Multiannual Top-Down Estimate of HFC-23 Emissions in East Asia

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Ⓢ *Supporting Information*

ABSTRACT: Trifluoromethane (CHF_3, HFC-23), with a 100-year global warming potential (GWP) of 12400, is regulated under the Kyoto Protocol. HFC-23 emissions in East Asia, especially in China, are currently thought to represent the majority of global HFC-23 emissions. This study provides both a bottom-up emission inventory and the multiannual top-down estimate of HFC-23 emissions in East Asia during 2007−2012. The new bottom-up inventory yields improved simulated HFC-23 mixing ratios compared to previous bottom-up inventories. The top-down estimate uses inverse modeling to further improve the model-measurement agreement. Results show that China contributed 94−98% of all HFC-23 emissions in East Asia. Annual a posteriori emissions from China were around 6.3 Gg/yr during the period 2007−2010 after which they increased to 7.1 ± 0.7 Gg/yr in 2011 and 8.8 ± 0.8 Gg/yr in 2012. For the first time, this study also provides a top-down estimate of HFC-23/HCFC-22 (chlorodifluoromethane, $CHClF_2$) coproduction ratios in non-CDM (Clean Development Mechanism) HCFC-22 production plants as well as in all HCFC-22 production plants in China.
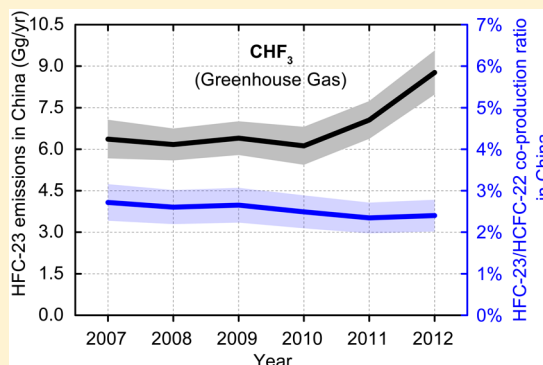
■ INTRODUCTION

Trifluoromethane (CHF_3, HFC-23) is a byproduct in the production of chlorodifluoromethane ($CHClF_2$, HCFC-22) which is widely used in air conditioning and refrigeration and also used as a feedstock in pentafluoroethane (CF_3CHF_2, HFC-125) production and fluoropolymer manufacture.[1−3] Current HCFC-22 production technology uses $CHCl_3$ and HF, creating HFC-23 as a byproduct when over fluorination occurs in the multistop fluorination process according to

$$CHCl_3 + 2HF \rightarrow CHClF_2 \ (HCFC\text{-}22) + 2HCl$$

Main reaction

$$CHClF_2 + HF \rightarrow CHF_3 \ (HFC\text{-}23) + HCl \quad \text{Side reaction}$$

HFC-23 generated from this side reaction is a waste gas that, without further measures, would be emitted to the atmosphere. HFC-23 is a potent greenhouse gas with a 100-year global warming potential (GWP) of 12,400.[4] Due to its long lifetime of 222 years and infrared-absorbing properties,[4] HFC-23 was included in the Kyoto Protocol,[5] under which the participating Annex I (mainly developed) countries are obligated to report their annual HFC-23 emission values to the United Nations Framework Convention on Climate Change (UNFCCC). In contrast, non-Annex I (mainly developing) countries have no obligations for emission reporting, and information regarding annual emissions from each non-Annex I country is therefore lacking. Previous studies showed that since about 2001 developing countries emit more HFC-23 than developed countries due to a substantial increase in HCFC-22 production since the 1990s.[6] With respect to global climate policies, HFC-23 emissions are currently of great concern for policymakers and researchers, since the global HFC-23 emissions were estimated to 128 Tg/yr CO_2-equivalent and contributed 22% to total HFC CO_2-equivalent emissions in 2010 calculated from estimates by Rigby et al.[7]

China is assumed to be the largest HFC-23 emitter in the world.[1] Some bottom-up and top-down estimates of HFC-23 emissions are available for China and other East Asia (except for Japan, all other East Asian countries belong to the non-Annex I category); however, these studies are insufficient in many aspects. First, compared to the two or three decades typically covered in the bottom-up studies,[1,8,9] all published

top-down studies[10−14] only report emission estimates for ca. one year (e.g., November-2007 to December-2008 in Li et al.[11]). Second, some inconsistencies are found among the top-down estimates and bottom-up estimates. For example, some top-down estimates[11−13] are on par with the bottom-up estimate[1] only when taking into account the large uncertainties of these estimates, while others reported emissions that were much lower.[14] In addition, many of the previously reported emissions utilize the tracer ratio method with relatively large uncertainties, such that validation of the relatively small changes in the long term bottom-up may prove difficult. The uncertainties in the inverse method, when implemented correctly, are generally considered lower and could be more useful for this purpose.

