A high-frequency and advanced monitoring study for the halogenated greenhouse gas inventory in East Asia　（Abstract of the Final Report）

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1. Introduction

Halocarbons such as chlorofluorocarbons(CFCs), hydrochlorofluorocarbons(HCFCs), per-fluorocarbons(PFCs), hydrofluorocarbons(HFCs), and sulfur hexafluoride(SF_6) are greenhouse gases with high global warming potentials[1]. Production and use of CFCs and HCFCs have been phased out under the Montreal Protocol. Most CFC emissions have already started to decrease, but the emissions of HCFCs, which are temporary substitutes for CFCs, are still growing in some countries. HFCs are used as substitute gases for HCFCs, and some of them are being rapidly accumulated in the atmosphere. HFCs, PFCs and SF_6 are included in the group of gases listed in the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). These halocarbon emissions are expected to grow rapidly in East Asia as the result of recent economic growth. However, there is limited information for their emissions in this area, and top-down approach based on high-precision and high-frequency observation is needed to know their emission strength from each country.

In the present project, we aim to (1) know the year-to-year, seasonal and day-to-day variations of halocarbons in East Asia, (2) improve the analytical method for a wide variety of halocarbons measurements, and (3) estimate the regional emission fluxes of each halocarbon, based on the high-frequency measurements and model calculation.

2. Method

(1) *In situ* high frequency monitoring and trend analysis of halocarbons on Hateruma Island and at Cape Ochiishi

High frequency measurements of CFCs (CFC-11, CFC-12, CFC-113, CFC-114, CFC-115), HCFCs (HCFC-22, HCFC-141b, HCFC-142b, HCFC-123, HCFC-124, HFC-125), HFCs (HFC-23, HFC-134a, HFC-152a, HFC-32), PFCs (PFC-116, PFC-218, PFC-318), SF_6 and halons (H-1301, H-1211) have been continued at the ground monitoring stations on Hateruma Island (123.8°E, 24.1°N) and at Cape Ochiishi (145.5°E, 43.2°N). HFC-227ea, HFC-143a, HFC-245fa, HFC-365mfc and CFC-13 have newly been included in the target compounds. Air is sampled at the top of a high tower (40m at Hateruma, 50m at Ochiishi), and is analyzed every hour with an automated halocarbon measurement system based on cryogenic preconcentration and capillary gas chromatography/mass spectrometry (GC/MS). Calibration is performed with gravimetrically prepared standard gases (Taiyo Nippon Sanso Co. Ltd.) with dry mole fraction concentration ranges of 100–500 ppt. Concentrations were given as "NIES-08 scale" after the recalibration of

the working standards with NIES primary standard. All the operations are automated, and occasional MS tuning are done by remote-control.

(2) Refinement of atmospheric halocarbon measurements.

Three capillary columns (InertCap-1, alumina (Al$_2$O$_3$/KCl) PLOT, and GS-GasPro) were investigated to select the best column in terms of resolution of wide boiling range of halocarbons and conditions suitable for use in conjunction with an automated halocarbon measurement method. Using the two best columns (InertCap-1 and PoraBOND-Q, as described below), a multi-dimensional gas chromatographic system based on a Deans switch was developed.

(3) Collaborative model study of halocarbon emissions from East Asia.

(Cooperated with Norwegian Institute for Air Research, Seoul National University, Chinese Academy of Meteorological Sciences, etc.)

An international collaborative model study was done to determine the halocarbon emissions from East Asia. The emissions of three HCFCs (HCFC-22, HCFC-141b and HCFC-142b) and three HFCs (HFC-23, HFC-134a and HFC-152a) from five East Asian countries (regions) (China, North Korea, South Korea, Japan and Taiwan) for the year 2008 were determined by inverse modeling[2]. The inverse modeling is based on *in-situ* measurements of these halocarbons at Hateruma and Ochiishi stations as well as the Chinese station Shangdianzi (40.7ºN、117.1ºE) and the South Korean station Gosan (33.3ºN、126.2ºE).

