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Asia-Pacific GAW on Greenhouse Gases

Newsletter

Volume No.6
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KMA Korea Meteorological Administration

GAW

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Contents

Recent activities on Global Atmosphere Watch in Korea

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Korea Meteorological Administration (KMA) began the atmospheric composition watch in association with the Global Atmosphere Watch (GAW) Programme of World Meteorological Organization (WMO) in 1987. KMA has produced many kinds of measurement data from twelve sites in the fields of GAW and has run the World Calibration Centre (WCC) for SF_6 to help the GAW stations keep traceability and compatibility for atmospheric SF_6 measurements.[1] Here we introduce the GAW related activities of KMA carried out in 2015, especially in terms of integration of the GAW-related measurement activities as well as expanding the measurement networks in Korea.

Korea Aerosol LIDAR Observation Network (KALION)

We constructed the Korea aerosol LIDAR Observation Network (KALION) to cope with aerosol-related atmospheric environmental issues, e.g., Asian dust, smog, haze, volcanic ashes, and fire plumes, originating both from the Asian Continent and in the Korean Peninsula.

An aerosol LIDAR (Light Detection and Ranging) instrument retrieves vertical profiles of information on aerosols so that it has advantages in monitoring of transport of aerosols, unlike conventional in-situ instruments. The KALION, which consists of fourteen LIDAR measurement sites to monitor transport of aerosols over the Korean Peninsula, is run by ten institutes in Korea National Institute of Meteorological Sciences (NIMS), National Institute of Environmental Research (NIER), Seoul Research Institute of Public Health and Environment (SRIPHE), Seoul National University (SNU), Mokwon University (MU), Hanbat University (HU), Gwangju Institute of Science and Technology (GIST),

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Ulsan National Institute of Science and Technology (UNIST), Gangneung-Wonju National University (GWNU), and Hankuk University of Foreign Studies (HUFS) (Figure 1).

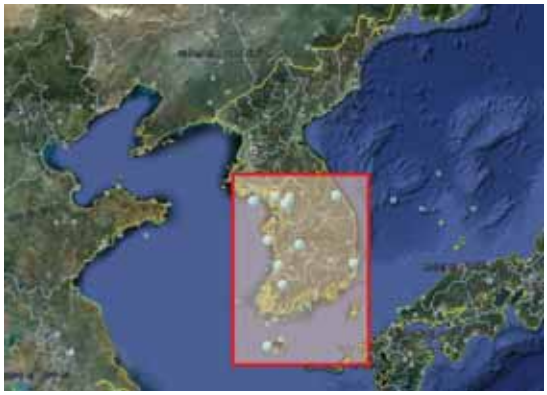

Figure 1

Observation sites of the Korea Aerosol LIDAR Observation Network (KALION).

In KALION, continuous observations are carried outat six sites and event observations in the other eight sites. There are also two intensive observation campaigns a year, during March to May and September to November. KALION members run the elastic-backscatter or inelastic-backscatter (Raman) LIDAR instruments with at least two wavelengths.

They basically share the range-corrected raw data and produce the vertical information on aerosols in real time using a unified analysis algorithm; i) aerosol optical properties, e.g., backscattering coefficients, depolarization ratios, and color ratios, ii) aerosol classification, e.g. Asian dust, pollutants, and clouds, and iii) aerosol mass concentrations (Figure 2).

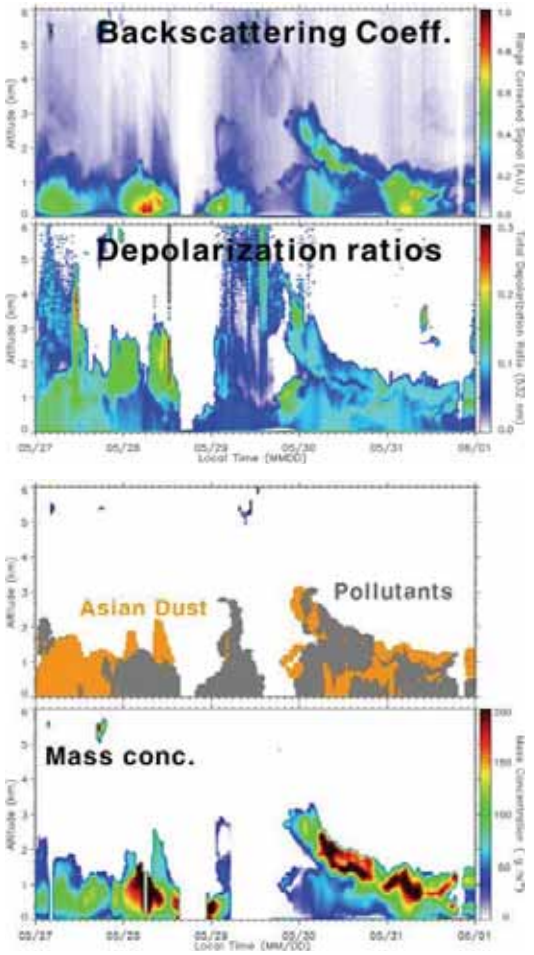

Figure 2

Examples of products from KALION. Backscattering coefficients, depolarization ratio retrieved from the LIDAR signals, vertical profiles aerosol classification and mass concentration (from top to bottom).[2]

Vertical distribution of particle mass concentrations was estimated with optical properties from the aerosol LIDAR, aerosol optical depth (AOD) data from collocated radiometer, e.g. sun-sky radiometer and sun-photometer, and PM_{10} concentrations from ground-based in-situ instruments. LIDAR ratio and mass extinction efficiency were determined from AOD and ground-level PM_{10} concentrations,

which were used as constraints to estimate particle mass concentrations. See Kim et al. (2015) for the detailed information on the retrieval of mass concentrations, classification of aerosols and schematic diagram for calculation of aerosol mass concentrations.[2]

The retrieved data are publicly served through the KALION webpage (www.kalion.kr). We have a plan to join the GAW Aerosol LIDAR Observation Network (GALION) after it is settled down.

Integration of the GAW related activities at Gosan, Jeju

There are two regional GAW stations, Jeju Gosan station (JGS) and Gosan station (GSN), at the Gosan area in Jeju island, Korea. The JGS station, which is all run by the KMA, comprises a comprehensive set of measurements under the umbrella of the GAW Programme. The JGS station produces data of greenhouse gases, reactive gases, aerosols, stratospheric ozone and ultraviolet radiation, atmospheric radiation, and atmospheric chemistry. The GSN station is known as a supersite where the International Global Atmospheric Chemistry Program (IGAC) has conducted the Aerosol Characterization Experiment (ACE-Asia) from March to May in 2001.[3] There are many institutes that conduct the atmospheric composition measurements in the supersite, e.g. KMA, SNU, Kyungpook National University (KNU), Yonsei University (YU), Korea University (KU), and Jeju National Universities (JNU) (see Table 1). The greenhouse gas measurement system operated by KNU is a part of the Advanced Global Atmospheric Gases Experiment (AGAGE) network.

We are integrating the two stations, GSN and JGS, into one station and share our out-

Table 1. Atmospheric componentsmeasured by KMA at JejuGosanstation(JGS), SNU, Kyungpook National University (KNU), Yonsei University (YU), Korea University (KU), and JejuNational Universities (JU), and Korea Environment Corporation (KEC)at the Gosan supersite (GSN)

Institute	Greenhouse Gases	Reactive gases	Aerosols	Precipitation Chemistry	Others
KMA	CO_2, CH_4, N_2O	CO, NO_x, SO_2, O_3	Physical[1]		
KNU	CO_2, CH_4, SF_6, PFCs[2], HFCs[3], Isotopes	CO			
SNU			Physical[4], Optical[5]		
KEC			Ions	Acidity, Conductivity, Ions	
JNU			Metals, Ions		Rn-222
KU			EC/OC[6]		
YU			Physical[7]		

1) $PM_{1,2.5,10}$, size distribution (0.5-20 μm), Condensation Particle Counter (0.01-3 μm) 2) Perfluorocarbons; 3) Hydrofluorocarbons; 4) $PM_{1,2.5,10}$, size distribution (0.5-20 μm, 0.01-5 μm), Condensation Particle Counter (0.003-3 μm) 5) Aerosol optical depth, scattering coefficients, absorption coefficients, and vertical profiles of backscattering coefficient, depolarization ratio, and color ratios 6) Element carbons/ organic carbons; 7) Condensation Particle Counter (0.003-3 μm)

put, which is resulting in enhancing usage of the data. To fulfill the integration, we are going to renovate infrastructure of the site and install new inlets for greenhouse gases and aerosols in accordance with the GAW recommendations. New parameters and methodologies are also secured and applied, e.g. greenhouse gas isotopes. KMA has a strong scientific supporting program with appropriate data analysis and interpretation in cooperation with research institutes and universities involved in the integration of the site. To enhance the effectiveness and application of the long-term measurements within GAW, we also cooperate with the atmospheric measurement networks worldwide along with focusing on the quality assurance and control.

The stationis well-suited to become a global GAW program given the long-term measurements of a large number of parameters carried out there, and the location of the site. We hope to register the integrated station as a global station in the GAW network.

Participation in the inter-comparison campaign

To maintain traceability and compatibility and secure the level of measurements, we have taken part in the inter-comparison campaigns under the auspices of Quality Assurance and Scientific Activity Centers (QA/SAC), in particular on greenhouse gases and precipitation chemistry. Recently we participated in the sixth round-robin comparison (RR6) organized by the WMO GAW Central Calibration Laboratory (CCL) in NOAA, and methane reference gas inter-comparisons organized by the World Calibration Centre for CH_4 (WCC-CH_4) in Japan Meteorological Agency (JMA).

In terms of precipitation chemistry, we participated in the GAW annual laboratory inter-comparison studies organized by World Data Centre for Precipitation Chemistry (WDCPC) in May and October 2015, with the result of three unknown samples in the interquartile range (IQR, 25th – 75th) indicating it was good.

Taking audit by WCC-Empa

We took a system and performance audit at the Anmyeon-do (AMY) station for CO_2 and CH_4 by WCC-Empa, which is run by Federal Laboratories for Materials Sciences and Technology in Switzerland, from 27 - 29 October 2014 in agreement with the WMO/GAW quality assurance system. Monitoring and research activities at the AMY are coordinated by KMA as one of the Korean contribution to the WMO/GAW program. No previous audit at the AMY station has been conducted by WCC-Empa. The report of the audit available on the WMO/GAW webpage describes “The Regional GAW station Anmyeon-do comprises a very comprehensive set of measurements. The AMY station a very important contribution to the GAW programme. The assessed greenhouse gasmea-

surements were of high quality. To date, not all of the parameters measured at AMY are considered as being part of the GAW programme by KMA, but KMA is working towards the integration of all measurements under the umbrella of GAW. WCC-Empa strongly encourages this process, since the available data would be a very valuable contribution to GAW. The continuation of the AMYmeasurement series as well as the inclusion of the reactive gases measurement programme as GAW parameters is highly recommended."[4]

Asia-Pacific GAW workshop on Greenhouse gases (APGG)

The Asia-Pacific GAW Workshop on Greenhouse Gases (APGG) has annually been held by KMA since 2009. The APGG has become a venue for cooperation on the greenhouse gases (GHGs) activities. The APGG has been designed to introduce the measurement technologies, quality control/assurance methodologies, and new monitoring stations as well as to share major research findings. It provides a good opportunity to share our knowledge on greenhouse gas measurements. The APGG-2015, in which ~60 peoples from 12 countries take part, is in connection with the technical training/education course in part of the WCC-SF_6 activities.

World Calibration Centre for SF_6

World Calibration Centre (WCC), one of the GAW central facilities, maintain calibration standards and provide instrument calibrations and training to the stations, that is, link observations to World Reference Standards and ensure networks comparability and compatibility through inter-comparison campaign and regular audits. World Calibration Centre for SF_6 (WCC-SF_6) was designated to be established in KMA in 2012, and has been operated since 2013. WCC-SF_6 conducts the missions for the traceability and compatibility of the SF_6 measurement in the GAW network. The main tasks and detailed information of the WCC-SF_6 are described in H. Lee et al. in this Newsletter. We hope to get a regional training and education centre for atmospheric SF_6 measurements established in KMA.

Measurement stations and variables

KMA operates the measurement stations to collect and provide reliable scientific data and information on the chemical composition of the atmosphere, its natural and anthropogenic change, helping improve the understanding on climate change. There are the three main stations for the atmosphere watch, which are located in the west (at Anmyeon, Chungnam Province), south (at Gosan, Jeju), and east (at Ulleung, Gyungbook Province) of the Korean Peninsula, in aim of monitoring of transportation of the atmospheric substances and variation in the atmospheric composition over the Korean Peninsula (Figure 4).

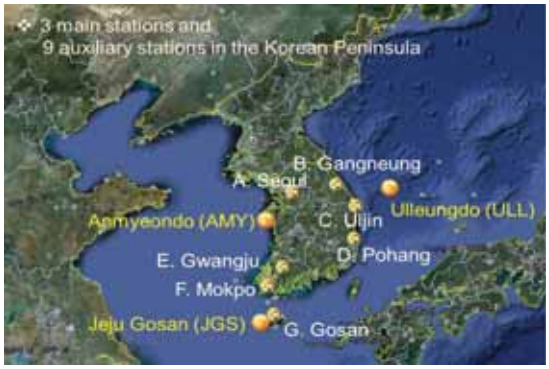

Figure 4

Location of the atmospheric watch stations operated by KMA in the Korean Peninsula. Three main stations (yellow) located in the west, south, and east of the Korean Peninsula are operated by KMA. The eight auxiliary stations (white) designated by KMA are run by Seoul National University (SNU), Yonsei University (YU), and Sookmyung Women's University (SMWU)at Seoul, Gwangju Institute of Science and Technology (GIST) at Gwangju, Jeju National University (JNU) at Gosan, and KMA regional offices at Gangneung, Uljin, Pohang, and Mokpo. An auxiliary station in King Sejong Base in Antarctica is run by the Korea Polar Research Institute (KOPRI).

From the three stations, KMA collects the atmospheric observation data of thirty seven components in the fields of greenhouse gases, aerosols, reactive gases, stratospheric ozone, atmospheric radiation including ultraviolet (UV) radiation, and precipitation chemistry, in accordance with the measurement recommendations of the GAW Programme.[5] There are ten auxiliary stations, where nine stations are in the Korean Peninsula and one is in the Antarctica, designated by KMA to collect more specific data, e.g. radioactivity (Radon), ozone sonde, total columns of ozone and water vapor, vertical profiles of aerosol optical properties from LIDAR, and ultraviolet (UV) (see Table 2). The Sookmyung Women's University (SWU) at Seoul, which was designated in 2015, produces the vertical profiles of ozone and water vapor in the stratosphere and the mesosphere.