Stohl et al. is the only study on HFC-23 emissions in East Asia using the method of inverse modeling.[13] One significant shortcoming of the HFC-23 emission inversions in that study was the a priori HFC-23 emissions used. Those a priori emissions were for the year 2005 (information for 2008 was not available at that time); however, the target year of that inversion study was 2008.[13,15] Moreover, those a priori emissions were geographically widely distributed over most of China,[13,15] while in reality HFC-23 is emitted mainly from tens of HCFC-22 plants. Thus, this study aims to improve the inversions by compiling a priori estimates of HFC-23 emissions from each plant.

Many production facilities today participate in UNFCCC CDM (Clean Development Mechanism) projects under which, beginning in 2003, certain facilities in developing countries were eligible to produce Certified Emission Reduction credits for the destruction of their coproduced HFC-23. While detailed statistics of production information are known for the CDM facilities, this is not the case for non-CDM plants. In particular, the coproduction ratio of HFC-23/HCFC-22, which is crucial for bottom-up HFC-23 emission inventorying, is not available for the non-CDM plants. For example, a recent study of Fang et al. used coproduction ratios of HFC-23/HCFC-22 from CDM production lines in China to estimate HFC-23 emissions from non-CDM plants in China.[1] Another example is that Miller et al. used HFC-23/HCFC-22 coproduction ratios from CDM production lines to estimate global HFC-23 emissions even though these include emissions from non-CDM plants.[6] Using the inversion results of HFC-23 emissions over 6 years and annual HCFC-22 production information, this study provides the first top-down estimate of HFC-23/HCFC-22 coproduction ratios in non-CDM plants in China.

■ METHODOLOGY

Measurement Data. Measurement data from three stations are used in this study: 1) Gosan (126.17°E, 33.28°N), located on Jeju Island south of the Korean peninsula, 2) Hateruma (123.81°E, 24.06°N), situated on a small island at the southwestern edge of the Japanese archipelago, and 3) Cape Ochi-ishi (145.50°E, 43.16°N), at the eastern coast of Hokkaido, at the base of Nemuro peninsula, Japan. Measurement data from the periods 11/2007−12/2012, 01/2007−12/2012, and 01/2007−12/2012 for the three stations, respectively, were used in this study. At Gosan, ambient mixing ratios of HFC-23 are measured every 2 h using a cryogenic preconcentration gas chromatography−mass spectrometry (GC-MS) "Medusa" system,[9,15] and at Hateruma and Cape Ochi-shi stations, HFC-23 mixing ratios are measured once per hour using a different technique that also couples a GC-MS

system with cryogenic preconcentration.[12,16] The measurements at Gosan are reported on the SIO-2007 calibration scale, while the measurements at the other two stations are reported on the NIES-2008 calibration scale. An intercomparison experiment between the two scales yielded a NIES-2008/SIO-2005 ratio of 0.995 ± 0.01. For the sake of consistency, we used this value to convert all NIES data from the NIES-2008 to the SIO-2007 calibration scale prior to the inverse modeling.

Lagrangian Backward Modeling. The Lagrangian particle dispersion model FLEXPART v-9.02[17,18] (http://www.flexpart.eu) was used to establish source-receptor relationships (SRR, often also called "emission sensitivities"), which are defined as the time that the particles reside in the surface grid cell, divided by the air density. We are interested only in the SRR involving the lowest model layer ("footprint" layer), as the HFC-23 emissions occur close to the ground. The model was driven by 2007−2012 operational 3-hly meteorological data of $1° \times 1°$ horizontal resolution and 91 vertical levels from the European Centre for Medium-Range Weather Forecasts (ECMWF). 10,000 particles were released every 3 h at the inlet altitude above model ground at each station and tracked 20 days backward in time.

Bayesian Inversion. The Bayesian inversion method used is almost the same as described and evaluated by Stohl et al.[13,19] and as used in a recent study of SF_6 emissions in East Asia by Fang et al.[20] Briefly, the Bayesian inversion method builds on least-squares optimization and aims at minimizing both the differences between observed and modeled mixing ratios and the deviation of retrieved emissions from an a priori emission field. The a priori mixing ratio baseline is derived from that parts of observed mixing ratios minus simulated mixing ratios, and the baseline values are unknowns in the inversion algorithm.[13,19] In this study, the a priori baseline uncertainty was determined by the range of a priori baselines when several very different a priori emission fields were used.

