B-6 Development of monitoring system for the halocarbon inventory in East Asia

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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...)[1]. Among them, ozone-depletion gases (CFCs and HCFCs) were banned or scheduled to be phased out under the regulations of the Montreal Protocol and its Amendments. HFCs (alternative compounds for CFCs and HCFCs), PFCs and SF_6 are targeted for reduction under the Kyoto Protocol, but are currently increasing. It has become an important issue to know the sources and the magnitudes of these halocarbons, in order to guarantee the measures' effectiveness as well as to predict their radiative effects on the global environment. It has been shown that high frequency measurement is a promising way to determine regional surface fluxes, combined with a three-dimensional chemical transport model. In this project, we develop monitoring system based on in-situ frequent measurements at Hateruma Island and aircraft sampling over Sagami-Bay for the halocarbon inventory in East Asia/Japan.

2.Research Objective

The first objective is to optimally determine the sources and magnitudes of halocarbons (PFCs, HFCs, SF_6, CFCs, HCFCs and some anthropogenic halocarbons) in East Asia / Japan from the observations. For this purpose, we develop a new high frequency monitoring system for the halocarbons, and have it run at Hateruma Island. The second objective is to know the long-term trend of atmospheric halocarbons, which would reflect the increased use of halocarbons in Asia. The third objective is to provide precise database of atmospheric halocarbons in East Asia to the global monitoring network.

This project consists of three sub-projects, (1) *In-situ* real-time monitoring of atmospheric halocarbons at Hateruma Station, (2) Aircraft monitoring of halocarbons over Sagami-Bay,

and (3) Simulation of halocarbon emissions in East-Asia based on a chemical transport model.

3. Results and Discussion

(1) *In-situ* real-time monitoring of atmospheric halocarbons at Hateruma Station

For the precise analyses of atmospheric halocarbons at a remote site, a new cryogen-free preconcentration / capillary GC-MS system has been developed. The instrument was installed in the ground monitoring station at Hateruma Island (123.8°E, 24.1°N) in February of 2004. Outside air was drawn from the top of the tower (40m high) through a teflon tube (1/2" ID), which was subsequently replaced with stainless steel tube, at a high flow rate. Part of this airflow was supplied to the preconcentration system in which 500 mL air samples were collected on a small trap containing Carboxene 1000 and Carbopak B cooled to -150°C in a small freezer (MMR, BIO-120). By increasing the trap temperature to -60°C, carbon dioxide and more volatile components than carbon dioxide were flushed out. Then the remaining components were thermally (200°C) desorbed and transferred to the second smaller trap cooled to -150°C. Then the second trap was heated to 200°C, and the desorbed components were transferred to a capillary column (Porabond Q, 0.32mm x 100m) for GC/MS (SIM) analyses. Target compounds included 3 PFCs, 4 HFCs, 5 HCFCs, 5 CFCs and 3 solvent halocarbons such as tetrachloroethylene (C_2Cl_4). Samples were analyzed once an hour, and after every five air analyses, standard gas (100-500 ppt) prepared gravimetrically was analyzed for quantification using the same procedure. All the operations were automated, and occasional MS tuning could be done by remote-control. This is the first *in-situ* high-frequency measurements of halocarbons under control by Kyoto-Protocol in Asia. More than 7000 datasets were obtained during the period of February 2004 – May 2005.

The whole datasets obdained for HFC-23, SF_6, HCFC-22, HFC-134a and C_2Cl_4 are shown as time-series in Fig. 1. HFC-23 and SF_6 had almost constant baseline concentration around 18 ppt and 5.2 ppt, respectively, and had occasional short-term increase during wintertime. HCFC-22, HFC-134a and C_2Cl_4 showed higher variability, and their baseline concentration changed greatly with the seasons. It can be seen their baseline concentrations of HCFC-22, HFC-134a and C_2Cl_4 are lower in the summertime when the oceanic air masses come to Hateruma from the south (lower latitudes) under the Pacific high-pressue system. In the other seasons, the site is mostly influenced by Asian Continental outflow. Among the twenty target halocarbons, most significant seasonal difference in the baseline concentrations were observed for the short-lived compounds such as C_2Cl_4 and C_2HCl_3, and some types of HFCs and HCFCs such as HFC-134a and HFC-152a which industrial use has been growing rapidly and have a large gradient in their latitudinal distribution. The average concentration