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Table 2. Atmospheric species related to the WMO GAW program, collected at three main stations (Anmyeon, Gosan, and Ulleung) and ten auxiliary stations managed by KMA and KMA-designated institutes in the Korean Peninsula

Site (Institute)	Greenhouse gases	Reactive gases	Aerosols	Stratospheric Ozone/UV	Atmospheric radiation	Precipitation Chemistry
Anmyeon (KMA)	CO_2, CH_4, N_2O, CFCs, SF_6	CO, NO_x, SO_2, O_3	Physical[1] Optical[2] Chemical[3]	TCO[4], UV-A,B	Solar Terrestrial	Acidity Conductivity Ions[5]
Gosan (KMA)	CO_2, CH_4, N_2O,	CO, NO_x, SO_2, O_3	Physical[6] AOD	TCO, UV-A,B	Solar Terrestrial	Acidity Conductivity Ions
Ulleung (KMA)	CO_2, CH_4, N_2O, SF_6	CO	Physical[7] AOD	UV-A,B	Solar Terrestrial	Acidity Conductivity Ions
Pohang (KMA)				TCO, Profile[8] UV-A,B		
Mokpo (KMA)				UV-A,B		
Uljin (KMA)						Acidity Conductivity Ions
Gangneung (KMA)				UV-A,B		
Gosan (JU)		Radon				
Seoul (SNU)	CO_2, H_2O					
Seoul (YSU)				TCO, UV-A,B		
Seoul (SMWU)	H_2O[9]			TCO		
Gwangju (GIST)			Optical[10]			
Antarctica (KOPRI)	CO_2,			TCO, UV-A,B		

1) $PM_{1,2.5,10}$, size distribution (0.01-32 μm), total suspended particle (TSP) 2) Scattering/absorption coefficients, aerosol optical depth (AOD), and vertical profiles of backscattering coefficient, depolarization ratio, and color ratios 3) Chemical ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and metals (Al Ca, Fe, K, Mg, Na, S, Ti, Mn, Zn, Cu, V, Cr, Co, Ba, Pb, U) 4) F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} 5) Total column ozone 6) $PM_{1,2.5,10}$, size distribution (0.5-20 μm), Condensation Particle Counter (0.01-3 μm) 7) $PM_{1,2.5,10}$, size distribution (0.5-20 μm) 8) Vertical profile of ozone measured by ozone-sonde 9) Vertical profile of water vapor measured by microwave radiometer 10) AOD, vertical profiles of backscattering coefficient, depolarization ratio, and color ratios

Recent activities of WMO GAW World Calibration Centre for SF_6

Haeyoung Lee[1*], Chulkyu Lee[1], Se-Won Kim[1], Seong-Kyoun Kim[1], Hee-Jung Yoo[2], Hong-Woo Choi[2], Sang-Ok Han[2], Sang-Boom Ryoo[2], Jeong-Sik Lim[3] and Jeong-Soon Lee[3]

Sulfur hexafluoride (SF_6) is known as one of the most potent greenhouse gases. Once emitted into the atmosphere, SF_6 is removed slowly while it is rapidly accumulating in the atmosphere due to its atmospheric lifetime of about 3200 years.[1] According to recent WMO Greenhouse Gas Bulletin(2015), atmospheric SF_6 concentration is about 8 ppt, twice of the level observed in the mid-1990s increasing nearly linearly.[2] It is not serious level in present but its Global Warming Potential is 22,800 times higher than carbon dioxide (CO_2) that these features have brought SF_6 into the climate change discussion aimed at reduction of emissions.

Under the GAW umbrella, 55 stations are monitoring atmospheric SF_6 with 17 global stations, 33 regional stations and 5 contributing stations to look at its global and regional state in the atmosphere (Figure 1). However, to understand its role, high quality, long-term, and globally harmonized observations are strongly required in a traceability chain and compatibility goal from Central Calibration Laboratory (CCL) in GAW.

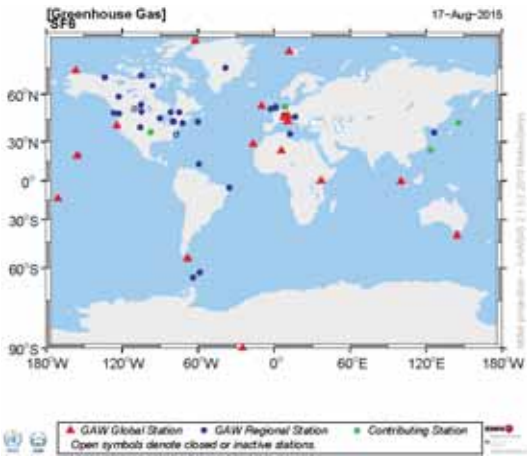

Figure 1

Distribution of GAW stations where monitor atmospheric SF_6 from GAWSIS(www.gaw.empa.ch/gawsis).

1. Climate Science Bureau, Korea Meteorological Administration, Seoul, Korea
2. National Institute of Meteorological Sciences, Korea Meteorological Administration, Jeju, Korea
3. Korea Research Institute of Standards and Science, Deajeon, Korea

To link between GAW stations and CCL, World Calibration Centre (WCC) acts as a bridge to support all stations with the following activities; a) assist WMO members operating GAW station to link their SF_6 observations to the WMO reference scale through comparisons with standards calibrated against CCL b) assist Scientific Advisory Group (SAG) on Greenhouse Gases in the development of the quality control procedures required to support the quality assurance of SF_6 measurement and ensure the traceability to WMO scale c) maintain laboratory and transfer SF_6 gas standards that are traceable to WMO scale d) perform regular calibrations and inter-comparison campaign involving all GAW stations and labs e) assistin provision of training and long-term technical help for the stations f) make public its involvement in the WMO GAW Programme.

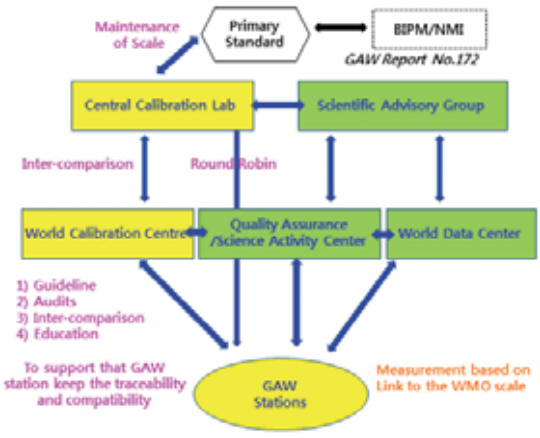

Figure 2
Conceptual framework of GAW quality assurance system.

In this newsletter, recent performances which are implemented by WCC-SF_6 are described.

Develop technical note for SF_6 analysis methods using GC-μECD

Many laboratories and stations have a difficulty to measure SF_6 using GC-μECD (Gas Chromatography - micro Electron Capture Detector) that recently WCC-SF_6 published a technical report for the analysis methods of atmospheric SF_6 as a GAW report No. 222. It described three methodologies with conventional GC-μECD, coupled with a pre-concentrator and fore-cutting/back-flush method. For conventional GC-μECD method, analytical conditions such as oven, sample loop, detector, column and etc. are described variously and applicable examples are given to enhance the peak area and to separate from other peaks such as N_2O and O_2. Secondly for pre-concentrator with GC-μECD was suggested one of the analytical methods. It is very useful to enhance the sensitivity of response with a process in which the ratio of the quantity of a desired trace element to that of the original matrix is increased. In this technical note, all concentration process including valve positions and cooling/heating steps are described. Practical analytic conditions were also showed with detailed information. Lastly Fore-cutting/ back-flush method is known as a candidate method to

avoid the interference of O_2 peak in the analysis of atmospheric SF_6 in short retention time. We described how to set up the system with 10- and 4-port valves according to column setting. Each column setting showed the appropriate examples with type of column.

This technical note showed a self-diagnosis flow chart to secure measurement conditions, restrict or information, flasks sampling materials and sample tubes. The report is available on the WMO GAW webpage (www.wmo.int/pages/prog/arep/gaw/gaw-report.html).[3]

Technical supports to monitoring station

To close the gaps between in situ stations and to get more information of atmospheric SF_6 in Asia, WCC-SF_6 visited IITM (Indian Institute of Tropical Meteorology) and supported their set-up of the system to monitor SF_6 and N_2O simultaneously with help of KRISS (Korea Research Institute of Standard and Science) during 19 to 23, September (Figure 3). We changed some conditions such as carrier gas from N_2 to P-5 (Ar 95% + CH_4 5%), column in oven from Hysep to Porapak-Q, and sample loop for an injection from 2 cc to 5 cc. SF_6 and N_2O were started monitoring together and to separate two peaks, some condition such as flow rate and oven temperature were adjusted. These activities were based on the published technical report by WCC-SF_6, WMO GAW report No. 222. Through these support, WCC-SF_6 contribute to enhancing monitoring activities and gathering high quality data.

Figure 3
WCC-SF_6 activities in IITM, India from 19 to 23 September, 2015.

WCC-SF_6 training and education course

Since 2014, WCC-SF_6 has held the training and education course on greenhouse gases. It is to assist GAW station members in a help for their monitoring activities. This year 2nd WCC-SF_6 training and education course was implemented during 3 days from 19 to 21 October in 2015, Anmyeondo station, Korea (Figure 4). Seven participants from India, Malaysia, Viet Nam, Indonesia, Jordan,

Tajikistan and Costa Rica attended the course in 2015. In the course, a theory of cavity ring down spectroscopy and gas chromatography, practical laboratoryexercises for flask sampling and its actual analysis performance were implemented. After the course, most participants wanted to expand the period of the course and have more practical activities. Therefore the course is going to not only focus on more classes which are applicable back to labs and in situ stations but also extend the period to one week from next year.

Figure 4

The 2nd WCC-SF_6 training and education course at Anmyeondo station from 19 to 21 October, 2015.

Inter-comparison experiment

Recently Central Calibration Laboratory in National Oceanic and Atmospheric Administration implemented the 6th WMO Round Robin Comparison Experiment to maintain the link to the WMO scales using normal operating procedures. For SF_6, 18 labs had participated and among them only 4 labs were within WMO compatibility goal, ±0.02 ppb. WCC-SF_6 is going to hold the inter-comparison experiment again in cooperation with KRISS and CCL in 2016. For this plan, we have developed the procedure of the inter-comparison experiment and technical method for tertiary/travelling SF_6 standard gases.

Plans for 2016

Next year, WCC-SF_6 is going to implement these activities: a) to publish a technical note of calibration method for SF_6, b) to have an audit and support the monitoring activity of SF_6 at Cape Point station in early of 2016, c) to hold 3rd WCC-SF_6 training and education course with extended period and expanded course, and d) to perform the 1st inter-comparison experiment from January 2016. All activities which were conducted from 2014 to 2015 will have submitted to WMO GAW this year.

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The WMO/GAW Cape Grim Baseline Air Pollution Station Air Archive

M.V. van der Schoot[1*], R.L. Langenfelds[1], P.J. Fraser[1], P.B. Krummel[1], J. Ward[2] and N.T. Somerville[2]

Introduction

Since April 1978 large volume air samples have been collected at the Australian Bureau of Meteorology operated Cape Grim Baseline Air Pollution Station (CGBAPS), creating a unique continuous archive of Southern Hemisphere marine boundary layer air, the Cape Grim Air Archive (CGAA). The CGAA is stored at the CSIRO Oceans & Atmosphere research laboratories at Aspendale, Victoria, Australia (Refer Figure 1.).

The motivation for starting this archive was to create a collection of background air samples, over a long period, which at some future time could be analyzed to recover information on past atmospheric composition. Over time this unique resource has facilitated a multitude of diverse research applications,

Figure 1

The Cape Grim Air Archive at CSIRO (Aspendale, Victoria).

allowing studies of new atmospheric trace gases (eg synthetic greenhouse gases) and provides the ability to take advantages of developments of new techniques for previously measured trace gases.

A detailed summary of the first 17 years of the CGAA has been reported previously.[1] and updated reports released since then.[2] These reports include details of the various

1. CSIRO Oceans & Atmosphere, Aspendale, Victoria, Australia
2. Cape Grim Baseline Air Pollution Station, Bureau of Meteorology, Smithton, Tasmania, Australia

aspects of the archive such as: archive containers and air sampling protocols, archive inventory, sub-sampling, and trace gas measurement techniques and stability verification. Here an update of the CGAA is presented, including the method of collection of an air archive sample.

Method

Although a range of compressed air cylinders; methods of drying and not drying, and sampling time protocols have been used over time, the CGAA routinely uses a filling method consistent with that employed for the very first archive samples. This method utilizes cryogenic assisted filling (liquid nitrogen bath), in the absence of active air sample drying, in stainless steel cylinders under "baseline" clean air sampling conditions at CGBAPS. Great care must be taken with this cryogenic technique but, done safely, it is suitable for the long term storage of many trace gas species. This is with the notable exception of atmospheric carbon dioxide, which is known to be susceptible to equilibration effects in the presence of surface moisture. Cylinder preparation technology, in particular the preparation and cleaning of the interior steel surfaces, has improved over time, with electro-polished (internally and externally) stainless steel containers being commercially available (Essex, USA, part number 80C-0008-8) for the successful long term storage of many trace gas species. As a result, since the 1980's these types of stainless steel air archive containers have proven to be generally very stable for most trace gases. These cylinders can be filled to a pressure of 900 psig.

The method for collection of an air archive sample at CGBAPS utilizes a cryogenic bath and an air sampling manifold with a metal bellows pump (Robbins & Meyers, USA, model KS-P330-BOWL) for filling and an oil-free diaphragm vacuum pump (Vacuubrand, Germany, model MD 1) for evacuation cycles (Refer Figure 2.). The final step involves removing the condensed water collected in the cylinder.

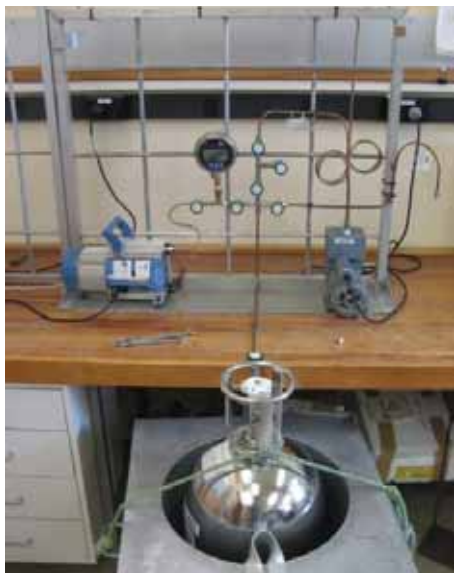

Figure 2

Air sampling system for CGAA.

