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Atmospheric Methane Characteristics in AMY, Korea, 2012

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The Fifth Assessment Report (AR5) of the United Nations Intergovernmental Panel on Climate Change (IPCC) published in September 2013 reported that there is a clear human influence on the ongoing global warming. In addition, atmospheric concentrations of carbon dioxide, methane, and nitrous oxide have increased to unprecedented levels in at least the last 800,000 years.

Especially, even though methane is the most important greenhouse gas next to carbon dioxide, the relative contributions to various processes that produce methane are uncertain while the sink is quite well understood indicating it arises primarily from the activity of hydroxyl radical which is involved in photochemical oxidation reaction.

Asia regions are well known for the main source of methane due to rice paddies, plateaus during monsoon, and tropical wetlands ^{[1], [2], [3], [4]}. For Korea, methane is released mainly from agriculture (40% methane emissions in total) and energy sector (30%) ^[5]. In Korea, methane studies are focusing on only emission source interestingly. However, atmospheric methane studies are very important to understand the growth rate because they reflect the global methane budgets which delicately balance large sink and sources at present.

The Korean Peninsula is not only located in downwind area from Asia continents due to westerly wind, but also affected by seasonal flow patterns indicating the main wind stream is southwesterly in spring, southerly in summer, easterly in autumn, and northwesterly in winter, respectively. Especially, Anmyeondo (AMY) is in western part of the Korean Peninsula and one of GAW (Global Atmosphere Watch) regional stations that AMY could monitor the methane not only from local area, but also from other Asia continents. In here, the evidence is presented from atmospheric trajectories that explain some of synoptic and seasonal scale variability in methane by relating it to flow patterns and locations of source and sink in AMY.

At AMY, methane had been measured from 1999 to 2003 from the inlet, 67m above the sea level, and has been measured from 87m using 40 m tower since 2004. Methane has been monitored using GC-FID (Gas Chromatography Flame Ionization Detector, Agilent 6890N) and calibrated with one point standard gas which has similar concentration with background concentration every 6 hours since 1999. When the data from GC-FID were compared with those from CRDS (Cavity Ring Down Spectrometer, model 2301, Picarro) which was calibrated with two point standard gases every two weeks, the values from GC-FID are in good agreement with those from CRDS as shown in Figure. 1.



Figure 1. Temporal variation of hourly mean of methane measured by GC-FID (red spots) and CRDS (black spots) in 2012, AMY, Korea (left) and the scatter plot of CRDS and GC-FID using hourly mean concentrations (right).

The seasonal mean concentrations of methane were high in the order of autumn>winter> summer>spring (Table 1.). Methane shows the lowest concentration in summer due to the OH radical and high mixing height generally. However, mean concentration of methane in summer at AMY was higher than that of spring, similar with winter's and its standard deviation was the highest indicating maximum concentration was the highest (2551 ppb) and the minimum concentration was the lowest (1773 ppb).

| Conc.(ppb) | Spring (MAM) | Summer (JJA) | Autumn (SON) | Winter (DJF) |
|------------|--------------|--------------|--------------|--------------|
| Mean | 1937 | 1953 | 1961 | 1954 |
| Std. | 37 | 116 | 67 | 43 |
| Median | 1927 | 1926 | 1940 | 1941 |
| Maximum | 2138 | 2551 | 2407 | 2179 |
| Minimum | 1836 | 1773 | 1826 | 1792 |
| Ν | 1675 | 2172 | 2183 | 2161 |

Table 1. The results of methane measured with GC-FID at AMY in 2012

To understand its characteristics in the summer of AMY, ten-day backward trajectories were analyzed using FLEXPART (from Norwegian Institute for Air Research in the Department of Atmospheric and Climate Research). According to the back trajectory analysis, three cases were categorized into: (a) when it was affected by North Pacific air mass directly, it indicated the baseline with lower concentration than other periods (Figure. 2(a)). (b) Under the stagnated conditions, high concentration of methane (daily mean of 2050 ppb) comes from the agriculture around the stations ^{[6],[7]} as showing no relationship between methane and carbon monoxide (Figure. 2(b)) (c) There was another case of high concentration when it was affected by long-range transported air mass from Asia continent. Carbon monoxide and methane trends are similar in that case (Figure.2(c)).



Figure 2. The ten-day backward trajectory of FLEXPART (left column) and CO and CH4 concentrations from GC-FID and CRDS respectively (right column) in (a) the low concentration case, (b) the high concentration case under the stagnated condition and (c) the high concentration case due to long-range transported air mass from the Asia continent during summer period, 2012, AMY.

To remove the effects of local sources under the stagnated condition from the data, hourly means with wind speed above 6m/s were selected and showed in Figure. 3. It indicated the high concentration in the order of winter>autumn>spring>summer, indicating it was similar to the global seasonal variation. From summer to winter, methane showed higher level with easterly wind, compared to other wind directions. However, spring period showed the highest concentration with south westerly wind that reflects the methane derivation from the Asian continent. Summer had the large variation of methane by wind direction due to strong north pacific air mass from sink region while this variability was reduced with the cessation of the north pacific wind from methane sink region in winter period.



Figure 3. Methane concentrations from GC-FID by the wind direction in spring (green), summer (blue), autumn (orange), and winter (red) when the wind speed was above 6m/s.

The seasonal mean methane showed the high concentration in the order of autumn>winter> summer>spring, while it showed winter>autumn>spring>summer with the similar pattern of global methane after removing the stagnated condition. Therefore, local sources would be the most important factor to select the background concentration from the data at AMY. Even though the local effects were removed from the data, it implied that changes in the methane linked to air flow patterns. Year-to-year changes in transport could affect estimate of the methane growth rate and the study of long range transported methane is needed to understand its growth rate in the future.

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NOAA Measurements of Long-lived Greenhouse Gases

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Introduction

NOAA Earth System Research Laboratory, Global Monitoring Division, Carbon Cycle Group (CCG) began monitoring CO_2 from discrete flask samples in the late-1960s, and has since added measurements of other important long-lived greenhouse gases and related tracers, including isotopes through collaboration with the University of Colorado, INSTAAR, from these flasks. Our group also has programs to measure CO_2 and CH_4 continuously at NOAA's background observatories, measure CO_2 and other tracers from tall towers, and measure long-lived greenhouse gases (LLGHG) from discrete samples collected on light aircraft. Our group, in collaboration with another group in our division, has also developed a standards program that provides SI-traceable standards to our NOAA programs and the WMO GAW community. Here some key results from CCG's global cooperative air sampling network are given for CO_2 , CH_4 , N_2O , and SF_6 .

Sampling and analysis methods

Air sample pairs are collected approximately weekly in 2.5 L flasks from ~60 sites (as of 2013) in NOAA's global cooperative air sampling network ^[1] (also http://www.esrl.noaa.gov/gmd/ccgg/flask. html). Flasks are flushed and pressurized to ~1.2 atm with a portable sampler. Samples are collected under conditions when air is representative of large, well-mixed volumes of the atmosphere to facilitate comparison with simulations from chemical transport models that have relatively large grid-scale resolution. Analytical methods are as follows: CO₂: NDIR; CH₄: GC/FID; N₂O/SF₆: GC/ECD. All instrument responses are calibrated with standards on the respective WMO GAW mole fraction scales maintained at NOAA and reported as dry-air mole fractions (CO₂ and CH₄ data path: ftp://aftp.cmdl.noaa.gov/data/trace_gases/<co2 or ch4>/flask/surface/). To calculate means representative of large spatial scales, data from a subset of globally-distributed remote boundary layer sites were fitted with curves to smooth variability with periods less than ~40 days ^[1]. Synchronized points were extracted from these curves at approximately weekly intervals and smoothed as a function of latitude to define an evenly spaced matrix of surface LLGHG mole fractions as a function of time and latitude. This matrix was used to calculate global and zonal averages.

Results

CO₂: Since 1750, ~385 billion tons of carbon has been emitted into the atmosphere as CO₂ by combustion of fossil fuels and production of cement. About half of these emissions have occurred since the mid-1970s ^[2]. This carbon is partitioned into three mobile reservoirs: atmosphere, oceans, and terrestrial biosphere. Atmospheric CO₂ has increased from about 278 ppm (ppm= μ mol mol⁻¹) at the start of the industrial revolution to more than 390 ppm today. The atmospheric increase contributes ~1.85 W m⁻² of radiative forcing (see e.g., http://www.esrl.noaa.gov/gmd/aggi/). CO₂ that enters the ocean increases the acidity (decreased pH) of surface waters through carbonate chemistry. This can have detrimental effects on organisms that contain calcium carbonate, for example the shells of plankton near the bottom of the ocean food chain and corals. Increasing acidity will cause calcium carbonate to dissolve, destroying these creatures.

The fate of fossil fuel derived CO_2 is important to climate, because different reservoirs have different residence times and different susceptibilities to human interference. Therefore much current carbon cycle research is dedicated to understanding the partitioning of fossil CO_2 into the ocean and terrestrial biosphere. One method used to understand the partitioning of fossil CO_2 between biosphere and ocean is stable C isotopes in CO_2 . Figure 1 shows CO_2 mole fraction (top panel) and $\delta^{13}C$ in CO_2 from weekly samples at Cape Kumukahi, Hawaii. The long-term decline in $\delta^{13}C$ results from fossil carbon being depleted in ¹³C relative to atmospheric CO_2 . There is a seasonal cycle in both CO_2 mole

fraction and δ^{13} C, but they are of opposite phase. As the biosphere takes up CO₂ in the spring and summer, it favors ¹²C; this enriches the atmosphere in ¹³C (less negative δ^{13} C values). Inter-annual variation in the balance between photosynthesis and respiration is seen in the subtle variations in the long-term δ^{13} C trends. For example, air temperatures were cool in 1992 because of the short-lived effect of aerosols after the eruption of Mt. Pinatubo. This likely resulted in decreased respiration relative to photosynthesis, and offset the decreasing trend in δ^{13} C from fossil fuel combustion. The opposite effect, an increase in the ratio of respiration to photosynthesis is seen in warm years such as 1998.



