

# Large Emissions of Perfluorocarbons in East Asia Deduced from Continuous Atmospheric Measurements

TAKUYA SAITO,<sup>\*,†</sup> YOKO YOKOUCHI,<sup>†</sup>  
ANDREAS STOHL,<sup>‡</sup> SHOICHI TAGUCHI,<sup>§</sup>  
AND HITOSHI MUKAI<sup>†</sup>

National Institute for Environmental Studies, Tsukuba, Japan,  
Norwegian Institute for Air Research, Kjeller, Norway, and  
National Institute of Advanced Industrial Science and  
Technology, Tsukuba, Japan

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The atmospheric mixing ratios of perfluorocarbons (PFCs), extremely potent greenhouse gases, have been continuously measured at two Japanese stations (Cape Ochiishi and Hateruma Island) since 2006, to infer their global and regional emissions. The baseline mixing ratios of the measured C<sub>2</sub>–C<sub>4</sub> PFCs [PFC-116 (C<sub>2</sub>F<sub>6</sub>), PFC-218 (C<sub>3</sub>F<sub>8</sub>), and PFC-318 (c-C<sub>4</sub>F<sub>8</sub>)] showed slight annual increases of 1%–3%. Enhanced mixing ratios above baseline were occasionally observed at both sites in air masses that had passed over metropolitan regions in East Asia, suggesting high PFC emissions from those regions. We applied transport models to these pollution events and an inversion technique to estimate national emissions. The results suggest that, among the studied regions (China, Japan, North Korea, South Korea, and Taiwan), China was the largest PFC emitter, accounting for more than half of the regional emissions, followed by Japan. The estimated total emissions of each PFC from East Asia were 0.86 Gg yr<sup>-1</sup> for PFC-116, 0.31 Gg yr<sup>-1</sup> for PFC-218, and 0.56 Gg yr<sup>-1</sup> for PFC-318. They contributed greatly to global emissions as derived from the annual increases in the baseline mixing ratios, accounting for more than 75% of global PFC-218 and PFC-318 emissions and for approximately 40% of global PFC-116 emissions.

## Introduction

Perfluorocarbons (PFCs) are very long-lived halocarbons (atmospheric lifetime, 3000–50,000 years (1)) that strongly absorb infrared radiation and thus act as extremely potent greenhouse gases with a global warming potential about 4 orders of magnitude higher than that of CO<sub>2</sub>. All PFCs except CF<sub>4</sub> are believed to originate only from human activities. The fully anthropogenic PFCs, including PFC-116 (C<sub>2</sub>F<sub>6</sub>), PFC-218 (C<sub>3</sub>F<sub>8</sub>), and PFC-318 (c-C<sub>4</sub>F<sub>8</sub>), have been widely used in semiconductor manufacturing, such as for chamber cleaning and dry etching, since the late 1970s, and their use accelerated markedly in the early 1990s (2, 3). Certain PFCs are also produced as a byproduct of aluminum manufacturing (4). PFCs are emitted from the industries to the atmosphere, but

in response to concern about the contributions of PFC emissions to global climate change, their emissions, together with those of other greenhouse gases, are regulated in developed countries under the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC). The contracting countries to the protocol are required to submit national inventories of greenhouse gases to UNFCCC. These inventories, made in accordance with the UNFCCC recommended guidelines, have inherent uncertainties arising from the activity data used. To assess these bottom-up emission inventories, Harnisch and Höhne (3) have compared total emission estimates of PFC-116 from developed countries with an independent top-down emission estimate obtained by atmospheric measurements. They found that in the 1990s global emissions were dominated largely by emissions from developed countries. It is likely, however, that developing countries in East Asia now contribute considerably to PFC emissions as a result of their rapid industrialization. Since most East Asian countries, except for Japan, do not report national emissions of PFCs, observation-based estimates of regional emissions are necessary to ascertain the environmental impact of those emissions.

High-time-resolution data of a long-lived species derived from continuous in situ measurements can be used to estimate regional emissions. With the help of transport models, time-series data on hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have been used to derive regional emission source locations and strengths (5–7). However, few measurements of PFCs have been made (8). In this study, we present continuous atmospheric measurement data for C<sub>2</sub>–C<sub>4</sub> PFCs (PFC-116, PFC-218, and PFC-318) obtained at two Japanese monitoring stations. These stations are seasonally downwind of the Asian continent, so they often capture the continental outflow of Asian pollution. We used meteorological transport models to analyze variations in the high-frequency measurements of PFCs and estimate regional emissions in East Asia.