Sample collection frequency originally targeted four archive samples per year to try to capture general features of the seasonality variation of individual trace gases, although this was not always achieved consistently each year of the archive's history. Recently the annual collection target has been increased to six CGAA samples per year, to better characterize these seasonal cycles.

Analysis

After collection, each CGAA sample is analyzed for a range of trace gases at the CSIRO GASLAB laboratory and verified that the sample is consistent with concurrent Cape Grim in situ and flask data. Suspect air samples are then either scheduled for refilling as another CGAA sample or used for an alternative application.

Details of the CSIRO GASLAB analytical procedure for the atmospheric hydrogen (H_2) measurements presented here have been reported previously.[3] All reported atmospheric H_2 mole fractions are reported in the units "nmol mol^{-1}" (or ppb) on the "*WMO MPI 2009*" H_2 calibration scale.[4] A typical analysis history of a CGAA sample is shown in Figure 3. The H_2 stability is used as a useful indicator of the behavior of small atmospheric molecules stored under the CGAA conditions, over extended periods.

The long term internal consistency of the CGAA, relative to GASLAB flask measurements for H_2, is shown in Figure 4.

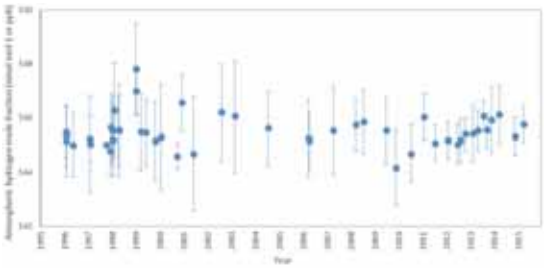

Figure 3

Typical CGAA sample (UAN 960051*) analysis history for atmospheric H_2 mole fraction (nmol mol^{-1} or ppb) (WMO MPI 2009 H_2 scale[4]) (* GASLAB assigned "Universal Analysis Number" a unique identifier for each air sample)

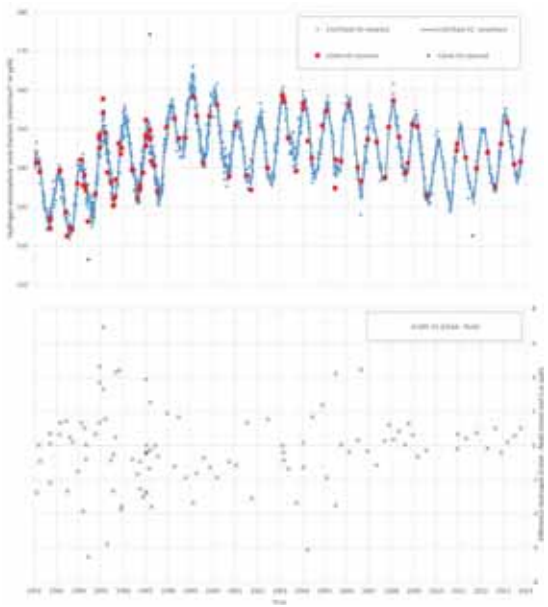

Figure 4

CGAA atmospheric H_2 history. Upper panel shows individual hydrogen analyses of CGAA samples (filled red squares=retained samples and black cross=rejected samples) against the GASLAB Cape Grim (CGO) flask record (blue diamonds = retained values with smoothed curve fit[5] in blue). The lower panel shows the difference between the retained CGAA sample and CGO smoothed flask record.

Research Applications

After 37 years of CGAA operation, more than 175 high pressure samples have been collected with approximately 100 to 150 surviving samples. Research applications using this archive have resulted in more than 100 publications covering more than 56 different gas species and more than 12 isotopic species. A selection of some of the most recent are presented in Table 1.

The CGAA has enabled the reconstruction of atmospheric trends of a diverse range of atmospheric species on a hemispheric to global scale. The archive has been particularly useful for the re-creation of time series for many of the synthetic greenhouse gases including chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC) and other strato-

Table 1. Recent CGAA research applications

Species	Research Application	Reference/Year
CFC-112, CFC-112a, CFC-113a, HCFC-133a	Detection and quantification of 4 previously undetected, anthropogenic stratospheric ODSs	Laube et al 2014[6]
NF_3	Demonstrated potential for significant emissions of NF3, a long lived and potent GHG, not included in 1st Kyoto Protocol for ODSs.	Arnold et al 2013[7]
$^3He/^4He$ isotopic ratio	Very few studies on noble gases especially as a time series. Aiming to define the trend in $^3He/^4He$ ratio (stable over million year time scales) which might be anthropogenically influenced through global fossil fuel use. Ne, Ar, Kr and Xe isotopes were stable over same period.	Brennwald et al 2013[8]; Mabry et al 2015[9]
N_2O and isotopes	Global N_2O sources and sinks attribution using measurements of the oxygen and nitrogen intra-molecular isotopes of N_2O to show major contribution from agricultural use of nitrogen-based fertilizers.	Park et al 2012[10]
SF_5CF_3	Showed that emissions trajectory of the potent long lived GHG SF_5CF_3 – from growth in 1950's to decline after late 1990's to effectively zero after 2003.	Sturges et al 2012[11]
c-C_4F_8 (PFC-118)	Reconstructed atmospheric time series of this long lived (→3000 year) perfluorocarbon and potent GHG and showed changes in industrial usage over time and discrepancies between bottom-up and top-down emissions estimates	Oram et al 2012[12]
C_4F_{10}, C_5F_{12}, C_6F_{14}, C_7F_{16}, C_8F_{18}	Reconstructed atmospheric time series and growth rates for the high molecular weight perfluorocarbon series of compounds.	Ivy et al 2012[13] and Laube et al 2012[14]
HFC-365mfc, HFC-245fa, HFC-227ea, HFC-236fa	Reconstructed atmospheric time series and emission estimates of 4 anthropogenic hydrofluorocarbons.	Vollmer et al 2011[15]
SF_6	Reconstructed atmospheric time series and emission estimates of SF_6.	Rigby et al 2010[16]

spheric ozone depleting substances (ODS) commonly used in various industrial applications (eg. refrigeration, air-conditioning, aerosol propellants, fire retardants, blowing agents, solvents, semi-conductor, and aluminium production) (Refer Table 1). The impact of these compounds, and their growth trajectories, on global radiative forcing can be calculated and the derived atmospheric observation based estimates ("top-down") can then be compared to the reported ("bottom-up") national/global industrial emission inventories.

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The JMA activities and network for GHG observation and recent topics

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Introduction

The Japan Meteorological Agency (JMA) has been operationally monitoring atmospheric greenhouse` gases (GHGs) in the western North Pacific region under the Global Atmosphere Watch (GAW) Programme. Especially, long-term observation data have been successfully obtained at ground-based stations. On the other hand, we have been operating aircraft observation and collaboration work with Japanese research groups since 2011.

GHG observation network

Figure 1 shows the GHG observation network of the JMA. We have three ground-based stations. One is the WMO GAW Global station of Minamitorishima (MNM). This station is located at a small isolated coral island about 2,000 km south east far from Tokyo.

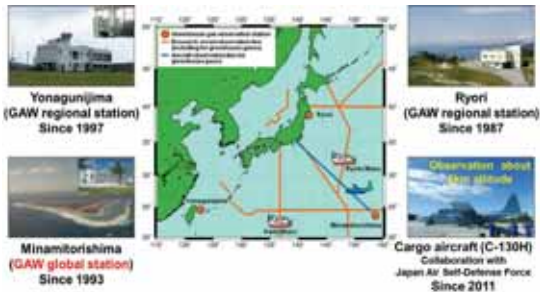

Figure 1
GHG observation network of JMA.

The site MNM is suitable for monitoring background GHGs, as is placed sufficiently far from industrial activities. We started its operation in 1993. We have the other two WMO GAW regional stations, Ryori (RYO) and Yonagunijima (YON). The site RYO is

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located on a hilly cape on the Pacific coast in the northern part of the Japanese main island. It has the longest monitoring history in Japan, which started in 1987. The site YON is the westernmost island of Japan near the Asian continent and its monitoring started in 1997. We unmanned it in 2008 and are operating the GHGs observation from headquarter, Tokyo, by a remote control system. We observe carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) and surface ozone (O_3) at every station. In 2011, we began an aircraft observation program, which collects air with flasks in the mid-troposphere (at an altitude of about 6 km), between Atsugi air base nearby Tokyo and MNM once a month. This observation is made by using a cargo aircraft C-130H of the Japan Ministry of Defense.

Outline of observation system

Figure 2 shows the outline of our observation system for continuously measuring atmospheric GHGs. Air sample is taken from an inlet mounted at a height of 20 m tower in order to minimize local effects from human and biospheric activities around the station. Taken air sample is filtered to remove dust, and then completely dried by through several processes before GHGs are analyzed. We are measuring CO_2 by non-dispersive infrared (NDIR) analyzer, CO by Gas Chromatograph with Reduction Gas Detector (RGD) and CH_4 by Gas Chromatograph with Flame Ionization Detector (FID). Air sample for O_3 is taken from different inlet mounted at a height of 8 m, made of Teflon to minimize O_3 loss during sampling processes. We are measuring O_3 by Ultraviolet (UV) absorption analyzer.

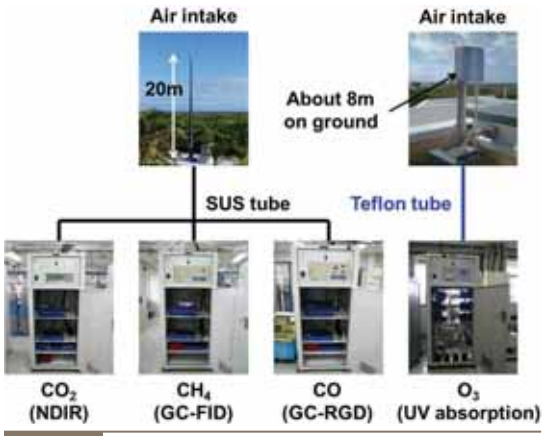

Figure 2

The outline of JMA observation system.

To keep enough precision of observation, we check out them periodically. Table 1 shows the details of analyzers and standard gas scales which we use. Our observations meet the precisions recommended by WMO GAW for all the parameters. Furthermore, all of our observations keep traceability to WMO scales, and we can quickly update when the scale is revised.

The JMA also uses a different measuring system for aircraft samples based on recently advanced laser based analyzers (Tsuboi et al., 2013[1]). Measurements of CO_2 and CH_4 are made by Wave Scan Cavity Ring Down Spectroscopy analyzer(WS-CRDS). On the other hand, CO and N_2O are analyzed by

Table 1. Analyzers detail used in ground-based station

Parameter	Analyzer(Method)	Precision	Standard Gas scale
CO_2	LI-COR LI-7000 (NDIR)	≦0.02ppm	WMO X2007
CH_4	Round Science RCG-1 (GC-FID)	≦2ppb	WMO X2004
CO	Round Science TRA-1 (GC-RGD)	≦2ppb	WMO X2004
O_3	Thermo Fisher Scientific 49i (UV ansorption)	≦1ppb	NIST

Table 2. Analyzers detail used for aircraft samples[11]

Analyzer(Method)	Parameter	Precision	Standard Gas scale
Picarro G2301 (WS-CRDS)	CH_4 CO_2	≦0.26ppb ≦0.014ppm	WMO X2004 WMO X2007
Los Gatos Research DLT100 (OA-ICOS)	N_2O CO	≦0.07ppb ≦0.08ppb	NOAA 2006A WMO CO X2004
LI-COR LI-7000 (NDIR)	CO_2	≦0.064ppm	WMO X2007
Aero-Laser AL5002 (VURF)	CO	≦0.28ppb	WMO CO X2004

Off-Axis Integrated Cavity Output Spectroscopy analyzer(OA-ICOS). For CO_2 and CO, conventional methods such as NDIR and Vacuum Ultraviolet Resonance Fluorescence (VURF) are also used for cross check between two different analyzers.

By using these methods, we have achieved better measurement precision than before (Table 2). In the future, we consider replacing the current analyzers with these laser based analyzers in the ground-based station observation system.

Result from observation

Figure 3 shows the time series of CO_2 concentration at ground-based stations. We can see a clear long-term increasing trend at every station. The concentrations seasonally vary in relation to photosynthesis and respiration in the biosphere. However, the amplitude of seasonal variation is different from each other. Figure 4 shows the time series of CO_2 annual growth rate and Southern Oscillation Index (SOI). One of the major factors that causes the year to year variation of the CO_2 concentration is the global climate variation correlated to the El Nino Southern Oscillation. We can see good coincidence between increases of CO_2 growth rate and decreases of SOI.