Figure 1.(a) CO_2 dry air mole fractions (NOAA ESRL) and (b) $\delta^{13}C$ in CO_2 (University of Colorado, INSTAAR) from weekly samples collected at Cape Kumukahi, Hawaii.

The globally averaged atmospheric CO₂ mole fraction in 2012 was 392.52 ± 0.10 ppm, and it increased 2.43 ± 0.09 ppm (see http://www.esrl.noaa.gov/gmd/ccgg/trends/). Despite fossil CO₂ emissions being predominantly in the Northern hemisphere, the rate of increase of atmospheric CO₂ is approximately the same everywhere.

CH₄: The contribution of CH₄ to anthropogenic radiative forcing, including direct and indirect effects, is about 0.7 W m⁻². While $\sim 2/3$ of its emissions are from anthropogenic sources, natural emissions of CH₄, predominantly from wetlands, are a potential strong climate feedback because emission rates depend strongly on temperature and precipitation. In the Arctic, where surface temperatures are increasing at twice the global rate, there is the potential for increases in CH₄ emissions from wetlands. The Arctic also contains large stores of organic carbon in permafrost and in hydrates, but increases in emissions from these climate-sensitive sources have not yet been detected in

atmospheric observations. Anthropogenic sources such as biomass burning are also susceptible to changing climate through changes in precipitation. Dry conditions during the strong El Niño of 1997 and 1998 resulted in an estimated 50% increase in CH₄ emissions from biomass burning in the tropics and high northern latitudes relative to normal ^[3].

After a decade of near-zero growth, atmospheric CH₄ began increasing again globally in 2007 ^{[4], [5]}, as shown in Figure 1. The increase was driven by increased Arctic and tropical emissions. CO measurements in the same air samples indicate little contribution from enhanced biomass burning since 2007. Likely drivers for increased emissions in 2007 are anomalously high temperatures and precipitation in wetland regions, particularly in the Arctic. Since



2007, atmospheric CH₄ continues to increase at ~6 ppb yr⁻¹. Despite continued warmth in the Arctic, emissions there returned to normal levels in 2008. The causes of the continued global increase are not clear, but greater than average precipitation in tropical wetland regions and increased anthropogenic emissions are likely the largest contributors. Unfortunately, the current atmospheric CH₄ observing network is not sufficient to determine with certainty the causes of the CH₄ increase since 2007.

 N_2O : Nitrous oxide contributes the third-most radiative forcing by LLGHGs since 1750, and its stratospheric ozone depletion potential-weighted emissions are now largest of all ozone depleting substances. Based on long-term continuous measurements at NOAA observatories, it has increased at ~0.78 ppb yr⁻¹ for more than 30 years (http://www.esrl.noaa.gov/gmd/hats/combined/N2O.html). Because N₂O has a long lifetime (~130 yr) and its emission rates are small, spatial gradients are small. This, in turn, requires a relatively high degree of internal consistency across measurement networks, if the observations are going to be used with a chemical transport model to calculate emissions at regional to continental scales. CCG has been measuring N₂O in discrete air samples since mid-1997. Despite poorer repeatability of the CCG N₂O measurements from flasks than from in situ analyzers, the greater spatial coverage of the CCG measurements has helped improve knowledge of the large

scale distribution of emissions ^[6]. In future, isotopic measurements of N₂O from CCG discrete samples may further improve our knowledge of the global N₂O budget.

SF₆: Sulfur hexafluoride is emitted almost entirely from anthropogenic processes. Because its lifetime is extremely long (~3200 yr) and it is well-mixed in the atmosphere, observations from relatively few sites can be used to estimate total global emissions. Such estimates show that emissions reported to the UNFCCC by Annex I countries are substantially underestimated ^[7]. As with N₂O, CCG measurements are useful in understanding the spatial patterns of SF₆ emissions. Additionally, the observations have been used to test transport in atmospheric chemical transport models. For example, Peters et al. ^[8] used CCG SF₆ measurements to show that the commonly used model "TM5" overestimates the latitudinal gradient of SF₆ by 19% and that mixing within the planetary boundary layer in the model is too slow.

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Ground-based monitoring of greenhouse gases (CO₂, CH₄) along the west coast of India: Role of Indian summer monsoon

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The paucity of ground-based greenhouse gas (GHG) monitoring over the Indian subcontinent has been posing a stringent limitation to the estimates of CO₂ sources and sinks. According to a recent report published by the Ministry of Environment and Forests (MoEF), Government of India (http://moef.nic.in/downloads/public-information/Report INCCA.pdf), the total GHG emissions in India have substantially increased from 1252 to 1905 million tons during 1994-2007 at an annual growth rate of 3.3%. With limited ground-based observational resources, it was seen that some sectors such as the cement production, electricity generation, and transport have provided greater contribution to this significant growth by 6%, 5.6%, and 4.5% respectively during this time. Estimates of total fossil-fuel CO₂ emissions from Indian subcontinent are: 189 TgC in 1990, 324 TgC in 2000, 385 TgC in 2005 and 508 TgC in 2009 with an increasing rate of about 7% per year during the past decade^[1] [source: Carbon Dioxide Information Analysis Center (CDIAC), USA]. One of intriguing sink factors is that some of the GHG emissions are likely to be compensated by vegetation uptake over the Indian subcontinent^{[2],[3]} which still remains an unresolved issue that warrants immediate attention. In response to land-sea thermal contrast, the largest volume of precipitation over the subcontinent is observed during the monsoon months [June through September (JJAS) in summer and December through February (DJF) in winter^{[4], [5], [6]}. As the southwesterly moist-laden winds during the Indian summer monsoon initially arrives at the west coast of India and then spreads over the subcontinent, the maritime transport mechanisms are imperative for accurate source region estimates. The influence of the continental air mass transport during DJF due to seasonal wind reversal is also equally important. More importantly, the GHG residence times over the oceanic and continental regions during their transport are of great importance. Therefore, the transport mechanisms associated with the monsoon meteorology in the vicinity of the complex mountainous regions constitutes the focal point of this study to understand the role of GHG transport and sinks in the west coast of Indian subcontinent using observational and modeling resources.

Currently, there are two operational stations along the west coast of India, one at Cape Rama (CRI), Goa (15.08° N, 73.83° E, elevation =50 m asl) (Fig. 1) that has a long observational record for more than a decade. The CO₂ seasonal behavior at CRI has clear signals driven by monsoon meteorology and terrestrial ecosystem variability^{[7], [8]}. Another GHG monitoring site located over the Western Ghats mountains is Sinhagad (SNG; 200 km from the Arabian sea; 73.75° E, 18.35° N, elevation = 1600 m asl) which is operational since 2010 that concatenates the CO₂ routine monitoring along the west coast of India (Fig. 1)^[9]. Similar to the features observed at CRI, SNG also consistently indicates

the seasonal changes of CO_2 to reversal of wind patterns. These two sites are predominantly influenced by maritime air masses during JJAS, while influenced by the continental air masses during DJF. Several recent observational and modeling studies have elicited the general connections associated with GHGs and the Indian summer monsoon ^{[10], [11], [12]}. However, these studies are not surface-based, but mostly restricted to mid-to-upper troposphere CO_2 obtained either from aircraft observations or from the model simulations. The surface-based observations at CRI and SNG will shed more insight to the understanding of the variability and seasonal changes. This study, in particular, is aimed at demonstrating the influence of the Indian summer monsoon on the GHG observations at CRI and SNG.



Figure 1.Observations sites Cape Rama (CRI) and Sinhagad (SNG) over India.

Figure 2 shows the monthly climatological mean of Normalized Difference Vegetation Index (NDVI), and rainfall (mm) during 2000-2010 valid over the site locations at SNG and CRI. NDVI ^{[14],} ^[15] and rainfall ^[16], 17] datasets archived at $1^{\circ} \times 1^{\circ}$ resolution are used in this study. NDVI is obtained from NOAA/AVHRR as well as from MODIS/AQUA. The rainfall dataset is based on 1803 rainfall gauges located over India. Zero NDVI means no vegetation and as high as 0.8 - 0.9 indicates the highest possible density of green leaves. NDVI shows minimum during April-May and maximum in October both at SNG and CRI. Indian summer monsoon rainfall at CRI (SNG) is maximum in May (June) month.



Figure 2.NDVI (left panel) and Rainfall (right panel) climatology at the Cape Rama (CRI) and Sinhagad (SNG) monitoring sites.

