Environmental Science & Technology

ARTICLE

pubs.acs.org/est

Emissions of Halogenated Compounds in East Asia Determined from Measurements at Jeju Island, Korea

Shanlan Li, Jooil Kim, and Kyung-Ryul Kim*

School of Earth and Environmental Sciences, and South Korea Research Institute of Oceanography, Seoul National University, Seoul, South Korea

Jens Mühle

Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, United States

Seung-Kyu Kim

School of Earth and Environmental Sciences (BK-21), Seoul National University, Seoul, South Korea

Mi-Kyung Park

School of Earth and Environmental Sciences, and South Korea Research Institute of Oceanography, Seoul National University, Seoul, South Korea

Andreas Stohl

Norwegian Institute for Air Research, Kjeller, Norway

Dong-Jin Kang

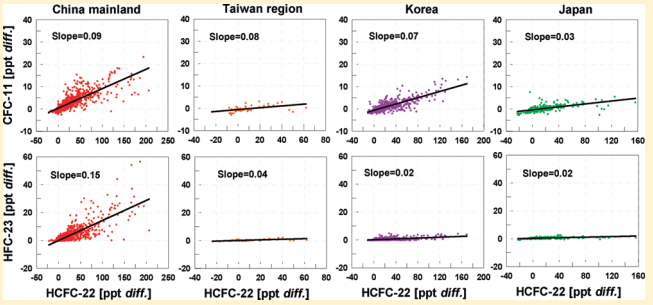
Korea Ocean Research and Development Institute, Seoul, South Korea

Tim Arnold, Christina M. Harth, Peter K. Salameh, and Ray F. Weiss

Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, United States

Supporting Information

ABSTRACT: High-frequency in situ measurements at Gosan (Jeju Island, Korea) during November 2007 to December 2008 have been combined with interspecies correlation analysis to estimate national emissions of halogenated compounds (HCs) in East Asia, including the chlorofluorocarbons (CFCs), halons, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6), and other chlorinated and brominated compounds. Our results suggest that overall China is the dominant emitter of HCs in East Asia, however significant emissions are also found in South Korea, Japan and Taiwan for HFC-134a, HFC-143a, C_2F_6, SF_6, CH_3CCl_3, and HFC-365mfc. The combined emissions of CFCs, halon-1211, HCFCs, HFCs, PFCs, and SF_6 from all four countries in 2008 are 25.3, 1.6, 135, 42.6, 3.6, and 2.0 kt/a, respectively. They account for approximately 15%, 26%, 29%, 16%, 32%, and 26.5% of global emissions, respectively. Our results show signs that Japan has successfully phased out CFCs and HCFCs in compliance with the Montreal Protocol (MP), Korea has started transitioning from HCFCs to HFCs, while China still significantly consumes HCFCs. Taiwan, while not directly regulated under the MP, is shown to have adapted the use of HFCs. Combined analysis of emission rates and the interspecies correlation matrix presented in this study proves to be a powerful tool for monitoring and diagnosing changes in consumption of HCs in East Asia.



Received: March 4, 2011
Accepted: May 26, 2011
Revised: May 19, 2011
Published: June 08, 2011

ACS Publications © 2011 American Chemical Society

INTRODUCTION

Many halogenated compounds (HCs) including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), bromine containing halocarbons (halons, CH_3Br), and long-lived chlorinated solvents (CCl_4, CH_3CCl_3) are regulated by the Montreal Protocol (MP) due to their role in the depletion of the stratospheric ozone layer.[1] Therefore, use of these anthropogenic ozone-depleting substances (ODSs) has generally been banned in non-Article 5 parties (mainly developed countries) since 1996 (2020 for HCFCs), but for the Article 5 parties (mainly developing countries) their continued use is generally permitted until their phase-out schedule is completed with a total ban by 2010 (2015 for CH_3CCl_3 and 2030 for HCFCs). Other HCs such as hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6) do not have direct impacts on stratospheric ozone but contribute to global warming. Hence, these compounds are regulated in developed countries under the Kyoto Protocol (KP) of the United Nations Framework Convention on Climate Change (UNFCCC). Global concentrations of CFCs in the atmosphere have stabilized or are declining as a result of compliance with the MP.[2] On the other hand, increased use of HCFCs and HFCs has led to a surge in their atmospheric concentrations.[3,4] HCFCs are interim replacement compounds for CFCs currently consumed mainly in developing countries. At present HFCs are dominantly consumed in developed countries as substitutes for both CFCs and HCFCs such as refrigerant blends (HFC-32, HFC-125, HFC-143a).[4]

Emissions of HCs in East Asia are of interest because they are expected to be a significant proportion of the global total[3] and also because these emissions will change as each country adapts differently to the MP and the KP. China and Korea are 'Article 5' countries in the MP and therefore have to complete the phase-out schedule of CFCs, halons, and CCl_4 by 2010, CH_3CCl_3 by 2015, and HCFCs by 2030. Japan is a "Non-Article 5" country and currently mandated to phase out consumption of all ODSs. Taiwan is not directly regulated under the MP and the KP, but still is reported to be implementing policies to control emissions of HCs.[5]

The changes in emissions of HCs in East Asia are not sufficiently understood to validate consumption changes in this region. The first attempt to characterize the emissions of HCs in Asia was the Transport and Chemical Evolution over the Pacific (TRACE-P) field campaign in 2001, which used aircraft measurements to estimate emissions of major HCs in China, Korea, and Japan.[6] Japan's 2001 emissions for a wide range of HCs were estimated also using separate aircraft measurements.[7] Aircraft studies can provide a snapshot of emissions but are usually limited by sampling frequency and cannot replace long-term monitoring. As a consequence, most of the recent studies have used in situ high-frequency measurements to derive emissions of HCs in East Asia,[8−12] however these studies only looked at a few HCs and/or were regional in scope, for example, the most recent study focused solely on HCs emissions from China.[8]

In this study, we estimate the emissions of 24 major HCs in China, Taiwan, Korea, and Japan for 2008, including CFCs (CFC-11, CFC-12, CFC-113, and CFC-114), HCFCs (HCFC-22, HCFC-141b, and HCFC142b), HFCs (HFC-23, HFC-134a, HFC-152a, HFC-32, HFC-125, HFC-143a, HFC-365mfc), halons (H-1211), PFCs (CF_4, C_2F_6 and C_3F_8), SF_6, and other chlorinated and brominated compounds (CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3CCl_3, and CH_3Br). Our top-down approach is based on high-frequency in situ measurements at Gosan (33.25°N, 126.19°E, Jeju Island, Korea), which has been shown to be an important site to understand the atmospheric outflow from East Asia.[8] The results presented in this study are based on measurements taken from November 2007 to December 2008. Both interspecies correlation matrix and derived emissions for 2008 are analyzed to characterize the emission patterns in East Asia and determine the effects of the MP in this region.