## Experimental Procedures

As a part of the National Institute for Environmental Studies (NIES) halocarbon monitoring project, in situ measurements of C<sub>2</sub>–C<sub>4</sub> PFCs have been performed at two remote monitoring stations in Japan, at Hateruma Island (24.1° N, 123.8° E) since 2004 and at Cape Ochiishi (43.1° N, 145.3° E) since 2006 (see Figure 3 for the locations). Hateruma is the southernmost inhabited island in Japan, with an area of 12.5 km<sup>2</sup> and a population of approximately 600; it is approximately 250 km east of Taiwan and 500 km southwest of Okinawa Island. The prevailing winds at Hateruma are southeasterly in summer and northwesterly in winter. The Ochiishi monitoring station is situated on a cliff at the southern tip of Cape Ochiishi, which projects southward from the eastern coast of Hokkaido into the western North Pacific; it is approximately 20 km south of Nemuro (population, ~30,000), the closest major city. Prevailing winds at Ochiishi are also southeasterly in summer and northwesterly in winter.

At each station, ambient air is analyzed every hour with a fully automated preconcentration/gas chromatography/mass spectrometry (GC/MS) system ((9), see Supporting Information). Halocarbons, including PFCs, are quantified with gravimetrically prepared standard gases (Taiyo Nippon Sanso Co. Ltd.), which are analyzed in the same manner as the ambient air samples after every five air analyses. Measurement uncertainty derived from repeat analyses (*n*

\* Corresponding author e-mail: saito.takuya@nies.go.jp.

† National Institute for Environmental Studies.

‡ Norwegian Institute for Air Research.

§ National Institute of Advanced Industrial Science and Technology.

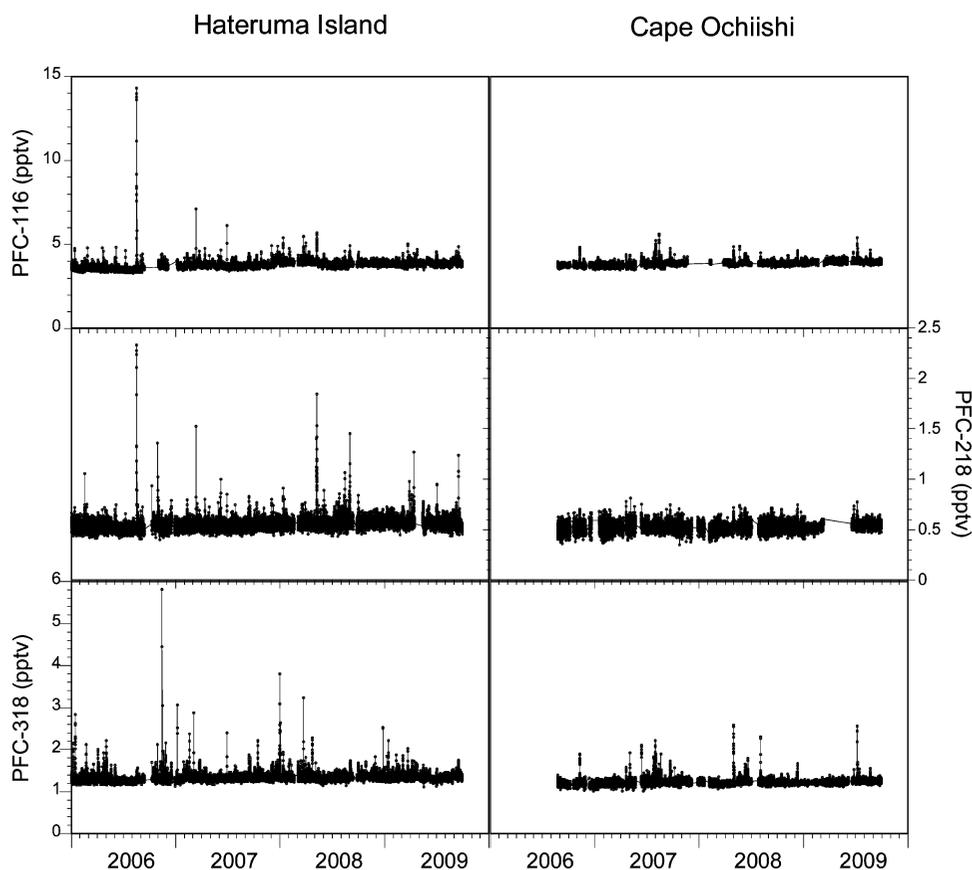


FIGURE 1. Atmospheric mixing ratios of PFCs measured at Hateruma Island and Cape Ochiishi.

= 10) of an ambient air sample in a canister was <2% for PFC-116 and PFC-318 and <4% for PFC-218.

## Results and Discussion

Atmospheric measurements of PFCs at Hateruma (January 2006 to September 2009) and Ochiishi (August 2006 to September 2009) showed low baseline values (from <1 to <5 pptv), along with short-term enhancements of the mixing ratios above baseline (Figure 1). We estimated the baseline mixing ratios for each month as follows: (1) the mean and standard deviation were calculated for each month; (2) data points beyond  $\pm 1\sigma$  of the mean were removed; (3) steps (1) and (2) were repeated with the residual data; and (4) the mean value calculated for the second residuals was used as the monthly mean baseline mixing ratio.