Figure 3 shows a comparison of daily mean atmospheric CO₂ observations at Mauna Loa (MLO) Hawaii, USA against the values at CRI and SNG. MLO daily mean CO₂ observations during 2009-2012 are used for comparison with CRI and 2010-2013 with SNG. As compared to MLO, CRI and SNG observations show stronger trend and seasonality. Marine (continental) winds dominate CRI during summer (winter) monsoon months ^[18]. In accordance to this, CRI and SNG indicated lower signatures of CO₂ during summer monsoon months as CO₂ signatures are richer in continental winds than in marine winds,

Figure 4 compares climatological mean of CO_2 and CH_4 concentrations observed at CRI, SNG, and MLO as well as at Seychelles (SEY;4.67 S, 55.17 E, 7m asl) and Cape Grim (CGO; 40.68 S, 14 4.68 E, 94 m asl) from the southern hemisphere. During summer monsoon months CRI observed CO_2 and CH_4 concentrations indicate lower values than observed at MLO (Fig.4a, b). Climatological mean of CH_4 concentrations observed at SEY and CGO generally indicate smooth variation during the entire year which implicates that these two sites are primarily dominated by the marine signatures.

The observations clearly indicate that greenhouse gas transport is strongly influenced by the monsoon circulation along the west coast of India. In the advent of changing climate era and the debatable strengthening and weakening of monsoonal flows, the carbon cycle has serious implications on the regional climate assessment over India^[13] owing to strong dependence of carbon sources and sinks from the neighboring regions. In lieu of this, a detailed further analysis of CO₂ observations as well as with the aid of full suite chemistry transport models are indispensable at this time towards an accurate regional identification of CO₂ and other tracer species for better understanding of regional carbon cycle over the Indian subcontinent.



Figure 3.Atmospheric CO₂ observations comparisons with Cape Rama and Mauna Loa (upper panel) and Sinhagad and Mauna Loa (lower panel).



Figure 4.Comparison of climatological mean of atmospheric (a) CO₂ observations Cape Rama and Mauna Loa (b) CH₄ observations at Cape Rama and Mauna Loa (c) CH₄ observations at Cape Rama, Sinhagad, Seychelles (SEY) and Cape Grim (CGO).

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Establishment of Continuous Greenhouse Gas Observation Capacity in Northern Vietnam through a Swiss-Vietnamese Collaboration

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I. Introduction

The project Capacity Building and Twinning for Climate Observing Systems (CATCOS)^[1]that will last from mid-2011 to 2013. The project is supported by the Swiss Agency for Development and Cooperation (SDC) with the Federal Office of Meteorology and Climatory MeteoSwiss as the coordinating partner on the part of Switzerland. The project addresses the need to improve climate observations world-wide, but particularly in developing countries and countries in transition. The Project focuses on atmospheric observations and will be implemented by the Paul Scherrer Institute (PSI, for the aerosol part), and by the Swiss Laboratories for Materials Testing and Research (EMPA, for the atmospheric trace gas part).

The **International partners and beneficiaries** of this project are countries in South America, in Africa, and in Asia. These are represented by the Bureau of Meteorology, Climatory and Geophysics (MMKG, Indonesia), the Dirección Meteorológica de Chile (DMC, Chile), the Kenya Meteorological Department (KMD, Kenya), and the National Hydro-Meteorological Service (NHMS, Vietnam). This report only focuses on the Establishment of Continuous Greenhouse Gas Observation Capacity in Northern Vietnam belong to the CATCOS project.

II. Preparation steps for the project in Vietnam

2.1 Expert Meeting

A first meeting took place at NHMS on 13 June, 2012. The meeting was chaired by Deputy Director General of NHMS Mr. Nguyen Van Tue, who also introduced NHMS. Dr. Jörg Klausen then introduced MeteoSwiss, the Global Atmosphere Watch, and the CATCOS project in three presentations. Dr. Nicolas Bukowiecki introduced technical aspects and requirements of the CATCOS project. During the ensuing discussion, the objectives of the visit of the Swiss delegation in Viet Nam were approved by the chair.

2.2 Site visit

The Swiss delegation then visited the Hydro-Meteorological and Environmental Station Network Center including their laboratories (Calibration, Analysis) and the automatic environmental station in Ha Noi. Subsequently, the delegation was introduced to the Vietnam Institute of Meteorology Hydrology and Environment (IMHEN).

The delegation visited six locations in Northern Vietnam suggested by NHMS and IMHEN:

Mau Son Climate Station Son La Climate Station Pha Din Climate and Radar Station Sa Pa Agrometeorological Station Sa Pa Climate Station Hoang Lien (previous climate station, re-establishment foreseen by 2020)

The suitability of these locations for representative atmospheric composition measurements was assessed in terms of

Geography (topography, land cover)

Climatology (available meteorological and atmospheric composition data)

Existing infrastructure



Figure 1.Overview of Sites Visited

2.3 Site selection

The **Pha Din Climate (and future Radar) Station** was identified to be the most suitable location to establish atmospheric measurements and was recommended for CATCOS and with a view of submitting this station to WMO as a Regional GAW station. Another, potentially suitable site located on a mountain saddle, namely **Hoang Lien**, could not be recommended at this point be-cause of a complete lack of infrastructure. The station **Mau Son** was initially considered because of its remote location on a hill top close to the Chinese border. However, upon inspection of the site, it became apparent that the anthropogenic activity in the vicinity of the station is likely to pro-duce excessive local emissions that would be too difficult to discern from the regional signal. Likewise, the stations at **Son La** and **Sa Pa** are very suitable for monitoring rural/urban back-ground, but were considered not to be clean enough for climate observations. The last candidate, **Cuc Phuong**, was initially considered but was eventually not visited by the delegation because of its location in a large forest reserve situated in a depression in the Red River Delta. The site is probably very useful for biosphere monitoring and research, but is likely not suitable for climate observation.

I. Detailed information for Pha Din (ĐèoPhaĐin)Climate Station

Pha Din station is a rural site in a hilly forested area in Northern Vietnam. Currently, Pha Din is a climate station with basic meteorology. The upcoming installation - planned for early 2014 - will enable the continuous in-situ ground-based observation of carbon dioxide, methane, carbon monoxide and ozone next to the new monitoring of optical properties of aerosols. Moreover, the project strongly focuses on know-how transfer, training and capacity building to ensure a sound and long-term operation of the equipment by NMHS also beyond the end of the project.

3.1 General description

The station represents a Level 3 NHMS meteorological station, providing manual readings every 6 hours for wind and wind speed. The station has been moved from a nearby site to this site in April 2012, because a radar tower is planned to be operational at the same site. The radar tower is already built, but the radar instrumentation itself is currently in the bidding process, operation is scheduled not before 2015. The station is permanently occupied with 3 staff persons (see station contacts above), recruited from local residents. Additional 5-10 technical staff persons will be on site by the time the radar will be operational. Staff housing is provided for 3-4 persons.

Pha Din is reachable all year long via a paved mountain road (10 h by car from Ha Noi via Son La). Airports in Son La and Dien Bien Phu with daily connections from Ha Noi (subject to changes). After heavy rainfalls the site the roads may be blocked due to landslides.

3.2 Meteorological conditions and geography

Prevailing wind directions: NE in winter and SW in summer (according to station staff)

Temperature: 25-30 °C in summer and down to 3 °C in winter. No snow or ice in winter.

Rainfall and humidity: The site is in clouds a considerable fraction of the year with a correspondingly high relative humidity all year long.

3.3 Infrastructure

Building: Standard NHMS building for meteorological stations. Brick or concrete, corrugated iron roof. Concrete ceiling approx. 10 cm (minimum). A room for the instruments is available in this

building. Available space: 5.2 m x 3.6 m, ceiling height approx. 4 m. One front door, one back door. Needs to be fitted with air conditioning.

Power: 380 VAC for the radar tower, meteorological station runs with 220 V / 50 Hz, Site has a high priority for power supply, power outages are rare. Surge protection advisable (also for data line).

Internet connection: Currently 3G, ADSL is planned by the time the radar will be operational.

Accommodation: Possibility to stay directly at the site (tent, in the lab). Staff can organize food.

Gas inlets: 1. Next to aerosol inlet, 2. Meteo mast (50+10 m from aerosol inlet), 3. Radar tower

potentially suitable, but belongs to different governmental department

Aerosol inlet: New roof transition necessary, inlet should be at least 1.5 m above roof.

IV. COMPONENTS AND MAJOR ACTIVITIES OF PROJECT

- Preparing the infrastructure for equipment installation;
- Equipment installation for GAW station in Viet Nam with the configuration as following [3]:
 - + Nephelometer Aurora 3000, Ecotech;
 - + Aethalometer AE-31, Aerosol d.o.o
 - + Picarro 2401 CO/CO₂/CH₄/H₂O analyzer
 - + NOAA Standards incl. Regulator
- Training activities

V. PROJECT APPROVAL

On 27 may 2013, Memorandum of Understanding (MOU) between Federal Office of Meteorology and Climatology MeteoSwiss and National Hydro-Meteorological Service of Viet Nam (NHMS) with reference to the project CATCOS has been signed. On 09 September 2013, the project is approved in the Decision No. 1692/QĐ-BTNMT by the Minister of Ministry of Natural Resources and Environment (MONRE, Viet Nam).

VI. CONSTRUCTION

At present, NHMS is preparing for the lab, air-conditioner, electricity, internet and sample mast.

The instrument is packed and shipped to Viet Nam in 4 December 2013. According to the announce ment of Swiss Embassy, the instrument expected to Viet Nam in 22 December 2013. Installation work s scheduled for February 2014. The Viet Namese side will transport equipment to Pha Din and c ollaboration with Swiss specialist to install the equipment.

The Pha Din Global Atmospheric monitoring station will go into operation in March 2014.