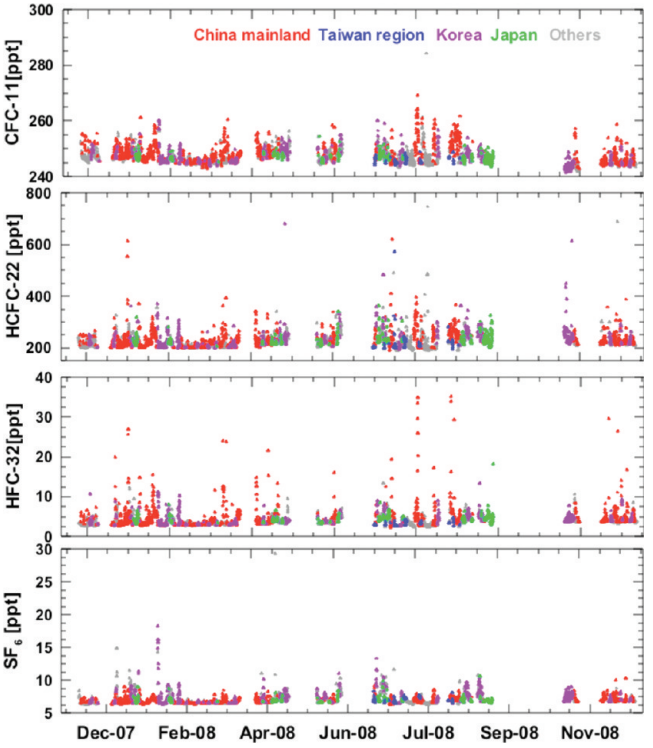


Figure 1. Time-series of CFC-11, HCFC-22, HFC-32, and SF_6 measurements at Gosan. The measurement data were affected by emissions sources from China mainland (34%) shown in red, Taiwan region (2%) in blue, Korea(19%) in purple, Japan (8%) in green, and mixed and unclassified data in gray.

MATERIALS AND METHODS

Sampling and Analysis. Ambient concentrations of halogenated compounds have been analyzed every two hours using the "Medusa" cryogenic preconcentration system with gas chromatograph and mass selective detector (GC-MSD)[13] as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) network. Precisions derived from repeated analysis (n = 12) of an ambient air sample in a tank are better than 1% for most compounds (see Supporting Information (SI) Table S1). The compounds measured here are on calibration scales developed at the Scripps Institution of Oceanography (SIO)[14] with the exception of HFC-125 and CH_2Cl_2 which are on the UB-98 scale (University of Bristol) and HFC-365mfc which is on the Empa-2003 scale (Swiss Federal Laboratories for Materials Science and Technology). The measurement results from November 2007 to December 2008 used in this study are shown in Figure 1.

Air Mass Characteristics at Gosan. Air-masses observed at Gosan are predominantly of northwesterly and northeasterly continental origin in the spring, fall, and winter seasons and therefore carry signals of pollution from China, Korea, and Japan.