(4) Regional perfluorocarbon emissions in East Asia deduced from atmospheric measurements

PFC-116 (C$_2$F$_6$), PFC-218 (C$_3$F$_8$), and PFC-318 (c-C$_4$F$_8$) are extremely potent greenhouse gases.   We inferred their global and regional emissions based on their atmospheric mixing ratios of PFC-116 (C$_2$F$_6$), PFC-218 (C$_3$F$_8$), and PFC-318 (c-C$_4$F$_8$) measured at Cape Ochiishi and Hateruma Island for the period of 2006-2009, and an inversion method. The inversion method used here is same to the one employed in Section (3).

(5) Simulation of annual emission rates of HCFCs and HFCs from China for 2006-2010

To simulate tracer concentration at the observation points we used global coupled Eulerian-Lagrangian transport model[3]. The surface fluxes for the global simulation were taken from EDGAR database ver.4.2 with some additional scaling to match global totals.   The difference between the simulated background and observation at Hateruma was used for the inversion model to estimate the surface fluxes of HCFC-22, HCFC-141b, HCFC-142b, HFC-23, HFC-134a and HFC-152a from China in each year. The inverse model domain has size of 35 deg East from 100E and 30 deg North from 20N.

3. Results and Discussion

(1) *In situ* high frequency monitoring and trend analysis of halocarbons on Hateruma Island and at Cape Ochiishi

During this study period (April 2009~), more than 17,000 measurements of halocarbons were obtained from each of Hateruma and Ochiishi. HFCs, HCFCs and SF$_6$ were found to have increased significantly, while CFCs showed a steady decrease. Together with the data from the previous project, we got over 7-year dataset from Hateruma and over 5-year dataset from Ochiishi for the species targeted from the beginning.   Figure 1 shows the temporal variations of selected species at the two sites; (a) HCFC-22, (b) HCFC-142b, (c) HFC-134a, (d) HFC-32, (e) SF$_6$, and (f) CFC-113. The changes in their annual baseline concentrations from 2005 to 2011 at Hateruma were 183.0 ppt $\rightarrow$ 221.4 ppt for HCFC-22, 19.8 ppt $\rightarrow$ 23.3 ppt for HCFC-141b, 17.8 ppt $\rightarrow$ 22.9 ppt for HCFC-142b, 41.6 ppt $\rightarrow$ 66.9 ppt for HFC-134a, 1.9 ppt $\rightarrow$ 6.2ppt for HFC-32, 5.6 ppt $\rightarrow$

7.6 ppt for SF$_6$, and 79.4 ppt → 75.3 ppt for CFC-113. Based on the radiative efficiency[4] for each halocarbon, we found those change of halocarbon concentrations led to