PACKING AND SHIPPING



Inside the lab





equipment for CO2, CH4 & CO observations 120cm x 80 cm x 136 cm, 130 kg.

calibration gases 6 separate boxes each box 136cm x 22cm x 22cm, 30 kg gases come without wooden pallett



Figure 2. The lab, planned sample mast and equipments

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Preliminary Results of Greenhouse Gases Observed at Lulin Atmospheric Background Station (LABS), Taiwan

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Introduction

The island of Taiwan is situated in a unique position in East Asia in terms of observing pollution outflows from Southeast Asia and the Asian continent. Regional meteorological conditions are favorable for the transport of air pollutants, such as dusts, acidic pollutants, and biomass burning emissions, from upwind source regions to Taiwan^{[1], [2]}. Thus, a high-elevation baseline station, Lulin Atmospheric Background Station (LABS), was established to measure baseline air pollutants and to study the atmospheric transport patterns. Official operation of LABS began on April 13, 2006, following the operating protocols of UN/WMO/GAW and US/NOAA/GMD sites. This station offers a great deal of opportunities to investigate the atmospheric chemistry of trace gases, aerosols, precipitation, mercury, and radiations, providing a distinctive contrast of atmospheric changes and impacts by a variety of air masses originated from relatively clean to emission source regions.

Site Description and Instrumentation

Lulin Atmospheric Background Station (23.47°N, 120.87°E; 2,862 m a.s.l.) is a two-story building (Figure 1) sitting on the summit of Mt. Front Lulin (Figure 2) in the Yu-Shan National Park in central Taiwan. The Lulin Astronomy Observatory is also located on the summit. There are no known point emission sources at the summit or in the surrounding area. The station is frequently within the free troposphere and is therefore an ideal site for making regional background air measurements. All of the instruments were placed on the second floor of the building, with the air intake line extruding to the roof and the inlet point approximately 10 m above ground. The instrument room is air-conditioned to keep constant air temperature around 25 °C. More detailed descriptions of the LABS can be found in the literature ^[3].

Flask air sampling of GHGs were performed once a week by a NOAA/GMD's PSU at LABS and Dongsha Island (20.70° N, 116.73° E; 8 m a.s.l.) since August 2006 and March 2010, respectively, measuring CO₂, CH₄, CO, N₂O, SF₆, H₂, and isotopes (CO₂¹³C and CO₂¹⁸O). A cavity ring-down spectroscopy (CRDS, Picarro G1301) analyzer continuously measures CO₂ and CH₄ at LABS since March 2011. Seven tertiary standard cylinders of CO₂ (369.86 ppm, 391.99 ppm, 409.23 ppm, 516.30 ppm) and CH₄ (1599.74 ppb, 1801.44 ppb, and 2024.64 ppb) purchased from NOAA/GMD were considered as our primary to verify the CO₂ and CH₄ mixing ratios in the working standards.



Figure 1. Photo of the LABS Figure 2. Aerial photo of the summit of Mt. Front Lulin

These working standards were then sent to the LABS for calibrating the CRDS analyzer on-site.

Results and Discussion

Temporal variations of CO_2 and CH_4 at LABS are illustrated in Figures 3 and 4, respectively. The mean mixing ratio of CO_2 is 387.9 ± 9.1 ppm based on the results of 7-year flask air samples, while the mean CH_4 level is calculated to be 1857.7 ± 37.9 ppb for the same period. The springtime maximum was most likely caused by the long-range transport of air masses from Southeast Asia, where biomass burning was intense in spring. In contrast, a greater Pacific marine influence contributed to the summertime minimum. CO_2 evidenced that in spring the excess CO_2 from biomass burning permeates the Western Pacific at an elevation of about 3 km. Until late fall, vegetation growth on land completely dominates the CO_2 signal as clean and stable as measured in Hawaii. The annual maxima and minima of CH_4 were seen in March and July, respectively, as well as other air pollutants such as CO, O_3 , and GEM (gaseous elemental mercury) ^{[3], [4]}.

As the diurnal cycles of CO_2 and CH_4 shown in Figure 5, a daily minimum of CO_2 with lager standard deviations was observed during daytime while the photosynthesis process is likely to be pronounced. In order to avoid the influences of CO_2 uptakesby plants surrounded, the sampling time was therefore adjusted to early morning (before 7 A.M.) since mid-September of 2012 (Figures 3 and 4). The diurnal pattern of CH_4 (Figure 5) is similar to that of other primary air pollutants (e.g. CO, GEM and PM_{10}), which is presumably the result of mountain-valley circulation as indicated by our previous studies ^[4].



Figure 3. Time-series CO₂ observed at LABS since August 2006. Open squares represent the preliminary results of NOAA/GMD flask air samples. Green lines represent the continuous CO₂ data measured by CRDS.



Figure 4. Time-series CH₄ observed at LABS since August 2006. Open squares represent the preliminary results of NOAA/GMD flask air samples. Brown lines represent the continuous CH₄ data measure by CRDS.



Figure 5. Diurnal patterns of CO₂ and CH₄ observed at LABS, averaged from March 2011 to July 2013.

LABS provide comprehensive and informative results of GHG measurements at 3 km elevation in the Western Pacific, which is not only sufficiently representative of the hemispheric background levels, but also responsive to the regional large-scale burning activities in Southeast Asia.

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Development of Southeast Asia-Australian Atmospheric Observation Capability

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In collaboration with a range of partners, Australia's Centre for Australian Weather and Climate Research (CAWCR) at CSIRO Marine and Atmospheric Research, is developing an integrated atmospheric observation network for greenhouse gases (GHG) and other climatically-active atmospheric species in the Southeast Asia-Australian region. This network is an extension of the Australian Greenhouse Gas Observation Network (AGGON) which has the Cape Grim Baseline Air Pollution Station (CGBAPS) as the central reference site. CGBAPS is a Global Atmospheric Watch (GAW) global station and one of only three designated "comparison" sites for GHG in the network.

The objectives of the expansion of the AGGON network are to:

- 1. Establish a continental Australian network to develop "top-down" emission verification tools (e.g. Australian coal seam gas fugitive emissions applications);
- 2. Understand key atmospheric processes in the Australian-Southeast Asian tropical region;
- 3. Quantify the changing Southern Ocean CO₂ sink, and
- Exploit new research platforms Australian blue water research vessel RV Investigator (expected to be operational early 2014)

Understanding the globally significant tropical atmospheric processes is a key focus of this research activity and therefore the expansion of the research capability in this region is an important step.

Currently the Southeast Asia-Australian tropical regional network includes two GAW global stations (Bukit Kota Tabang, Indonesia and Danum Valley, Malaysia) as well as more than ten other air sampling sites for GHG (Figure 1).

The main Australian contribution to this network is the development of the Australian Tropical Atmospheric Research Station (ATARS) at Gunn Point in Australia's Northern Territory – a GAW regional station in the Australian tropical savannah region (Figure 2). In the dry season (Austral winter) the prevailing synoptic easterly winds expose this site to the significant biomass burning events that regularly occur in the large expanse of the Australian tropical savannah. In the monsoon season (Austral summer) the Gunn Point site is exposed to air masses originating from the Southeast Asian region.



Figure 1. Southeast Asia-Australian tropical regional GHG observation network



Figure 2. Gunn Pt site with new 2nd container laboratory

The research program at Gunn Pt ATARS has developed significantly over the last year (Table 1) with significant expansion of the available laboratory space with a new 2nd container laboratory, and the installation of new equipment. This includes the installation of: a GC-ECD system to study short-lived halocarbons from marine biogenic sources (University of Cambridge, UK); an automatic weather station (AWS), and an Aerosol Diffusion Dryer (ARADD) system including ambient MET sensors on tower and an ultra-Dry 10Bar compressed air system.

An example of the data collected so far from the Gunn Pt site is shown in Figure 3 showing the time series of a range of greenhouse and related traces gases and isotopes from the flask air sample collection program. These results can be compared with the time series that have been collected at Cape Ferguson (East coast of Australia) (Figure 3).

| Atmospheric species / technique | Research Group | Period of |
|---|-------------------|------------------|
| | | Operation |
| In-situ CO ₂ & CH ₄ (CRDS) | CAWCR/CMAR | (2011 - present) |
| In-situ ¹³ CO ₂ / ¹² CO ₂ (CRDS) | CAWCR/CMAR | (2011-2012) |
| Flask CO ₂ , CH ₄ , ¹³ CO ₂ / ¹² CO ₂ , N ₂ O, CO, H ₂ | CAWCR/CMAR | (2011 – present) |
| Radon-222 | ANSTO | (2011 – present) |
| Short-lived halocarbons | University of | (Jul 2013 – |
| (CHBr ₃ /CH ₂ Br ₂ /CHCl ₃ /C ₂ Cl ₄ /CH ₂ CCl ₃ /CCl ₄) GC-ECD | Cambridge (UK) | present) |
| Automatic Weather Station | CAWCR/CMAR | (Jul 2013 - |
| (with 2nd anemometer on tower since 2011) | | present) |
| O ₃ (UV spectrometry) | CAWCR/CMAR | (2011 – present) |
| CO (NDIR) /NO/NO _X (chemiluminescence) | CAWCR/CMAR | (2011-2012) |
| Aerosols (nephelometer) | CAWCR/CMAR | (2011 – 2013) |
| Aerosols (absorption photometer) | CAWCR/CMAR | (2011 – 2012) |
| Proposed measurement program (N | EW container lab) | |
| In-situ CO/N ₂ O (Off-axis ICOS) | CAWCR/CMAR | (May/June 2014) |
| CO/NO/NO _X | CAWCR/CMAR | (May/June 2014) |
| PM2.5/PM10 | CAWCR/CMAR | (May/June 2014) |
| Aerosols & VOCs | CAWCR/CMAR | (May/June 2014) |

Table 1. Gunn Point ATARS atmospheric measurement program



Figure 3. Flask air samples trace gas time series for Gunn Pt (left panel) and Cape Ferguson (right panel).