The a priori emissions are particularly critical for the inverse modeling of HFC-23 because its emissions originate mainly from a small number (tens) of HCFC-22 plants without abatement measures, whereas widespread applications (such as fire extinguishing agents) contribute minimally to the emissions. This is very different from the distribution of most other halocarbons, where emissions occur in wide regions where these species are consumed. A priori values for HFC-23 emissions in East Asian countries were collected from several sources. Values for Japan were taken from Japan's National Inventory Report submitted to UNFCCC.[21] Values for North Korea were estimated from annual HCFC-22 production information reported in a project proposal,[22] an assumed value of HFC-23/HCFC-22 coproduction of 3.0% (by mass, hereafter),[23] and zero sales of HFC-23. Values for South Korea were estimated from CDM reports submitted by a HCFC-22 plant in Ulsan, South Korea,[24] and South Korea's National Greenhouse Gas Inventory Report.[25] Values for Taiwan were derived from Emission Database for Global Atmospheric Research (EDGAR) v4.2.[15] For point emissions in China, HCFC-22 production information for each plant was collected in this study, and HFC-23 emissions were estimated using annual HFC-23/HCFC-22 coproduction ratios estimated by Fang et al.[1] For the relatively minor area emissions (referring to widespread emissions from consumption) in China, information on sales of HFC-23 (estimated in this study to be ca. several hundreds Mg) were used. All the national a priori emissions in East Asia used in our study are listed in Table S1.
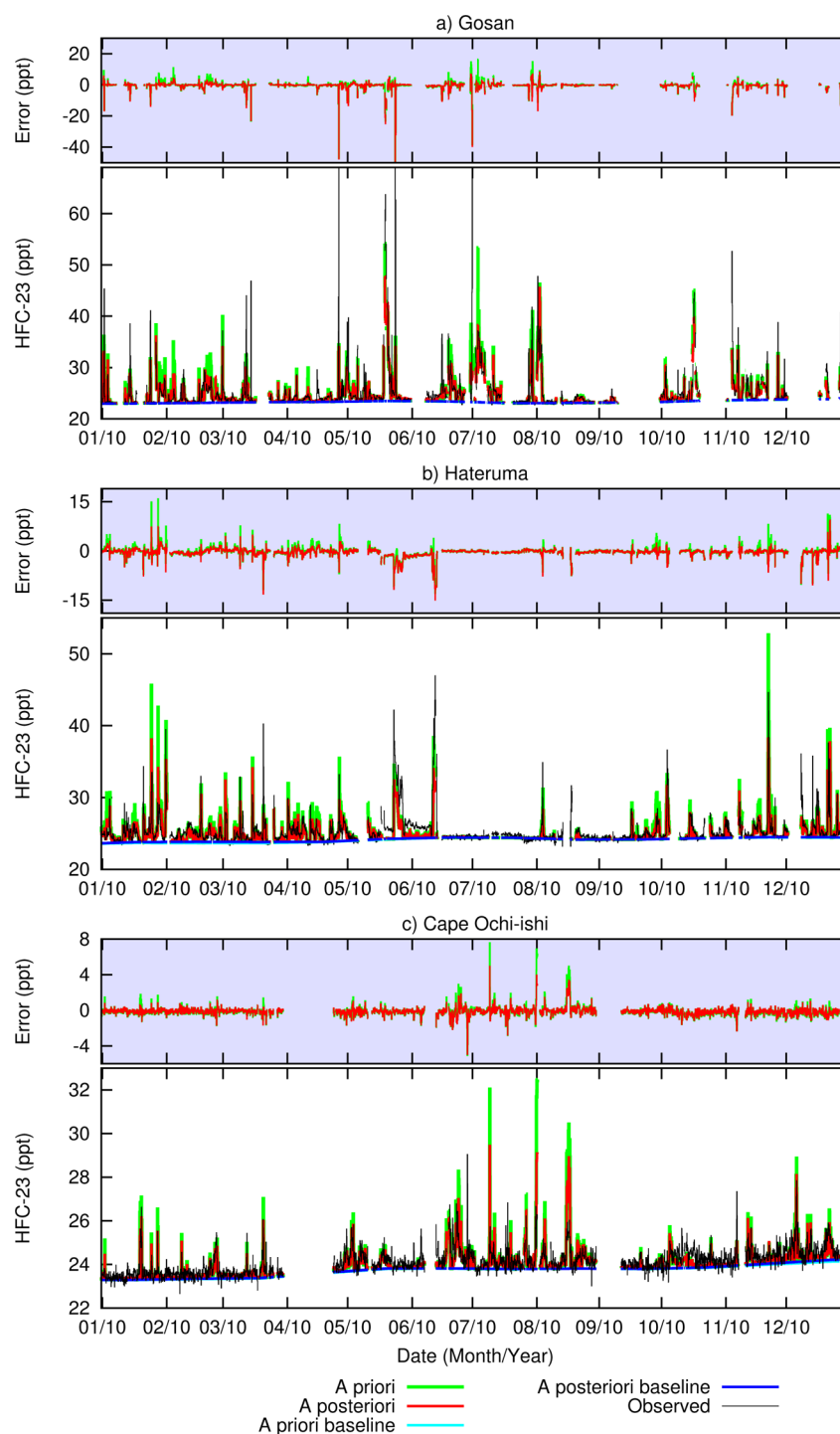
Figure 1. Observed and simulated HFC-23 mixing ratios at Gosan (top), Hateruma (middle), and Cape Ochi-ishi (bottom) in the year 2010.

The a priori emission values for 2010 were used as an approximation for 2011 and 2012 emissions, since detailed HCFC-22 production information for each HCFC-22 plant in 2011 and 2012 is currently not available. The emission inventory compiled for our study will hereafter be referred as the PKU-GHG inventory.

