Observational Study of Halocabon Greenhouse Gases to Infer Changes in Emissions in East Asia （Abstract of the Final Report）

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Total Budget for FY2005-FY2008 111,084,000Yen (**FY2008**; 25,284,000Yen)

Key Words Halocarbon, High-Frequency Measurement, Regional model, HFCs, HCFCs

1. Introduction

Halocarbons such as CFCs, HCFCs, PFCs, HFCs, and SF_6 are greenhouse gases with high global warming potentials (22200 for SF_6, 12000 for HFC-23…). Their emission is expected to grow rapidly in East Asia as the result of recent economic growth. However, there has been very limited observation of these halocarbons in Asia. In order to determine the importance of regional sources, we started measuring atmospheric halocarbons at Hateruma Island which had been a promising location for investigating Asian sources[1)], as well as at Cape Ochiishi in Hokkaido. Cape Ochiishi is occasionally influenced by the air masses from northern/eastern Japan. In this project, we continue the high frequency (~hourly) measurements of halocarbons at Hateruma Island and Cape Ochiishi. Based on the observational data, we determine the long-term and short-term trends of each halocarbon in East Asia, and estimate regional surface emissions combined with a transport model.

This project consists of two sub-projects, (1) In situ high frequency monitoring of halocarbons at Hateruma Island and Cape Ochiishi, (2) Model study of halocarbon emissions in East Asia.

2. Method

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

High frequency halocarbons monitoring has been done at the ground monitoring stations on Hateruma Island (123.8°E, 24.1°N) since March 2004 and at Cape Ochiishi (145.5°E, 43.2°N) since September 2006. Outside air drawn from the top of the 40-m tower is analyzed every hour with an automated halocarbon measurement system based on cryogenic preconcentration and capillary gas chromatography/mass spectrometry (GC/MS)[2)]. After every five air analyses, a gravimetrically prepared standard gas is analyzed for quantification using the same procedure. All the operations were automated, and occasional MS tuning could be done by remote-control. Target compounds include three PFCs, four HFCs, five HCFCs, five CFCs and SF_6. PFC-14 was also measured with a newly developed system installed at Ochiishi station.

(2) Model study of halocarbon emissions in East Asia.

Online tracer option of the regional meteorological model RAMS (Regional Atmospheric Modeling System) was employed for tagged simulation with the emission field in East Asia divided into 12 areas. The initial flux distribution was prepared with the 1° mesh geographic distribution provided by GEIA and the annual emission estimates for the year 2005 reported by

AFEAS. The period of the simulation was set from January 2005 to September 2007.Using the results of the on-line tracer forward calculation in combination with the hourly observation of HCFC-22 and HFC-134a at Hateruma, inversion calculations have been conducted based on Bayesian least-squares in order to estimate the unknown emission distribution in East Asia.

(3) Collaborative model study of global/regional halocarbon emissions.

An international collaborative model study was done to determine the regional and global emissions of halocarbon greenhouse gases. It exploits in-situe measurement data from a global network (AGAGE, SOGE and NIES-Hateruma) in Figure 1, and builds on backward simulations with a Lagrangian particle dispersion model. The emission information is extracted from the observed concentration increases over a baseline that is itself objectively determined by the inversion algorithm. The method was applied to HFC-134a, HFC-152a and HCFC-22 for the period January 2005 till March 2007.

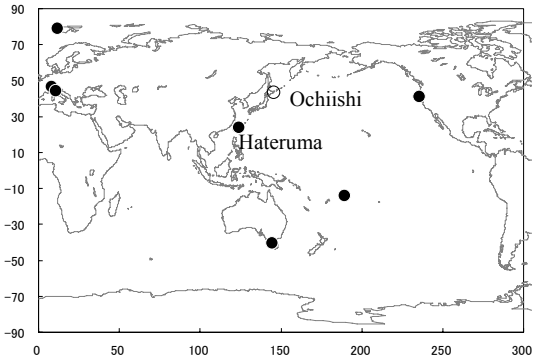

Figure 1. High frequency monitoring stations for halocarbon monitoring network employed for the model study (●).