The future plans for the development of the Gunn Pt site involve conducting a number of research campaigns at the site and further engagement with regional sampling sites, including inter-comparison activities. In May/June 2014 the "Savannah Early Dry Season Fire Experiment" will be conducted over a one month period. An accompanying campaign in the late dry season will also follow. The main objective of these experiments is to study the ageing of aerosols in biomass burning smoke plumes. The "Northern Australia Biomass Burning Experiment" (NABBEx) is also planned in the period 2016/17, which will include measurement programs onboard the new Australian RV Investigator research ship. Other plans include greater engagement with the Total Column Carbon Observing Network (TCCON) site located nearby in Darwin and to investigate vertical profiling experiments for GHG at the Gunn Pt site.

Forty Years of Baseline CO₂ Measurements at Baring Head, New Zealand

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Background

The sources of carbon dioxide (CO_2) emissions are greater in the northern hemisphere than in the southern hemisphere, resulting in inter-hemispheric differences of atmospheric CO_2 mole fractions. However the trends in the atmospheric CO_2 are comparable between hemispheres due to the fact that the species is long lived and transported to the south. The southern hemisphere geographically is dominated by oceans. Nearly a quarter of the CO_2 emitted to the atmosphere from fossil fuel burning, land use change and other human activities has been absorbed by earth's oceans, with the Southern Ocean playing an especially critical role in the carbon cycle. Several critical questions remain unresolved for the carbon cycles that are linked to southern hemisphere processes (e.g. trends in the Southern Ocean carbon sink, and uptake by southern hemisphere land masses). The National Institute of Water and Atmospheric Research (NIWA) maintain a network of stations in the New Zealand region that provide trace-gas observations, compatible with other GAW stations, that contribute to understanding carbon cycle processes.



Figure 1. Baring Head station is located on the southern tip of the North Island (Te Ika-a-Maui), and is frequently exposed to baseline air from the south.

Baring Head observations

Located on a south facing cliff on the southern coast of the North Island (41.4083° S, 174.8710° E) New Zealand, the NIWA operated Baring Head (BHD) monitoring station began observations of CO_2 in 1972 and is ideally situated to observe air masses that have not been in contact with terrestrial sources for thousands of kilometers and multiple days ^[1].Observations have always been made with direct ties to the central calibration laboratories to ensure compatibility with observations made elsewhere. A site specific filtering process is used to ensure that local topography and air flows are considered when selecting what is regarded as background, or baseline air representative of midlatitudes of the southern hemisphere. Filtering avoids air that has arrived at the site from the north, and excludes air that has been in contact with the South Island based on pressure differences between the east and west coasts. The full time-series is depicted in Figure 2, in black, and the filtered stable background data are shown in red.



Figure 2. CO_2 time series from BHD, black points are hourly averages for all directions while red are stable background, steady southerly periods where the variations are less than 0.1 ppm in a 6 hour period.

Footprints for the air arriving at Baring Head are developed using the high resolution Lagrangian model NAME III, where we release particles at the site and determine their trajectories "back in time" using meteorological input from the regional forecast model NZLAM-12. Clusters (Figure 3) can be formed from these particle trajectories, here we have characterized seven dominant clusters for the released particles. A southerly trajectory is shown to predominantly avoid local land areas, it is air from this cluster that is least perturbed by local effects for CO_2 and forms the majority of the background air data.



Figure 3.CO₂ footprint for air arriving at BHD using NAME III over a two year period. A 1- σ band for the trajectory spread is shown for this southerly cluster.

Time-series

We employ a seasonal time-series decomposition by Loess (STL) routine (Cleveland et al 1990) to interpret the 40 year time-series, and determine a seasonal amplitude of 0.95 ppm and a long-term growth rate (Figure 4) of 1.5 ppm yr⁻¹ with and increasing trend with time. During the last decade (2000-2009), we note a difference between BHD and, Scripps Institution of Oceanography at, Mauna Loa of -3.03 ppm primarily as a result of fossil fuel usage in the north hemisphere. A difference between BHD and South Pole over the same period of -0.05 ppm is an indication of the removal processes of the Southern Ocean between Antarctica and New Zealand.



Figure 4. CO₂ growth rate determined for Baring Head over a 40 year period.

By utilizing tagged tracer simulations from the fine grid version of Transport Model version 3 (TM3) ^[3], we are able to infer contributions of sources from different geographic regions to the seasonal cycle ^[4]. The simulations (Figure 5) use CarbonTracker-2010 fluxes ^[5] and were run from 2000-2009 with the first three years discarded to allow for spin-up. The atmospheric imprint of the southern hemisphere ocean flux at Baring Head has a peak in the autumn (May) and a trough in the early summer (Dec). While the northern hemisphere terrestrial flux influence at BHD is lagged by about six months due to transport time and has a phase and magnitude close to that of the southern hemisphere terrestrial flux, with peaks in late winter (Aug-Sep) and troughs in autumn (Mar-Apr).



Figure 5. Output from a tagged tracer experiment was the observations are plotted as circles. The TM3 model seasonal cycle is of the similar magnitude as the observations however the phase is advanced by one month.

Summary

A 40 year in situ record of atmospheric CO_2 has been acquired from the Baring Head site, this has proven to be an effective location for the observation of baseline air. When the time-series has been examined a long-term growth rate of 1.5 ppm yr⁻¹ has been determined with a mean peak to peak seasonal cycle of 0.95 ppm. Air mass origins or footprints have been modeled using NAME and trajectory clusters determined that demonstrate the effectiveness of the site to make observations of mid-latitude southern hemisphere air. A tagged tracer model simulation has provided insight into the components contributing to the seasonal cycle and their potential phasing. Further work is required to ensure the continued compatibility of observations with other network stations.

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The Greenhouse Gases Observation and Analysis at GAW stations in Malaysia

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Monitoring Activities

The GAW monitoring activities at GAW stations in Malaysia focuses on six classes of variables such as aerosol, greenhouse gases, reactive gases, O_3 , UV radiation and precipitation chemistry. The monitoring activities at GAW stations in Malaysia are as listed in Table 1.

| NO. | GAW FOCAL AREAS | TYPE OF INSTRUMENT | Danum Valley | Cameron Highlands | Petaling Jaya |
|-----|--|---|-----------------|----------------------|------------------|
| 1. | Aerosol - Aerosol Load - Back Seattering Coefficient - Absorption Coefficient - Aerosol Optical Depth | High Volume Air Sampler (TSP & P.M-10) and Tapered Element Oscillating Microbalance (TEOM) Nepholomotor Multi Angle Absorption Photometer (MAAP) Precision Filter Radiometer (PFR) | *** | V | Ń |
| 2. | Greenhouse Gases Carbon Dioxide (CO2) Methane (CH2) Nitrous Oxide (N2O) Sulphur Hexatluonde (SF6) | Lo Flo Mark II CO ₂ Analyzer & Flask Sampling Flask Sampling Flask Sampling Hask Sampling | へんたん | | |
| 3. | Reactive Gases Surface Ozone (O ₂) Carbon Monoxide (CO) Nitrogen Oxides (NO ₂) Sulphur Dioxide (SO ₂) Hydrogen (H ₂) | O_Analyzer OQAnalyzer & Flask Sampling NQAnalyzer SQAnalyzer SQAnalyzer Flask Sampling | 4 | ~~~ | |
| 4. | Ozone • Total Column Ozone | Brewer Spectraphotometer | | | V |
| 5. | UV Radiation | Brewer Spectrophotometer | | | 1 |
| 6. | Precipitation Chemistry | Ecotech Wet Only Rainwater Sampler Acid Precipitation Sampler (APS) | 4 | V V | √ √ |

Table 1. The monitoring activities at GAW stations in Malaysia.

This paper will only focus on the on-going greenhouse gases and selected reactive gases that related to greenhouse gases monitoring programmes at GAW stations in Malaysia. Some of the research findings based on the data analysis are discussed in this paper, including research conducted through Met Malaysia's collaboration with other research agencies. Several parameters related to the focus topic will be further discussed as follows:

Greenhouse Gases

Since 2004, Met Malaysia has collaborated with Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia in installing a LoFlo Mark II $CO_2Analyzer$ to monitor CO_2 concentration continuously at Danum Valley GAW Station. In the monitoring mode, each hour comprises 10 minutes measurement on the REF cylinder (REF cylinder air through both sample and reference cells of the LI-COR), followed by 50 minutes measurement of ambient air that has been dried using the Nafion dryer (backed up by the mop-up dryer). The first 6 minutes of the 10 and 50 minute blocks are used to provide ample opportunity for flow and pressure stabilisation; thus 'valid

data' comprises 4 minutes REF and 44 minutes of ambient air data each hour. Hourly averaged data is obtained from the mean of the 44 minutes values. In order to maintain the accuracy of the instrument and data collected is up to the international standard, the LoFlo Analyzer is calibrated every 4 to 6 weeks, while the yearly maintenance is done on a regular basis by an expert from CSIRO.