HFC-23 point emissions were assigned to both the grid box containing the respective plants and the neighboring four boxes weighted by distances to the center of each box (in principle, it would be best to only assign them to one grid box but transport model errors could make such a discrete distribution

problematic for the purpose of inverse modeling). The area emissions in the East Asian countries and emissions in all other countries (derived from UNFCCC database[26] and global emissions[6]) were disaggregated according to the population density.[27] The emission uncertainties in factory-containing grid boxes are large because of the strong point emissions there. The emission uncertainties in nonfactory-containing grid boxes were set according to their distance from factory-containing boxes using eq 1. The reason for choosing such a smooth decrease of the uncertainty from factory-containing grid boxes is to give the inversion some flexibility in terms of the location of the point

source, which may not always be captured accurately because of transport model errors. A posteriori uncertainty of the emissions in each grid box was calculated as described by Seibert et al.[28]

$$\sigma_{priori}^{j} = \max(p*E_{priori}^{j}, \sigma_{priori}^{1}*e^{(-\frac{d(j,1)}{L})}, \sigma_{priori}^{2}$$
$$*e^{(-\frac{d(j,2)}{L})}, ..., \sigma_{priori}^{i}*e^{(-\frac{d(j,i)}{L})}, ...\sigma_{priori}^{n}*e^{(-\frac{d(j,n)}{L})})$$

(1)

Here σ_{priori}^{j} is the a priori emission uncertainty in nonfactory-containing grid box j, E_{priori}^{j} is the a priori emission assigned to nonfactory-containing grid box j, p is the scaling factor of 120% used in this study, $d(i,j)$ is the midpoint distance of box j from the factory-containing box i, n is the number of HCFC-22 plants in East Asia, and L is the spatial decorrelation length scale of 40 km used in this study, determined from various tests.

■ RESULTS

Inversions with Improved a Priori Field. Table S2 shows a statistical comparison of the performance of simulations of HFC-23 mixing ratios at Hateruma and Gosan stations using the EDGAR v4.0 emission inventory for 2005 used in Stohl et al.,[13] the EDAGR v4.2 emission inventory for 2008, and the PKU-GHG emission inventory for 2008 compiled in this study, respectively (see maps in Figure S1). The EDGAR v4.2 is the latest emission inventory available in the EDGAR database.[15] The simulated mixing ratios were obtained from the gridded a priori emissions multiplied by the gridded FLEXPART-derived emission sensitivities. Results show that compared to EDGAR v4.0 and EDGAR v4.2, using the PKU-GHG inventory resulted in simulated mixing ratios with smaller mean bias (B_a), smaller root-mean-square error (RMSE, E_a) and higher Pearson correlation values (r_a^2) at both stations. For example, for Gosan, B_a values are 0.650, 0.898, and 0.166 ppt for the three inventories, and for Hateruma, B_a values are 0.561, 0.253, and 0.227 ppt, respectively, indicating substantial improvement of the emission distribution with the PKU-GHG inventory compiled in this study. A paired sample t test revealed that the simulated mixing ratios using PKU-GHG inventory are significantly closer to the observed mixing ratios than the simulated mixing ratios using EDGAR v4.0 emission inventory or EDGAR v4.2 emission inventory ($P < 0.01$).

Based on these results, annual PKU-GHG inventory estimates for the period 2007−2012 were used as the a priori information for the inverse modeling of HFC-23. Figure 1 shows the observed and simulated HFC-23 mixing ratios at Gosan, Hateruma, and Cape Ochi-ishi for the year 2010 as an example. The simulation captured most pollution episodes very well compared to the observations, but the mixing ratios simulated using the a priori emission inventory are higher than the measurements in some pollution events (see Figure 1). The simulation using a posteriori emissions obtained from the inversion fits better with the observed mixing ratios than the one using a priori emissions. For example, Pearson correlation values between the simulated and observed mixing ratios in 2010 increased from 0.50, 0.47, and 0.42 (r_a^2) to 0.54, 0.52, and 0.49 (r_b^2) for Hateruma, Gosan, and Cape Ochi-ishi, respectively.