. The breakdown is +0.012 W/m^2 from the increase of HCFCs, -0.007 W/m^2 from the decrease of CFCs and +0.007 W/m^2 from the increase of HFCs.
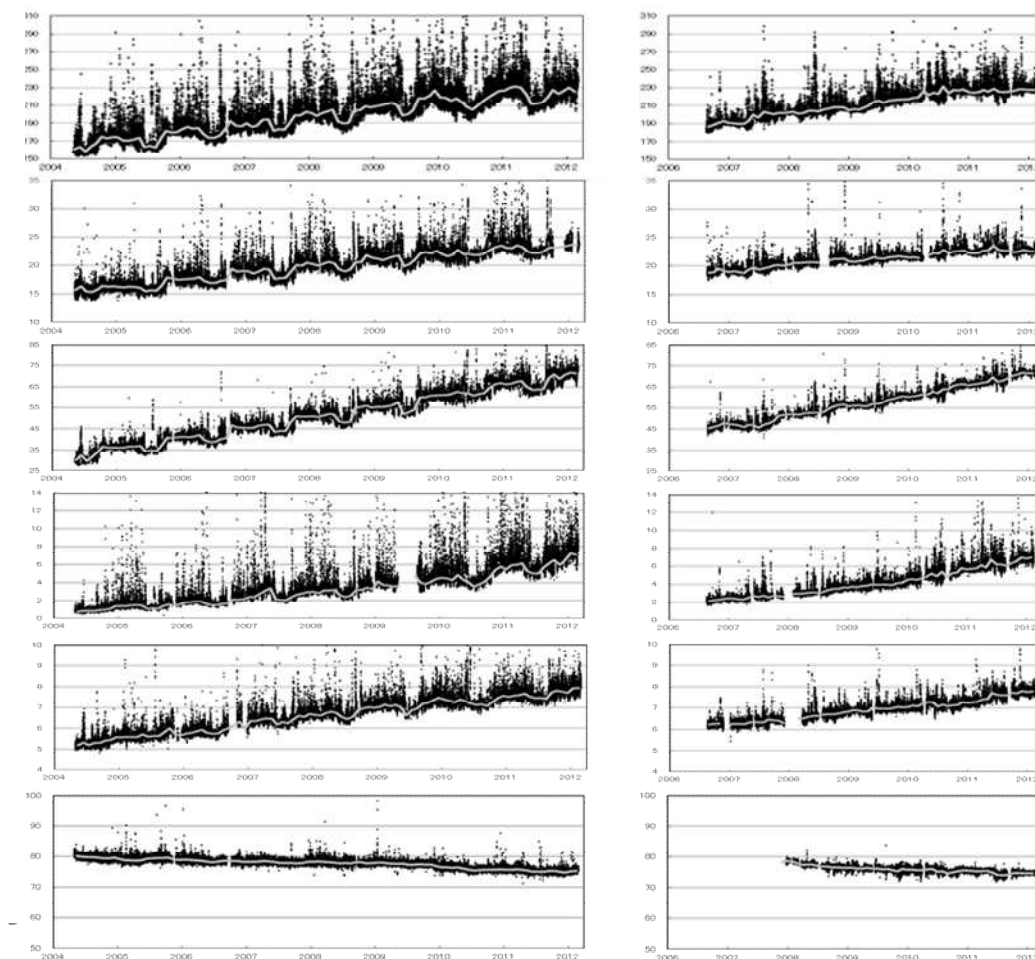

Figure 1. Atmospheric concentrations of (a) HCFC-22, (b) HCFC-142b, (c) HFC-134a, (d) HFC-32, (e) SF$_6$, (f) CFC-113 measured on Hateruma Island (May 2004〜February 2012：left hand) and at Cape Ochiishi (September 2006〜February 2012：right hand）

(2) Refinement of atmospheric halocarbon measurements

　　Both of the tested columns (GS-GasPro and alumina PLOT) showed excellent resolution for the fully halogenated hydrocarbons (i.e., PFCs, CFCs, and Halons, except carbon tetrachloride). However, alumina PLOT suffered from decomposition of certain halocarbons such as HCFC-152a and HFC-23, and InertCap-1 had a poor separation for low-boiling halocarbons although it showed better performance for the separation of some high-boiling halocarbons (e.g., carbon tetrachloride) than PoraBOND-Q. Thus, among the tested columns, there was no single column which has advantage for the measurements of wide boiling range of halocarbons over PoraBOND-Q.

　　To overcome this problem, we developed a multi-dimensional gas chromatographic system using PoraBOND-Q and InertCap-1 columns. The columns are connected to a Deans switch,

which controls an auxiliary gas flow (helium) for directing the carrier gas from the 1st separation column (InertCap-1) to either the 2nd separation column (PoraBOND-Q, and to a MSD) or the uncoated capillary column (and to a µECD).

The overall analytical procedure was evaluated in terms of reproducibility, linearity, and detection limit. The relative standard deviations (RSD) were <2% for most target compounds. The RSD for high-boiling polyhalocarbons, such as carbon tetrachloride and trichloroethane, were improved (<0.5%) compared to the measurements by the conventional GC/MS equipped with PoraBOND-Q column. All the halocarbons showed linear responses over a range of volumes (0-1 L). Detection limits (s/n = 2) for the low-boiling point analytes measured by MS were similar to those by the conventional GC/MS, but those for high-boiling point analytes (such as carbon tetrachloride) were lower owing to high resolution of InertCap-1 column and a high sensitivity of the µECD. Further, the multi-dimensional GC worked well to separate PFC-14 (CF_4), the lowest-boiling point analyte, from its interfering compound (krypton) by using a combination of the two columns.