On the other hand, Met Malaysia is also collaborating with National Institute of Environmental Studies, Japan (NIES) since 2010 in CO₂, CH₄, N₂O and SF₆ monitoring using Flask Sampling method in Danum Valley GAW Station. The flask air sample is collected automatically once a week (every Sunday at 10.00 - 10.10 pm local time) and after each sixth week, the air samples will be sent to NIES for analysis. The data then will be shared among the researchers from Met Malaysia and NIES.

Reactive Gases

Surface ozone (O₃) is measured continuously in Cameron Highlands GAW Station since 2003 using Thermo Model 49C UV Photometric O₃Analyzer, while at Danum Valley GAW Station, surface ozone (O₃) is measured continuously since 2006 using Thermo Model 49*i* UV Photometric O₃Analyzer. Similarly with greenhouse gases monitoring and in collaboration with NIES, reactive gases such as CO and H₂ are measured once a week using Flask Sampling since 2010.

Result and analysis

Carbon Dioxide (CO₂)

The following are some of the analysis of CO_2 concentration using LoFlo Analyzer and Flask Sampling. Figure 1 shows the time series analysis of annual average of CO_2 concentration both for Danum Valley (using LoFlo Analyzer) and Mauna Loa, Hawaii GAW stations from 2004 to July 2013. It is observed that the trend of annual average CO_2 concentration for both stations are quite similar with both are showing an increasing trend of 1.90 ppm/year for Danum Valley and 2.11 ppm/year for Mauna Loa. Annual Mean Global CO_2 also showing quite similar trend with both stations with an increasing trend of 2.02 ppm/year.



Figure 1.The time series analysis of annual average of CO₂ concentration at Danum Valley and Mauna Loa.

Figure 2 shows the comparison of CO_2 concentration measured using LoFlo Analyzer and Flask Sampling from June 2011 to June 2013 at Danum Valley GAW Station. The hourly mean CO_2 concentration by LoFlo Analyzer is chosen from the same hour of sampling time of Flask Sampling. From the comparison, the values from the both methods are showing quite a comparable trend with only less than 5% percentage difference.



Figure 2. The comparison of CO₂ concentration measured using LoFloAnalyzer and Flask Sampling.

Other Greenhouse Gases (CH₄, N₂O & SF₆) and Reactive Gases (CO & H₂)

The following analysis will try to explain the trend and time series of some greenhouse gases (CH₄, $N_2O \& SF_6$) and reactive gases (CO & H_2) concentrations at rainforest in the tropics (Danum Valley GAW Station) and coastal area in temperate zone (Hateruma, Japan contributing station). Figure 3, 4, 5, 6 and 7 shows the time series analysis of CH₄, N₂O, SF₆, CO and H₂ concentrations using Flask Sampling at Danum Valley and Hateruma (as a reference site) from January 2010 to June 2013. The flask air sample is collected automatically once a week at Danum Valley, while at Hateruma is once in 4 days. It is observed that the trends of CH₄, N₂O, SF₆, CO and H₂ concentrations for both stations are quite similar with N2O and SF6 are showing slight increasing trend, while CH4 and CO fluctuates throughout the period from January 2010 to June 2013. H₂ is showing stable trend except for period before November 2012 for Danum Valley. The value for H_2 concentration at Danum Valley is quite high before November 2012 because of contamination from Flask Sampling's old pump and the value become more comparable to the Hateruma after new pump is changed in October 2012. The concentrations of these three greenhouse gases at Danum Valley, namely CH₄ (1,792.35 - 1,942.5 ppb), N_2O (322.5 - 327.04 ppb) and SF_6 (6.99 - 8.25 ppt) are comparable with the range of the global average values as issued by the 2012WMO Greenhouse Gas Bulletin. The CO concentration at Danum Valley ranged between 73.5 - 249.72 ppb, while H₂ concentration at Danum Valley ranged between 536.04 - 1,127.25 ppb.



Figure 3.The time series analysis of CH₄ concentration at Danum Valley and Hateruma.



Figure 5.The time series analysis of SF_6 concentration at Danum Valley and Hateruma.



Figure 4.The time series analysis of N_2O concentration at Danum Valley and Hateruma.



Figure 6.The time series analysis of CO concentration at Danum Valley and Hateruma.



Figure 7.The time series analysis of H_2 concentration at Danum Valley and Hateruma.

Surface Ozone (O₃)

The surface ozone (O₃) concentrations at Cameron Highlands GAW Station from May 2012 to June 2013 and O₃ concentrations at Danum Valley GAW Station from August 2011 to August 2012 were analysed in the following analysis. Figure 8 shows the time series analysis of daily average of O₃ concentration for Danum Valley and Cameron Highlands GAW stations during the study period. It is observed that the concentration of O₃ in Danum Valley is generally less than the concentration of O₃ in Cameron Highlands. For Danum Valley the concentration fluctuated between 2.71 – 20.06 ppb with average value of 9.85 ppb. While for Cameron Highlands, the concentration recorded are higher with values fluctuated between 8.31 - 44.48 ppb with average value of 21.13 ppb.



Figure 8. The time series analysis of O_3 concentration at Danum Valley and Cameron Highlands GAW Stations.

Future Direction

The GAW stations in Malaysia especially in Danum Valley are able to provide good infrastructure for the research activities focusing on the environment, air quality and atmospheric composition as well as climate. As such Met Malaysia welcome any institution to participate and collaborate with us in an extensive research works and subsequently produce research findings that will be beneficial to the country and the world population as a whole. In the near future, Met Malaysia is planning to expand its greenhouse gases monitoring programme to include other greenhouse gases analyzer namely methane (CH₄) and nitrous oxide (N₂O) at Danum Valley GAW Station as well as to install another CO₂analyzer in Langkawi Meteorological Station. In addition to address the urban environmental issues in Klang Valley, Malaysia, Met Malaysia is proposing to the Malaysian Government to participate in the WMO GAW Urban Research Meteorology and Environment (GURME) in 2014.

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Gravimetric standards of Greenhouse gases at ambient levels

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1. Introduction

The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) serves as an international framework aimed at maintaining the traceability chain for Greenhouse Gases observation passing through the Central Calibration Centre (CCL) and World Calibration Centre (WCC). The Korea Research Institute of Standards and Science (KRISS) and the Korea Meteorology Administration (KMA) agreed to host WCC-SF₆(World Calibration Center for SF₆) and started to improve the analytical capability of SF₆.^[1]

In this newsletter, we present new gravimetric standard scales of SF_6 for supporting WCC task. Furthermore, N₂O scale will be introduced. Each standard was developed according to the ISO 6142. ^[2] And the uncertainties of prepared cylinders are individually evaluated to meet virtually no errors on the regression of the sets of standards covering ambient levels. We hope this primary scale will contribute to strengthen the WMO traceability chain. Therefore, the comparison of KRISS and NOAA scale is planned in order to ensure the equivalence between them. Before leaving this letter, the comparison of CO₂, CH₄ standard will be also introduced to report the deviation between KRISS and NOAA standards.

2. Primary standards developments

2.1 Overview

In this letter, we will present our recent achievements on new standards of N_2O in air and SF_6 in air. Impurity analysis of pure gases of SF_6 , N_2O , N_2 , O_2 and Ar were performed and every dilution steps are gravimetrically controlled according to ISO 6142. Particularly, SF_6 of which mixing ratio at atmospheric is pmol/mol, careful investigation on SF_6 impurity in air matrix was rigorously carried out to pick out sub-ppt level of SF_6 , which provides slightly positive bias on the certified mixing ratio. For this purpose, the pre-concentrator-GC-ECD was brought to ensure the SF_6 trace in matrix. To verify dilution steps, analyses were performed using KRISS-calibrated gas chromatograph with thermal conductivity detector or electron capture detector (GC-TCD and ECD, respectively) according to ISO 6143.^[3] For SF_6 /air scale, 5 cylinders were gravimetrically prepared as a function of mixing ratio in the range of ambient levels (5~15 pmol/mol). In case of N_2O scale covering ambient

level (305~345 nmol/mol), overall procedure was identical with SF₆ standards in spite of dilution step.

2.2 SF₆and N₂O scale in the range of ambient levels

SF₆ scale in the range of 5~15 ppt was prepared using automatic weighing technique. SF₆pure gas, of which purity was assigned to 99.989 % by the impurity analysis, was diluted through7 steps with pure N₂ gas. Then, in the final step, O₂ and Ar were added in 10 L aluminium cylinders (Luxfer, UK), of which inner surfaces were electrochemically polished. Considering trace level of SF₆at ambient level, even 0.01 ppt of SF₆ impurity in artificial air matrix has a power to exhibit a positive bias resulting in ~0.15% increase in a final mixture.^[1] To nail down this effect, we measured SF₆ impurity in pure gases of N₂, O₂ and Ar by the aid of cryogenic pre-concentrator. It was shown that the SF₆ impurity in N₂, O₂ and Ar was not detected where a LOD of our precon-GC-ECD system is 0.002 ppt. By the uncertainty evaluation of the primary standards, which includes the uncertainties during impurity analysis, gravimetric weighing and verification, ~0.23% (2 sigma) were given to final uncertainties of every bottle. A least square fit of quadratic response curve of SF₆ scale returned great agreement with theoretical value, leaving negligible residuals. (Figure 1) These results suggest that KRISS SF₆ scale can reduce the potential error of analyser calibration and offer great comparability after all.



Figure 1. Calibration curve of KRISS SF_6 scale in the range of 5~15 ppt. The response curve was approximated by a least square fir of a second-order polynomial with an agreement of $R^2 = 0.09999997$. Residuals which are the differences between certified mole fraction and theoretically calibrated value are given in the table.

