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CONTINUOUS MEASUREMENTS OF ATMOSPHERIC HALOGENATED COMPOUNDS AT JEJU ISLAND, KOREA FOR ESTIMATION OF EMISSION FROM EAST ASIA

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Abstract: Ambient concentrations of halogenated compounds have been analyzed every two hours using the "Medusa" cryogenic pre-concentration system with gas chromatograph and mass selective detector (GC-MSD) at Gosan (Jeju Island, Korea) from Nov. 2007. Our analysis results identified country based emission ratios and correlation patterns among measured species. The emissions of these compounds in East Asia estimated by interspecies correlation method account for over ~30% of global emissions, and emphasize the importance of atmospheric measurement in this region.

Keywords: Halogenated compounds, Jeju Island, emission, East Asia.

1. INTRODUCTION

Many halogenated compounds including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) bromine containing halocarbons (halons, CH_3Br), and long-lived chlorinated compounds (CCl_4, CH_3CCl_3) are regulated by the Montreal Protocol (MP) due to their role in the depletion of the stratospheric ozone layer. Other halocarbons 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 developing countries under Kyoto Protocol (KP). Accurate measurements of these compounds are essential to monitoring the emissions strength and reduce effort.

Measurements of trace halogenated compounds in East Asia are of interest because they are expected to be a significant proportion of the global total and also because these emissions will change as each country adapts differently to the MP and the KP.

Here, we summarize the recent finding from measurements of halogenated compounds at Gosan for quantifying the emissions of these species in East Asia. A brief description of the analytical methodology used at the station is followed by a discussion of the results derived from our measurements, as reported in recent literature (Li et al. 2011; J. Kim et al. 2010).

2. MEASUREMENT

The measurement system at Gosan is comprised of GC-MSD system (Figure 1) for measuring ~40 halogenated compounds, which is optimized for remote site in situ field operations as well as the advanced pre-concentration, desorption and chromatographic characteristics (Miller et al. 2008). The measurements of the GC-MSD system reported using calibration scales developed by the Scripps Institute of Oceanography under Advanced Global Atmospheric Gases Experiment (AGAGE). Typical precisions seen by the measurements are better than 1% of background atmospheric concentrations. The GC-MSD system has been installed as part of AGAGE network at Gosan on Nov. 2007 for monitoring emission strength of ozone depletion compounds and greenhouse gases from East Asia.

Figure 1.'Medusa' GC-MSD system at Gosan for measurements of halogenated compounds.

Measurement precisions of Medusa system can be deduced from the measurements of the quaternary standard gas, which is repeated between every ambient air measurement results of the precisions estimated for each measured compound is displayed in Table 1, along with average ambient concentrations measured at Gosan, all for 2009. The precisions measured on the medusa are mostly less than 1% of the ambient concentrations, signifying the excellent measuring capabilities of the medusa system.

Table 1. Average concentrations and measurement precision of the Gosan observations.

Compound Name	Avg. Conc. (2009, ppt)	Avg. Prec. (2009, ppt)	Compound Name	Avg. Conc. (2009, ppt)	Avg. Prec. (2009, ppt)
CFC-11	245.63	0.64	H-1211	4.52	0.04
CFC-12	538.16	0.50	H-1301	3.33	0.06
CFC-13	2.91	0.04	H-2402	0.48	0.01
CFC-113	76.20	0.13	CH_3Cl	645.60	1.19
CFC-114	16.51	0.04	CH_2Cl_2	98.44	0.72
CFC-115	8.42	0.05	$CHCl_3$	19.16	0.15
HCFC-22	241.62	0.57	CCl_4 (prelim)	89.83	0.73
HCFC-124	1.67	0.04	CH_3CCl_3	9.68	0.10
HCFC-141b	25.83	0.10	CH_3Br	11.23	0.06
HCFC-142b	23.47	0.08	CH_2Br_2	1.38	0.02
HFC-134a	61.24	0.17	$CHBr_3$	2.19	0.01
HFC-152a	9.91	0.08	CH_3I	1.23	0.02
HFC-23	24.41	0.18	C_2H_6	1753.95	2.97
HFC-32	5.48	0.16	Benzene	226.97	1.74
HFC-125	8.60	0.04	Toluene	6.68	0.03
HFC-143a	10.99	0.09	COS	645.24	2.92
CF_4	78.70	0.08	TCE	6.66	0.11
C_2F_6	4.15	0.03	PCE	6.52	0.05
C_3F_8	0.56	0.01	SO_2F_2	1.78	0.02
SF_6	7.47	0.03			

Gosan station is located on the south-western tip of Jeju Island, south of the Korean peninsula (126°9' E, 33°17' N, 72m asl, Figure 2(a)). Located on a remote hill-top by the coast, effects from local contamination can be assumed to be minimal, and allow for research of long-range transport from the surrounding region. The wind patterns at Gosan are typical of the Asian Monsoon pattern, with strong northern winds in the winter time, and southern influence during the summer season. These wind patterns are favourable for monitoring air masses passing through East Asia, especially from China and Korea. Air masses passing through Japan are relatively less frequent and constrained to the spring and fall seasons (Figure 2(b)). Clean "baseline" conditions are observed when a clean stream of air flows in directly from the northern Siberia region (in winter) and during transport of southerly oceanic winds (in summer).