Figure 2 shows maps of the HFC-23 a priori emissions, a posteriori emissions, and emission uncertainty reduction in 2010. The a priori and a posteriori emission maps show that the biggest emission sources are located in eastern China and
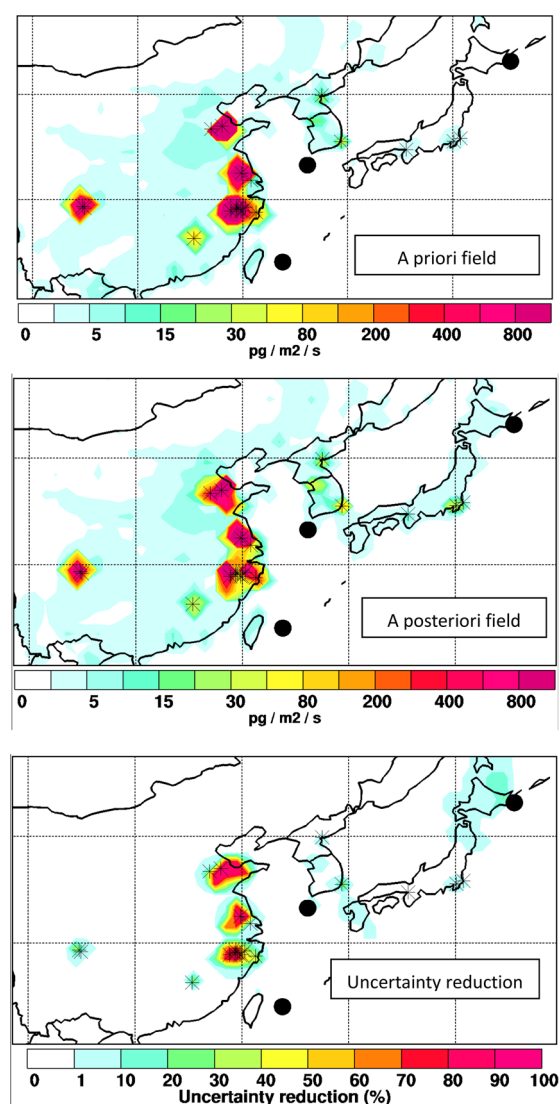

Figure 2. Maps of HFC-23 a priori emissions (top), a posteriori emissions (middle), and gridded emission uncertainty reduction (bottom) in 2010. Measurement stations are marked with black dots.

middle-western China (Sichuan Province) and that only minimal emission sources exist in other East Asian countries. The uncertainty reduction map shows significant error reductions of 70% or more in boxes containing HCFC-22 production plants with high HFC-23 emissions as well as high absolute HFC-23 emission uncertainties. Almost no error reduction was achieved in most of the low-emission areas.

National a Posteriori Emissions in Countries Other than China. Table 1 presents the annual a posteriori emissions for each East Asian country during the period 2007−2012. We got similar national a posteriori emissions using $1° \times 1°$ 6-hly National Center for Environmental Prediction (NCEP) Final (FNL) Operational Model Global Tropospheric Analyses data (http://rda.ucar.edu/datasets/ds083.2/) (see Supporting Information text and Table S3). Sensitivity tests of inversion results to different magnitudes of a priori emissions showed that a posteriori emissions for China in 2010 varied by only ∼6%, while the a priori emissions for China varied by 50%, and a posteriori emissions for other East Asian countries were similar in different inversions, which suggests that a posteriori emissions for China and other countries are not strongly

Table 1. National a Posteriori HFC-23 Emissions (Gg/yr) for East Asian Countries during the Period 2007−2012

|	2007	2008	2009	2010	2011	2012
Mongolia	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
China	6.4 ± 0.7	6.2 ± 0.6	6.4 ± 0.6	6.1 ± 0.7	7.1 ± 0.7	8.8 ± 0.8
Taiwan	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
North Korea	0.01 ± 0.00	0.04 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
South Korea	0.06 ± 0.01	0.11 ± 0.01	0.09 ± 0.01	0.08 ± 0.01	0.09 ± 0.01	0.10 ± 0.01
Japan	0.12 ± 0.02	0.23 ± 0.02	0.05 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	0.08 ± 0.01
East Asia	6.6 ± 0.7	6.6 ± 0.6	6.6 ± 0.6	6.3 ± 0.7	7.3 ± 0.7	9.0 ± 0.8
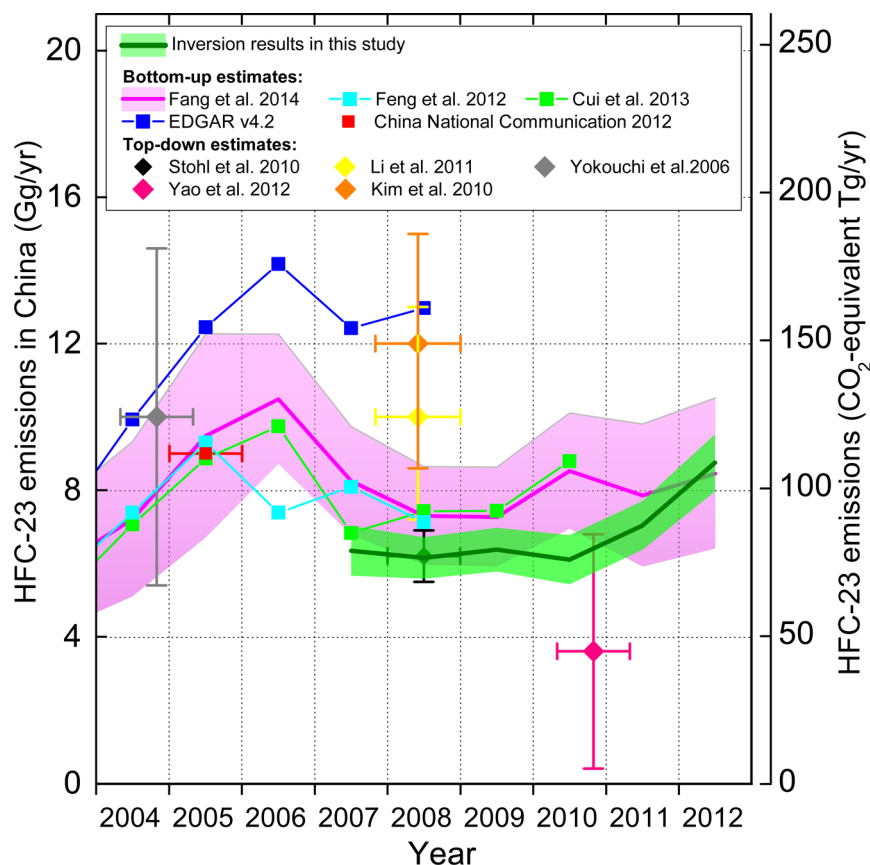
Figure 3. Comparison with other published estimates of HFC-23 emissions in China, as specified in the legend at the top. X-error bar in the plot represents the span of the target period in the respective study, for example, 14 months of Nov-2007−Dec-2008 in Li et al.[11] or 12 months of Jan-2008−Dec-2008 in Stohl et al.[13]