 N_2O scale in the range of 305~345 ppb was gravimetrically prepared. Overall procedure including 5-step dilution, verification and the specification of cylinder is similar with the case of SF₆ standards preparation. The uncertainties of gravimetric preparation are given to be around 0.21% (2 sigma) and calibrated mole fractions of every standard are greatly fitted into theoretical regression curve of 2nd polynomial, which also shows nonlinearity of N₂O response, to leave residuals less than 0.03%. (Figure 2)



Figure 2. Calibration curve of KRISS N₂O scale in the range of $305 \sim 345$ ppb. The response curve was approximated by a least square fir of a second-order polynomial with an agreement of R² = 0.099997. Residuals which are the differences between certified mole fraction and theoretically calibrated value are given in the table.

3. Comparison of KRISS and NOAA CO₂/CH₄standards

KRISS and NOAA CO₂ and CH₄ standards at ambient levels have been compared to give a degree of equivalence. Analytical system was GC-FID (Agilent 6890A). In case of CO₂ analysis, methanator was coupled to secure sufficient sensitivity. Brief introduction of analytical condition is as follows. Porapak-Q column for CO2 and Molsieve 5A packed column for CH4were applied. N2 as a carrier gas was feed with appropriately adjusted flow rate. To load constant amount of sample (reference) gas mixture, well calibrated MFC (Bronkhorst) was coupled to sampling gas line. Venting parts of gas lines are protected by the restrictor in case of the necessity of instrument isolation from laboratory pressure tolerance. As references for this comparison analysis, CO₂/CH₄ gas mixture provided by NOAA as Central Calibration Laboratory for CO₂ and CH₄ were used. Since NOAA standards are very well scaled and used analyzer shows great linearity of detector response to the substances of CO₂ and CH₄, it seemed to be sufficiently reasonable that one KRISS gravimetric standard were calibrated against NOAA scale in order to give reliable result for full comparison. In case of KRISS CO₂ standards, perfect match with NOAA scale was found. Response curve made by NOAA standard is straight and residuals are given less than 0.07 ppm (Table 1), which satisfies the recommended WMO network comparability goal of 0.1 ppm even considering analytical uncertainty (<0.05 %) of applied analytical system. Upon this calibration curve, KRISS values were perfectly overlapped, showing great equivalence of KRISS and NOAA standards. But, CH₄comparison shows that negative bias of KRISS standard as much as ~0.13 %. (Table 2) As a consequence, an application of conversion factor to KRISS standard should be considered to meet WMO compatibility.

| | CO ₂ | Mole fraction [µmol/mol] | C _{calibrated} [µmol/mol] | Residual [µmol/mol] | Difference [%] |
|-------|-----------------|-----------------------------|---------------------------------------|------------------------|-------------------|
| | CB09838 | 351.72 | 351.69 | -0.04 | -0.01 |
| | CB09734 | 381.12 | 381.19 | 0.07 | 0.02 |
| NOAA | CB09738 | 410.93 | 410.89 | -0.04 | -0.01 |
| | CB09906 | 448.67 | 448.67 | 0.00 | 0.00 |
| KRISS | 075-009 | 410.7 | 410.67 | -0.03 | -0.01 |
| | D929150 | 381.92 | 382.02 | 0.10 | 0.03 |

Table 1. Comparison result of KRISS and NOAA CO₂ standards. Residuals of certified mole fraction from the theoretically calibrated value are given.

Table2. Comparison result of KRISS and NOAA CH_4 standards. Residuals of certified mole fraction from the theoretically calibrated value are given.

| | CH ₄ | Mole fraction [nmol/mol] | C _{calibrated} [nmol/mol] | Residual [nmol/mol] | Difference [%] |
|-------|-----------------|-----------------------------|---------------------------------------|------------------------|-------------------|
| | CB09838 | 1674.17 | 1674.02 | -0.15 | -0.01 |
| NOAA | CB09734 | 1810.73 | 1811.01 | 0.28 | 0.02 |
| NOAA | CB09738 | 1875.21 | 1875.09 | -0.12 | -0.01 |
| | CB09906 | 1995.72 | 1995.63 | -0.09 | 0.00 |
| KRISS | ES0008646 | 1872 | 1870 | -2.50 | -0.13 |
| | D929150 | 1800 | 1798 | -2.09 | -0.12 |

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Intercomparison experiments for Greenhouse Gases Observation (iceGGO) in Japan

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1. Introduction

Under the WMO GAW programme, the Japan Meteorological Agency (JMA) serves as the GAW World Calibration Centre (WCC) for CH_4 in Asia and the South-West Pacific. In order to ensure traceability to GAW international standards and maintain the accuracy of the measurements, JMA has carried out CH_4 reference gas intercomparisons since 2001, and three-intercomparisons have finished by 2013.

In Japan, the intercomparison experiments named iceGGO (Inter Comparison Experiments for Greenhouse Gases Observation) started in 2012 through collaboration among observation laboratories and the national metrology institute. IceGGO-1 (CH₄) is one of these intercomparison experiments. The purposes of this intercomparison experiment are to compare the CH₄ standard gases used by observation laboratories with the SI traceable standard gases and to clarify the detailed differences of the standard gases with a wide range of CH₄ mole fractions.IceGGO-1 (CH₄) was conducted in combination with the 3rd round CH₄ reference gas intercomparison conducted by the GAW WCC in Asia and the South-West Pacific.

2. CH₄ reference gas intercomparison in Asia and the South-West Pacific.

Table 1 shows the overview of the 1st - 3rd rounds CH₄ reference gas intercomparisons conducted as the activity of WCC for CH₄ in Asia and the South-West Pacific. In these intercomparisons, two standard gases prepared by using purified natural air and pure CH₄ gas were circulated in Asia, the South-West Pacific and Japan. JMA and following ten observation laboratories from five countries (Australia, China, Japan, Korea and New Zealand) participated, namely China Meteorological Administration (CMA), Commonwealth Scientific and Industrial Research Organization (CSIRO), Korea Meteorological Administration (KMA), Korea Research Institute of Standards and Science (KRISS), Meteorological Research Institute (MRI), National Institute for Environmental Studies (NIES), National Institute of Advanced Industrial Science and Technology (AIST), National Institute of Polar Research (NIPR), National Institute of Water & Atmospheric Research Ltd. (NIWA) and Tohoku University (TU).

| Intercomparison Round | Period of Intercomparison | Participants | CH₄ mole fractions of circulated two standard gases [ppb] |
|--------------------------|------------------------------|---|---|
| 1st | 2001.04 - 2005.03 | JMA, CMA, KMA, CSIRO, NIWA, TU, NIES | 1800, 1950 |
| 2nd | 2005.07 - 2010.01 | JMA, CMA, KMA, KRISS, CSIRO, NIWA, NIES, TU | 1700, 1875 |
| 3rd | 2008.05 - 2013.02 | JMA, KRISS, KMA, CMA, CSIRO, NIWA, NIPR, AIST, MRI, NIES, TU | 1665, 1850 |

Table 1. Overview of the 1st - 3rd rounds CH₄ reference gas intercomparisons.

Figure 1 and figure 2 show the differences of measured CH_4 mole fractions between observation laboratories which participated in the 1st - 3rd rounds CH_4 reference gas intercomparisons and JMA. The concentration drifts of the standard gases used in these intercomparisons were considered in these figures. JMA has used the WMO mole fraction scale propagated from the CCL (Central Calibration Laboratory) of NOAA since 2006, so some of JMA's values used in figure 1 were recalculated values from the values measured by using JMA scale for the adoption of the NOAA04 scale. These figures show that the differences of measured CH_4 mole fractions were gradually reduced in order from the 1st to the 3rd round, and it seems to be presumably caused by an increase in the laboratories using the NOAA04 scale (Table 2).



Figure 1. Differences of measured CH_4 mole fraction from those of JMA in the 1st and 2nd rounds CH_4 reference gas intercomparisons (left: 1st round, right: 2nd round).



Figure 2. Differences of measured CH_4 mole fraction from those of JMA in the 3rd round CH_4 reference gas intercomparisons.

Table 2. Standard gas scales used in JMA and ten laboratories participated in the 1st - 3rd rounds CH_4 reference gas intercomparisons

| Intercomparison round | JMA | СМА | KMA | CSIRO | NIWA | TU |
|--------------------------|--------|--------|-------|-----------|--------|-------------------------|
| 1st | NOAA04 | AES | CMDL | CSIRO1994 | NIST | TU Gravimetric Scale |
| 2nd | NOAA04 | AES | KRISS | NOAA04 | NOAA04 | TU Gravimetric Scale |
| 3rd | NOAA04 | NOAA04 | KRISS | NOAA04 | NOAA04 | TU-X08 |
| Intercomparison round | NIES | KRISS | NIPR | AIST | MRI | |
| 1st | NIES94 | | | | | |
| 2nd | NIES94 | KRISS | | | | |
| 3rd | NIES94 | KRISS | NIPR | AIST | MRI | |

In the result of the 3rd round, the differences of measured CH₄ mole fractions between each laboratory using the NOAA04 scale and JMA range from about -2 to about +0.5 ppb. On the other hand, the differences between each laboratory not using the NOAA04 scale and JMA had a different tendency, and the differences at the higher CH₄ mole fraction (1850 ppb) tended to be larger than ones at the lower CH₄ mole fraction (1665 ppb) in whole. Some of the differences at the higher CH₄ mole fraction were about +4 ppb. This result suggests that these differences may increase as the absolute CH₄ mole fraction increases. In order to clarify this tendency in detail, it is necessary to conduct the CH₄ reference gas intercomparison by using the multiple standard gases which cover a wide range of CH₄ mole fractions.