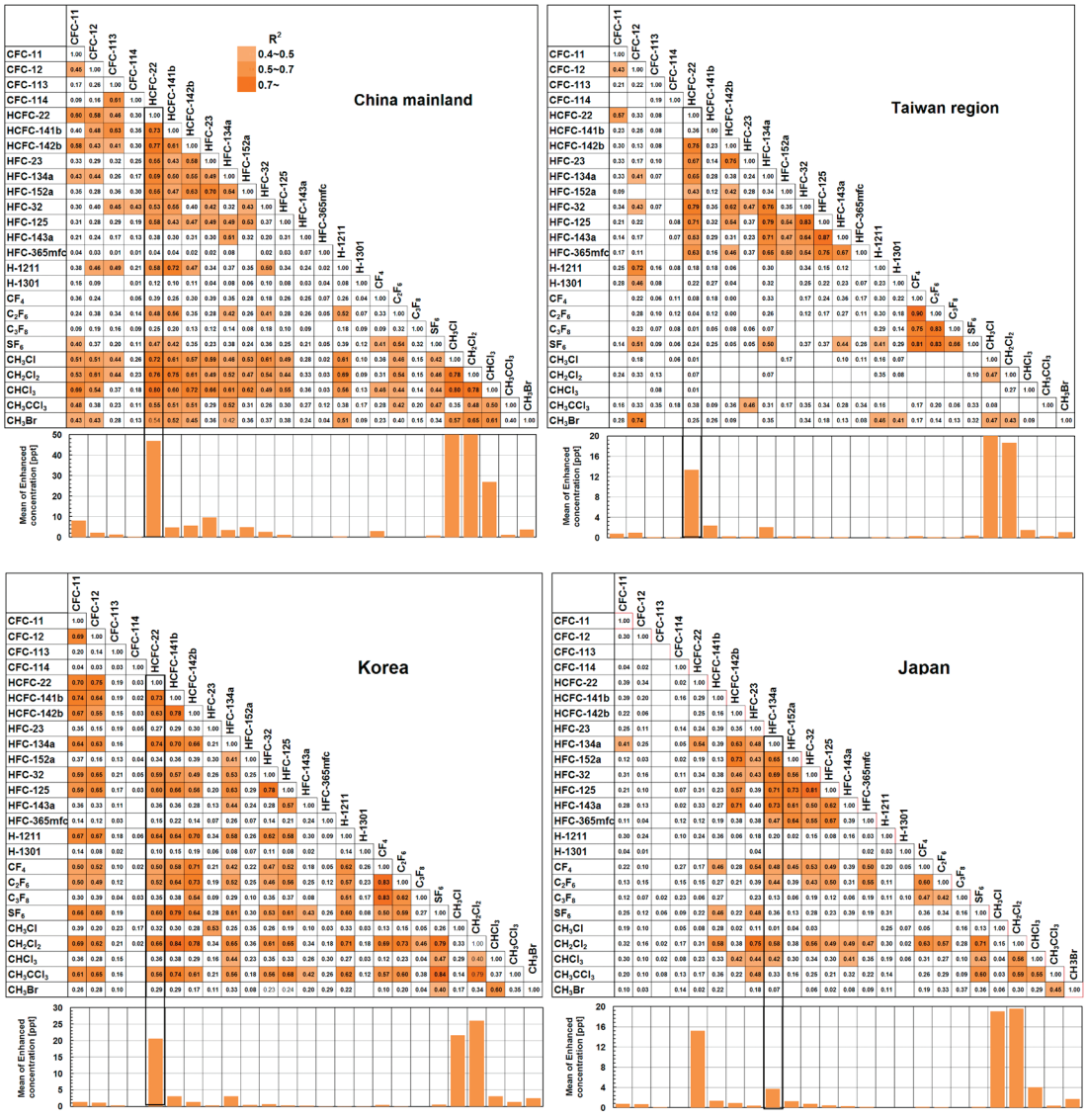


Figure 2. Interspecies correlation coefficient (R^2) for each country in East Asia ($P < 0.05$). When R^2 is less than 0.4 (poor correlation indicating that the two compounds do not have common sources and/or that emissions of one or both compounds are very low) the value is shown on a white background; All other R^2 were grouped in three groups: (1) $R^2 = 0.4-0.5$ (some correlations indicating that some sources of the two compounds are colocated or the same), 0.5−0.7 and larger than 0.7 (good and excellent correlations which indicates that many or most sources of the two compounds are colocated or the same). The lower plot shows the mean of enhanced concentrations above baseline concentration for each compound.

The monsoon brings oceanic background air from the southern regions to Gosan in summer (see SI Figure S2).

To separate emission influences for each country in East Asia, we combined air-mass back-trajectory analysis with a tracer method based on the HFC-23/HCFC-22 ratio (explained in detail in the SI). Results of our source region classification analysis showed that most air-masses (34%) are affected by mainland China, whereas 2%, 19%, and 8% of air-masses are affected by Taiwan, Korea, and Japan, respectively. Periods with mixed air events (15% for China and Korea mixes, and 4% for Korea and Japan mixes) were excluded from further analysis. The other 18% of air-masses were thought to be not affected by the four source regions, which represent clean air-masses originating from the Pacific in the south and from Siberia in the north.

Emission Estimates by Interspecies Correlation. Emission rates for each country were estimated using an interspecies correlation method, in which the emission rates of comeasured, correlating compounds can be calculated from the ratio to a reference tracer with known emission rates.[6−9] This method is based on the assumption that correlating compounds have colocated emission sources, which may be reasonable for many of the compounds considered in this study with similar industrial uses and emissions. To determine a suitable reference tracer for estimating the national emissions in East Asia, an interspecies correlation matrix was derived for each country along with mean enhanced concentrations calculated for each compound (Figure 2). A good reference tracer should ideally show both statistically significant correlation with most other compounds and a high emission rate to achieve lower uncertainties. The mean enhanced concentrations are thought to be proportional to emission rates of the compound for each emissions country.

For China, Korea, and Taiwan, HCFC-22 was determined to be the most suitable reference tracer because of good correlation with most other compounds and its high mean enhanced

Table 1. Emissions of Halogenated Compounds from China Mainland, Taiwan Region, Korea, and Japan (kt/a) and Contributions to Global Emissions from November 2007 to December 2008[a]

	emissions (kt/a)									
compound	China mainland		Taiwan region		Korea		Japan		total	(% global)[c]
CFC-11	**11**	(9−15)	**0.3**	(0.2−0.4)	**0.9**	(0.8−1.1)	**1.1**	(0.7−1.4)	**13.3**	16
CFC-12	**6.1**	(4.4−8.5)	**0.2**	(0.1−0.3)	**0.8**	(0.7−0.9)	**0.9**	(0.7−1.1)	**8.0**	10
CFC-113	**3.2**	(2.5−3.8)	*		*		*		**3.2**	64
CFC-114	**1.3**	(0.9−1.8)	*		*		*		**1.3**	
HCFC-22	**83**[b]	(64−109)	**2.1**[b]	(1.6−2.7)	**8.4**[b]	(8−8.8)	**11**	(10−13)	**104.6**	29
HCFC-141b	**15**	(11−21)	**0.5**	(0.2−0.8)	**2.2**	(2.0−2.5)	**1.6**	(1.2−2.0)	**19.3**	32
HCFC-142b	**9**	(6.9−13)	**0.12**	(0.07−0.18)	**0.8**	(0.7−0.9)	**0.9**	(0.7−1.1)	**10.8**	26
HFC-23	**10**	(7.2−13)	**0.07**	(0.04−0.10)	**0.11**	(0.08−0.13)	**0.3**	(0.2−0.3)	**10.5**	78
HFC-134a	**8.3**	(6.2−11)	**0.5**	(0.3−0.8)	**1.7**	(1.5−1.8)	**4.7**[b]	(4.5−5)	**15.2**	9
HFC-152a	**5.4**	(4.0−7.4)	**0.08**	(0.04−0.13)	**0.11**	(0.08−0.13)	**1.2**	(1.0−1.4)	**6.8**	24
HFC-32	**4.0**	(2.9−5.6)	**0.05**	(0.03−0.07)	**0.21**	(0.18−0.23)	**0.4**	(0.3−0.5)	**4.7**	129
HFC-125	**3.1**	(2.3−4.3)	**0.07**	(0.04−0.10)	**0.27**	(0.24−0.31)	**0.7**	(0.7−0.9)	**4.2**	20
HFC-143a	**0.6**	(0.4−0.8)	**0.04**	(0.02−0.06)	**0.08**	(0.07−0.09)	**0.4**	(0.3−0.4)	**1.1**	3.5
HFC-365mfc	**		**0.01**	(0.007−0.017)	**		**0.2**	(0.2−0.3)	**0.21**	7
H-1211	**1.5**	(1.0−2.0)	**		**0.10**	(0.09−0.12)	**		**1.6**	26
CF_4	**2.1**	(1.4−2.9)	**		**0.22**	(0.19−0.26)	**0.3**	(0.2−0.3)	**2.6**	29
C_2F_6	**0.5**	(0.4−0.7)	**		**0.10**	(0.09−0.12)	**0.2**	(0.1−0.2)	**0.8**	44
C_3F_8	**0.09**	(0.06−0.13)	**		**0.04**	(0.03−0.04)	**		**0.13**	31
SF_6	**1.2**	(0.9−1.7)	**		**0.38**	(0.33−0.44)	**0.4**	(0.3−0.5)	**2.0**	26.5
CH_3Cl	**239**	(176−327)	**		**5.7**	(4.6−6.9)	**		**239**	
CH_2Cl_2	**169**	(126−230)	**		**18**	(16−20)	**17**	(14−20)	**204**	
$CHCl_3$	**44**	(33−60)	**		**2.1**	(1.7−2.5)	**3.4**	(2.8−4.2)	**49.5**	
CH_3CCl_3	**1.7**	(1.3−2.4)	**0.13**	(0.08−0.18)	**1.5**	(1.3−1.7)	**0.6**	(0.5−0.7)	**3.9**	
CH_3Br	**5.4**	(3.9−7.5)	**		**1.1**	(0.9−1.4)	**		**5.4**	
Per group										
CFCs	21.6		0.5		1.7		2		**25.3**	15
HCFCs	107		2.7		11.4		13.5		**134.6**	29
HFCs	31.4		0.8		2.5		7.9		**42.6**	16
PFCs	2.7				0.4		0.5		**3.6**	32
Total	**162.7**		**4.0**		**16**		**24**		**206**	**34**