3. Results and Discussion

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

The whole datasets obtained for HFC-134a, HFC-152a, HFC-23, HCFC-22, and HCFC-142b are shown in Fig. 2. The most striking feature is the occasional short-term enhancement of concentrations over hours to days, which was more frequently observed during winter and spring at Hateruma Island. Their baseline concentrations observed at Hateruma Island show a clear seasonal variation, being lower in summer than in other seasons, while the data obtained from Cape Ochiishi showed less prominent seasonal variation. The increases of their baseline concentrations from 2004 to 2008 were 37.0ppt to 51.6 ppt for HFC-134a, 4.8ppt to 7.1ppt for HFC-152a, 20.0ppt to 22.8ppt for HFC-23, 1.5ppt to 3.0ppt for HFC-32, 173ppt to 201ppt forHCFC-22, 19.1ppt to 21.1ppt for HCFC-141b, and 16.4ppt to 20.2ppt for HCFC-142b at Hateruma. The baseline concentrations of PFCs were 77.8 ppt for PFC-14, 3.9 ppt for PFC-116, 0.6 ppt for PFC-218, and 1.3 ppt for PFC-318 at both of the stations in 2008. PFC-116 observed at Hateruma Island showed slight increasing trend at a rate of approximately +0.07 ppt/yr. PFC-14 also showed increasing trend with +0.84 ppt/yr at Ochiishi.

Short-term enhancement (or pollution events) of halocarbons could be related to one or more potential sources surrounding Hateruma Island and Cape Ochiishi. The potential source region for each pollution event was identified using a tagged simulation of HCFC-22 from three-dimensional transport model. The simulations showed that the pollution events at Hateruma were mainly attributed to China and Taiwan, while those observed at Ochiishi were assigned to Japan. The relative ratios of the enhancements of the HFCs and HCFC-22 and their ratios to the increase in atmospheric CO concentration are expected to reflect the ratios of their emission strengths in each source region. If the emission rate of one species (Er, Gg/y) from an area is known, then the emission rates of all the other compounds (Ex, Gg/y) in the same dataset can be calculated from the enhancement (ΔC) at the pollution event by using the following equation:

$$E_x = E_r \times \Delta C_x/\Delta C_r \times M_x/M_r$$

where M_x and M_r are the molecular weights of species x and reference compound r, respectively, and ΔC_x and ΔC_r are expressed in ppt.

Using this approach and available data for CO emissions, we tentatively estimated HFCs emissions from China. The annual emission rates of HFC-23, HFC-134a, HFC-152a and HCFC-22 from China were estimated to be around 11 Gg/y, 4.2Gg/y, 4.6Gg/y and 56Gg/y, respectively.

Furthermore, using the relative enhancement ratios of PFCs to HCFC-22 concentrations and the known emission estimates of HCFC-22 in China, Japan, and Taiwan, annual emission rates of PFCs were calculated; as for PFC-116, 0.69 Gg in China, 0.23 Gg in Japan, and 0.19 Gg in Taiwan. Based on 16 pollution events during 2005-2008, the emission strengths ratios from China were estimated to be HCFC-22: 50%, HFC-23: 17%, HCFC-141b: 13%, HCFC-142b and HFC-152a: 5%, HFC-134a: 4% on a weight base. Converted to the ratios of their potential impacts on the global warming using the GWP for each compound, they were HFC-23: 62%, HCFC-22: 23%, SF6: 5%, HCFC-141b and HCFC-142b: 3%.

