–10.2	14.1	15 (11–21)	12.1 ± 1.6	–	58
HCFC-142b	7.5	3.3–11.7	10.3	8.6–12	–	9 (6.9–13)	7.3 ± 0.7	12 (10–18)	48
HFC-134a	6.4	3.4–9.3	5.7	4.7–6.7	16.1[c]	8.3 (6.2–11)	12.9 ± 1.7	–	180

[a] Global top–down emissions for 2009 are estimated from the global emissions for 2008 and the annual growth rate, derived from Keller et al. (2012) and Montzka et al. (2011). Global emissions of CFC-113 are taken from Vollmer et al. (2009) for 2007.
[b] See Section 2.2.
[c] Emissions of HFC-134a from mobile air conditioners (MACs) for 2010 under the combined scenario (HFC-134a is primarily used in MACs in China) (Wan et al., 2010).
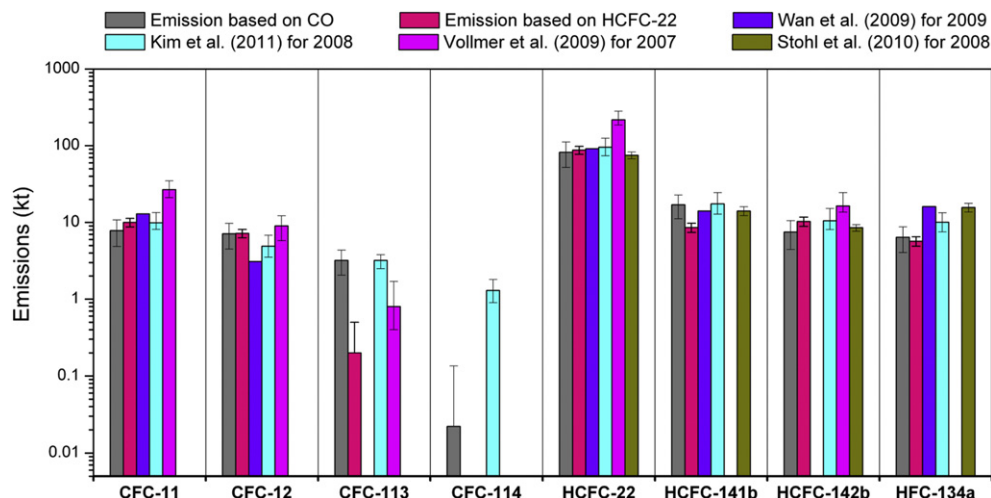
Fig. 2. Chinese emissions found by this study for 2009 and by other studies for 2007 or 2008 (in Table 2). The 2007 or 2008 emissions were extrapolated to 2009 by applying the estimated annual rates of change of these halocarbon emissions in China. The annual rates of change of the CFC-11, CFC-12, HCFC-22 and HCFC-141b emissions (for 2007–2009) were derived from Wan et al. (2009). These values were -10.0%, -19.8%, 15.0% and 16.7%, respectively. The annual rate of change of the HFC-134a emissions (for 2005–2006), 21.4%, was derived from Stohl et al. (2009). No information on the rates of change can be found for the HCFC-142b, CFC-113 and CFC-114 emissions for China. We assumed that the rate of change of HCFC-142b emissions was the same as that of HCFC-141b emissions and that the emissions of CFC-113 and CFC-114 remained the same. Note that the Y-axis is on a logarithmic scale.

Note that our estimates of HFC-134a emissions, as well as the estimates using ratio method by Li et al. (2011), are lower than the bottom–up estimates and inverse modeling estimates. Our suggested explanation is that HFC-134a emission sources (within urban areas and between cities) are more widely distributed than HCFC-22 emission sources (commonly within urban areas). Compared with CFC-11, CFC-12 and HCFC-142b, HFC-134a presented a lower Pearson correlation coefficient with HCFC-22 (Table 1), which suggests that HFC-134a emission sources are relatively not well co-located with HCFC-22 emission sources. The wider distribution of HFC-134a emission sources may lead to quicker dispersion of HFC-134a than HCFC-22 during the pollution episode, which may result in lower slopes than expected between HFC-134a and HCFC-22 at the receptor. But further quantitative studies are needed.