[a] *, No pollution events were observed at Gosan in air masses from these regions. **, The emissions were not calculated in this study due to low correlations with the reference tracer. [b] The emissions of the reference tracers were calculated by inverse model FLEXPART. [c] Global emissions of CFC-11, CFC-12, CFC-113, HCFC-22, HCFC-141b, HCFC-142b, and H-1211 are taken from Vollmer et al.,[11] HFC-23 from Montzka et al.,[16] HFC-125 from O'Doherty et al.,[17] HFC-365mfc from Vollmer et al.,[18] and SF_6 from Rigby et al.[19] All others are taken from EDGAR[20] and extrapolated to year 2008 which can introduce significant uncertainties. Global emissions of HFC-23 were mostly attributable to emissions from China, occurring as byproduct during HCFC-22 production. For HFC-32 our estimates exceeded global emission estimates, which we attribute to underestimated emissions reported in EDGAR.[8]

concentrations, while HFC-134a was chosen for Japan based on identical criteria. Emissions of the reference tracers were calculated with the inverse method based on FLEXPART transport model analysis, explained in detail in Stohl et al.[10] The implementation of the inverse model is identical to that of Kim et al.[8] constrained by observations at Gosan. Of note, using only Gosan measurements in the model, the emissions were higher by ∼25% for HCFC-22 from China and by ∼50% for HFC-134a from Japan than those deduced from measurements at multiple sites in East Asia using a practically identical method.[10]

The uncertainty in emissions calculated using this method, shown in Table 1, take into account the uncertainties in the emissions of the reference tracer and in the slope. The largest source of uncertainty comes from the inversion of the reference tracer, which are derived by assuming a 50% uncertainty range for the a priori emissions used for the inversion calculations. The inversion process reduces this to 27% for China, 23% for Taiwan, and 5% for Korea and Japan, respectively. Uncertainties of the slope (typically ∼5−10%, except ∼15% for Taiwan, attributable to a smaller data set for this region) are calculated using a Williamson-York linear least-squares fitting method[15] which takes into account the measurement uncertainties of both the target and reference compounds. Another important source of uncertainty in our calculations is the inherent uncertainty of the global meteorological data used in the FLEXPART inversions (operational and 3 h forecast 1° × 1° meteorology from ECMWF), which could not be explicitly determined this study, and is the subject of further research

Of note, air-masses from Taiwan were only observed during summer when air-masses originate from the Southern Hemisphere

(SH) (Figure 1). This could be an additional source of uncertainty for estimating emissions from Taiwan using measurements at Gosan. However, the interspecies ratios do not vary seasonally,[8] suggesting that emissions of halogenated compounds are relatively constant throughout the year. Therefore the emission results of this study are assumed to be minimally affected by the seasonal sampling distribution.

RESULTS AND DISCUSSION

Our estimates of national emissions of halogenated compounds and the fractions to global emissions[11,16−20] for 2008 are shown in Table 1. Overall, the emissions of major HCFCs and HFCs from China and Japan were higher than those reported by Stohl et al.[10] but agree within uncertainty for Taiwan and Korea. Good agreement was also found for emissions of C_2F_6 and C_3F_8 within uncertainty when compared to those reported by Saito et al.[9] (see SI Table S2 for a detailed comparison).

In the following sections, the emissions and interspecies correlations for each country are further analyzed. The interspecies correlation matrix reveals consumption patterns which may not be readily noticeable from quantified emissions alone (Figure 2).

Interspecies Correlations and Emissions in China. For CFCs from China, emission rates are found to have declined since 2001 by 50% for CFC-11 and 80% for CFC-12,[6] in good agreement with bottom-up emissions projected for China[21] (see SI Figure S3 for the comparison to previous studies). However, the significant emission rate and some correlation ($R^2 = 0.4-0.6$) with many other compounds suggest that CFCs are still being emitted in China. Consumption of all CFCs reportedly ended in 2008,[22] and future changes in the CFCs emissions and correlations could be a good indicator of the phase out of these compounds.

The good correlations (R^2 = 0.5−0.7) found among the HCFCs indicate the dominant use of these species in China. This is also supported by the large emission rates found for these species. Of note, the emissions we derive for HCFCs are smaller than the reported consumption of HCFCs in China,[22] suggesting that HCFCs are being accumulated in banking time usage in China (as suggested by Stohl et al.[10] and Montzka et al.[3]).