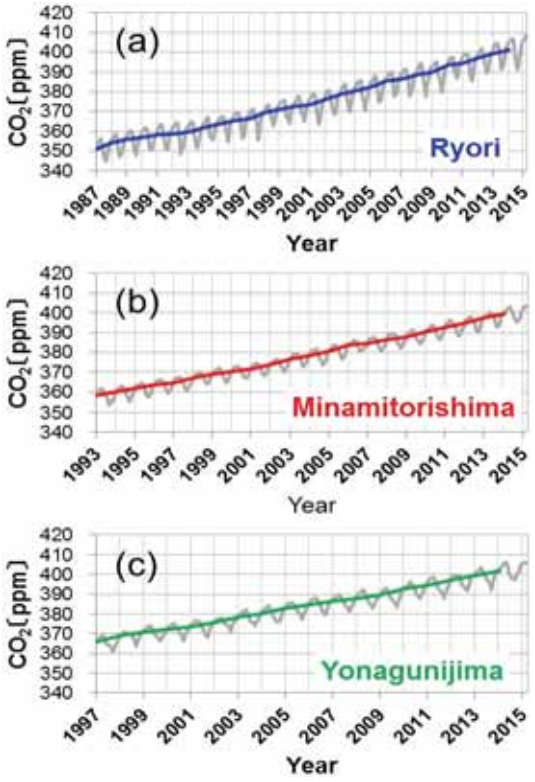

Figure 3

Timeseries of CO_2 concentration. (a) RYO (b) MNM (c) YON

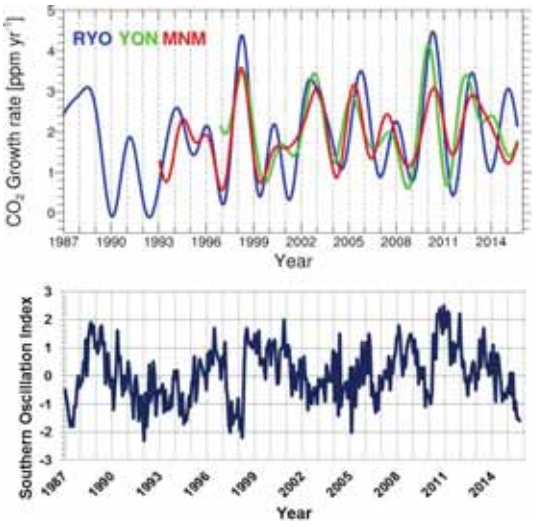

Figure 4

Top: time series of annual growth rate. (Blue: RYO Red: MNM Green: YON) Bottom: Time series of SOI

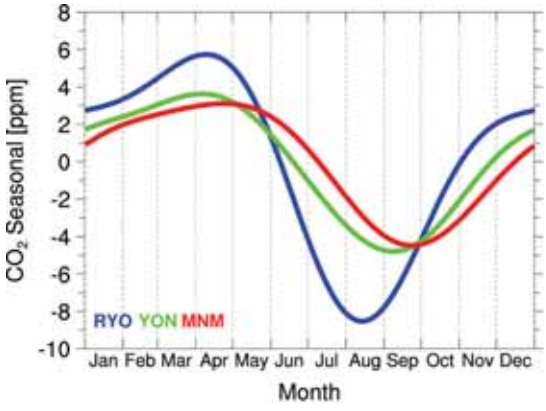

Figure 5

Averaged seasonal cycle of CO_2.
(Blue: RYO Red: MNM Green: YON)

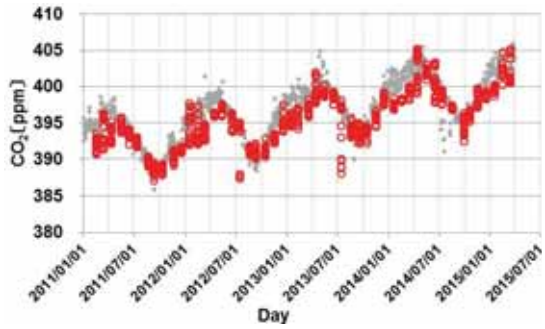

Figure 6

Time series of CO_2 concentration.[2] (Red: Altitude over 5km Gray: MNM)

Figure 5 shows the average seasonal cycle of CO_2. Concentration of CO_2 at RYO has larger seasonal variation than those at MNM and YON. This is because RYO is located at higher latitude and significantly influenced by activity of terrestrial biosphere in the Asian continent. Also, the figure shows that the seasonal maximum and minimum at MNM appear later than YON despite both the stations are located at almost the same latitude. This reflects the influence of emissions from the

Asian continent, to which YON is located closer. Figure 6 shows the time series of CO_2 concentration observed at MNM and by aircraft at cruising altitude over 5 km. Both of their seasonal cycles are similar, however the seasonal cycle of aircraft observation is delayed to that at ground. This indicates that it takes time for atmospheric convection to uplift high CO_2 air masses from the ground to the mid-troposphere.

Introduction of JMA collaboration work

Since 2011, Japanese research institutes have started a new joint research to elucidate the carbon cycle. This collaborative research is constructed by Meteorological Research Institute (MRI, one of JMA facility), National Institute for Environmental Studies (NIES) and National Institute of Advanced Industrial Science and Technology (AIST). We, JMA, offer the MNM platform to the other institutes and contribute to the joint research. They have been measuring various parameters shown in Table 3. This is also useful to understand GHG variations observed by JMA. The result of this research has been published (e.g., Ishidoya et al., 2014[3]), and the data will be submitted to World Data Centre for Greenhouse Gases (WDCGG) operated by JMA from corresponding researchers.

Furthermore, MRI has been conducting the observation of hydrogen and Radon-222 (^{222}Rn) at all the three stations. They are useful tracers for data selection (Wada et al., 2013[4]). Figure 7 shows the time series of ^{222}Rn and CO_2, CO and CH_4 at MNM and YON in Dec. 2012. Because ^{222}Rn is mainly originated from a soil and it is a radioactive gas with a half-lifetime of 3.824 days, it is useful to estimate emissions of greenhouse gases in East Asia. Some peaks of ^{222}Rn are coincident with those of other gases. These tight relations demonstrate the transport of continental air masses passing over the anthropogenic emissions over the continent.

Table 3. Measuring parameters in the joint research

Measurement Laboratory	Parameter	Sampling Type
Meteorological Research Institute (MRI)	H_2, ^{222}Rn	Continuous
National Institute for EnvironmenStudies (NIES)	O_2/N_2, $^{14}CO_2$, Halocarbons	Flask
National Institute of Advanced Industrial Science and Technology (AIST)	CO_2 isotope ratio($\delta^{13}C$, $\delta^{18}O$), $\delta O_2/N_2$, $\delta Ar/N_2$, $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, $\delta^{40}Ar$	Flask

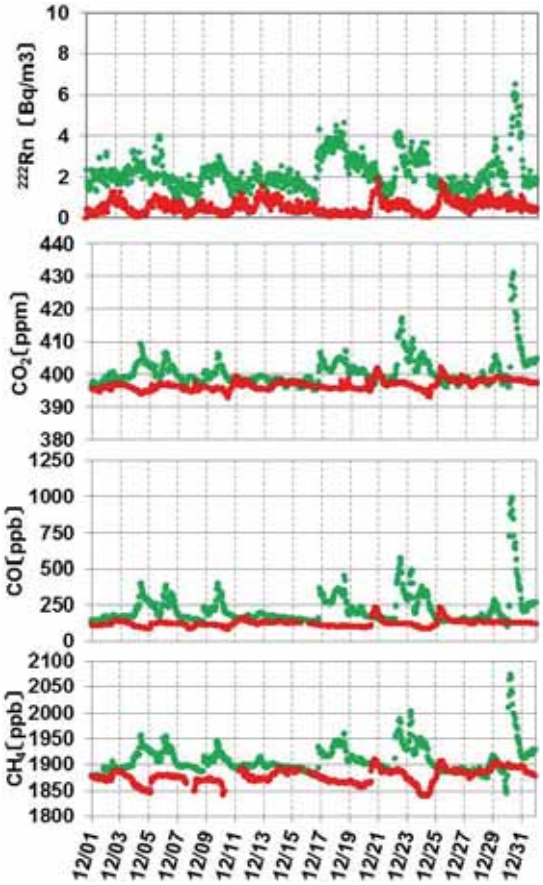

Figure 7

Time series of ^{222}Rn, CO_2, CO and CH_4 in Dec. 2012. (Red: MNM Green: YON)

Summary

The JMA has been operating three ground-based stations and obtained long-term observation data. Furhtermore, we have started to use the advanced laser based analyzers, and achieved better measurement precision. To elucidate the carbon cycle in detail, we have started the collaboration work with the Japanese research institutes. The data related to GHGs have been accumulated for four years.

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Improving estimates of pollution outflow at Gosan using ^{222}Rn

S.D. Chambers[1*], C-.H.Kang[2], A.G. Williams[1], J Crawford[1], A.D. Griffiths[1] and W-.H. Kim[2]

The best understanding of climatic, ecological and health effects from increasing Southeast Asian emissions will likely be achieved by models coupled to detailed emission inventories and remote sensing data. To improve model accuracy and forecast horizons, careful evaluation against appropriate observations is essential. To minimize the chance of misleading comparisons, it is important to ensure ground-based reference observations are well matched with the model output, especially regarding fetch regions and scales of observation. To quantify upstream emissions based on ground-based observations it is necessary to: (i) understand the measurement "footprint", (ii) identify observations most representative of air that has been in good contact with the surface over which it has travelled, and has not been significantly diluted by fronts or deep convection in transit, (iii) ensure observations are representative of the whole boundary layer (BL), (iv) minimize the influence of local emissions, (v) characterize changes in mixing depth, and (vi) characterize evolving "background" concentrations.

Trace gas sampling at Gosan is conducted by the Korean Ministry of Environment, and meteorological observations by the Korean Meteorological Administration. CO measurements are made by NDIR absorption (detection limit 0.03 ppm and accuracy was 10%), and SO_2 by UV fluorescence (detection limit 0.5 ppb and an accuracy of 3.2%).[5] Direct, hourly radon observations have also been made at Gosan since 2001.[4] Radon is an unreactive poorly-soluble radioactive gas of terrestrial origin that is an ideal tracer of transport and mixing.[1,2,3] The detector is calibrated monthly, has a lower limit of de-

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tection of ~0.04 Bq m^{-3}, and uncertainty of ~12%. JejuIsland is sparsely populated, so the main Gosan pollution sources are: China (500 km west), Kyushu, Japan (200 km east), and mainland Korea (100 km north).

The seasonal radon cycle (Figure. 1) was characterized by a winter maximum and summer minimum, corresponding to extremes of terrestrial influence during the winter and summer monsoon periods (e.g. Figure. 2). Although sparsely populated, under certain conditions local emissions can contaminate Gosan observations. The diurnal radon cycle (Figure. 3a) is characterized by a morning maximum and afternoon minimum. In the afternoon, when the BL is well-mixed, the measurement footprint is large (representative of distant fetch regions). At night, radon accumulates until sunrise. Since radon has a terrestrial source, and the nearest alternative land is over 100 km away, the nocturnal radon accumulation must be a result of local influences. The diurnal CO cycle (Figure. 3b) is similar to radon. Therefore the observed nocturnal CO accumulation is also from local sources. By contrast, there are few large SO_2 sources on Jeju, so at night, when the nocturnal inversion isolates surface observations from the influence of remote sources, a gradual (1.3% h^{-1} in summer) decline in SO_2 is observed until sunrise (Figure 3c). Consequently, when using Gosan observations to characterize emissions from remote fetch regions, a 4-5 hour diurnal sampling window near midday should be imposed.

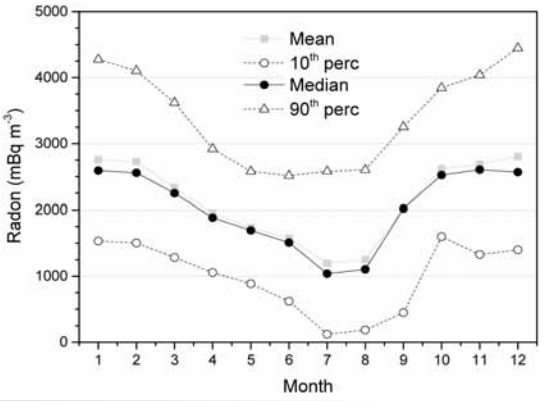

Figure 1

10-year composite monthly mean and distribution of Gosan radon concentrations.

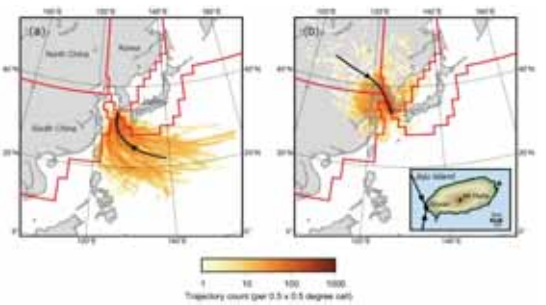

Figure 2

Trajectory density plots for Gosan fetch during the summer and winter monsoons.

A corollary of these observations is that Gosan aerosol samples integrated over 24-hour periods may contain a “local source” bias. Furthermore, ground-based observations reported when the BL is well-developed are better suited to model evaluation, since model spatial or vertical resolution may be insufficient to resolve the nocturnal boundary layer or island effects.

The dominant terrestrial fetch regions contributing to anthropogenic pollution observed at Gosan are: South China, North China,

Korea and Japan (Figure. 2). Fetch regions were assigned hourly based on the mean air mass location over its most recent 24 hours of land contact, as indicated by 5-day NOAA Hysplit v4.0 back trajectories. Radon's physical characteristics ensure that an air mass' radon concentration will be closely linked to terrestrial influence over the past 2-3 weeks. For a given fetch, the higher an air mass'radon concentration, the longer it has spent in contact with surface sources, or the less dilution it has been subjected to, and the more likely observations are to be representative of surface-based emissions over that fetch. Here, "dilution" is understood to be a result of either (i) tropospheric injection, during fronts or other severe weather events, or (ii) deep convection, which can vent emissions from the BL[6, 7].

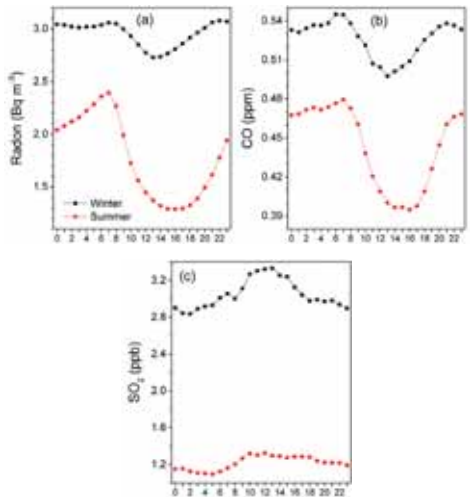

Figure 3

Summer and winter diurnal cycles of (a) radon, (b) CO and (c) SO_2, at Gosan.

To select observations most representative of emissions from each fetch region, we (i) selected only observations within the 5-hour diurnal sampling window to exclude local influences and mixing effects, (ii) retained only those air masses with radon greater than the monthly median value for each fetch region (assuming that low radon events are poorly representative of surface-based sources due to dilution or limited interaction with the corresponding BL).

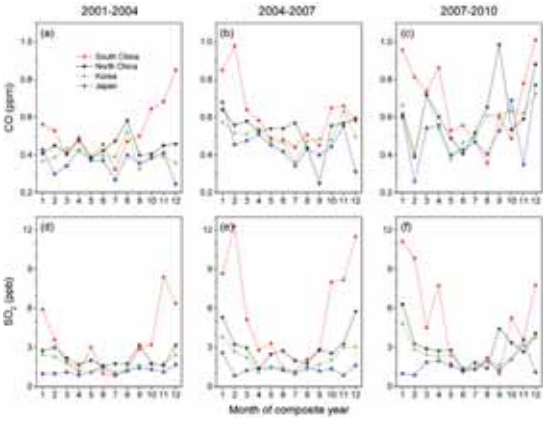

Figure 4

Monthly-mean CO and SO_2 for each fetch region across the decade, based on measurements within the diurnal sampling window and upper 50% of radon concentrations.

Mean monthly CO and SO_2 values by fetch region based on the sampling method proposed here are summarized in Fig. 4. Across the decade, results have been grouped in three 4-year composites: 2001-2004; 2004-2007 and 2007-2010. In general, emissions increased across the decade, were highest from South China and lowest from Japan.