The calculated monthly mean baseline mixing ratios of PFCs tended to increase slightly with time at both sites. The rates of annual increase were determined by least-squares fitting to the monthly mean baseline mixing ratios (Table 1). The resulting rates of increase of each PFC were similar at both sites: PFC-116,  $0.08\text{--}0.10\text{ ppt yr}^{-1}$  or  $2\text{--}3\% \text{ yr}^{-1}$ ; PFC-218,  $0.01\text{--}0.02\text{ ppt yr}^{-1}$  or  $2\text{--}3\% \text{ yr}^{-1}$ ; and PFC-318,  $0.01\text{--}0.02\text{ ppt yr}^{-1}$  or  $1\text{--}2\% \text{ yr}^{-1}$ . The PFC-116 and PFC-218 values are consistent with previously reported values obtained from the late 1980s to the late 1990s ( $0.09\text{ ppt yr}^{-1}$  for PFC-116 and  $0.01\text{ ppt yr}^{-1}$  for PFC-218) (2, 10, 11), but the PFC-116 value is higher and the PFC-218 value lower than those obtained in 2004 ( $0.05$  and  $0.04\text{ ppt yr}^{-1}$ , respectively) (8). By assuming that these rates of increase represent those in the global atmosphere and neglecting loss processes, we estimated global emissions of PFCs from the total number of moles of air in the atmosphere ( $1.77 \times 10^{20}$  moles) and the molecular weights of the PFCs. The resulting estimates of global emissions are  $2.2 \pm 0.3\text{ Gg yr}^{-1}$  for PFC-116,  $0.4 \pm 0.1\text{ Gg yr}^{-1}$  for PFC-218, and  $0.6 \pm 0.2\text{ Gg yr}^{-1}$  for PFC-318. These

TABLE 1. Mean Baseline Mixing Ratios (pptv) and Growth Rates ( $\text{pptv yr}^{-1}$ ) Observed at Hateruma (January 2006–September 2009) and Ochiishi (August 2006–September 2009)

station	PFC-116		PFC-218		PFC-318	
	mixing ratio	growth rate <sup>a</sup>	mixing ratio	growth rate <sup>a</sup>	mixing ratio	growth rate <sup>a</sup>
Hateruma	3.79 (2.6 ± 0.3)	$0.10 \pm 0.01$	0.55 (3.0 ± 0.4)	$0.02 \pm 0.002$	1.33 (1.5 ± 0.2)	$0.02 \pm 0.003$
Ochiishi	3.88 (2.1 ± 0.3)	$0.08 \pm 0.01$	0.52 (1.9 ± 0.4)	$0.01 \pm 0.002$	1.22 (1.1 ± 0.3)	$0.01 \pm 0.004$

<sup>a</sup> Numbers in parentheses represent growth rates ( $\% \text{ yr}^{-1}$ ).

estimates are in reasonable agreement with previously reported estimates:  $2\text{--}2.6\text{ Gg yr}^{-1}$  in the 1990s (3) and  $2.7 \pm 0.16\text{ Gg yr}^{-1}$  in 2001 (12) for PFC-116;  $0.48\text{ Gg yr}^{-1}$  for PFC-218 during 1992–1997 (2); and about  $0.7\text{ Gg yr}^{-1}$  for PFC-318 during 1978–1997 (13). Our estimates are higher by 9% for PFC-116, 20% for PFC-218, and 97% for PFC-318 than the global emissions calculated using a technology based emission factor approach for 2005 by the Emissions Database for Global Atmospheric Research (EDGAR) (14).

We found a remarkable difference in the measurements between the two sites with respect to the frequency and magnitude of above-baseline (“pollution”) events, both of which were higher at Hateruma than at Ochiishi (see Figure 1), reflecting the fact that Hateruma is closer than Ochiishi to the major East Asian source regions. The frequency of pollution events was higher in summer at Ochiishi. Such seasonal variation at Ochiishi was attributed to prevailing southerly winds occasionally bringing pollution from the Japanese mainland in summer, whereas air masses brought

by northwesterly winds in winter travel over remote, less-polluted areas (e.g., western Siberia).

To estimate East Asian PFC emissions, we analyzed the observation data by two methods: the tracer ratio method and the inversion method. Each method has been described previously and used successfully to estimate regional halocarbon emissions (15, 16).