3.3. Global perspective on Chinese halocarbon emissions

To explore the contribution of Chinese emissions to global totals, the fractions of total global emissions represented by Chinese emissions were calculated (shown in Fig. 3 for 2009). The largest values of these fractions were found for HCFC-22, HCFC-141b and HCFC-142b, all approximately 20%. These results are consistent with the fractions of 17% for HCFC-22, 22% for HCFC-141b and 17% for HCFC-142b reported for 2008 (Stohl et al., 2010). The next highest fractions of global emissions were found for CFC-11 and CFC-12, approximately 10%. The smallest fraction was found for HFC-134a, less than 5%. This ranking agrees with the patterns of current Chinese halocarbon consumption. With the exception of certain exemptions, the production and consumption of CFCs in China have been banned since 2007 (Wan et al., 2009). The emissions of CFCs only reflect the presence of banks containing these species. These measures have produced a decrease in CFC emissions. HCFCs play the dominant role in China's current halocarbon consumption (Li et al., 2011; Wan et al., 2009). According to the statistical data furnished by the United Nations Environment Programme, China's consumption of HCFCs represents approximately one-half of global HCFC consumption (UNEP, 2011). HFCs were recently introduced to China, and the magnitude of HFC consumption is much smaller than that of HCFCs.

The total ODP-weighted or GWP-weighted emissions are calculated by summing the emissions of each species multiplied by their corresponding ODP values (UNEP, 2009) or GWP values (100-year time horizon, IPCC (2007)), respectively. In terms of ODP, the halocarbon emissions for 2009 are estimated to be 24.3 (13.3–35.3) kt and 23.8 (19.7–27.9) kt, based on CO and HCFC-22 reference tracers, respectively. These values represent 14.0 (7.7–20.3)% and 13.7 (11.4–16.1)% of the total global emissions. In terms of GWP, the combined halocarbon emissions from China for 2009 are 312.3 (171.2–452.5) Mt and 319.6 (271.5–368.0) Mt, based on CO and HCFC-22, respectively. These values represent approximately 14.1 (7.7–20.5)% and 14.5 (12.3–16.7)% of the total global emissions. These values are lower than the fractions for 2008 estimated by Kim et al. (2010), 19 (14–27)% in terms of ODP and 20 (15–26)% in terms of GWP. Note that the target species were not the same in these two studies. One reason for the discrepancies in the ODP-weighted emission is that the previous study included CCl_4 emissions of 15 kt a^{-1} for China in 2008 (representing approximately 35% of the total emissions of Chinese ODSs in terms of ODP and 28% of the global total emissions of CCl_4
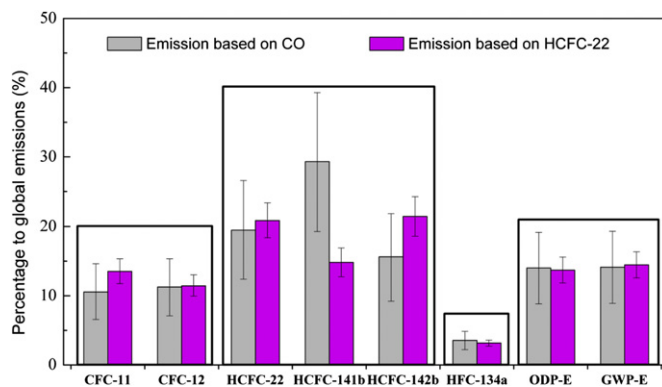

Fig. 3. Chinese anthropogenic halocarbon emissions estimated with two approaches in this study, expressed as a percentage of the global totals. Values of global totals for 2009 are given in Table 2. "ODP-E" and "GWP-E" represent the combined ODP-weighted and GWP-weighted emissions for these halocarbons, respectively.

calculated from Kim et al. (2010)), whereas the current study only includes CFCs, HCFCs and HFCs. Another reason for the discrepancies in the ODP-weighted emission is that the halocarbon emissions changed from 2008 to 2009. For example, the CFC-11 emissions for 2009 estimated by this study are approximately 3 kt lower than the 2008 values in Kim et al. (2010). The reason for the discrepancies between the studies in the fractions calculated in terms of GWP may be that emissions of other HFCs (in addition to HFC-134a), PFCs and SF_6 from China were not included in our estimates, whereas Chinese emissions of these compounds constituted large proportions of the global totals (89%, 26% and 19% for HFC-23, CF_4 and SF_6, respectively, calculated from Kim et al. (2010)). Therefore, a reasonable range of values for the combined Chinese halocarbon emissions, expressed as a fraction of the global totals, would be 10–20% in terms of either ODP or GWP. This result suggests that the emissions of halocarbons from China contribute significantly to the global totals.

3.4. Trends in Chinese halocarbon emissions

Trends in Chinese anthropogenic halocarbon emissions (2001–2009), estimated in different studies (all using top–down approaches), are shown in Fig. 4. The plots show that the emissions of CFC-12 have declined by approximately 75% since 2001. This declining trend is consistent with the bottom–up estimate (Wan et al., 2009). Surprisingly, the emission pattern for CFC-11 shows an inverted V shape. A possible reason for this result is that the emissions of CFC-11 for 2007 derived from Vollmer et al. (2009) were overestimated. A previous study shows that the peak year for CFC-11 emissions in China was 1999 and that the emissions of this species have decreased gradually since then (Wan et al., 2009). For this reason, the CFC-11 emissions from China should show a decline during 2001–2009.