influenced by a priori emissions (see Supporting Information text).

For Mongolia and Taiwan, national a posteriori emissions were estimated to be about 0.01 Gg/yr or less for all 6 years, which are negligible compared to the emissions in other countries. For North Korea, in 2007, the estimated emissions were 0.01 ± 0.00 Gg/yr, which is consistent with the fact that due to a fire, there was no production of HCFC-22 in 2007.[22] Since 2008, a posteriori HFC-23 emissions have ranged between 0.02 and 0.04 Gg/yr which is consistent with the reported HCFC-22 production of 0.5 Gg/yr[22] and a possible HFC-23/HCFC-22 coproduction ratio of 4%.[23] For South Korea, national total emissions in 2007−2012 were relatively constant at 0.06−0.11 Gg/yr.

For Japan, national a posteriori emissions were 0.12 ± 0.02 Gg/yr in 2007 and 0.23 ± 0.02 Gg/yr in 2008, after which the emissions dropped to ca. 0.05−0.08 Gg/yr. National a posteriori emissions for Japan were larger than the reported

emissions in Japan's National Inventory Reports (NIRs).[29] According to Japan's NIRs, Japanese HFC-23 emissions decreased because all manufacturing facilities were equipped with recovery/destruction units in 2004, and since 2009 emissions have become even smaller due to efforts made in improving the management and maintenance of the destruction facilities.[29] This reduction step in 2009 is consistent with our findings.

National a Posteriori Emissions in China. Table 1 shows that China contributed 94−98% of all HFC-23 emissions in East Asia. Annual a posteriori emissions from China did not change much during the period 2007−2010, being 6.4 ± 0.7 Gg/yr, 6.2 ± 0.6 Gg/yr, 6.4 ± 0.6 Gg/yr, and 6.1 ± 0.7 Gg/yr, respectively, after which they increased to 7.1 ± 0.7 Gg/yr in 2011 and 8.8 ± 0.8 Gg/yr in 2012. Considering the increasing amount of incinerated HFC-23 in 2007−2010,[1] the constant emissions imply that the actually produced HFC-23 must have
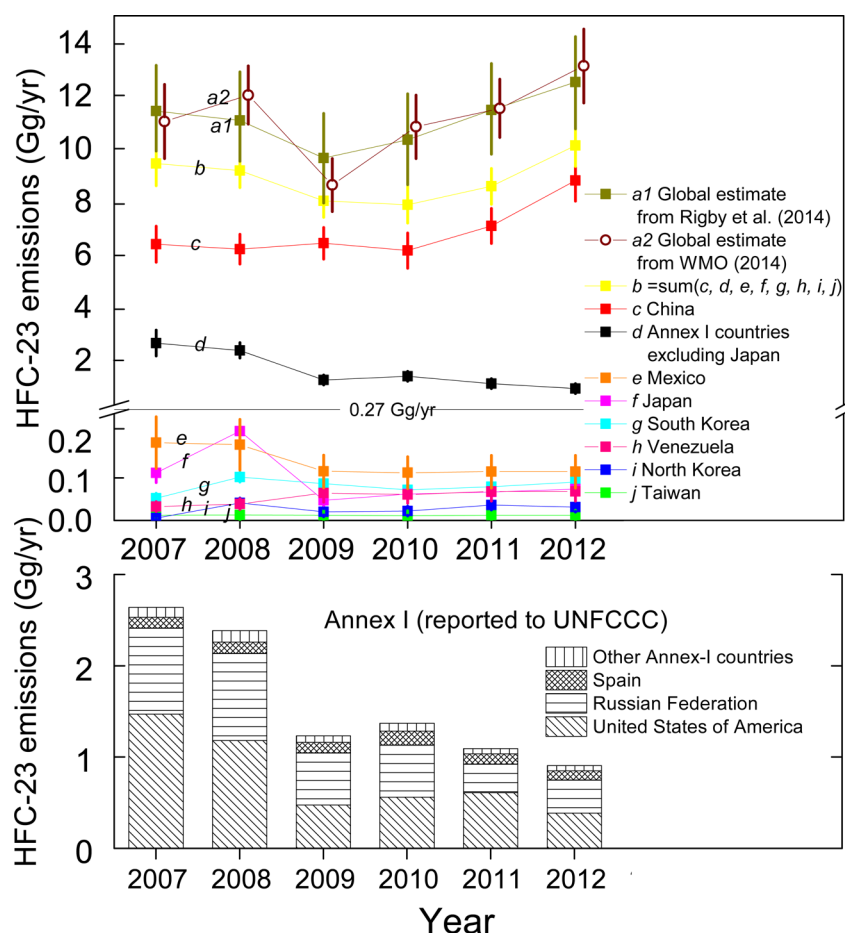
Figure 4. Global emission estimates from Rigby et al. (2014) and from WMO (2014), Annex I countries' bottom-up estimates, East Asian countries' inversion results and estimates of emissions in Mexico and Venezuela (upper panel), and emissions in Annex I countries reported to UNFCCC (bottom panel).