during the period of September-August of 2004 and January-February of 2005 were 162.8 ppt and 177.2 ppt for HCFC-22, 15.5 ppt and 16.3 ppt for HCFC-142b, 5.3 ppt and 5.6 ppt for SF_6, 18.5 ppt and 21.0 ppt for HFC-23, 30.4 ppt and 37.4 ppt for HFC-134a, 540.1 ppt and 541.0 ppt for CFC-12, and 1.3 ppt and 5.8 ppt for C_2Cl_4, respectively. PFCs and CFCs did not show significant seasonal change.

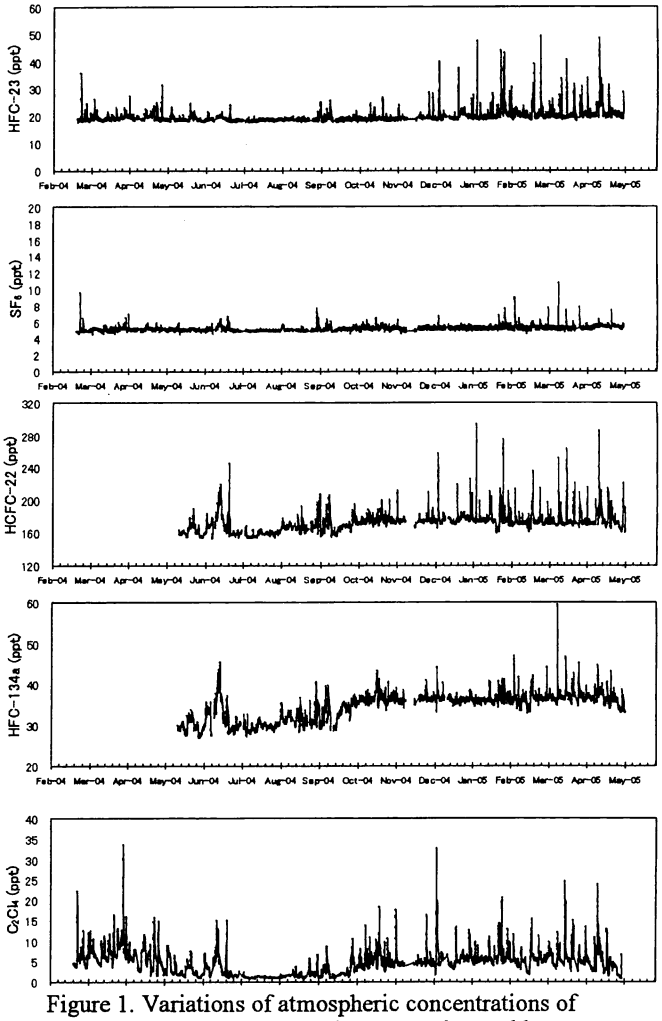

Figure 1. Variations of atmospheric concentrations of HFC-23, SF_6, HCFC-22, HFC-134a, and tetrachloroethylene measured at Hateruma (20 February 2004–8 May 2005).

(2) Aircraft monitoring of halocarbons over Sagami-Bay

Regional- and national-scale emission rates of halocarbons have been a great concern in the field of global environmental studies and policy making. Emissions have been inventoried mainly by bottom-up approaches, which involve adding up emissions from various industrial sources. To verify and supplement those bottom-up inventories, top-down approaches based on measurements of air concentrations are required. In this study, aircraft monitoring over Sagami Bay, Japan (lat 35.04°N, long 139.28°E), was used to estimate the emission ratios of halocarbons (PFCs, HFCs, CFCs, HCFCs, and others) from Japan. The halocarbons showed higher and more variable concentration at lower altitude (500 – 1000 m) as expected for gases with their sources at surface. The enhancements of selected halocarbons at low altitudes compared to those in the free troposphere should be largely affected by their source strength around Sagami Bay. The enhanced concentrations in the boundary layer of air masses having traveled over Japanese mainland were used for the calculation under the assumption that the air masses over Sagami Bay represented average emission ratios for anthropogenic halocarbons on a countrywide basis. Given their emission ratios, a single compound with a credible emission rate can yield the emission estimates for all the other compounds. When we employed an inventory-based emission estimate of