**Tracer Ratio Method.** The tracer ratio method is based on the idea that the relative enhancement ratio of two species in a pollution event reflects the ratio of their emission strengths in the source region, as long as they are neither produced in, nor removed from, the air mass during transport. From simultaneous measurements of two species, if the emission rate of one species is known (reference compound), the emission rate ( $E_x$ , Gg yr<sup>-1</sup>) of the other (target compound) can be calculated by multiplying the emission rate ( $E_r$ , Gg yr<sup>-1</sup>) of the reference compound by the relative enhancement ratio of the target compound ( $\Delta C_x$ , mol) to that of the reference compound ( $\Delta C_r$ , mol) in the pollution event as follows:

$$E_x = E_r \times \frac{\Delta C_x}{\Delta C_r} \quad (1)$$

We used HCFC-22, the most abundant HCFC in the atmosphere, as the reference compound because its regional emission rate in East Asia has been studied relatively well. The enhancement for a compound ( $\Delta C$ ) at each event was determined by the difference of the mixing ratio at the peak top time and the peak base time which were set for the HCFC-22 peak.

We identified the potential source region of each pollution event by comparing the timing of the HCFC-22 pollution event with that in a tagged simulation of HCFC-22, which treats HCFC-22 emitted in a certain region as a separate tracer. The tagged simulation was obtained by using the three-dimensional transport model STAG (17), following the approach of Yokouchi et al. (15). The model was driven by meteorological inputs from the European Centre for Medium-Range Weather Forecasts (ECMWF, horizontal resolution, 1.125° × 1.125°; 60 vertical levels; time resolution, 6 h). The simulations of HCFC-22 in East Asia were performed separately for four emission regions: China, Japan, Korea, and Taiwan. We used emission inventory data estimated by Aucott et al. (18), which were distributed to the model grid by population density. National emissions from China and Japan were scaled in a post-processing step to 70.6 Gg yr<sup>-1</sup> and 7.8 Gg yr<sup>-1</sup>, respectively, as of 2006, on the basis of recent inversion results (16). The emission from Taiwan was scaled to 2.2 Gg yr<sup>-1</sup> under the assumption that half of the consumption amount reported by Tsai and Chou (19) would be emitted to the atmosphere. We assumed constant emissions of the PFCs throughout the measurement periods. The model reproduced the timing of the major pollution events fairly well (see Supporting Information, Figure S1 for the comparison of the observations with the modeled mixing ratios for Hateruma in November 2006).

By classifying all pollution events in the entire Hateruma and Ochiishi data sets, we identified the pollution events observed at Hateruma as being from "China" ( $n = 53$ ) or "Taiwan" ( $n = 9$ ) and those at Cape Ochiishi as being from "Japan" ( $n = 7$ ). The classified events were nearly evenly distributed in each year. We excluded pollution events influenced by more than one source region because they could not be used for emission estimates. The relative enhancement ratios varied substantially. Some excessively high or low ratios can be attributed to low correlations between PFCs and HCFC-22, in part because of low analytical precision in relation to the small mixing ratio enhancements and temporal and spatial differences in their emission