The developed instrument has been deployed at Cape Ochiishi monitoring station since June 2011. The multidimensional GC measurements showed low scatter in the time series of carbon tetrachloride and trichloroethane compared to those by the conventional GC owing to the better precision of the multidimensional GC. Atmospheric measurements of PFC-14 at Ochiishi demonstrated baseline mixing ratios (ca. 79.5 ppt), along with short-term enhancements of the mixing ratios above baseline.

(3) Collaborative model study of halocarbon emissions from East Asia.

The model calculation of regional halocarbon emissions was done by Dr. Andreas Stohl. The model results were generally well correlated with the halocarbon measurements, and the best correlation was found for Ochiishi (ex. r^2 for HCFC-22 ; 0.63). Best estimates of Chinese emissions for the year 2008 were 65.3±6.6 kt/yr for HCFC-22, 12.1±1.6 kt/yr for HCFC-141b, 7.3±0.7 kt/yr for HCFC-142b, 6.2±0.7 kt/yr for HFC-23, 12.9±1.7 kt/yr for HFC-134a and 3.4±0.5 kt/yr for HFC-152a. Those for Japanese emissions were 6.0±0.3 kt/yr for HCFC-22, 1.1±0.1 kt/yr for HCFC-141b, 0.6±0.1 kt/yr for HCFC-142b, 0.21±0.03 kt/yr for HFC-23, 3.1±0.2 kt/yr for HFC-134a and 0.9±0.1 kt/yr for HFC-152a. Halocarbon emissions in China are much larger than the emissions in the other countries together and contribute a substantial fraction to the global emissions. Particularly, China accounts for more than 50% of the global HFC-23 emissions. Best estimates of Japanese emissions for HCFC-22, HCFC-142b and HFC-134a were similar to their bottom-up estimates (PRTR or GIO), but that for HCFC-141b was much lower than its PRTR emission estimate, and those for HFC-23 and HFC-152a were lower than their GIO emission estimates.

(4) Regional perfluorocarbon emissions in East Asia deduced from atmospheric measurements

Atmospheric measurements of PFCs at Hateruma and Ochiishi showed slight annual increases of the baseline mixing ratios (1%–3%) in the period of 2006-2009. We applied the inversion technique to the time series in order to estimate national emissions in East Asia. 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^{-1} for PFC-116, 0.31 Gg yr^{-1} for PFC-218, and 0.56 Gg yr^{-1} 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. The significant regional emissions of the PFCs in East Asia has recently been supported by the regional emission estimates based on the AGAGE measurements[5].

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 (0.196 Gg yr^{-1}) were higher by a factor of approximately 1000 than the emission rate associated with aluminum production (0.2 t yr^{-1}), suggesting that most PFC-116 is not emitted by aluminum production but by other industries (i.e., semiconductor industries).

(5) Simulation of annual emission rates of HCFCs and HFCs from China for 2006-2010

The fluxes were inverted by species and by year (2006-2010). The inverted fluxes were collected for each country using the country map at $1^{\circ}\times1^{\circ}$ resolution of GISS. The estimated fluxes for China are given in Table 1 for each year. The obtained fluxes were generally in good agreement with the results from Section (3) except for HFC-23 and HFC-152 which had almost double values. The interannul variations of the Chinese emissions in Table 1 suggest HFC-23 and HFC-152a emissions were highest in 2007 and have been decreased since then, while HFC-134a emission was highest in 2009. Calculated annual flux maps suggested HCFC-22 emission from Seoul vicinity increased substantially in 2009 and 2010.

year	HFC-134a	HCFC-141b	HCFC-142b	HFC-152a	HCFC-22	HFC-23
2006	9.5	12.9	7.1	7.2	65.3	11.7
2007	11.5	17.2	8.4	7.4	73.3	14.5
2008	11.6	17.4	8.6	7.2	65.3	13.2
2009	13.1	17.4	7.7	7.0	67.0	12.0
2010	10.7	16.5	7.0	6.6	75.1	12.7

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