Despite relatively large emissions, poor correlations were observed among HFC-125, HFC-32, and HFC-143a. This indicates that emissions of these compounds do not occur from the consumption of zero-ODP refrigerant blends. In support of these findings, the HFC-32/HFC-125 ratio for China (slope = 2.2) was significantly different from Taiwan (slope = 1.81), Korea (slope=1.86) and Japan (slope = 1.34). Emissions of these HFCs, especially HFC-32, probably occur from fugitive leaks in production.[9] Among all HFCs, the best correlation against HCFC-22 was found with HFC-134a, which is used in automotive air conditioning.[23] Emissions of HFC-134a were found to have more than doubled since 2005 (3.9 ± 2.4 kt/a),[12] and are expected to continue to rise as China's automotive industry matures. China's large emissions of HFC-23 occur during the production of HCFC-22.[24]

The poor correlation found between CF_4 and C_2F_6 (R^2 = 0.33) is likely to be a result of the fact that two emission sources with significantly different CF_4/C_2F_6 emission ratios coexist in China, namely primary aluminum production and electronics manufacture (semiconductor and liquid crystal displays). This may also explain the better correlations found between C_2F_6 and SF_6 (R^2 = 0.54), as these compounds are emitted more dominantly from electronics manufacturing. Emissions of PFCs from China are of great interest, due to China's large aluminum production (35% of global production in 2009[25]) and a separate study is in progress to further analyze these emissions.

Excellent correlations ($R^2 = 0.7-0.8$) between CH_3Cl, CH_2Cl_2, and $CHCl_3$were observed for China. Emissions of these compounds in China have been reported to occur from various industrial processes including film production, pharmaceutical use, manufacturing of cleaning solvents, and other chemical production uses.[26] Of note, the significant correlations found between these chlorinated solvents and HCFCs and some HFCs suggest that emissions during industrial processes are important for these compounds.

Interspecies Correlations and Emissions in Taiwan. The interspecies correlation matrix for Taiwan is especially interesting since very little information is available regarding Taiwan's consumption and emissions of HCs. Our results show poor correlation among CFCs in contrast to good correlation among most HCFCs and HFCs, suggesting that CFCs have been mostly phased out and replaced with HCFCs and HFCs. The correlations among refrigerant blends (HFC-32, HFC-125, and HFC-143a) are found to be excellent (R^2 = 0.6−0.8). The high correlations found among PFCs and SF_6 (R^2 = 0.7−0.8) are likely a signal from Taiwan's semiconductor industry.

HFC-365mfc is predominantly used in Europe[27] for polyurethane structural foam blowing as a replacement for HCFC-141b, and to a minor extent as a blend component for solvents. Here we find small emissions of 0.01 kt/a in Taiwan in agreement with the potential use of HFC-365mfc reported for Taiwan[5] (0.022kt in 2004).

CH_2Cl_2, CH_3Cl, and $CHCl_3$ show little correlation with HCFCs and HFCs, despite ∼60% of the measurements being classified as pollution events. This suggests that these chlorinated solvents have emission sources which are significantly different from the sources of HCFCs and HFCs in Taiwan.

Interspecies Correlations and Emissions in Korea. While both emissions and consumptions of CFCs are found to have decreased substantially since 2001 (by ∼70% and ∼80%, respectively)[6,22] (see SI Figure S3), CFC-11 and CFC-12 still show good correlations with many other compounds. Combined with the dominant emission rate of HCFCs in Korea, our results suggests that CFCs continue to be emitted from remaining banks as they become replaced with HCFCs under the MP. In addition, good interspecies correlations are found among the HCFCs (HCFC-22, HCFC-141b, HCFC-142b), further confirming the wide use of these CFCs replacement compounds in Korea. Of note is that the emissions derived in our study are only half of the consumed HCFCs reported to UNEP for 2008 in Korea. This suggests that HCFCs in Korea may also be accumulating in banking time usage (similar to China), with implications for later phase-out baseline levels.

While both the emission quantities and interspecies correlation suggest that HCFCs are dominantly used, interspecies correlation among the HFCs indicate that HFC refrigerant blends are starting to be used as well. HFC-125 and HFC-32 show excellent correlation, suggesting the use of the R-410a refrigerant blend (1:1 mixture of HFC-32 and HFC-125) to replace HCFC-22. In addition, some correlation between HFC-143a and HFC-125 could indicate the use of the R-507a refrigerant blend (1:1 mixture of HFC-143a and HFC-125). Continued monitoring should help to characterize Korea's shift from HCFCs to HFCs.