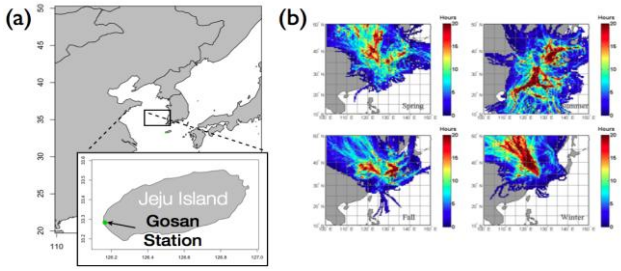

Figure 2.(a) Location of Gosan, Jeju Island (Korea) and (b) General wind pattern observed at Gosan, shown as residence time of air-mass back-trajectories prior to arriving at Gosan.

For source region (China, Korea, and Japan) classification we combined air-mass back-trajectory analysis. We defined regional grid boxes representing each country in East Asia as shown in Figure 3, and for each 4-day kinematic back trajectory arriving at Gosan we calculated the residence time. If a trajectory stayed below the planetary boundary layer (2000m) for more than 1 hour in one of the four regional boxes, the air mass was retained in our analysis and classified accordingly.

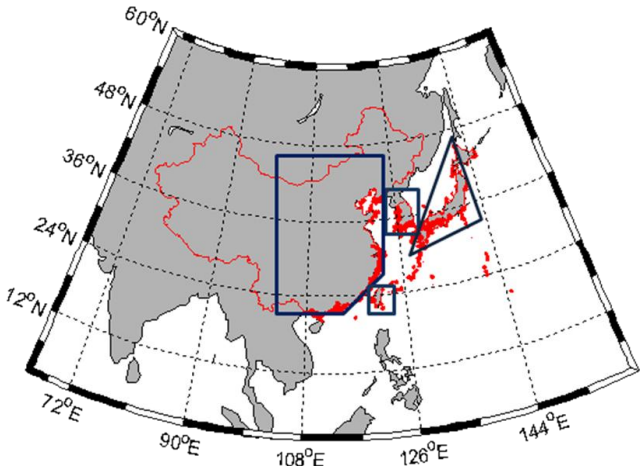

Figure 3. Map showing the measurement station at Gosan, Jeju Island, Korea as a star in the inset along with the four source regions.

3. RESULTS AND DISCUSSIONS

The results of the measurements reveal frequent pollution events of almost all measured species, reflecting the large emissions of many halogenated compounds in East Asia (Figure 4, example of HCFC-22). Concentrations during these baseline conditions agree well with the baseline concentrations at other background sites in North Hemisphere, such as Mace Head (Ireland) and Trinidad Head (California, US).

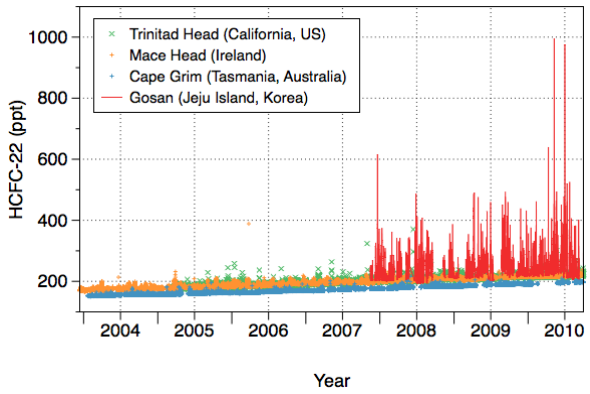

Figure 4.Measurements of HCFC-22 at Gosan by comparing that observed at Trinidad Head, Mace Head, and Cape Grim.

Emission rates for China, Korea, and Japan were estimated using an interspecies correlation method, in which the emission rates of co-measured, correlating compounds can be calculated from the ratio to a reference tracer with known emission rates. This method is based on the assumption that correlating compounds have collocated emission sources, which may be reasonable for many of the compounds considered in this study with similar industrial uses and emissions (Figure 5). The emissions result was

shown in Figure 6 by each country and each group compounds (CFCs, HCFCs and HFCs).