However, top–down estimates of the annual HCFC emissions from China are limited, especially for the years in which the widespread use of HCFCs in China began. The changes in these annual emissions can only be plotted for recent years because the data are only available for those years (Li et al. (2011) and Stohl et al. (2010) for 2008, Vollmer et al. (2009) for 2007, Stohl et al. (2009) for 2006 and 2005, Yokouchi et al. (2006) for 2005) (Fig. 4). The emissions of HCFC-22, the major HCFC in China, increased from 52 (18–86) kt in 2005 to 70.7 kt in 2006 and 83 (64–109) kt in 2008, whereas the emissions of HCFC-141b increased from 15.0 (11–21) kt in 2008 (derived from Li et al. (2011); the emission value of the same year derived from Stohl et al. (2010) is smaller, 12.1 ± 1.6 kt) to 17.0 (11.2–22.8) kt in 2009 (CO-based estimates, this study). These results show that the emissions of HCFC-22 and HCFC-141b increased during these years. The trend in the annual emissions of HCFC-142b appears to be downwards. However, it is possible that this trend results from the overestimation of the value for 2007 by Vollmer et al. (2009), discussed above. In summary, all the studies using top–down approaches suggest that an increase in HCFC emissions has accompanied the decrease in CFC emissions in China.

The patterns of the discrepancies between consumption and emissions are different for CFCs and HCFCs in China. The trends in the ODP-weighted emissions of CFCs and HCFCs were presented in Fig. 4 in conjunction with the consumption data reported to UNEP (UNEP, 2011). Previous studies show that CFC-11, CFC-12 and CFC-113 represented more than 99% of all CFCs consumed in China (Wan et al., 2009). For this reason, only these three species were used in this study's calculations of the total ODP-weighted emissions of CFCs. The plots in Fig. 4 show a decrease in both the combined consumption and the emissions of CFCs in terms of ODP. Moreover, the estimated emissions are
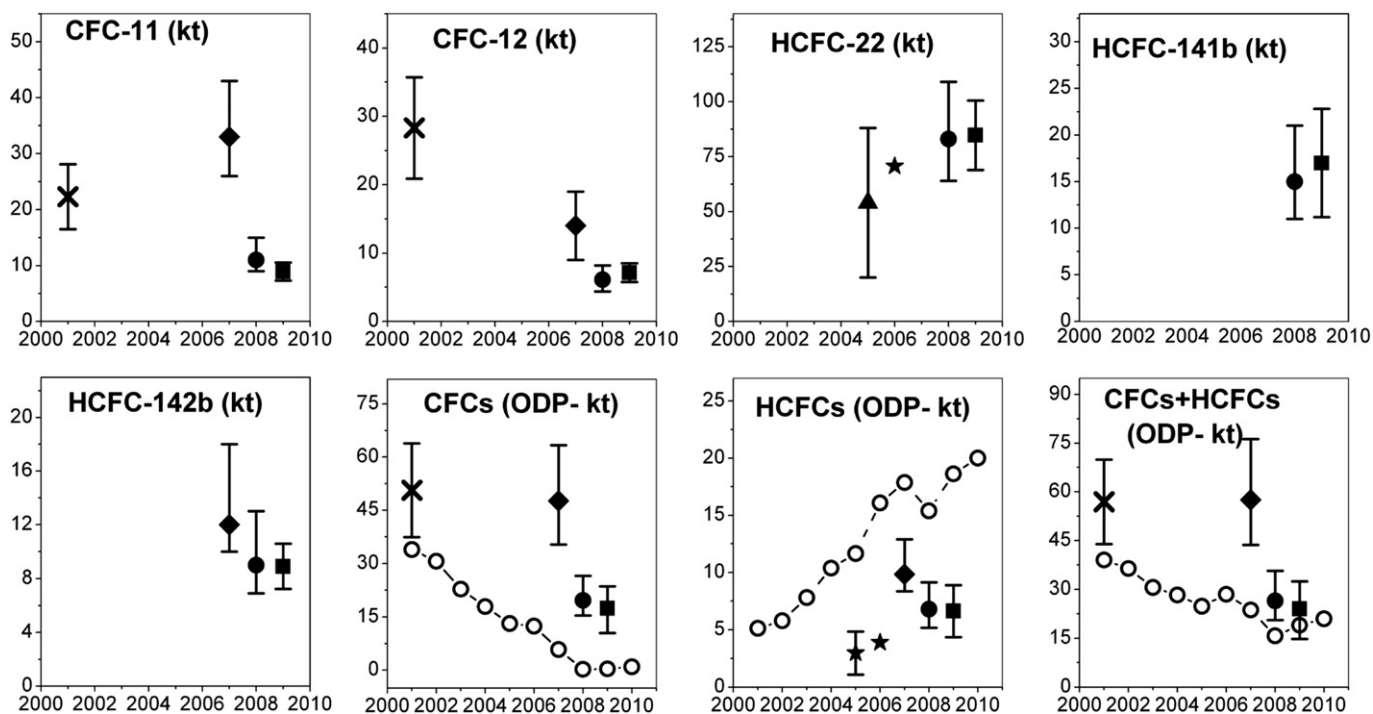