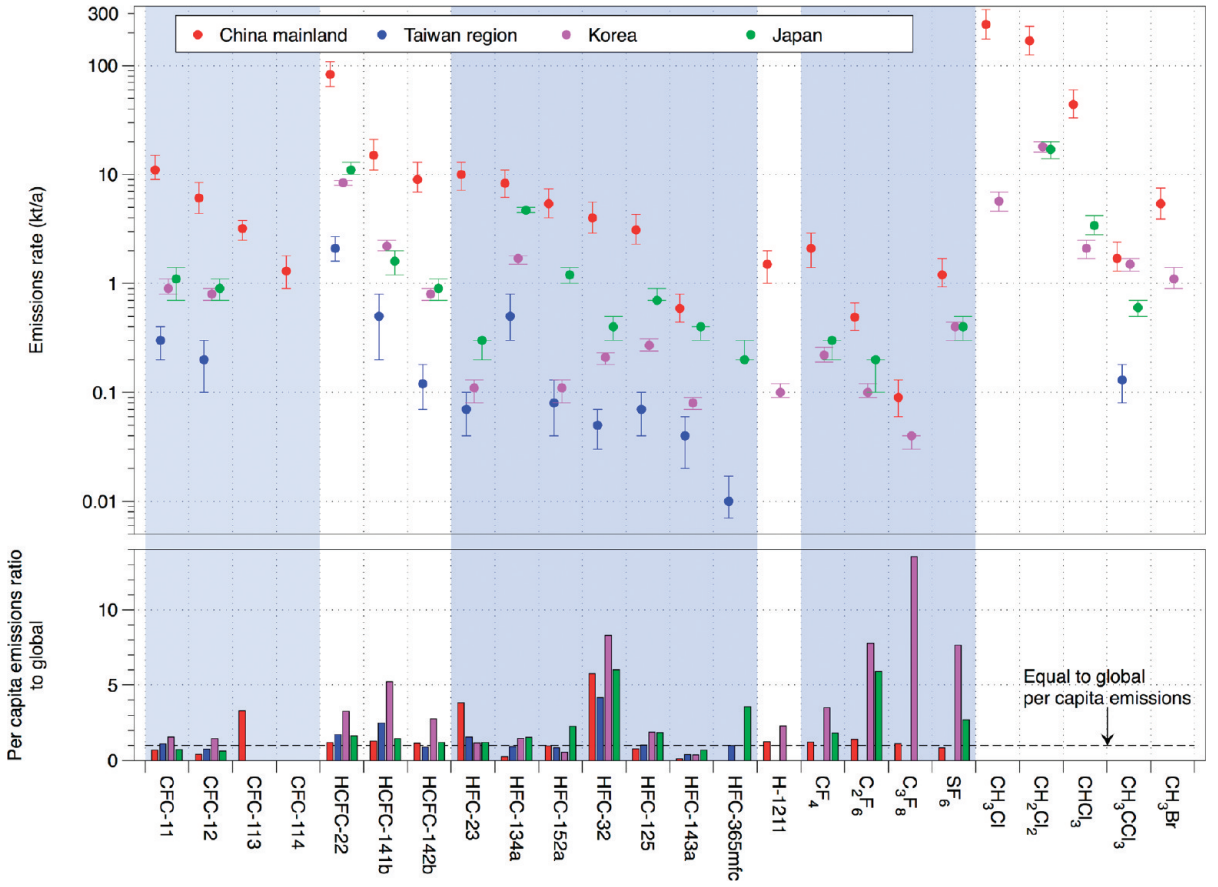


Figure 3. Emissions rate for China mainland, Taiwan region, Korea, and Japan are shown in the top plot. The ratios of national per capita emissions to global per capita emissions are shown in the lower plot.

The good correlations among the PFCs and SF_6 are indicative of emissions from Korea's semiconductor and electronics industries, however the relatively large emissions of SF_6 may indicate that additional sources for this compound exist. The good correlations of CH_2Cl_2 and CH_3CCl_3 with many other compounds suggest that these solvents are also widely used in Korea.

Interspecies Correlations and Emissions in Japan. For CFCs emissions from Japan, our results are in line with ~70% reduction\ since 2002[6] (see SI Figure S3), suggesting long-banking time emissions of CFCs have been continuing for a decade. Our results also show ~30% reduction in the emissions of HCFCs (HCFC-22, HCFC-141b, and HCFC-142b) since 2002. Of note is that Japan was the only country in our study that did not have good correlations with HCFC-22 although significant emission rates were estimated for this compound (11 kt/a). Along with good interspecies correlations found among refrigerant species (HFC-134a, HFC-32, HFC-125, and HFC-143a), results of our study suggest that Japan has already moved the majority of its refrigerant consumption to HFCs.

Good interspecies correlations (R^2 = 0.5−0.7) were found between HCFC-142b and many HFCs (HFC-134a, HFC-152a, HFC-32, HFC-125, and HFC-143a). HCFC-142b is normally used as a foam blowing agent, and consumption of this compound in developed countries (including Japan) is virtually completed with a ban in place by 2020. The correlations found in our study suggest that consumption of HCFC-142b continues in Japan,[28] although good correlation of replacement HFCs (HFC-152a, HFC-134a) with HCFC-142b also suggest that phase-out of HCFC-142b is in progress. Compared to Taiwan, we find larger Japanese emissions of HFC-365mfc (0.2 kt/a) which is surprising as Japan does not report any HFC-365mfc consumption to the UNFCCC.[29]

Correlations among CF_4 and C_2F_6 (R^2 = 0.6) are likely from Japan's semiconductor and electronics industries, as emissions of C_2F_6 in Japan were reported to be from these sources. In addition, some correlations are found between HFC-23 and these PFCs, which could indicate that HFC-23 is emitted from similar sources.[29]

Emission Contributions within East Asia. Our results show that for most compounds emissions from China constituted more than 80% of East Asian emissions (see SI Figure S4). Especially, contributions to HFC-23 emissions from China account for approximately 98% of total emissions from East Asia.

For some compounds, however, significant contributions from Korea, Japan and Taiwan were also found. HFC-134a and HFC-143a emissions in Taiwan, Korea, and Japan were equal to approximately two-thirds of Chinese emissions. SF_6 was found to be emitted mostly in China and Korea with emissions from Korea to be close to half of Chinese emissions. Emissions of CH_3CCl_3 were found to be approximately equal for China and Korea. Emissions of HFC-365mfc in East Asia were found for Taiwan and Japan.

In contrast to China's dominant contribution to global emissions, the per-capita emissions were highest in Korea (Figure 3), especially for PFCs and SF_6 they are approximately five times higher than global per capita emissions. On the other hand, the

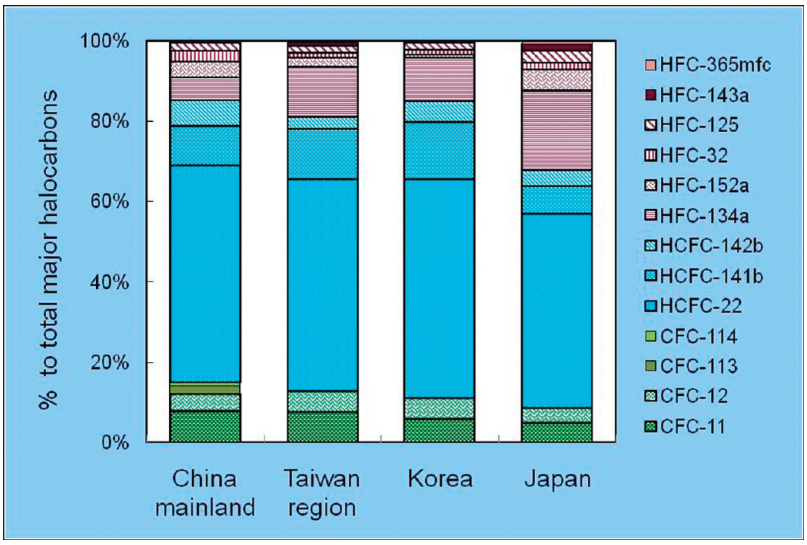


Figure 4. Fractions of each compound to total halocarbons (CFCs, HCFCs, and HFCs) emissions for 2008 in each country.

per capita emissions for China, Japan, and Taiwan are close to the global per capita emissions for most compounds. Our results show that emissions of HCs from Korea are still important despite the relatively small contribution to global emission totals.