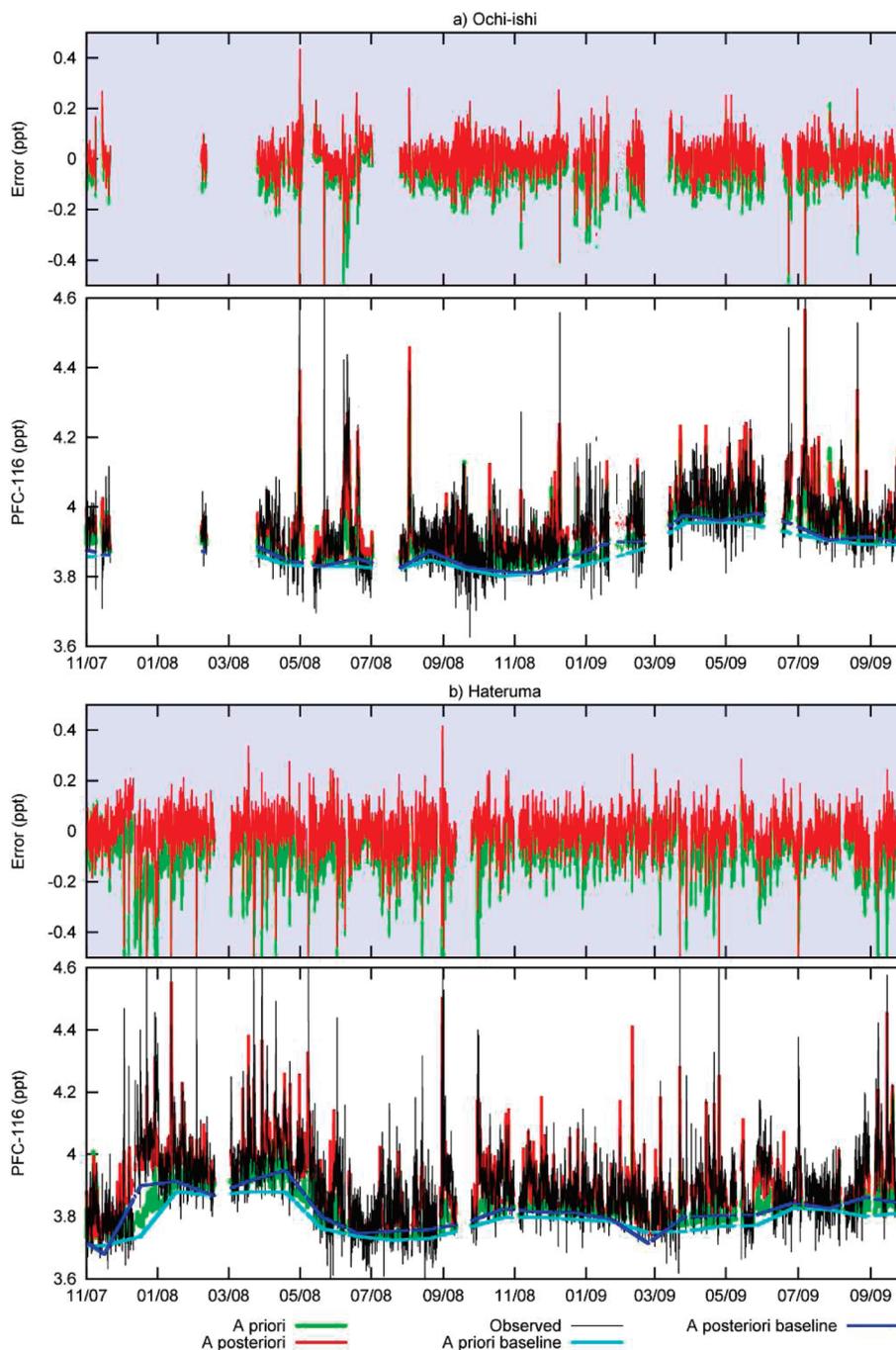
sources. Therefore, we considered median ratios to be more reliable than mean ratios. We multiplied the median enhancement ratios for China, Japan, and Taiwan by the corresponding HCFC-22 emissions described above to obtain national PFC emission rates. These emission estimates are discussed below, together with those obtained by the inversion method.

**Analytical Inversion Method.** The inversion method used in this study is an analytical approach that corrects the emission distribution (a priori) by comparing the observations with the simulated mixing ratios to yield a posteriori emission distributions that best fit the observations. Technical details of the method are reported by Stohl et al. (16) and Stohl et al. (20) who describe a nearly identical setup for East Asia for other halocarbons, so we give only a brief description here. The method uses the Lagrangian particle dispersion model FLEXPART (21) to determine potential source contributions at the receptor sites, Hateruma and Ochiishi, of this study. FLEXPART was driven by meteorological fields generated by ECMWF with 1° × 1° horizontal resolution and 91 vertical layers; it calculated 20 day backward trajectories from Hateruma or Ochiishi for 40000 virtual particles released every 3 h to obtain the emission sensitivity of each grid cell. The emission sensitivity was multiplied by the a priori emission distributions to yield the simulated mixing ratios at the receptor sites. The simulated mixing ratios containing emission information from the past 20 days were compared with the observed short-term enhancements, which were calculated by subtracting a baseline mixing ratio from the observations. The comparison was made using the inversion algorithm to find the optimized a posteriori emission distribution achieving the best fit between the modeled and observed mixing ratios, while also keeping the deviation of a posteriori emissions from the a priori emissions at a minimum, considering uncertainties of emissions, observations, and model calculations.

The a priori emissions of PFCs (see Supporting Information, Table S1) used in the inversion were obtained from UNFCCC inventories for 2007 for countries where such data were available, except for Japan. For the other countries, including most East Asian countries, our global emission estimates, less the UNFCCC emissions used above and the Japanese emissions described below, were distributed according to population density (22). For Japan, annual emissions of PFC-116 have been reported to UNFCCC, but the value (0.2 t in 2007) is only for emissions associated with aluminum production, and thus is not used here. Instead, for Japan, emissions related to semiconductor and liquid crystal manufacturing were used as the a priori emissions. These emissions of PFC  $i$  ( $E_i$ , t) were estimated from the purchased amount of PFC  $i$  ( $C_i$ , t), the fraction of PFC  $i$  fed into process ( $F_i$ , %), the use rate for PFC  $i$  ( $U_i$ , %), the fraction of PFC  $i$  destroyed by the emission control technology ( $d_i$ , %), and the installation fraction of removal equipment ( $a_i$ , %) by using the following equation (23):

$$E_i = C_i \times F_i \times (1 - U_i) \times (1 - d_i \times a_i) \quad (2)$$

These parameters, other than the installation fraction of removal equipment, were obtained from the national emission inventory of Japan (23). Although the installation fraction of removal equipment was not available, under the assumption that the parameter (14%) was the same for all PFCs, we could calculate the emission of each PFC from the reported total PFC (sum of PFC-14, PFC-116, PFC-218, and PFC-318) emissions (23) related to the two industries. As a result, we estimated the PFC emissions associated with semiconductor and liquid crystal manufacturing in 2007 to be 192 t for PFC-14, 178 t for PFC-116, 61 t for PFC-218, and 8 t for PFC-318, which together account for 87% of total PFC emissions in