Fig. 4. Trends in Chinese anthropogenic halocarbon emissions (kt) estimated by different studies using top–down approaches. The emission values for 2009 are derived in this study as an average of the results of the two tracer methods (solid squares, except for the HCFC-141b emissions determined with the CO tracer). The values are obtained from Li et al. (2011) (solid circles) for 2008, from Vollmer et al. (2009) (solid diamonds) for 2007, from Stohl et al. (2009) for 2006 (solid pentagrams, only HCFC-22), from Yokouchi et al. (2006) for 2005 (solid triangles, only HCFC-22) and from Palmer et al. (2003b) for 2001 (solid crosses). The consumption data reported to UNEP (UNEP, 2011) were also plotted (hollow circles).

much greater than the reported consumption. This result shows that the CFCs in China are emitted primarily from the banks in which they occur and that these banks will diminish gradually due to the annual emissions. However, because of the critical or essential uses and laboratory analytical uses of CFCs in China after 2007, hundreds of metric tons of CFCs are annually consumed (FECO, 2012; UNEP, 2011), contributing a small part of the current emissions. Unlike the emissions of CFCs, the combined ODP-weighted emissions of HCFCs are not more than one-half of the reported consumption of HCFCs. This result suggests that HCFCs in China are accumulating in banking time usage, in agreement with previous findings (Li et al., 2011; Stohl et al., 2010).

The decrease in the ODP-weighted emissions of CFCs was partly offset by the increase in HCFCs in China. The emissions of CFCs and HCFCs were combined to calculate the total ODP-weighted emissions. The results show a decrease in the combined emissions of CFCs and HCFCs, declining from 54.5 (41.3–67.7) kt in 2001 to 24.5 (18.4–30.7) kt in 2009 (Fig. 4). Note that the total consumption has increased slightly since 2008. This increase will continue until the beginning of the HCFC phase-out in China. Although top–down estimates of other ODS emissions (such as CH_3Br, halons and CH_3CCl_3, whose emissions would decrease along with the phase-out process in China) are limited and were not included in this study, the combined ODP-weighted emissions of ODSs in China are believed to be decreasing.

4. Conclusions

In this study, a comparison between the correlations obtained from halocarbon/CO methodology and from halocarbon/HCFC-22 methodology was performed. The results of this comparison showed that most target species are significantly correlated with these two reference tracers ($P < 0.01$). According to these results, both HCFC-22 and CO are suitable reference tracers. HCFC-22 is preferable for use because HCFC-22 is more strongly correlated with the target species than CO. The comparisons between our estimated emissions for 2009 and other results estimated using bottom–up and top–down approaches (including interspecies correlation methods and inverse modeling methods) show that our estimated values agree with these results within uncertainties. This finding suggests that the approach based on interspecies correlations will be a useful method for assessing halocarbon emissions from certain areas.

The estimates of Chinese emissions, represented as a fraction of the global totals, show that HCFCs constitute the largest fractions (approximately 20%), followed by CFC-11 and CFC-12 (approximately 10%) and HFC-134a (approximately 5%). This result is consistent with the dominant role of HCFCs in the current patterns of Chinese halocarbon consumption. The time series of emissions for 2001–2009 estimated by different studies using top–down approaches show an evident decrease in CFC emissions and an accompanying increase in HCFC emissions. The combined ODP-weighted emissions of CFCs are much greater than the reported consumption. This finding shows that these species are primarily emitted from the banks in which they occur. However, the combined ODP-weighted emissions of HCFCs are not more than one-half of the reported consumption. This result suggests that HCFCs are accumulating in banks and that these banks will continue to grow in China. The emissions of CFCs and HCFCs were combined to calculate the total ODP-weighted emissions, and the results of this calculation show that the total emissions of CFCs and HCFCs, in terms of ODP, are decreasing in China, declining from 54.5 (41.3–67.7) kt in 2001 to 24.5 (18.4–30.7) kt in 2009.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2012.08.010.

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