In addition, the fraction of each compound to total halocarbons (CFCs, HCFCs, and HFCs) emissions by country can show how each country is adapting to the MP in phasing out CFCs and HCFCs (Figure 4). The successful phase out of CFCs was observed for four countries with a lower fraction of CFCs to total halocarbon emissions than HCFCs and HFCs. A different picture was observed for HCFCs and HFCs in Japan. The lowest fraction of HCFCs (59%) and the highest fraction of HFCs (32%) in Japan suggest the faster transition from HCFCs to HFCs among the four countries. In terms of individual compounds, the largest contributions are found for HCFC-22 in each country, most likely a sign of its wide use as a refrigerant in East Asia. A significant contribution of HFC-134a suggests the common usage in Japan.

Global Perspective of East Asia. The Ozone Depletion Potential (ODP)[2] weighted emissions of major HCs in East Asia (form the four countries) during 2008 were 51 kt ODP and the Global Warming Potential (GWP, CO_2 equivalent, 100 year time horizon)[30] weighted emissions were 754 Mt of CO_2. These values represent ~19 (14−27) % of global emissions of corresponding species in terms of their ODPs, and ~24 (18−31) % in terms of their GWPs. In terms of per-capita emissions from East Asia, the GWP weighed emissions (493 kg of CO_2) were larger than the global levels (450 kg of CO_2), however in terms of ODP East Asia's per-capita emissions (0.022 g ODP) were found to be lower than global levels (0.028 g ODP). Our results suggest that the emissions of HCs in East Asia contribute substantially to the global total.

The interspecies correlation analysis presented in this study enables a comprehensive analysis of the emissions of almost all important HCs in East Asia, and shows detailed changes in emission patterns that are not always apparent from analysis of emission rates alone. Continued monitoring and analysis of the interspecies correlation patterns will help to further understand changes in consumption patterns of HCs in this region, and support global efforts to reduce the overall emissions of these species.

■ ASSOCIATED CONTENT

Supporting Information. A detailed description of source region classification is presented with Figure S1.The residence time analysis of back-trajectories arriving at Gsoan for year 2008 was shown in Figure S2. Measurement precision are shown in Table S1. Derived emissions in this study are compared with other studies[9,10] in Table S2. Emissions in this study are compared with previous studies in Figure S3. Figure S4 shows the national emission contributions for the four East Asian countries discussed here.This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +82 2 880 6751; fax:+82 2 885 7164; e-mail: krkim@snu.ac.kr.

■ ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0029119). Contribution from A. Stohl was supported by the Norwegian Research Council (SOGG-EA project). AGAGE and SIO operations were funded by the NASA Upper Atmosphere Research Program.

■ REFERENCES

(1) *Handbook for the Montreal protocol on Substances that Deplete the Ozone Layer. Ozone Secretariat*, 8th ed.; United Nations Environment Programme (UNEP): Nairobi, 2009.

(2) World Meteorological Organization (WMO), *Scientific Assessment of Ozone Depletion: 2010*, Global Ozone Research and Monitoring Project-Report No. 52, chap. 1, Geneva, Switzerland, 2011.

(3) Montzka, S. A.; Hall, B. D.; Elkins, J. W. Accelerated increases observed for hydrochlorofluorocarbons since 2004 in the global atmosphere. *Geophys. Res. Lett.* **2009**, *36*, L03804.

(4) Velders, G. J. M.; Fahey, D. W.; Daniel, J. S.; McFarland, M.; Andersen, S. O. The large contribution of projected HFC emissions to future climate forcing. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106* (27), 10949–10954.

(5) Tsai, W. T. Energy and environmental policies relating to hydrofluorocarbons (HFCs) emissions mitigation and energy conservation in Taiwan. *Energy Convers. Manage.* **2006**, *47* (15−16), 2308–2318.

(6) Palmer, P. I.; Jacob, D. J.; Mickley, L. J.; Blake, D. R.; Sachse, G. W.; Fuelberg, H. E.; Kiley, C. M. Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data, *J. Geophys. Res.* **2003**, *108* (D24).

(7) Yokouchi, Y.; Inagaki, T.; Yazawa, K.; Tamaru, T.; Enomoto, T.; Izumi, K. Estimates of ratios of anthropogenic halocarbon emissions from Japan based on aircraft monitoring over Sagami Bay, Japan. *J. Geophys. Res.* **2005**, *110* (D6).

(8) Kim, J.; Li, S.; Kim, K. R.; Stohl, A.; Mühle, J.; Kim, S. K.; Park, M. K.; Kang, D. J.; Lee, G.; Harth, C. M.; Salameh, P. K.; Weiss, R. F. Regional atmospheric emissions determined from measurements at Jeju Island, Korea: Halogenated compounds from China. *Geophys. Res. Lett.* **2010**, *37*, L12801.

(9) Saito, T.; Yokouchi, Y.; Stohl, A.; Taguchi, S.; Mukai, H. Large emissions of perfluorocarbons in East Asia deduced from continuous atmospheric measurements. *Environ. Sci. Technol.* **2010**, *44* (11), 4089–4095.

(10) Stohl, A.; Kim, J.; Li, S.; O'Doherty, S.; Muhle, J.; Salameh, P. K.; Saito, T.; Vollmer, M. K.; Wan, D.; Weiss, R. F.; Yao, B.; Yokouchi, Y.; Zhou, L. X. Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling. *Atmos. Chem. Phys.* **2010**, *10* (8), 3545–3560.

(11) Vollmer, M. K.; Zhou, L. X.; Greally, B. R.; Henne, S.; Yao, B.; Reimann, S.; Stordal, F.; Cunnold, D. M.; Zhang, X. C.; Maione, M.; Zhang, F.; Huang, J.; Simmonds, P. G. Emissions of ozone-depleting halocarbons from China. *Geophys. Res. Lett.* **2009**, *36*, L15823.

(12) Yokouchi, Y.; Taguchi, S.; Saito, T,; Tohjima, Y.; Tanimoto, H.; Mukai, H. High frequency measurements of HFCs at a remote site in east Asia and their implications for Chinese emissions, *Gephys. Res. Lett.* **2006**, *33* (21).

(13) Miller, B. R.; Weiss, R. F.; Salameh, P. K.; Tanhua, T.; Greally, B. R.; Mühle, J.; Simmonds, P. G. Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds. *Anal. Chem.* **2008**, *80* (5), 1536–1545.