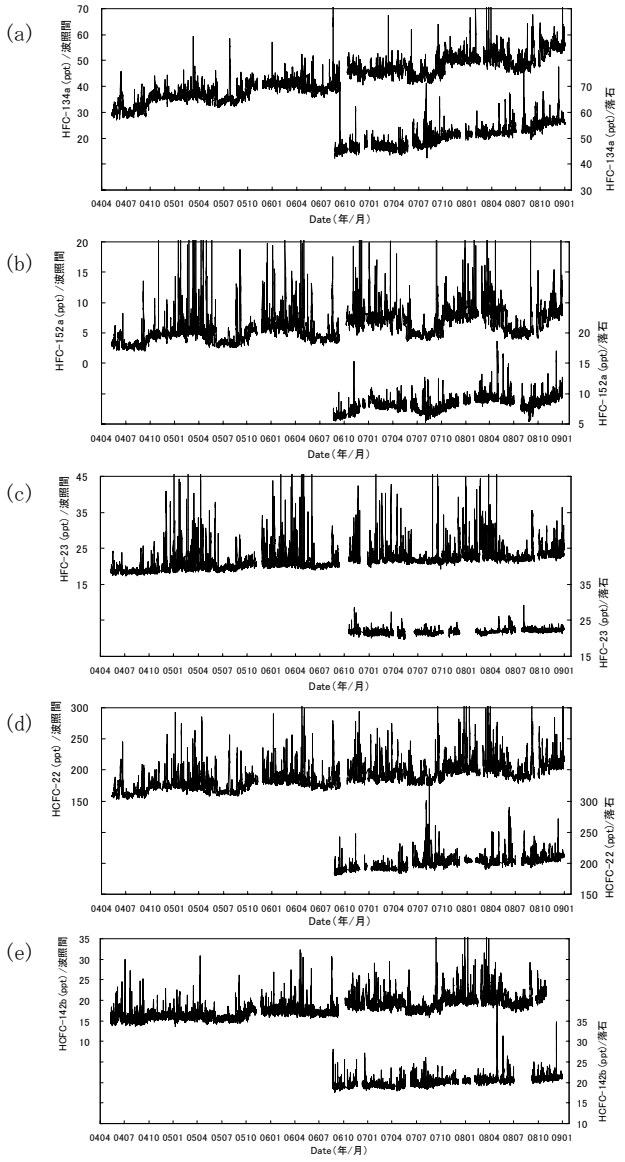

Figure 2. Atmospheric concentrations of (a) HFC-134a, (b) HFC-152a, (c) HFC-23, (d) HCFC-22, (e) HCFC-142b measured at Hateruma Island(May 2004 ～ December 2008：left scale) and at Cape Ochiishi (September 2006～ December 2008：right scale)

(2) Model study of halocarbon emissions in East Asia.

We calculated the concentration of RAMS online tracers by tagged simulation using12 source regions and compared it with the halocarbon data for HCFC-22 and HFC-134a at the Hateruma and Ochiishi observation station. The model reproduced the short period cycle (~3-4days) and the seasonal change of the baseline concentration at Hateruma but the amplitude of the variation did not always agree with observed variation. Considering signal to noise ratio for HCFC-22 and HFC-134a observation, the baseline variation affect little to HCFC-22 but affect significantly to HFC-134a.

Figure 3 shows the time series of observed HFCF-134a, HCFC-22 and calculated tracer concentrations at Hateruma. The calculated values are the sum of all the tracer concentrations. For each sharp peak observed during the period, the calculated values give one or more corresponding peaks at the same timing, assuring the validity of the transport model simulation. However, when comparing the intensity of the observed and calculated peaks, the result using the initial emission (the solid line in Figure 3c) was far smaller than observed HCFC-22, suggesting the underestimation of the emission inventory employed. The dashed line and the dotted line in Figure 3c are the result factored by 5 and the result when only emission from China has been factored by

15, respectively. By comparing the area of calculated and observed peaks exclusively originated from China (peaks 1-4 in Figure 3), judged by the tagged simulation, the difference in the emission used in the simulation and actual emission was estimated. Derived mean difference between calculated and observed peaks was a factor of 14.8 (± 4.6) which can be converted to the annual emission of 43(±14) Gg by multiplying the China emission used in the model.