increased gradually in 2007−2010, which is consistent with the increasing HCFC-22 production estimated in Fang et al.[1]

A comparison of our results with other published estimates for HFC-23 emissions in China is shown in Figure 3. The comparison shows that EDGAR v4.2 estimates for China after 2004 are larger than all other estimates. Indeed, EDGAR emissions are likely too large since they reach or even exceed the top-down estimated global emissions. The bottom-up estimates in previous studies[8,9] and Second National Communication from China to UNFCCC[30] agree relatively well with each other since they were derived from similar input, though there are some differences in HCFC-22 production and coproduction ratios of HFC-23/HCFC-22 and HFC-23 incineration. Our inversion results are lower than these bottom-up estimates and lower than the latest bottom-up estimate by Fang et al.[1] for the years 2007−2011. However, this is not very surprising, because Fang et al.[1] based their estimates on HFC-23/HCFC-22 coproduction ratios obtained from CDM facilities that started HCFC-22 production before 2002. They have also used this coproduction ratio for newer plants for which no information was available. However, newer plants may well have lower HFC-23/HCFC-22 coproduction ratios, leading to lower emissions. Our inversion results agree well with the only other inversion study,[13] which is not surprising given methodological similarities. Some differences are found when compared to other top-down estimates based on the tracer ratio method.[10,11,14] Our inversion results meet within

the high uncertainty range of the estimate based on measurements at Shangdianzi Station,[14] while our inversion results are lower than that the estimates based on measurements at Gosan station.[10,11]

Figure 4 shows global HFC-23 emission estimates using the top-down inversion approach,[7,31] emission estimates for Annex I countries from National Inventory Reports to UNFCCC,[26] inversion results for the East Asian countries from this study, and estimates of emissions in Venezuela and Mexico from this study (see details in the Supporting Information). The uncertainties of emissions reported by Annex I countries were derived from the reported uncertainties in the annual National Inventory Reports.[32] Figure 4 shows that China is responsible for more than half of global HFC-23 emissions. Although there are some differences between the global HFC-23 emission estimates by Rigby et al.[7] and by WMO,[31] both estimates show a similar trend for global HFC-23 emissions. The sum of estimated emission values for the countries in Figure 4 and different years is 1.6−2.9 Gg/yr less than the corresponding best estimate of global emissions by Rigby et al.,[7] although the estimates of the two data sets agree within uncertainties. Of note is that not all countries in the world are included in Figure 4, so the sum of emissions from countries in Figure 4 does not account for all global emissions. A top-down estimate by Keller et al. found that HFC-23 emissions in Western European countries officially reported to UNFCCC were under-reported by 60−140% (0.05−0.13 Gg/yr) for July

Table 2. Calculated HFC-23/HCFC-22 Coproduction Ratios in HCFC-22 Production Plants in China

	2006	2007	2008	2009	2010	2011	2012
coproduction ratio in non-CDM plants[a]		2.58% ± 0.70%	2.42% ± 0.69%	2.49% ± 0.74%	2.21% ± 0.67%	2.03% ± 0.56%	2.14% ± 0.54%
coproduction ratio in CDM plants[b]	3.25% ± 0.22%	2.93% ± 0.25%	2.84% ± 0.43%	2.83% ± 0.46%	2.81% ± 0.48%	2.79% ± 0.45%	2.78% ± 0.45%
coproduction ratio in all plants		2.72% ± 0.44%	2.61% ± 0.41%	2.65% ± 0.42%	2.49% ± 0.40%	2.34% ± 0.37%	2.40% ± 0.38%
number of CDM projects[c]	4-	9-	10-	11-	11	11	11

[a]Some of the 11 CDM plants had not started CDM abatement projects during 2006−2009, thus "coproduction ratio in non-CDM plants" represents combined coproduction ratio in non-CDM plants and CDM plants that had not yet started CDM abatement projects during 2007−2009. For the period 2010−2012, "coproduction ratio in non-CDM plants" represents coproduction ratio in all non-CDM plants. [b]Some of the 11 CDM plants had not started CDM abatement projects during 2006−2009, thus "coproduction ratio in CDM plants" represents coproduction ratio in CDM plants that had started CDM abatement projects during 2006−2009. For the period 2010−2012, "coproduction ratio in non-CDM plants" represents coproduction ratio in all CDM plants. [c]"-" means that CDM abatement projects in HCFC-33 production plants may have not been in operation for the whole year since some projects were not launched on January 1 in the respective year.