HCFC-22 from the Pollutant Release and Transfer Register (PRTR) system 2002 of Japan (9.1 Gg/y) as the reference, the estimated emission rates of HCFC-141b, HCFC-142b, CFC-12, chloroform, and trichloroethylene for 2002 were consistent with their PRTR values within 10%. Emissions of carbon tetrachloride (CCl_4) and 1,1,1-trichloroethane (CH_3CCl_3) were much higher than their PRTR values, suggesting that their sources are not adequately accounted for in the current inventories. This study also presents probable annual emission rates for individual HFCs and PFCs that previously had no reported estimates; for example, 4.4 Gg/y for HFC-134a as of 2002.

In the free troposphere over Sagami-Bay, the increase of HCFC-22, HCFC-142b, HCFC-141b have been slowed down in 2003, while HFC-134a has increased linearly through the period of 2001-2004, and HFC-152a showed significant increase during 2005 winter.

(3) Simulation of halocarbon emissions in East-Asia based on a chemical transport model.

Emissions of HCFC-22 in East Asia were analyzed using hourly observations at Hateruma during May to December 2004. We defined pollution events and background conditions in the time series of the observations. Eighteen pollution events were defined as high concentrations periods with maximum concentrations higher than 180 ppt. We call periods not assigned to pollution events as background conditions. Analyses were conducted with a global atmospheric transport model of STAG (Simulator of Tracer transport of the Atmosphere in Global scale). It has 1.125x1.125x60L and 6 hourly resolution. Meteorological data were an operational analysis of ECMWF (European Centre for Medium Range Weather Forecasts) of 2004. Analysis were composed of the following four steps; (a) consistency check using some observations running the model 26 years with emissions and removal processes started with zero concentrations, (b) relative contributions from 7 areas on the globe using 26 years simulations, (c) detection of pollution events from 18 areas on the globe, (d) linear fitting of these 18 emissions using synthesis inversion.

(a) Global emissions of HCFC-22 estimated by AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) and geographical distributions of the emissions estimated by RCEI (Reactive Chlorine Emission Inventory)[2)] were emitted into the model atmosphere. Removal by the reaction of OH (Spivakovsky et al., 2000) with reaction coefficients recommended by JPL(Jet Propulsion Laboratory). Simulated concentrations were compared with monthly observations of vertical profile at Sagami-Bay in 2002 and hourly observations at Hateruma Island in 2004. Simulated concentrations at Sagami-Bay agreed with the observations at 1- 7 km within 5pptv. Simulated concentrations at Hateruma underestimated 50 ppt in polluted events, although they agreed within 5 ppt in background conditions. A remarkable feature of this simulation was that a short term low concentration events at Hateruma could be attributed to the intrusion of low concentrations air mass of

Southern Hemisphere when Typhoon passed near the island. In fact 9 typhoons passed near Hateruma island only in these seven months.

(b) Global emissions were decomposed into 7 area, namely Europe(28.5%), India and Russia(4.5%), China and Korea(2.2%), Taiwan (0.2%), Japan (6.9%), North America (51.0%), and the Southern Hemisphere (6.7%). Simulated concentrations in 2004, relative contributions in background conditions were proportional to the emission rate.

(c) 18 areas were set on the globe as potential emission areas and were used for STAG simulations of 12 month starting from January, 2004. We could detect the Asian sources (Shanghai area, Taiwan area, Korea area, west-Japan area and their combinations).

(d) Emissions of 18 areas were estimated to fit the simulated concentrations with the observations in the least square sense using a synthesis inversion technique. Some cases with different uncertainties in prior estimate produced a wide range of posterior flues. In most of the case, we obtained negative value in posterior flux which is unlikely. It was suspected that some of the high concentration events are spatially too narrow for STAG to make. Also time variations of the emissions which we ignored in the current analysis might take place.

As a summary, AFEAS emissions, RCEI emissions distributions, Spivakovsky's OH, JPL recommendations in reaction coefficients, STAG and the observations were in principle consistent. Major discrepancies were the size of pollution event that were largely underestimated by STAG. Possible causes of this underestimate are: (1) width of high concentration area is narrower than the size of grid interval of STAG, (2) emissions are sporadic which we ignored in the current analysis.

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