Using the data from the high frequency monitoring at Cape Ochiishi, we tried to interpret the time series of observed HCFC-22 by comparison with the forward simulation result from July 2006 to September 2007 with the same settings as those for Hateruma Island. The result of forward simulations indicated that the high-concentration events observed at Ochiishi were mainly due to the emission from Hokkaido and/or East Japan. Throughout a year, there were little cases of direct transport from China to Ochiishi. Focusing on reducing the uncertainty of the emission from China in this study, we used only the Hateruma result in the following discussion of emission estimate by inversion technique.

Figure 4 shows the inversion results from winter in 2005-2007. The total uncertainty for Chinese emission was reduced from 50% (a priori) to 15% (a posteriori) by the inverse calculation. The estimated annual emission of HCFC-22 from all 4 source regions in China ranged from 3-16 Gg, and the total annual emission was estimated to be 32(±5) Gg. This result was generally consistent with the annual emission from the China of 52(±34) Gg estimated using the tracer-ratio technique mentioned above.

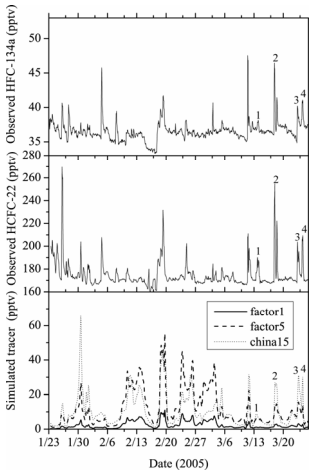

Figure 3. Observed concentration of a) HFC134a and b) HCFC-22 and c) simulated tracer concentration at Hateruma station. (Solid line: factor=1, dashed line: factor=5 applied to all emissions, dotted line: factor=15 applied to the emissions from China only. See text for the peak numbers shown in late March.

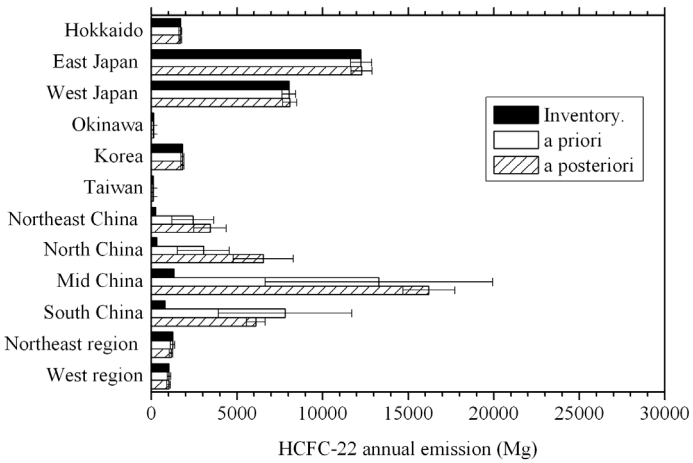

Figure 4. Results of the inverse calculation of HCFC-22 mean annual emission for 2005-2007. Error bars show covariance before and after the inversion.

(3) Collaborative model study of global/regional halocarbon emissions.

The model calculation of global/regional halocarbon emissions was done by Stohl et al. and was published[3]. It was found that the global a posteriori emissions of HFC-134a, HFC-152a and HCFC-22 all increased from the year 2005 to 2006. Large increases (by 21%, 16%, 18%, respectively) from2005 to 2006 were found for China, whereas the emission changes in North America and Europe were modest.An internat. Emissions frm Japan and China in 2006 were estimated to be 4.0 Gg/y and 11.9 Gg/y for HFC-134a, 1.3 Gg/y and 3.7 Gg/y for HFC-152a, and 7.8 Gg/y and 70.7 Gg/y for HCFC-22, respectively.

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