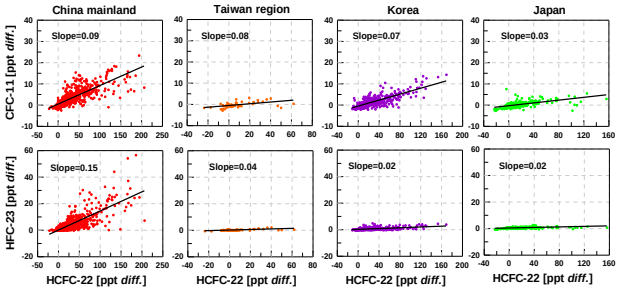

Figure 5. Scatter plotting of CFC-11 and HFC-23 versus the HCFC-22, which influenced by each main emission source regions (China, Taiwan, Korea and Japan).

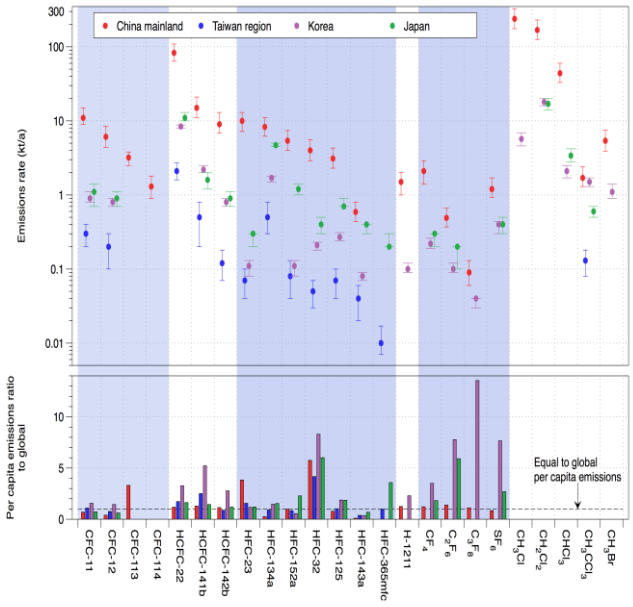

Figure 6. Emissions rate for China, Taiwan, Korea and Japan are shown in the top plot. The ratios of national per capita emissions to global per capita emissions are shown in the lower plot.

While the total emissions (Figure 7) of halogenated compounds are largest in China, per-capita emissions (Figure 8) are significantly larger in Korea than in China. This shows that emissions in Korea, while relatively small quantitatively, are still a cause for concern. In addition, if China's per-capita emissions were to reach Korean levels, as China follows Korea's path in economic development, the increase in Chinese emissions would have a significant impact on the global budgets of these compounds. As such, continued monitoring of emissions is essential for this region.

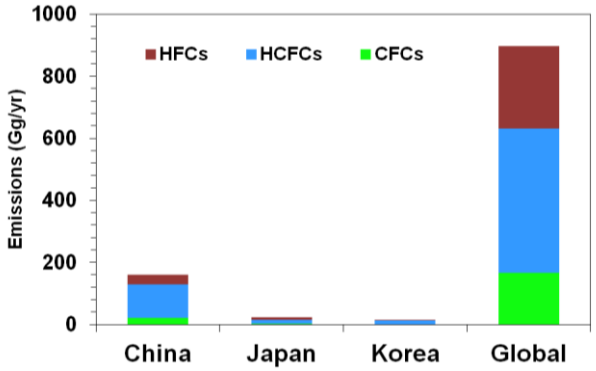

Figure 7.Total emissions of halogenated compounds in China, Korea and Japan for 2008.

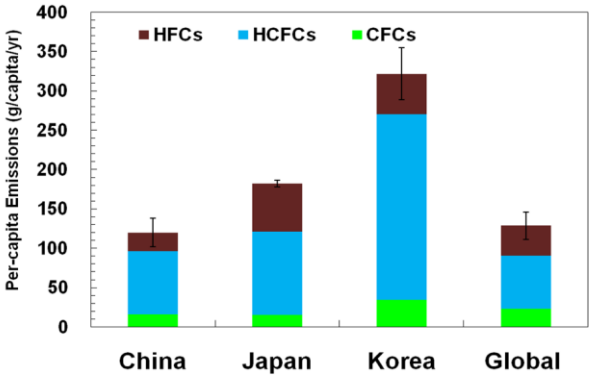

Figure 8.Per-capita emissions of halogenated compounds in China, Korea and Japan for 2008.

4. CONCLUSIONS

The continuous measurements of trace halogenated compounds at Gosan are important to defining the current state of emissions in East Asia, which serves as a baseline for future changes. Emissions derived from measurements (so-called "top-down" emissions) are crucial to validate "bottom-up" emissions and to ultimately reach the emission reduction goals set forth by the international community (Nisbet and Weiss 2010). The measurements at Gosan will provide the data needed to assess the emissions of the halogenated species, both now and in the future.

5. REFERENCES

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