Figure. 5 compares seasonal mean SO_2 across the decade from South China based on all hourly data, and the procedure described here. Our findings indicate that unless local influences are minimized, and representative air masses sought, emissions from South China are likely to be substantially underestimated (less so in the case of the other fetch regions). Furthermore, unless appropriate care is taken to ensure observations are representative of their intended fetch regions, and to better match vertical and horizontal scales of observations to model grid cell dimensions, results of subsequent evaluations could be misleading.

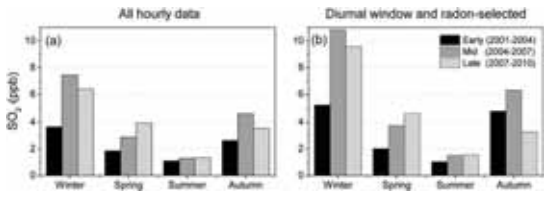

Figure 5

Seasonal mean SO_2 across the decade from South China based on (a) all hourly data, and (b) the sampling method proposed in this study.

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Measuring mixing ratio of N_2O using Thermo IRIS 4600 mid-IR laser based spectroscopy at global GAW station Bukit Kototabang (Indonesia)

Agusta Kurniawan

Introduction

The greenhouse gas (GHG) monitoring activities at the Global GAW Station Bukit Kototabang (0.20194°S, 100.31805°E, 864 m a.s.l.) consist of many observations. Since in January 2004, the GHG activities in Bukit Kototabang was started with the installation of the NOAA Flask Sampling that collected the ambient air into two 2.5-liter flasks containing ambient air taken from a 32 m height inlet[1]. Measurement CO_2 mixing ratios in Bukit Kototabang was installed by Kyoto University in the early 2000s. In October 2008, a Picarro G1301 $CO_2/CH_4/H_2O$ analyzer was installed at the station. The instrument provides a continuous measurement, allowing the observers to get near-real time data. A year later, an automated inlet and calibration system were added to support the measurement of the existing Picarro.[1] The system, which was installed by MeteoSwiss and WCC-Empa, enables the instrument to automatically measure the GHG mixing ratios of ambient air from three height levels, as well as to perform calibration up to three different concentrations. In June 2013, the latest GHG monitoring instrument, Thermo IRIS4600 N_2O Analyzer, was installed in Bukit Kototabang. The analyzer also shares the same inlet and calibration system with the Picarro for supporting the automated ambient air/standard gas intake.[1] Unfortunately in early 2015, Picarro has been stopped working due to instability of the electricity at the

Indonesia Meteorology, Climatotology and Geophisic Agency (BMKG:BadanMeteorologi, Klimatologidan Geofisika)

station. So in 2015, Greenhouse gases measurement at Bukit Kototabang only rely on NOAA Flask Sampling and Thermo IRIS 4600 Mid IR Laser. In this study, we want to display variability mixing ratio of N_2O measured by Thermo IRIS 4600 and based on seasonal basis/ monthly aggregate.

Methodology

In this section, we want to show the performance of Thermo IRIS 4600 Mid IR based Spectroscopy. The performance of this analyzer was examined in the last system and performance audit by WCC-Empa, May 2014 and reported in WCC-Empa Report 14/1.

Principle of Operation Thermo IRIS 4600[2]

The IRIS 4600 analyzer is controlled via an internal computer, which can be accessed via the Ethernet port on the front panel, which provides the basic user control and diagnostic interfaces. The averaging time, for example, can be controlled via the software interface by connecting the system to an external computer using Windows Remote Desktop.

After the inlet assembly, the stream enters the optical sensing cell where the instantaneous concentration of nitrous oxide gas and water vapor is measured by high resolution laser absorption spectroscopy in the mid infrared spectral region. The associated concentrations are determined using a standard "Beer's Law" analysis, which relates the strength of the measured optical absorption to the absolute nitrous oxide and water vapor concentrations. Both temperature and pressure are simultaneously measured to enable precise calculation of the concentrations. The IRIS 4600 analyzer measures discrete "rovibrational" absorption "fingerprints" for nitrous oxide and water vapor at extremely high frequency resolution across the full absorption lineshape, providing an unambiguous and highly quantitative nitrous oxide concentration measurement. The laser is approximately 100 times narrower in frequency than the intrinsic absorption linewidth, and sweeps continuously in frequency through the associated lines at a repetition rate of 500 Hz. Both water vapor and nitrous oxide absorption lines are measured with each sweep, providing an instantaneous measurement of the two gases to produce the dry mole fraction nitrous oxide data.

After the nitrous oxide has been sensed in the optical cell, the air stream passes through the diaphragm pump and out of the exit port. The pump is used in a "puller" mode to avoid particulate contamination from the diaphragm membrane as it wears. The sample cell pressure is maintained at a nearly constant value using a control loop (with the pressure measurement data) of the pump speed. The sampling flow rate through the instrument is set at the factory for optimum stability of the internal cell pressure, which is kept under vacuum during the measurement time. Some time is required for the cell to

equilibrate to a constant pressure after starting the system (typically a few minutes). After passing through the flow assembly, the air is exhausted from the IRIS 4600 enclosure through a small bulkhead fitting. This exhaust port can also be used as a flow return in special sampling applications where the inlet of the IRIS 4600 is connected to an environment at either positive or negative pressure (with respect to ambient).

The IRIS 4600 accepts a universal A.C. power input (100-240 VAC, 50/60 Hz). The A.C. power is diverted to internal D.C. power supplies.

The measured concentration of nitrous oxide and water vapor are displayed in real time on the IRIS 4600 LCD readout, and provided digitally via Ethernet or memory download via USB. The measured data is logged internally into files for subsequent downloading to an external device. The Ethernet port also serves to link to an external PC for programming operating parameters of the IRIS 4600 (e.g., logging period, measurement averaging time, calibration constant, etc.).

The technology to measure nitrous oxide absorbance is Tunable Diode Laser Absorbance Spectroscopy (TDLAS). Higher sensitivity is attained by coupling TDLAS with Difference Frequency Generation (DFG) to result in a mid- infrared laser source. This technique uses exquisite tuning and wavelength resolution of diode lasers to access a single absorption line of gas. The advantages of using a tunable laser source include:

- High throughput to minimize the impact of optical losses
- High directionality to couple with multiple pass cells
- Fast dynamical response for signal detection strategies and integration
- High spectral resolution to efficiently sample absorbance lines relative to other lines and non-absorbing baseline

The basic measured quantity is light hitting a detector that carries varying amount of loss due to nitrous oxide absorbance, according to Beer's Law:

$$A = \ln\left(\frac{I_0}{I}\right) = \varepsilon b C$$

A is termed the 'absorbance' of light, which is linear with concentration C. I_0 and I are the intensities of light detected, absent absorbance (I_0) and with absorbance (I). The parameters ε and b are both constant: ε is the absorption coefficient of the nitrous oxide, and b is the path length across which it is sampled.

These features of the IRIS 4600 analyzerprovide nitrous oxide measurement typically to ppb levels and lower, and water vapor measurement to under 0.01% absolute humidity, with high linearity and dynamic range, with stable accuracy, and with durability and low cost of ownership.

Data Analysis

Period of N_2O data from June 2013 to October 2015. We make monthly aggregate data from 1,10 second resolution, We used Microsoft Excell to make plot of time series data.

Result

Performance of Thermo IRIS 4600 Mid IR based Spectroscopy

Result of Comparisoncited from WCC-Empa Report 14/1.[3]

- Date of Audit: 2014-05-22
- WCC-Empa N_2O Reference: NOAA laboratory standards (WMO-2006A scale)
- N_2O Transfer Standard [TS]: TS calibrated against the WCC-Empa laboratory standards
- Analyser Model: Thermo IRIS 4600 #1210052268-128/83
- Range of calibration: 320 – 363 ppb

The comparison involved repeated challenges of the BKT instrument with randomized nitrous oxidelevels using WCC-Empa travelling standards. The following equations characterize the instrument bias, and the results are further illustrated in Figure 1with respect to the WMO GAW DQOs (WMO, 2009, 2011):

For the comparison, data of the instrument was corrected based on two working standards with N_2O numbers assigned by WCC-Empa(130822_CB10280, 120307_CB08975). These two standards were purchased by BKT from Empa before the audit. It should be noted that the instrument itself has nouser calibration implemented, which means that the reported values always need to be corrected-based on reference gas measurements. Thermo IRIS 4600 #1210052268:

- Unbiased N_2O mixing ratio: XN_2O (ppb) = (N_2O + 8.86) / 1.0259
- Remaining standard uncertainty: uN_2O (ppb) = sqrt (0.14 ppb^2 + 1.01e-07 * X_{N2O}^2)

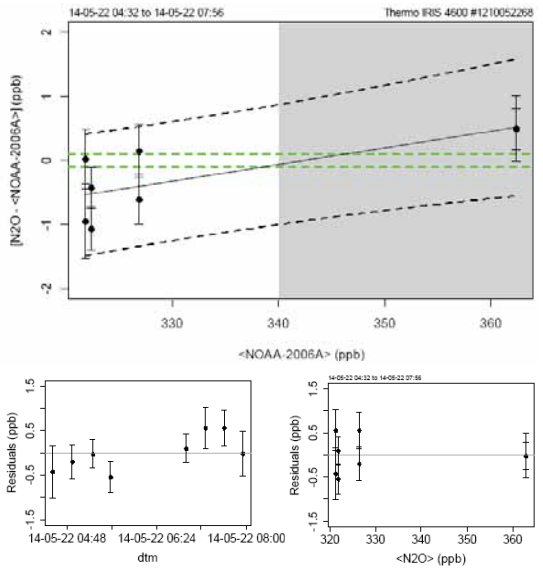

Figure 1

Top: Bias of the BKT Thermo IRIS 4600 #1210052268 nitrous oxide instrument with respect to the WMO-2006A reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for BKT, whereas the green lines correspond to the DQOs. Each point represents theaverage of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Bottom: Regression residuals (time dependence and mole fraction dependence).

The results of the comparisons can be summarized as follows:

The result of the BKT Thermo IRIS 4600 instrument exceeded the WMO/GAW DQOs of ±0.1 ppb for N_2O. The reason is the relatively poor stability of the instrument during the comparison. The averaging time was also relatively short (10 min). Longer averaging times of one hour will further improve the agreement if no significant drift is observed.

Mixing Ratio of N_2O (ppb) at Bukit Kototabang

We can see from Figure 2 seasonal variation/fluctuation of N_2O from June 2013 until recent. It's related with wet and dry season in the site. From the figure 2, it can be seen that there is a slight increasing trend of the N_2O mixing ratios. One of the possibilities that cause this trend is the fact that the farming activity surrounding the site has been more active in the period of observation. The gap on the data, covering the period February 2015 to May 2015, is due to instability of the electricity at the station.

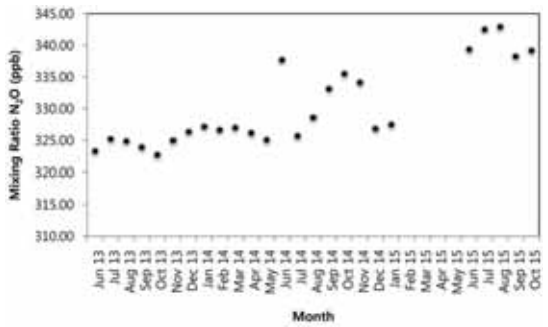

Figure 2

Seasonal variation of N_2O at Bukit Kototabangon monthly aggregate (Period June 2013 to Oct 2015).

And statistical descriptive data showed in Table 1.

Table 1. Statistical Descriptive Data

Average	330.14	
Max	342.87	Jul-15
Min	322.67	Oct-13
N (Sample)	25	
Stdev	6.47	

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Advantages and difficulties of greenhouse gases observations at the National Hydro-Meteorology Service (NHMS), Vietnam

Han Thi Ngan

Introduction

The hydro-meteorological sector was established in Vietnam more than 100 years ago. On the 25th April, 1900, the Governor of Indochina issued Decree No. 421 that approved the construction of the Indochinese Department of Meteorology's main building at Phu Lien Hill (Kien An District, Hai Phong City), both the design and the construction of which were done by the French. Since then, along with the rise and fall of the national history, the hydro-meteorology sector in Vietnam has been maintained and developed. Vietnam's hydro-meteorological sector joined the World Meteorological Organization (WMO) on the 7th May, 1975, which was its mark of integration and international cooperation.

Network

Vietnam is located in the tropical monsoon climate. It has a complex geographical location and varied terrain, therefore, its NHMS's network of climate change observation stations are distributed widely all over the country, both in the mainland and in the islands.

The current stations are divided according to their specific professional tasks as following:

- 194 meteorological stations;
- 233 hydrological stations;
- 17 upper air meteorological stations;
- 18 oceanographically stations;
- 26 air monitoring stations(at meteorological station sites)- include 11 greenhouse gages stations;
- 61 water monitoring stations(at hydrological and oceanographically station sites);
- 68 salty monitoring points;
- 01 GAW station (Pha Din).

National Hydro-Meteorology Service, Vietnam

Each type of stations is operating according to the industry's regulation by the Government of the Social Republic of Vietnam. Each station has its monitoring staff trained in terms of profession, observation and measurement skills as well as data processing and transmission skills. Every year, Vietnam suffers from 8 to 17 storms and tropical low pressure. Therefore, before rainy season each year, the NHMS often sends its technical inspection team to the stations in order to enhance the staff's profession and check the monitoring equipments.

The location of each station was investigated in scientific researches in order to reach the goal of basic weather and climate investigation and forecast. Typical monitoring stations are designed to match different type of terrain and climate. At the site of major rivers and large lakes, the stations are to monitor flow characteristics and hydraulic. Sea stations play an important role in forecasting storms. During over the last 10 years, environmental stations have collected a precious dataset on air and water quality with high reliability. Environmental stations are located in association with meteorological, hydrological, and marine stations. The salinity measurement positions are set in the hydrological stations to evaluate the salinization of the estuaries. GAW station (Pha Din) has been carefully investigated in terms of itsposition on the northwestern highland of Vietnam.