2008−July 2010.[33] However, such top-down HFC-23 emissions estimates are not available for other Annex I countries including the three biggest reported contributors of HFC-23 emissions, U.S.A., Russia, and Spain (see Figure 4 bottom panel).[26] HCFC-22 production plants and HFC-23 emissions might also exist in countries other than those included in Figure 4. For example, there are several HCFC-22 production plants in India, and some of them have participated the CDM projects.[34] However, currently there is no detailed information available for these emissions in countries other than those included in Figure 4. In the absence of better bottom-up information, better regional top-down constraints are needed which, however, would require a denser observation network.

HFC-23/HCFC-22 Coproduction Ratio Derived from Inversion Results. There are in total 11 HFC-23 CDM projects in China.[1,35] Four CDM projects started in 2006, five in 2007, one in 2008, and a final project in 2009.[1,35] All plants that participated in the CDM projects started HCFC-22 production before 2002 as required by the CDM baseline methodology, so facilities and technologies in those plants are relatively old. On average, HFC-23/HCFC-22 coproduction ratios in the CDM production lines were estimated to decrease from 2.93% in 2007 to 2.78% in 2012.[1] The HFC-23/HCFC-22 coproduction ratios in non-CDM plants in Table 2 were calculated using the inversely determined HFC-23 emissions divided by the difference between national total HCFC-22 production and HCFC-22 production from CDM projects. This method assumes that a negligible amount of HFC-23 was emitted from CDM projects, thus the inversely determined HFC-23 emissions are equal to coproduced HFC-23 amounts in non-CDM plants. Table 2 shows the calculated HFC-23/HCFC-22 coproduction ratios in non-CDM plants since the year 2010 were about 2.1%, which is about 25% lower than corresponding values for CDM plants. A value of ∼2.1%, albeit low, is not unrealistic. For example, a HFC-23/HCFC-22 coproduction ratio of 1.37% was achieved by one of the largest facilities in the developed world.[36,37] HFC-23/HCFC-22 coproduction ratios for HCFC-22 production facilities in Japan were 2.01% in 2010, 1.53% in 2011, and 1.60% in 2012.[29] Furthermore, the HFC-23/HCFC-22 coproduction ratio in Changshu Haike Chemical Co., Ltd., one of the main HCFC-22 production plants in China and a CDM facility, was reported as about 1.64% on average, and in this plant the coproduction ratio even reached the lowest value of 1.11% during December 1, 2008 to April 30, 2009.[38] Possible reasons for the lower coproduction ratios in non-CDM plants

compared to CDM plants are as follows: 1) All CDM facilities in China came into operation before 2002, which is required by the CDM credit methodology. Most of the non-CDM facilities came into operation after 2002, and some were installed in 2006, 2007, and 2010. Thus, the facilities and the technology in non-CDM plants are probably more advanced than in the CDM facilities. 2) Since HFC-23 is a waste gas, non-CDM plant operators have great motivation to improve management to lower the HFC-23/HCFC-22 coproduction ratios over time to get less HFC-23 emissions and more HCFC-22 production.

For each year, we also calculated the HFC-23/HCFC-22 coproduction ratios in all HCFC-22 production plants in China by summing the inversely determined HFC-23 emissions and incinerated HFC-23 amounts and then dividing this sum by the total HCFC-22 production in China. Annual incinerated HFC-23 amounts were derived from the estimates in Fang et al.,[1] and annual total HCFC-22 production were estimated in this study. Table 2 shows the calculated HFC-23/HCFC-22 coproduction ratios in all HCFC-22 production plants were 2.72% ± 0.44% in 2007 with a decreasing trend to 2.40% ± 0.38% in 2012, due to more HCFC-22 production from non-CDM plants and relatively constant HCFC-22 production from CDM plants. To date, this is the first study estimating HFC-23/HCFC-22 coproduction ratios in non-CDM HCFC-22 plants as well as in all HCFC-22 plants in China.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Information of bottom-up estimation of HFC-23 emissions in Venezuela and Mexico is provided. Discussion on sensitivity of inversion results to the choice of meteorological data and a priori emissions is provided. The national a priori emissions in East Asia used in our study are shown in Table S1. Performance comparison of simulating HFC-23 mixing ratios using three a priori fields is presented in Table S2. National a posteriori emissions from inversions using different meteorological data are shown in Table S3. Maps of EDGAR v4.0 HFC-23 emission inventory for 2005, EDGAR v4.2 HFC-23 emission inventory for 2008, and the PKU-GHG emission inventory for 2008 are shown in Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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