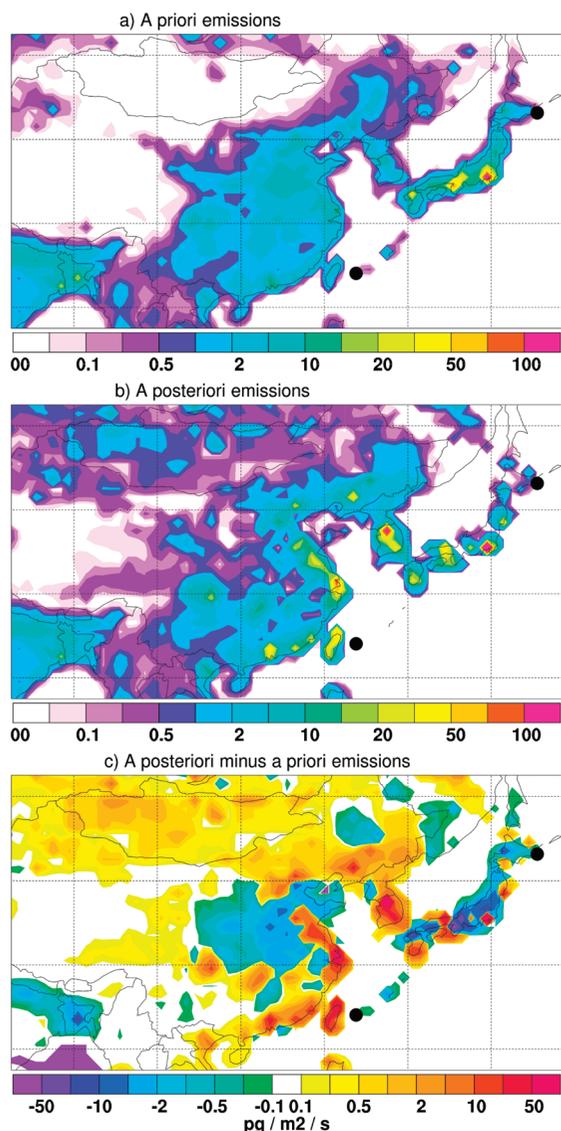


**FIGURE 2.** PFC-116 time series for (a) Ochiishi, and (b) Hateruma. For both stations, the lower panels show the observed mixing ratios (black lines) as well as the mixing ratios simulated by using the a priori (green lines) and a posteriori (red lines) emissions and the a priori (cyan lines) and a posteriori (blue lines) baseline emissions. Upper panels show the model errors based on the a priori (green lines) and the a posteriori (red lines) emissions.

Japan. No national emission data for PFC-318 are available from UNFCCC; therefore, we distributed our global emission estimate of  $0.6 \pm 0.2 \text{ Gg yr}^{-1}$  according to population density after subtracting the Japanese emissions. In addition to the a priori emissions described above, we used an alternative emission distribution as a priori data to quantify the uncertainty of the inversions. In this scenario, our global emission estimates were distributed simply according to population density. For both scenarios, we performed the inversions with 50%, 100%, and 200% of the emissions, and we characterized the uncertainties of the inversion results by the standard deviation of the six inversions.

For the inversions, emission grid boxes near the measurement sites have a resolution of  $1^\circ \times 1^\circ$ , whereas the

resolution was lower in the regions of low emission sensitivity (16). We assumed constant global emissions of individual PFCs. To avoid possibly strong trends in the time interval used for the inversion, we performed the inversion calculations only for the period from November 2007 to September 2009. Figure 2 shows the time series of the measured and the simulated PFC-116 mixing ratios at Hateruma and Ochiishi, as well as the corresponding errors. The model reproduced the observed short-term enhancements of the mixing ratios fairly well, whereas the simulated magnitudes of some major events were somewhat lower than the observations, even in the models of the a posteriori emissions. As we shall see, the a priori emissions used for our inversions were far too low. Given that a posteriori emissions are bound to the a priori



**FIGURE 3.** Maps of (a) a priori and (b) a posteriori PFC-116 emissions, and (c) the difference between the a posteriori and a priori emissions for the period from November 2007 to September 2009. Black dots indicate the locations of the measurement stations.

values by assuming an uncertainty (standard deviation) of 100%, a posteriori emissions are likely to be on the low side of real emissions, too. We do not show the comparison data for the other PFCs, but the model performance was similar for all of them.