According to the network planning, from now until 2020, apart from opening new hy

List of climate change monitoring stations (planning)[1]

No.	Station's Name	Location
1	Dien Bien	Thanh Xuong Commune, Dien Bien
2	Muong Lay	Song Da Precinct, Muong Lay Town
3	Pha Din	Tua Chua Commune, Tuan Giao District, Dien Bien
4	Son La	Chieng Le Precinct, Son La City
5	Moc Chau	Moc Chau Town, Moc Chau District, Son La
6	Hoa Binh	Tan Thinh Precinct, Hoa Binh City, Hoa Binh
7	Sapa	Sapa Town, Sapa District, lLao Cai
8	Yen Bai	Minh Tan Precinct, Yen Bai District, Yen Bai
9	Ha Giang	Nguyen Trai Precinct, Ha Giang Town, Ha Giang
10	Tuyen Quang	Phan Thiet Precinct, Tuyen Quang Town, Tuyen Quang
11	Thai Nguyen	Trung Vuong Precinct, Thai Nguyen City, Thai Nguyen
12	Lang Son	Quang Lac Precinct, Lang Son City, Lang Son
13	Co To	Co To Town, Co To Island District, Quang Ninh
14	Phu Lien	Tran Thanh Ngo Precinct, Kien An District, Hai Phong City
15	Thai Binh	Vu Ninh Commune, Kien Xuong District, Thai Binh
16	Ninh Binh	Dinh Tien Hoang Street, Ninh Binh City
17	Nam Dinh	Con Mo Commune, Nghia Hung District, Nam Dinh

List of climate change monitoring stations (planning)[1]

No.	Station's Name	Location
18	Thanh Hoa	Quang Thinh Commune, Quang Xuong District, Thanh Hoa
19	Hoi Xuân	Hoi Xuan Town, Quan Hoa District, Thanh Hoa
20	Vinh	Cua Nam Precinct, Vinh City, Nghe An
21	Tuong Duong	Hoa Binh Town, Tuong Duong District, Nghe An
22	Ky Anh	Ky Anh Town, Ky Anh District, Ha Tinh
23	Huong Khe	Huong Pho Commune, Huong Khe District, Ha Tinh
24	Dong Hoi	Bac Ly Precinct, Dong Hoi City, Quang Binh
25	Hue	Thuy Bang Commune, Huong Thuy District, Thua Thien Hue
26	Da Nang	Hoa Thuan Precinct, Da Nang
27	Quang Ngai	Tran Phu Precinct, Quang Ngai City, Quang Ngai
28	Quy Nhon	Tran Phu Precinct, Quy Nhon City, Binh Dinh
29	Nha Trang	Vinh Nguyen Precinct, Nha Trang City, Khanh Hoa
30	Phan Thiet	Phu Trinh Precinct, Phan Thiet City, Binh Thuan
31	Kon Tum	Quyet Tien Precinct, Kon Tum City, Kon Tum
32	Buon Me Thuot	Tu An Precinct, Buon Me Thuot City, Dak Lak
33	Dak Nong	Gia Nghia Commune, Dak Nong
34	Da Lat	I Precinct, Da Lat City, Lam Dong
35	Rach Gia	Vinh Thanh Precinct, Rach Gia City, Kien Giang
36	Can Tho	Xuan Khanh Precinct, Can Tho City

dro-metrological stations, there are 36 monitoring climate change stations will be newly established.

Advantages

Assigning the task of monitoring greenhouse gases to the stations under the NHMS has some advantages.

1. Facilities

To make use of the facilities of the stations has brought a big advantage since the equipments that have operated through many years have been frequently renewed, changed or supplemented. Taking advantage of the stations' infrastructure also helps saving great cost for building new stations and facilities equipment.

2. Human resource

Monitoring staff working at the stations have good knowledge of meteorology so training them in terms of greenhouse gases observation is not a difficult task.

3. Favorable observation position

The meteorological stations have been thoroughly investigated and adjusted through years of operation so that their observation positions are assured scientifically and the data collected through many years (in some cases over 100 years) is helpful for scientific researches and forecast work.

The selection of these stations as places for installing monitoring equipments aims to reduce the cost of investigation on station placement. It is also for the purpose of making use the stations'hydro-meteorological data in order to scientifically support the assessment of climate change.

4. Government's concern and investment

The Vietnamese Government is very concerned about climate change issues in general and greenhouse gas monitoring in particular. Vietnam is a developing country and its economy remains difficulties in terms of finance. However, aiming to the objective of sustainable development, the Vietnamese Government has invested in greenhouse gases monitoring for many years. Currently, the GHG statistics are made every year and every 10 years[2] there is the government's report on greenhouse gases statistics. Taking advantage of the government's support, the NHMS has enhanced its role and improved its capacity in the monitoring of greenhouse gases.

5. International organizations' support

The issue of greenhouse gases has always received a great concern of the international community because the atmosphere is shared in the whole humanity. The countries that have modern science and technology development are always willing to help Vietnam in many fields including the monitoring of greenhouse gases. Learning from their experience and receiving their modern equipments have been done very well by the NHMS.

Difficulties

For more than 10 years of monitoring greenhouse gases, the NHMS has faced many difficulties, those are as follows:

1. Measurement instruments not adapt to Vietnam's nature conditions: air humidity, tropical rain, storm, and insects

All the devices are imported from abroad while foreign manufacturers have not taken into account the natural conditions in Vietnam, which has led to the fact of technical errors or equipments and components have been frequently broken. In some cases, insects of various kinds scraw into the equipments and cause damage to the device. In 2012, a station was down by lightning, its entire operation had to be shutdown and then many equipments had to be replaced by new ones.

2. Untimely supply of spare parts

The components have been imported either. When any component is fully depreciated or suddenly broken, there is a number of complicated administrative procedure required to be completed. The proposal of purchasing new spare part(s) needs to wait for the approval of different levels of authority. Ultimately, waiting for foreign suppliers to transport the spare part(s) to Vietnam requires another amount of time.

3. High cost of maintenance

In a context of a developing country, the price of the greenhouse gases monitoring equipments is very high in comparison to Vietnam's financial capacity. Investing on a greenhouse gases monitoring station requires a great effort of many branches in the society. Therefore, the cost of maintenance is also a difficulty to the NHMS.

4. High technology not regularly updated

The Vietnam's science and technology are still underdeveloped, thus updating modern technology from developed countries has faced with many difficulties in terms of technological access, perception, and application.

5. Deficient experience of work management and operation.

The management and organization of greenhouse gases monitoring activities at the NHMS are inexperienced and no indepth work has been done, accordingly expected effects have not been reached.

Solution

Based on the analyses above about advantages and difficulties in monitoring greenhouse gases at the system of stations run by the NHMS, such solutions as belowed have been put forward:

- Continue taking advantages of the network of the NHMS's observation stations; Convince the Government and related sectors to continue to take advantages of the network of the NHMS' stations in order to get optimal sesult; program of climate change, environmental observations, and acid rain monitoring should be carried out at the NHMS
- Find appropriate technological solutions that are suitable for Vietnam's natural condition;
- Use equipments at the best-case;
- Strengthen human resources;
- Improve ability of technology through international cooperations;
- Advance organizational mechanism.

Conclusion

It could be said that climate change monitoring is an urgent task set out by the Vietnamese Government with in the context of the international concern on climate change and its impacts on people's living standard. For many years, especially since the last 10 years, climate change monitoring has received concerns of the country's leaders and the scientists. Even though the economy is still developing and financial situation has still faced with difficulties, the Vietnamese Government has directed the annual implementation of collecting data on greenhouse gases, which has facilitated scientific researches on climate change and contributed to the forecast work as well as climate change response.

For the future, developing advantages and overcoming difficulties are very important activities at the NHMS. It requires the effort of

not only its leaders and staff but also of the government. Apart from that, drawing more concern of the society and calling more investment of both the government and international organizations are essential work that need to be done in order to raise the awareness of the public about environmental protection as well as to better the greenhouse gases monitoring and improve the living standard for every people.

Figure 1

Monitoring climate change stations network-plan.

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Monitoring methane (CH_4) and other greenhouse gases (GHGs) emissions in the sector of wastewater in Jordan.

Captain Haytham Malkawi

Jordan is a mere contributor to the global GHG emissions with only a marginal emission rate of 0.01% of total global emissions. However, we committed to its role and reputation as a global pioneer in the implementation of the various UN conventions. Jordan also believes it has a major responsibility in addressing Climate Change challenges while adhering to its national priorities and developmental objectives. Jordan released "climate change policy of the Hashemite Kingdom of Jordan 2013-2020" which is the first of its kind in the region.[1]

Jordan is one of the world's most arid countries. In addition, it is affected by the impacts of global climate change in the form of increasing temperatures and decreasing rainfall. Due to high birth rates and the continuous stream of refugees, the population is growing rapidly. There has likewise been a growth in industrial activities as well as traffic and construction. As a result, in the medium term Jordan will be faced with rapidly increasing greenhouse gas (GHG) emissions. As a signatory to all key environmental agreements, including the UN Framework Convention on Climate Change (UNFCCC) and the Kyoto Protocol, Jordan has geared its national climate policy towards reducing its greenhouse gas emissions and adapting to climate change.

Enabling Activities for the Preparation of Jordan's Third National Communication Report to the UNFCCC (TNC) Project aims at assisting Jordan with the enabling activities necessary to undertake the Third National

The Royal department for Environmental Protection Public Security Directorate, Jordan

Greenhouse Gas Inventory and to prepare and report the Third National Communication to the Conference of Parties in accordance with guidance of the UN Framework Convention on Climate Change (UNFCCC). In addition, this project will help strengthen Jordan's capacity to fulfill its commitments to the UNFCCC on a continuing basis. The structure of this project is based on the country's previous experience and studies already identified under a stocktaking exercise.[3] And the main expected outcomes of the project is an inventory of greenhouse gases for the base year 2006 and time series 2000-2005; and beyond if applicable.

A national inventory of anthropogenic emissions by sources and removals by sinks of all greenhouse gases for base year 2006 is an extensive research based activity that collects emission data from activity sources and then processes the data to a form reported to UNFCCC

Waste water sector

Water demand and the water shortage will drastically increase in the future due to population growth and anticipated socio-economic development. Water management in Jordan is supply-based and, despite significant improvements in water-supply infrastructure, a critical and serious supply demand imbalance remains.

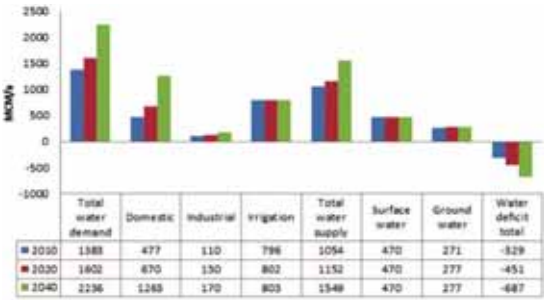

Figure 1

Expected shortage of water supply up to year 2040.

The handling of wastewater streams with high contents of organic material, including domestic and commercial wastewater and some industrial wastewater streams can emit significant amounts of methane.

Methane has the second largest share of Jordan's greenhouse gas emissions. CH_4 emissions were estimated to be 147Gg at 10.8% of Jordan's total greenhouse emissions in the year 2006. the contribution of the domestic and commercial wastewater was estimated to be around 1.4% of the total (around 2Gg CH_4) generated methane.

Industrial waste methodology

MCF was made as an assumption of 5% as the method used in the three zones is activated sludge – extended aeration (aerobic treatment). Wastewater Handling Facility Efficiency and Output Aerobically treated may be subject to anaerobic conditions due to poorly managed and functioning facilities. Methane producing capacity was taken as default 0.25 Kg Ch_4/Kg BOD. The default (theoretical) value for BOD is 0.25 kg

CH_4/kg BOD for wastewater and for sludge (Lexmond et al., 1995) if sludge is disposed of in landfills then the resulting emissions is already accounted for in the IPCC/OECD SWDS emission methodology. In this case, to ensure that emissions are not counted twice an "MCF" of zero should be used in this methodology for sludge disposed in SWDSs.

Domestic and commercial wastewater methodology:

65% of Jordan population is connected to the sewer system, the other 35% discharge their sewage either to the treatments plants by tanks (those will be calculated with influent of the treatment plants), or discharge it illegally. There were 22 working treatment plants in Jordan, 2006 managed by Water Authority of Jordan which aim to develop and protect water sources, provision of water and sewerage services to ensure the requirements of citizens, and improvement of infrastructure to preserve environment and public health.

Indirect Nitrous oxide (N_2O) emissions from human sewage

Nitrous oxide (N_2O) is associated with the degradation of nitrogen components in the wastewater, and the indirect nitrous oxide emissions from human sewage calculated to be 0.375 Gg N_2O/yr.

Uncertainty

The quality of CH_4 emissions estimates for wastewater handling is directly related to the quality and availability of the waste management data used to derive these estimates.

- Organic Wastewater Quantity and Composition were available in all data sources considered.
- Physical and Chemical Data Country-specific data on wastewater characteristics are available.
- Wastewater Handling Facility Efficiency and Output for Aerobically treated wastewater by handling plants may be subject to anaerobic conditions due to poorly managed and functioning facilities so MCF was made as an assumption of 0.05.
- MCF for domestic/commercial wastewater was taken default value.
- Max. Methane producing potential B0D was taken default value.

Climate change strategic objectives on reporting and monitoring of GHG emissions:

1. To improve the national capacity on aspects of the measurement and reporting of GHG emissions and the reporting of climate change actions in Jordan, with emphasize on aspect of measurement, reporting, and verification (MRV) in line with the Bali Action Plan provisions and post-2012 international climate change agreements in this regard;
2. To strengthen the knowledge on the current volume and sources of GHG emissions in the country

3. To gain insight in the possible impact of future developments and policies on future GHG emissions as a basis for policy-making on adopt regulation to facilitate data collection from emitters, especially in private sector, to the purpose of the inventory

The national climate change policy of the Hashemite Kingdom of Jordan 2013-2020 strategic goals

1. To support research-oriented programs and projects on improvement of the GHG inventory in Jordan, elaboration of GHG scenarios and assessment of mitigation options.
2. To support research-oriented programs and projects of observation, monitoring and estimation of climate change impacts on all affected sectors (water, agriculture/food security, biodiversity, desertification, health, tourism, coastal areas, infrastructure, etc.) including interactions between sectors and impact categories;
3. To support research-oriented programs and projects on assessment of technology needs and technology transfer options in the Jordanian context (local R&D capacity, local markets)
4. Strengthen Jordan's system for reporting and verification of emissions, mitigation potential and activities in line with any international obligations that Jordan has/will be committed to. The reporting and verification system will support the identification and assessment of mitigation priorities, emission projections/scenarios, as well as provide data for the monitoring and reporting

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Monitoring carbon dioxide and other greenhouse gases in GAW Danum Valley station

Aminah Ismail* and Mohd Firdaus Jahaya

Introduction

Greenhouse gases are very closely linked to global warming and climate change, where it is carefully monitored to ensure that GHG emissions are always low. In view of the global GHG concentrations they showed an increase in pattern, and one of them is because of human activities.[1] Monitoring program such as for Carbon Dioxide (CO_2) and other elements of GAW focal area has been entrusted to Malaysian Meteorological Department (MetMalaysia) through Danum Valley GAW Station and two other regional GAW Stations i.e. Cameron Highlands and Petaling Jaya. MetMalaysia cooperated with the National Institute for Environment Studies (NIES), Japan to monitor the CO_2 using flask sampling method starting 2010 and in 2014 NIES have added CO_2 analyzer using continuous monitoring method in 4 stations i.e. Danum Valley, Kuala Lumpur International Airport (KLIA), Kota Kinabalu and Tawau.