(14) Prinn, R. G.; Weiss, R. F.; Fraser, P. J.; Simmonds, P. G.; Cunnold, D. M.; Alyea, F. N.; O'Doherty, S.; Salameh, P.; Miller, B. R.; Huang, J.; Wang, R. H. J.; Hartley, D. E.; Harth, C.; Steele, L. P.; Sturrock, G.; Midgley, P. M.; McCulloch, A. A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.* **2000**, *105* (D14), 17,751–17,792.

(15) Cantrell, C. A. Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems. *Atmos. Chem. Phys.* **2008**, *8* (17), 5477–5487.

(16) Montzka, S. A.; Kuijpers, L.; Battle, M. O.; Aydin, M.; Verhulst, K. R.; Saltzman, E. S.; Fahey, D. W. Recent increases in global HFC-23 emissions. *Geophys. Res. Lett.* **2010**, *37*, L02808.

(17) O'Doherty, S.; Cunnold, D. M.; Miller, B. R.; Mühle, J.; McCulloch, A.; Simmonds, P. G.; Manning, A. J.; Reimann, S.; Vollmer, M. K.; Greally, B. R.; Prinn, R. G.; Fraser, P. J.; Steele, L. P.; Krummel, P. B.; Dunse, B. L.; Porter, L. W.; Lunder, C. R.; Schmidbauer, N.; Hermansen, O.; Salameh, P. K.; Harth, C. M.; Wang, R. H. J.; Weiss, R. F. Global and regional emissions of HFC-125 (CHF_2CF3) from in situ and air archive atmospheric observations at AGAGE and SOGE observatories. *J. Geophys. Res.* **2009**, *114*, D23304.

(18) Vollmer, M. K.; Miller, B. R.; Rigby, M.; Reimann, S.; Mühle, J.; Krummel, P. B.; O'Doherty, S.; Kim, J.; Rhee, T. S.; Weiss, R. F.; Fraser, P. J.; Simmonds, P. G.; Salameh, P. K.; Harth, C. M.; Wang, R. H. J.; Steele, L. P.; Young, D.; Lunder, C. R.; Hermansen, O.; Ivy, D.; Arnold, T.; Schmidbauer, N.; Kim, K. R.; Greally, B. R.; Hill, M.; Leist, M.; Wenger, A.; Prinn, R. G. Atmospheric histories and global emissions of the anthropogenic hydrofluorocarbons HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa. *J. Geophys. Res.* **2010**, *116*, D08304.

(19) Rigby, M.; Mühle, J.; Miller, B. R.; Prinn, R. G.; Krummel, P. B.; Steele, L. P.; Fraser, P. J.; Salameh, P. K.; Harth, C. M.; Weiss, R. F.; Greally, B. R.; O'Doherty, S.; Simmonds, P. G.; Vollmer, M. K.; Reimann, S.; Kim, J.; Kim, K. R.; Wang, H. J.; Olivier, J. G. J.; Dlugokencky, E. J.; Dutton, G. S.; Hall, B. D.; Elkins, J. W. History of atmosphere SF_6 from 1973 to 2008. *Atmos. Chem. Phys.* **2010**, *10* (21), 10305–10320.

(20) Emission Database for Global Atmospheric Research (EDGAR). *Emission Database for Global Atmospheric Research (EDGARv4)*, release version 4.0; European Community Joint Research Centre: Brussels, 2010; http://edgar.jrc.ec.europa.eu).

(21) Wan, D.; Xu, J. H.; Zhang, J. B.; Tong, X. C.; Hu, J. X. Historical and projected emissions of major halocarbons in China. *Atmos. Environ.* **2009**, *43* (36), 5822–5829.

(22) *Ozone Secretariat Data Access Centre*; United Nations Environment Programme (UNEP): Nairobi, 2009; http://ozone.unep.org/Data_Reporting/Data_Access/.

(23) Hu, J. X.; Wang, D.; Li, C. M.; Zhang, J. B.; Xu, Y. Forecasting of consumption and emission of HFC-134a used in automobile air conditioner sector in China. *Adv. Clim. Change Res.* **2010**, *1* (1), 20–26.

(24) Miller, B. R.; Rigby, M.; Kuijpers, L.J. M.; Krummel, P. B.; Steele, L. P.; Leist, M.; Fraser, P. J.; McCulloch, A.; Harth, C.; Salameh, P.; Mühle, J.; Weiss, R. F.; Prinn, R. G.; Wang, R. H. J.; O'Doherty, S.; Greally, B. R.; Simmonds, P. G. HFC-23(CHF_3) emision trend response to HCFC-22 ($CHClF_2$) production and recent HFC-23 emission abatement measures. *Atmos. Chem. Phys.* **2010**, *10* (16), 7875–7890.

(25) *Report on the Aluminum Industry's Global Perfluorocarbon Gas Emissions Reduction Programme- Results of the 2008 A Node Effect Survey*; International Aluminum Institute: London, 2009.

(26) Guo, H.; Ding, A. J.; Wang, T.; Simpson, I. J.; Blake, D. R.; Barletta, B.; Meinardi, S.; Rowland, F. S.; Saunders, S. M.; Fu, T. M.; Hung, W. T.; Li, Y. S. Source origins, modeled profiles, and apportionments of halogenated hydrocarbons in the greater Pear River Delta region, southern China. *J. Geophys. Res.* **2009**, *114*, D11302.

(27) Stemmler, K.; Folini, D.; Ubl, S.; Vollmer, M. K.; Reimann, S.; O'Doherty, S.; Greally, B. R.; Simmonds, P. G.; Manning, A. J. European emissions of HFC-365mfc, a chlorine-free substitute for the foam blowing agents HCFC-141b and CFC-11. *Environ. Sci. Technol.* **2007**, *41* (4), 1145–1151.

(28) Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel (IPCC/TEPA). *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, prepared by Working Groups I and III of the Intergovernmental Panel on Climate Change, and the Technical and Economiv Assessment Panel; Cambridge University Press: Cambridge, U.K., 2005.

(29) Greenhouse Gas Inventory Office of Japan (GIO). *National Greenhouse Gas Inventory Report of Japan*; Center for Global Environmental Research, National Institute for Environmental Studies: Tsukuba, 2010; pp 2−8, http://www-gio.nies.go.jp/index.html.

(30) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; and Dorland, R. V. *Changes in Atmospheric Constituents and in Radiative Forcing, in Climate Change 2007: The Physical Science Basis; Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Solomon, S., Qin, D., Manning, M., Chen, Z., Marguis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: Cambridge, U.K., 2007; pp 129−234.