The a priori and a posteriori emission maps for PFC-116 are shown in Figure 3, as well as a difference map between a posteriori and a priori emissions. The a priori map shows a few high emission areas in Japan but otherwise fairly uniform emission distributions because it is based on the population distribution in each country. In contrast, the a posteriori map shows many regions with increased emissions compared with the a priori emissions. Large emission increases were generally found in and around large cities (Shenyang, Beijing, Shanghai, Xiamen, Shantou, and Hong Kong) along or near the coast of China and in Taiwan (Taipei), Japan (Tokyo), and South Korea (Seoul). Since industry, including semiconductor and liquid crystal manufacturing, is concentrated in these metropolitan areas, the collocation of the high-emission regions and the urban areas is reasonable. The a posteriori map and the difference map also show weak increases in emissions in some vast remote areas (e.g.,

Mongolia and inland China). Because these remote areas are too far from our measurement stations to constrain strongly their emissions, we attribute these increases to an artifact of the inversions: that is, small variations in baseline data probably because of instrumental noise were fitted to the small emissions in these remote areas by the inversions. However, these artificial increases have little effect on our discussion of national emissions because they are negligibly small compared with the large emission increases derived from major pollution events. Emission maps for PFC-218 and PFC-318 are not shown because their emission patterns are similar to those of PFC-116. The national emission estimates of all studied PFCs derived from the a posteriori emission maps are discussed below.

**National Emission Estimates.** We compared estimated national emissions of PFCs between the tracer ratio and inversion methods (Table 2). In general, emissions derived by the inversion method were larger than the a priori emissions (see Supporting Information, Table S1 and Table 2), suggesting substantial PFC emissions from East Asian nations. National emission estimates by the tracer ratio method were not made for the two Koreas because no pollution events could be attributed exclusively to these countries. Comparison of the emission estimates obtained by the two methods shows broad agreement, except in the case of PFC-318 emissions from China. However, the central tendency of these estimates is shown by different statistics (i.e., median and interquartile range for the tracer ratio method, arithmetic mean and standard deviation for the inversion method), and the values, in particular those estimated by the tracer ratio method, are associated with relatively large uncertainties. The largest uncertainties in both methods were found in the emission estimates of PFC-218, which we attribute to our PFC-218 measurements having the lowest signal-to-noise ratios among the PFC measurements (see Figure 1). Because of the low signal-to-noise ratios, the uncertainty in the a priori emissions of PFC-218 was not reduced by the inversions as much as the uncertainties of the a priori PFC-116 and PFC-318 emissions, with the result that the relative standard deviation of the a posteriori emissions was much higher for PFC-218 (19%–50%) than for PFC-116 (7%–15%) or PFC-318 (6%–11%). We attributed the large uncertainties for PFC-218 in the tracer ratio method mostly to poor correlation between PFC-218 and HCFC-22 pollution events, which are partly attributable to the low signal-to-noise ratios.

Even when the large uncertainties are taken into account, the PFC-318 emission estimate for China obtained by the tracer ratio method is higher ( $0.73 \text{ Gg yr}^{-1}$ ) than that obtained by the inversion method ( $0.422 \text{ Gg yr}^{-1}$ ), which can be only partly explained by the different measurement periods used to derive the estimates (i.e., even if data from the same period were used for both methods, the tracer ratio-based emission estimate ( $0.62 \text{ Gg yr}^{-1}$ ) would still be higher than the inversion-based estimate). Considering that the tracer ratio-based estimates exceeded our global emission estimate for PFC-318, the difference is likely due to overestimation by the tracer ratio method rather than to underestimation by the inversion method, while we cannot rule out the possibility of underestimation by the inversion method, as mentioned above. This overestimation might reflect poor regional representativeness of the pollution events in terms of the PFC-318:HCFC-22 ratios, partly because the Chinese pollution events used in the tracer ratio method originated mostly in metropolitan regions (e.g., Shanghai) in southern China and rarely in northern Chinese regions.

According to our best estimates by the inversion method, total emissions from East Asia (China, Japan, North Korea, South Korea, and Taiwan) were  $0.859 \text{ Gg yr}^{-1}$  for PFC-116,  $0.310 \text{ Gg yr}^{-1}$  for PFC-218, and  $0.562 \text{ Gg yr}^{-1}$  for PFC-318.