Thus, the main objective of this study is to observe the pattern of CO_2 concentration at Danum Valley Station as well as to show the comparison of the short term pattern data from these two different instruments to see whether there is significant difference in the measurement of the concentration of CO_2.

Measurement and analysis

As one of the Global Watch Station, Danum Valley involved in the monitoring and measurement of air quality and weather elements. Among the instruments available at Danum Valley other than flask sampling are LoFlo Mark II, Precision Filter Radiometer, Nephelometer, Multiangle Absorption Photometer, Tapered Element Oscillating Microbalance, Wet-Only Rain Sampler,

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Multigas Analyzer, Passive Sampler and Filter Pack.

For this study, the data is from two different instruments. One is from flask sampling and the other one is CO_2 analyzer. CO_2 measurement system that has been developed by NIES, comprising four cylinder of CO_2 standard gases for calibration periodically, inlet tube for sampling air, CO_2 detection and data logger. The flask sampling recorded a weekly data, whereas CO_2 analyzer recorded hourly data. The time series analysis is used to observe the pattern of CO_2 concentrations.

In this study the pattern of CO_2 concentrations in different areas such as KLIA, Tawau and Kota Kinabalu are also being observed. In addition, CO_2 concent ration is compared with other tropical GAW Stations within the same time frame such as Mauna Loa.

Results and discussion

Figure 1 (a) showed the pattern of CO_2 concentrations for Danum Valley from February until August 2015. The concentration is relatively lower as compared to other sites with a range between 376 – 469 ppm. As we know, Danum Valley is one of the largest pristine lowland forests covering 438 km^2. CO_2 concentration recorded in Kota Kinabalu, Tawau and KLIA is ranged from 384 – 495 ppm, 391 – 512 ppm and KLIA 394 – 670 ppm respectively. Figure 1 (d) showed that KLIA has CO_2 concentration higher than other sites. The air quality in KLIA most probably is influenced by the emission from the aircraft.

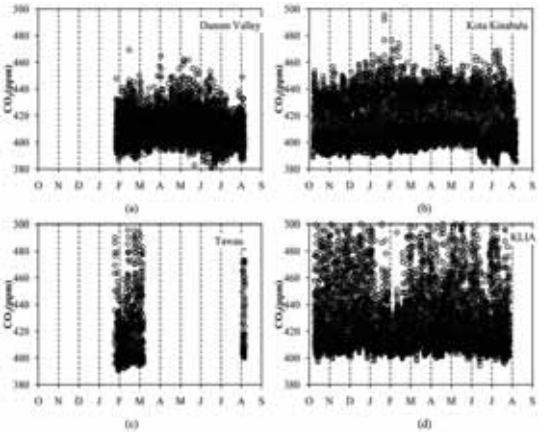

Figure 1

CO_2 measurement for (a) Danum Valley, (b) Kota Kinabalu, (c) Tawau and (d) KLIA in 2014-2015(Source: NIES).

Daily mean data of the first six months of 2015 is compared between two instruments shown in Figure 2, CO_2 Analyzer recorded higher reading value of concentrations with range 404 – 421 ppm, with the difference between 0.3 – 5.7% as compared to flask sampling. In general, the pattern of CO_2 concentration between these two instruments is quite comparable, where CO_2 concentrations range for flask sampling is 396 – 410 ppm.

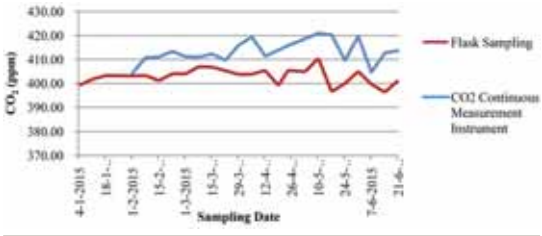

Figure 2

Average CO_2 Concentration from different instruments.

Figure 3 shows the pattern of CO_2 concentration and fluctuation in different sites such as KLIA, Tawau, Danum Valley and Kota Kinabalu. From the analysis, diurnal variations of CO_2 concentration for KLIA, Tawau and Kota Kinabalu showed greater values as compared to Danum Valley.

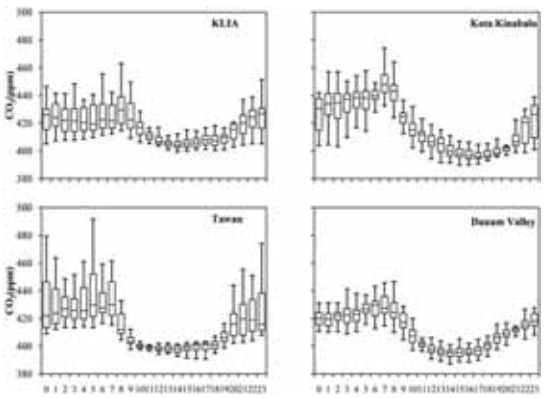

Figure 3

The distribution of hourly data for February 2015. (Source: NIES)

Figure 4 shows the monthly mean of CO_2 concentration between Mauna Loa and Danum Valley, where the pattern for both sites are comparable. Danum Valley recorded higher concentration during August – October 2011 and lower in April – August 2012 than Mauna Loa. Monthly mean CO_2 concentration of Danum Valley range between 390.01 – 395.33 ppm and Mauna Loa 389.04 – 396.78 ppm.

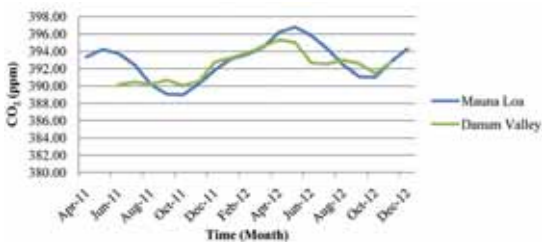

Figure 4

The time series analysis of CO_2 Concentration at Danum Valley and Mauna Loa.

Conclusion

Continuous monitoring and measurement of GHG is important to observe the fluctuation and the general pattern of GHG emissions as well as providing information for the early warning. It also important to provide the information on the changes in atmospheric composition in the forest that may affect the flora and fauna. Besides, the information will provide a better understanding in regard to the patterns of absorption and emission of GHG in tropical forests.

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Continuing efforts on greenhouse gases monitoring in India

Yogesh K. Tiwari*, Tania Guha, and Supriyo Chakraborty

The Carbon Dioxide Information Analysis Center (CDIAC), USA, estimates the total fossil-fuel CO_2 emissions from India as 189 TgC in 1990, 324 TgC in 2000, 385 TgC in 2005 and 508 TgC in 2009, and the annual rate of increase as ~7% per year during 2005-2009. Some of these emissions may be compensated by vegetation uptake. Between 1994 and 2007, some of the sectors indicate significant growth in Greenhouse Gases (GHGs) emissions such as cement production (6.0%), electricity generation (5.6%), and transport (4.5%). In order to improve our understanding in this field, we are working on: i) ambient CO_2 and other GHGs monitoring at the surface ii) air sample analysis using WMO/GAW calibration standards, iii) airborne campaigns at different locations over India iv) carbon flux monitoring at different ecosystems in India. Present study has discussed about GHGs monitoring efforts over Indian subcontinent.

Details of monitoring sites and instrumentation

1) Surface GHGs concentration monitoring

Among the greenhouse gases of anthropogenic origin, the increase of atmospheric carbon is of concern because carbon is not removed from the atmosphere by chemical reactions in the atmosphere unlike other greenhouse gases. India has one of the largest and fastest growing economies in South Asia and is emerging as a major contributor to CO_2 emissions among developing nations (Figure 1). However, there has been relatively little monitoring of atmospheric CO_2 over India to date. To infer estimates of CO_2 sources and sinks we need good coverage of stations and high quality of measurements.[1][2] GHGs monitoring in India on various platforms are discussed in references.[3a][3b][4][5]

Centre for Climate Change Research, Indian Institute of Tropical Meteorology, Pune, India

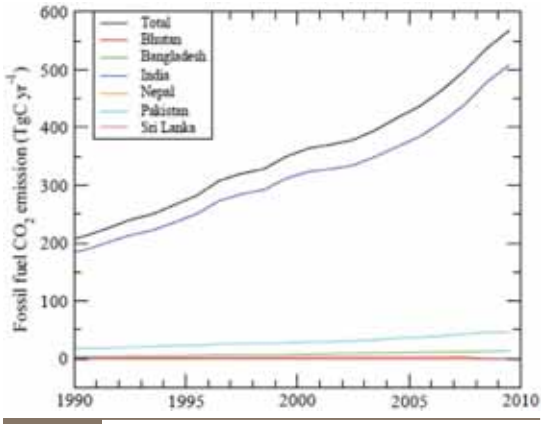

Figure 1

CO_2 emissions due to fossil fuel and cement production over South Asia during 1990-2009.[6]

Systematic GHGs monitoring over this country is started at the mountain site Sinhagad (SNG) Pune India and at a coastal site- Cape Rama Goa India. SNG, 200 km east of the Arabian Sea (73.75o E, 18.35o N, elevation = 1600 m asl) is located over the Western Ghats mountains (Figure 2). Routine air sampling at SNG, collected from a 10 meter meteorological tower at weekly intervals, has been operational since November 2009. This site is free from major vegetation and has prevailing light winds from the south and south-east during afternoon hours. The mean wind speed at the time of sampling is typically about 0.5 to 1 m s^{-1} so that the samples are free from the effects of vegetation and local influences. Ambient temperature ranges from 25 to 30°C. The air sampling methodology at SNG is described in detail in reference.[5] Recently, Korea Meteorological Administration (KMA) has helped us to start SF_6 monitoring at our GC lab at Pune India. KMA standards are used for SF_6 calibrations and NOAA Boulder standards are used for calibrating of CO_2, CH_4 and N_2O observations.

Figure 2

GHGs monitoring at Sinhagad (SNG) Pune India (upper pictures), and gas chromatograph lab at the IITM (lower pictures).

Another surface site Cape Rama (CRI), Goa (15.08°N, 73.83°E, elevation = 50 m asl) has monitoring records during 1993-2002 and 2009-2013 which were maintained by CSIRO Australia but this site is now discontinued. The CRI site is located closer to the shoreline and isolated from local anthropogenic influences.[1] The mean wind speed at the time of sampling CRI varies from about 10 to 12 m s^{-1} in the summer monsoon and 4 to 6 m s^{-1} during the winter monsoon. Air samples were collected in two separate 0.5 liter glass flasks from 6 meters above ground. The filled glass flasks were then analyzed at the Commonwealth Scientific and Industrial Research Organization (CSIRO) Atmospheric

Research GASLAB (Global Atmospheric Sampling LABoratory), Australia for CO_2 and other related trace gases.[1]

There are two more observational sites which are coming up soon, the first one is Sagar located at central India, and second is Cape Rama located at the west coast of India (Figure 3). Sagar site will be equipped with 72 meter tall tower and GHGs will be monitored at five levels. Apart from this we will monitor soil CO_2, eddy co-variance CO_2 flux at 3 meter, reactive gases such as O_3, CO, NO_x, SO_2 etc. This is very important site because it is located at central Indian region and air-mass received here represents only Indian land mass (no oceanic air-mass) during every season. On the other hand coastal site Cape Rama will be equipped with 20 meter tower at the coast for GHGs monitoring. This site represents oceanic air-mass during Indian summer monsoon months (JJAS) and continental air-mass during winter months (DJF) i.e. it witnesses seasonal reversal of wind pattern. Figure 4 shows climatological mean of CO_2 concentration over Cape Rama (CRI) and Sinhagad (SNG) observations sites. Both the sites show CO_2 peak during adjacent months whereas drawdown is in same month. September peak is due to local emissions on the scale of 500 km when lots biomass is removed from the surface during this month.

Figure 3

Surface GHGs monitoring sites Sinhagad (SNG), Cape Rama(CRI) and Sagar (SGR). (Map of India adopted from Forest Survey of India- http://www.fsi.nic.in/sfr_2009.htm).

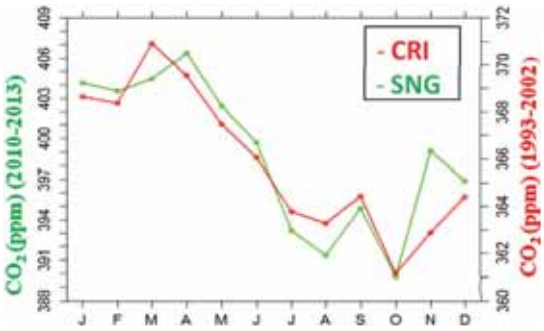

Figure 4

Climatological mean of CO_2 concentration over Cape Rama (CRI) and Sinhagad (SNG) surface observations sites.

2) Carbon flux measurement network

A network of carbon flux monitoring is in operational in India since 2014. This network consists of five sites located in different ecosystems such as natural forests: Selembong

Forest at Darjeeling district (DJI), West Bengal and Kaziranga National Park (KNP), Assam, both in North East India; coastal: Lakshwadeep (LKD) and Port Blair (PBL); mangrove: Pichavaram (PCV) (Figure 5). Multi-level instrumentations are installed such as: Eddy Covariance (EC) systems at two levels consisting of fast-response 3D sonic anemometer-thermometer, closed-path CO_2-H_2O analyzer and data logger; soil temperature sensor at 5 levels; soil heat flux plates at 2 levels; multi-component weather sensors at 4 levels; infra-red thermometer; Photosynthetic Active Radiation (PAR) quantum sensor; and net radiometer.

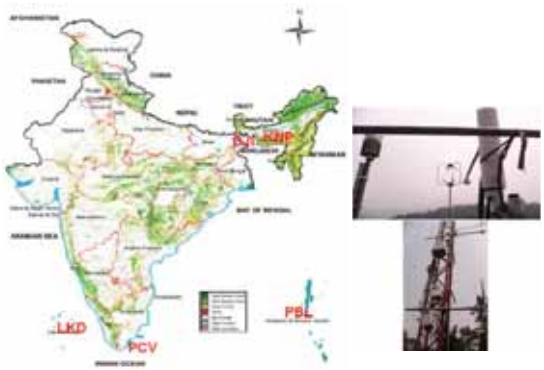

Figure 5

Carbon flux monitoring network in India, Darjeeling (DJI), Kaziranga National Park (KNP), Lakshwadeep (LKD), Port Blair (PBL), and Pichavaram (PCV) (left panel). Tower and instruments installed at forest sites (right panel). (Map of India adopted from Forest Survey of India- http://www.fsi.nic.in/sfr_2009.htm).

3) GHGs concentration monitoring at Aircraft platform

Apart from above, aircraft is used for GHGs monitoring over Indian continent and adjacent oceanic regions. Beech-craft B200 twin engine aircraft was used for the campaigns during Indian summer monsoon months of 2010, 2014, and 2015 over India. Airplane campaign 2014 was conducted over Ganga river basin located near the foothills of Himalaya. This basin is hot spot for GHGs emissions due to densely populated habitat as well as for several industries. GHGs observations are not available over this region and so model simulated lower to upper troposphere transport are need to be validated over this region. CRDS technique based instrument Picarro G2401-m instrument was used during 2014 and 2015 campaigns and NOAA standard gases were used to calibrate the observations. Calibration was done at the ground before start of airborne observations because cylinders were not allowed flying in the aircraft. Output data were stored at every two second interval, post-processing is done with the help of co-located meteorological data from other instruments on board the aircraft. Figure 6 shows the vertical profile of CO_2, CH_4, CO, H_2O concentrations during one flight in 2014. Figure 7 shows the aircraft campaign photographs during calibrations before the flights using NOAA standards.

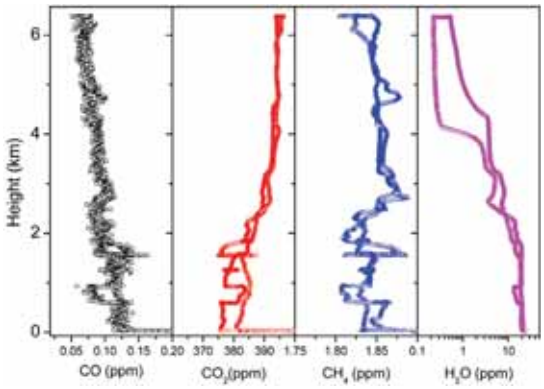

Figure 6

Vertical profile of CO_2, CH_4, CO, H_2O concentrations of one flight during aircraft campaign 2014 over India.

Figure 7

Aircraft campaign 2014 & 2015 over India

Outlook

Greenhouse gases (GHGs) monitoring in India started in 2009 whereas aircraft based observations were started in 2010 and carbon flux monitoring in 2014. GHGs monitoring outputs at surface site Singahad (SNG) is in agreement with the Cape Rama (CRI) as both sites generally samples more or less similar air-mass on continental scale. Aircraft campaigns are very promising to understand vertical profile of GHGs over India; this will help us understand model simulated CO_2 transport from lower to upper troposphere during different seasons over the Indian region. Air sample analysis lab with gas chromatography was established at the IITM Pune India in 2009 and now part of CH_4 inter-comparison program among Asian labs (Japan, Korea, etc). Such comparison exercises will help us in maintaining high precision of GHGs monitoring at the surface sites in India. SF_6 monitoring started recently with the help of KMA, Korea. KMA team visited IITM Pune during Sept. 2015 and worked on optimization of gas chromatograph instrument to get SF_6 peak. KMA has provided SF_6 calibrations standards whereas all other gases are calibrated using NOAA standards. We hope to get valuable data during coming years which will ultimately help us in understanding regional carbon balance as well as reduce model uncertainties in carbon sources and sink estimations.[7]

Acknowledgement

I sincerely thank to my previous student Dr. K Ravi Kumar for helping me in setting of GHGs observational program in India. Also, I am grateful to Director IITM for supporting me on this research.

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Experimental probing long-term stability of SF_6 in dehumidified and pressurized air sample by using preconcentrator-GC-μECD

Jeong Sik Lim[1*], Dongmin Moon[1], Jin-bok Lee[1], Kwang-sup Kim[1], Kahae Kim[1], Haeyoung Lee[2], and Jeongsoon Lee[1]

Introduction

Air Archive might stand for the (dry) air samples stored for a long period of time after being collected into a pressurized gas cylinder or an air sampling canisters. Accordingly, it can be said that the Air Archive has a very high value as an important standard that can provide abundant information about the temporal and regional variations of particular gaseous species in order for the reconstruction of the past air composition. For instance, CSIRO (Commonwealth Scientific and Industrial Research Organization) has been continuing the Cape Grim Air for (CGAA) Program that symbolizes the temporal variation in the background atmosphere of the southern hemisphere since 1978, and this background-atmospheric sample of the southern hemisphere was used in restoring the temporal changes in the past atmospheric concentration of important greenhouse gases such as SF_6, N_2O, NF_3, and PFCs.[1][2][3][4] CGAA was also used as absolute reference of the verification of real-time measurement and flask sampling network. Furthermore, the Air Archive can provide potential values for new species to be detected by new technology and new interests at some point.

Consequently, national specific Air Archive system is highly required to be built for establishing a history of the background atmosphere of Korean Peninsula. To this end, we intend to carry out base studies for a construction of the Air Archive system. First of

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all, we intended to select SF_6, which is a representative anthropogenic greenhouse gas, for a study on the long-term stability of dry air sample which will be collected in various gas cylinders and to develop a precise analysis method using a Gas Chromatography – Electron Capture Detector (GC-ECD) combined with a preconcentrator to trace the change in the concentration inside the cylinder as a function of time

Results and discussion

1) Sampling strategy: change in the SF_6 concentration at the AMY depending on the wind direction

As Anmyeon-do Climate Change Observatory (AMY), which is one of the candidates for the site of air archiving, is located on the west coast of Korean Peninsula, air masses with different natures flow into this area depending on the wind direction. It is an area which has diversity in acquiring the information about the inflow of air mass from China and about the greenhouse gas discharge in the inland of Korean Peninsula. Accordingly, in collecting dry air samples for monitoring the background-atmospheric concentration of greenhouse gas, the variability of wind direction is required to be considered, and, as a result of comparing the meteorological data and the background atmosphere observation data produced by the AMY, it could be confirmed that the background-atmospheric concentration of SF_6 was high when the air mass from the southern part of Gyeonggi-do and the northern part of Chungcheongbuk-do, in which IT industry was concentrated, flowed in and the wind was blowing from the northeast. (Figure 1).

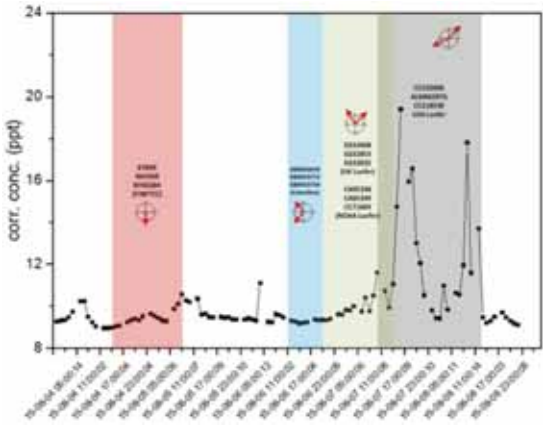

Figure 1

Change in the background atmospheric concentration of SF_6 with time observed in the Anmyeon-do Climate Change Observatory (August 4 ~ August 8, 2015)
The red arrows added are the variations in the wind direction during the relevant time bands. The observed data is produced using a GC-ECD (Data provided by: Anmyeon-do Climate Change Observatory).

Based on this, to secure the representativeness as the northern hemisphere background atmosphere, introduction of an acceptance sector depending on the wind direction should be considered or sampling in Gosan (Jeju Island) which is well known as a super site should be considered. Accordingly, a sampling methodology by sector is required to be developed through synchronization of the wind direction information during air sampling. Figure 2 shows a schematic dia-

gram of the sampling device that collects the wind direction information from an Automatic Weather Station and synchronizes it with the on/off state of the pressurizing pump. Granulated $Mg(ClO_4)_2$ is used as a filter for removal of particles and a chemical trap for removal of moisture. The entire system can be fully automated by synchronizing the pressure sensor and the power of the pump when the cylinder pressure reaches the set pressure. To prevent contamination of the collected sample, a cylinder in vacuum state (< 10^{-5} Torr) with clean internal surface is used. For this, the surface of the cylinder is heated (> 60 ℃) while it is vacuum processed to induce desorption and discharge of the adsorbed gas. The gas piping should be purged without fail from the sampling tower to the background atmosphere before operating the pump, and the normal operation condition of various safety devices should be checked in the state the cylinder tank valve is closed.

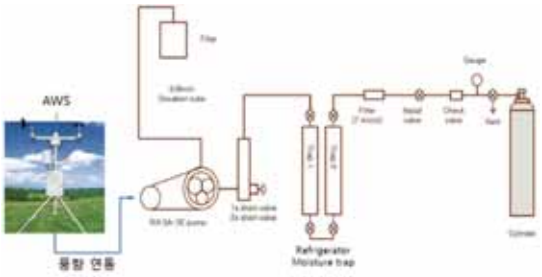

Figure 2

Sketch of dry air sample collection device using a high pressure cylinder. The Automatic Weather Station (AWS) is connected to enable the switch of the pump to be turned on and off in accordance with the wind direction.

2) Development of the method to analyze the atmospheric concentration of SF_6

The Global Warming Potential (GWP) of HFCs (Hydrofluorocarbons) which are alternative refrigerants is comparable to that of CFC (Chlorofluorocarbon), but as the demand in the industrial sector is continuously increasing, it is very intriguing to look into a possibility of HFCs for being archived. But analytical methods using gas chromatography are suffered by low sensitivities in HFCs in ECD and MSD (Mass Selective detector). Therefore, it is very difficult to track a change of HFCs concentrations in a sampling cylinder along entire storage period. As an alternative to this, SF_6 might be a good indicator for the test of the long term stability of sampling cylinders. The background- atmospheric concentration of SF_6 is of 8 to 10 ppt level globally and SF_6 is known to be a greenhouse gas with a moderate daily variation. Considering that the atmospheric concentrations of HFCs are of several tens of ppt, the study on the stability of a few ppt SF_6 has diverse advantages as sufficient sensibility for tiny concentration change in a cylinder can be secured by using ECD. It is a very important factor in preparing the evidence for the stability of long-term storage. The analytical methods applying a back-flush technique coupled with Porapak Q column and inter-injection baking method with activated alumina F1 column has been introdeced.[5][6] In this study, an SF_6 analytical

method using a preconcentrator with GC-ECD is investigated for the inspection of SF_6 stability in various cylinders. The preconcentrator can also provide a chance to explore the possibility to detect the stabilities of HFCs by GC methods. When preconcentrator is applied, we can expect not only noticeable improvement in the sensitivity but also the effect of mitigating the drift by effectively isolating the instrument from the laboratory environment, that is to say, the pressure change. The reason is because the change in the flow rate of the sample resulting from the change in the external pressure is small when the concentration technique is applied as the sample passes through the gas piping filled with an adsorbent (Carboxen) instead of using the sample loop which has vacant internal space and is directly connected to the atmosphere differently from the back-flush and baking technique introduced earlier. For this reason, one can expect low drift to improve an uncertainty caused by drift correction. As a result of testing the drift of the equipment while carrying out the measurements of reference – sample – reference (3 injections each) which is the unit sequence of this bracketing method, the SF_6 response was grasped to change by 0.7 % when the pressure of the laboratory changed by about 0.1 %. An effect of small drift could be obtained by isolating the analysis equipment from the laboratory environment in such a way, through which we can expect analysis precision of 0.1 % or better when quantitatively analyzing SF_6.

Figure 3

Preconcentration system which is coupled with GC-ECD. The process of concentrating gas is divided into the following six steps: 1) High-purity He is injected into the trap with the three valves turned off, and the temperature of the pre-concentrator is set at about -65℃; 2) With the pre-concentrator valve and sample injection valve turned on, the sample is adsorbed in the trap; 3) With the sample injection valve turned off, high-purity He is used to purge the non-adsorbed O_2 and the sample on the line; 4) With the pre-concentrator valve turned off, the temperature of the pre-concentrator is raised to 100°C or higher to remove the sample adhered in the trap; 5) With the other two valves turned on, the carrier gas enters the detector with the gas loaded in the trap so that SF_6 and other analytes such as N_2O and CFCs can be detected; 6) During the measurement, the pre-concentrator is returned to the initial state for the next pre-concentration cycle.

In this study, to evaluate the long-term stability of various cylinders widely used for gas analysis, dry air samples were collected into the products of 4 companies which are made of different materials and of which the internal surfaces are treated differently, and their SF_6 concentrations were measured. As shown in Table 1, the difference between KRISS-measured SF_6 in pressurized cylinders and the observation values which are generated by on-line GC-ECD is not big, indicating no

Table 1. Characteristics of the gas cylinder of each manufacturer and initial certification value of SF_6 after the dry air sample is collected

Cylinder No.	Manufacturer	Material	Sampling Date	SF_6 Concentration (ppt)	Analysis Uncertainty (%)	Observation (ppt)
D232832	A	Aluminum /electropolished	Aug. 7	12.73	0.1	9 ~ 20
D232853	A	Aluminum /electropolished	Aug. 6	9.21	0.19	About 9
CC71604	B	Aluminum /electropolished	Aug. 8	10.21	0.15	9 ~ 17
CC218540	B	Aluminum /electropolished	Aug. 7	13.28	0.16	9 ~ 20
EB0033750	C	Aluminum	Aug. 6	9.32	0.1	About 9
NY00284	D	Mn-steel	Aug. 6	9.45	0.18	About 9

error during sampling. The analytical precision was evaluated to be below the level of 0.2 % (0.05 ppt) in most of the measurements, which might be good measurements. In near future, we plan to complete the test of the long-term stability using the SF_6 standard gas newly manufactured for stability test of the selected cylinders with time.

Plan to utilize the study result and the effects expected

The scientific grounds for the Unique National Air Archive can be secured by obtaining the data of the study on the stability of sample storage cylinder for long-term storage of atmosphere samples. Also, we can expect proliferation of the analysis system that can be used to study the temporal change in the major atmospheric constituents and greenhouse gases, or unknown ingredients, as well as proliferation of the method of storing atmosphere samples for a long period of time. The long-term stability evaluation of cylinders to be carried out in the future can be utilized as the standard procedure for long-term stability evaluation of standard gases. Moreover, it is the base technology that can be utilized for long-term stability evaluation of the traveling standard gas produced and supplied through WCC-SF_6 (World Calibration Centre for SF_6) being operated by the Korea Meteorological Administration. Finally, the atmosphere sample of Korean Peninsula which has regional characteristics stored and built for a long period of time can be utilized for preparation of the strategy to cope with the geopolitical environmental issues.

We can secure measurement technology and domestically produced data to utilize them for implementation of an observation system suitable for the unique national atmospheric environment and topography, which in the near

future can contribute to tracing the temporal change in the new gas species which have not been the observation items and can contribute to the restoration of the temporal variability data of isotopic ratio of HFCs, CFCs and major greenhouse gases as potential candidates.

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