**TABLE 2. Estimated PFC Emissions<sup>a</sup> in East Asia Using the Inversion Method<sup>b</sup> and the Tracer Ratio Technique<sup>c</sup>**

country	PFC-116		PFC-218		PFC-318	
	inversion	tracer ratio	inversion	tracer ratio	inversion	tracer ratio
China	0.499 ± 0.038	0.57 (0.36–0.90)	0.157 ± 0.030	0.08 (0–0.17)	0.422 ± 0.045	0.73 (0.56–1.26)
Taiwan	0.059 ± 0.004	0.13 (0.05–0.17)	0.024 ± 0.012	0.05 (0.04–0.07)	0.009 ± 0.001	0.01 (0.01–0.01)
North Korea	0.013 ± 0.002		0.007 ± 0.002		0.010 ± 0.001	
South Korea	0.092 ± 0.006		0.031 ± 0.008		0.032 ± 0.002	
Japan	0.196 ± 0.018	0.16 (0.12–0.20)	0.091 ± 0.019	0.07 (0.03–0.09)	0.089 ± 0.006	0.10 (0.05–0.15)

<sup>a</sup> Gg yr<sup>-1</sup>. <sup>b</sup> Mean ± stdev. <sup>c</sup> Median and interquartile range in parentheses.

The PFC-218 and PFC-318 values are surprisingly high, accounting for more than three-quarters of our global emission estimates. The contribution of PFC-116 to the global estimate is also high, accounting for approximately 40%.

China is suggested to be the greatest PFC emitter among the studied regions, followed by Japan. Approximately 20%, 40%, and 70% of the global emissions of PFC-116, PFC-218, and PFC-318, respectively, are estimated to be emitted from China, despite China's relatively low share (7% in 2005) of the global semiconductor manufacturing capacity (24). However, semiconductor production capacity is not a good proxy for actual emissions because emissions vary with plant utilization, product type and complexity, and with the use of emission reduction technologies. Given that PFC-218 and PFC-318 have become more common since 1999–2000 as drop-in replacements for PFC-116 in the semiconductor industry (25), the higher estimated Chinese contributions of PFCs other than PFC-116 suggest that these relatively new gases are widely used by China's rapidly growing semiconductor industry and that emission reduction technologies may be less widely used. At least in the case of PFC-116, emissions as byproduct of aluminum manufacturing are also important, because China is the world's largest aluminum producer, accounting for a third of the world's production (26). PFC-116 emissions from aluminum manufacturing can be estimated from the amount of aluminum production (13,177 Gg yr<sup>-1</sup> (26)), and the corresponding emission factor (kilograms PFC-116 emitted per ton of aluminum produced), but the emission factor can vary by a factor of 10 depending on the production technology. If we use the emission factor (0.014 (27)) for the point-feed prebake technology employed by some Chinese smelters (4), PFC-116 emissions would be 0.18 Gg yr<sup>-1</sup>, accounting for approximately 30% of our emission estimate for China.

The total estimated PFC emissions from Japan, South Korea, and Taiwan account for substantial fractions (16% for PFC-116, 35% for PFC-218, and 22% for PFC-318) of the global emissions; however, these numbers are lower than what might be predicted, given that these countries are world leaders in semiconductor manufacturing. These low values probably reflect the successful reduction of PFC emissions by these countries, which adhere to a voluntary PFC reduction plan committed to by their semiconductor industry associations (as members of the World Semiconductor Council). The estimated emission rates of PFC-116 from Japan (tracer ratio method, 0.16 Gg yr<sup>-1</sup>; inversion method, 0.196 Gg yr<sup>-1</sup>) were higher by a factor of approximately 1000 than the emission rate associated with aluminum production (0.2 t yr<sup>-1</sup> (23)), suggesting that most PFC-116 is not emitted by aluminum production but by other industries (i.e., semiconductor industries). Japanese PFC emissions in 2003 have been estimated by the tracer ratio method using airborne measurements over Sagami Bay, Japan (28). Our estimates are consistent with those for PFC-116 (0.19 Gg yr<sup>-1</sup>) and PFC-218 (0.06 Gg yr<sup>-1</sup>), but higher by about 80% than that for

PFC-318 (0.02 Gg yr<sup>-1</sup>). The difference for PFC-318 may reflect a year-to-year change in the emissions or the representativeness of the measured enhancement ratios. North Korean PFC emissions are the lowest among the studied regions, consistent with the minor role of the semiconductor industry there; moreover, part of the estimated emissions for North Korea may be attributable to an artificial spillover of emissions from South Korea because of the limited model resolution (20).

The present top-down emission estimates suggest that the PFC emissions in East Asia, where most countries (except for Japan) do not report national emissions of PFCs, contribute substantially to the global emissions and to the increases in the mixing ratios. Current mixing ratios of the PFCs are still low and thus they play a relatively minor role in the Earth's radiative forcing compared to the major greenhouse gases, such as CO<sub>2</sub>; however, assuming continuous PFC emissions at the current rates, the resulting radiative forcing of the PFCs at a steady-state mixing ratio would account for 3%–10% of that for CO<sub>2</sub> stabilization scenarios (CO<sub>2</sub>: 350–800 ppm) in the distant future.

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### Supporting Information Available

Details of experimental method, regional PFC emissions used as the a priori in the inversion method (Table S1), and simulation of HCFC-22 mixing ratios compared with observations (Figure S1) are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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