3. Intercomparison experiments for Greenhouse Gases Observation (iceGGO) in Japan

In harmony with the WMO/BIPM cooperation in the international community, JMA and active observation laboratories in Japan have established a national alliance with the National Metrology

Institute of Japan (NMIJ), which is part of AIST, to compare standard gas scales each other. In the framework of this alliance, we started intercomparison experiments named iceGGO in 2012.IceGGO-1 (CH₄) is its first experiment, and was conducted in cooperation with the observation laboratories and the national metrology institute in Japan for the first time.

Table 3 shows the overview of iceGGO-1 (CH₄). In this experiment, seven laboratories participated, and six standard gases with a range of CH₄ mole fractions from about 1665 ppb to about 2240 ppb were circulated from Oct. 2012 to Mar. 2013 in the following sequence: JMA, NIPR, AIST, MRI, NIES, TU and JMA again. Four of the six standard gases were prepared by using purified natural air as a diluent gas and pure CH₄ gas. CH₄ mole fractions in these standard gases ranged from about 1665 ppb to about 1920 ppb. These gases were provided by JMA, and two of these gases were used for CH₄ reference gas intercomparison as the activity in the GAW WCC in Asia and the South-West Pacific. The other two standard gases were SI traceable, and were prepared by a gravimetric method of NMIJ using synthetic air (mixture of pure N₂, O₂ and Ar) and pure CH₄ gas. CH₄ mole fractions in these the gases were prepared additionally at the time of CCQM-K82 intercomparison, which is the preparative comparison of CH₄ in air at ambient level.

| Period of Intercomparison | Oct.2012 - Mar.2013 |
|-----------------------------|---|
| Participants | JMA, NIPR, AIST, MRI, NIES, TU and NMIJ(7 participants) |
| | <4 cylinders> |
| | Provider: JMA |
| | CH ₄ mole fraction: about 1665 - 1920 ppb |
| | These cylinders were prepared using purified natural air and pure CH ₄ gas. |
| Detail of standard gases | <2 cylinders> Provider: NMIJ CH ₄ mole fraction: about 1830, 2240ppb These cylinders were prepared by a gravimetric method using synthetic air and pure CH ₄ gas. CH ₄ mole fractions in these cylinders were SI traceable. |

Table 4 lists the standard gas scales and analytical methods used in seven laboratories that participated in iceGGO-1 (CH₄). Figure 3 shows the differences in measured CH₄ mole fractions from those of JMA at the beginning of circulation. The analytical precisions for all laboratories were around 1-2 ppb, and the expanded uncertainties of NMIJ gravimetric values were 1.3 ppb (k=2). The differences of measured CH₄ mole fractions of JMA between the end and the beginning of circulation were within the range of ±0.8 ppb.

The plots in Figure 3 show a consistent dependency between the differences of measured CH_4 mole fractions at each laboratory from JMA and the absolute CH_4 mole fraction levels, although their values have systematic differences. Figure 4 shows differences of measured CH_4 mole fractions from NMIJ gravimetric values. The differences except JMA were distributed within about ±3 ppb.

| | JMA | NIPR | AIST | MRI | NIES | TU | NMIJ |
|---|----------------------|--------------------|----------------------|--------------------|-------------------|-------------------|----------------------|
| Standard gas scale | NOAA04 | NIPR | AIST | MRI | NIES94 | TU-X08 | Gravimetric blending |
| Range of standard gas scale [ppb] (Number) | 1622 - 2109 (5) | 1390 - 2282 (4) | 1007 - 2534 (4) | 1599 - 2102 (5) | 512 - 3012 (7) | 899 - 2503 (5) | |
| Instrument (GC-FID) | GC-14BPF SHIMADZU | GC-8A SHIMADZU | GC-14BPF SHIMADZU | AG-1F Yanaco | HP5890 Agilent | 6890NF HP | |
| Average o [ppb] | 2.0 | 1.8 | 1.6 | 0.9 | 1.0 | 1.2 | |

Table 4. Standard gas scales and analytical methods used in seven laboratories participated in iceGGO-1 (CH_4)



Figure 3. Differences of measured CH₄ mole fractions from those of JMA.



Figure 4.Differences of measured CH₄ mole fractions from NMIJ gravimetric values.

4. Conclusion

JMA and active observation laboratories in Japan have established a national alliance with NMIJ to compare standard gas scales each other. In this framework, we started intercomparison experiments named iceGGO in 2012.

The first experiment named iceGGO-1 (CH₄) was conducted with SI traceable standard gases provided by NMIJ, in combination with the 3rd round CH₄ reference gas intercomparison conducted by the GAW WCC in Asia and the South-West Pacific. The result of this experiment shows that most of the differences in measured CH₄ mole fractions from those of JMA are positive and the differences increase with absolute CH₄ mole fraction values.

In addition to CH_4 , the alliance will continue to conduct the series of the intercomparisons for other gases such as CO and CO₂, for the purposes of clarifying the relation among various standard gas scales used by laboratories and ensuring their stability.

Current Activities of World Calibration Center for SF₆

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Sulfur hexafluoride (SF₆), one of the important greenhouse gases regulated by Kyoto Protocol, has no natural sources and only comes from human related activities. Aluminum industry and semiconductor manufacturing are major emission sources of SF₆, and electrical transmission equipment including circuit breakers are also emits SF₆ in the atmosphere. In 1970s, the concentration of atmospheric SF₆ was about 0.3 ppt ^[1], and reached 7.5 ppt in 2012 ^[2]. Many researchers report that there is a big gap between the emissions based on air measurements and estimated by the emission database ^{[3],[4]}. This shows that the reliable observation is important to verify the global and regional emissions of SF₆.

World Meteorological Organization / Global Atmosphere Watch (WMO/GAW) programme has a unique quality assurance (QA) system to provide reliable scientific data and information. This QA system is supported by five types of central facilities, including Central Calibration Laboratory (CCL), World / Regional Calibration Center (WCC/RCC), and so on. In the case of greenhouse gases including SF₆, Earth System Research Laboratory / Global Monitoring Division (ESRL/GMD) of National Oceanic and Atmospheric Administration (NOAA) plays an important role as a CCL. In 2012, based on the considerable experience in the field of quality assurance and quality control for the analysis of atmospheric SF₆, Korea Meteorological Administration (KMA) was designated as WCC for SF₆ (WCC-SF₆) by signing the Memorandum of Understanding (MoU) with WMO. To improve the greenhouse gases measurement technique, KMA has cooperated with Korea Research Institute of Standards and Science (KRISS), the national metrology institute of Korea, since 2002. Using the advanced measurement technique of KRISS, KMA started to monitor atmospheric SF₆ in its Korea GAW Center (KGAWC) located in Anmyeondo in 2007.

According to the MoU between WMO and KMA, KGAWC/KMA has its own important missions as WCC-SF₆, such as to develop and to publish quality control procedures required to support the quality assurance of measurements; to prepare and maintain laboratory standards traceable to the WMO reference scale; to perform intercomparison campaigns, system/performance audits, and to provide a training and long-term technical help for those who work for WMO/GAW stations. To implement of its own missions, WCC-SF₆ established several systems for preparing laboratory and transfer standard gas mixtures, including polish treated aluminum cylinders and cylinder evacuation system, LIX air compressor, sampling and mixing systems to prepare the dry compressed air. A gas chromatograph with micro electron capture detector (GC/ μ ECD) is used for SF₆ analysis, which is calibrated with five standard gas mixtures linked to the NOAA-2006 SF₆ scale.



Figure 1. System and condition for SF₆ analysis (left) and its chromatogram (right)

To ensure that the reference scale which is maintained at WCC-SF₆ is traceable to the WMO reference scale, the first intercomparison between CCL for greenhouse gases and WCC-SF₆ has been conducted in early 2013. Dry compressed air in 6 L aluminum cylinders were used as gas samples for this experiment, and those nominal values of SF₆ concentration were 6 and 8 ppt. To analyze SF₆ in gas samples, a 4 m length of activated alumina F-1 (80/100 mesh) packed column (Restek, USA) was installed in the GC/ μ ECD (Agilent 7890N, China). Gas samples were injected to the GC by the Valco 6-port sampling valve with a sample loop with 6 mL volume. More detailed system for SF₆ analysis and its chromatogram are shown in Figure 1. The limit of detection (3×S/N) of this measurement condition was approximately 0.15 ppt.

In this experiment, four standard gas mixtures were used to make sure of the linear range in the GC/ μ ECD and to apply the multi-point calibration method to the analysis result. To correct the instrumental drift during the measurement, we employed one working standard (WS) gas contained dry compressed air with ambient level of SF₆. The working standard gas was analyzed every before and after standard (STD₆, STD₈, STD₁₀, and STD₁₂) and sample (SP_A and SP_B) gases measurement, as shown in Table 1. From this A-B-A' method, the response ratio of each standard and sample gas against the working standard gas were obtained. Figure 2 shows the non-linear response curve of the GC/ μ ECD in the range of 6 ppt to 12 ppt.

| Gas mixture | WS | SPA | WS | STD ₈ | WS | SP_B | WS |
|-----------------------------|------------------|--------|------------|------------------|-------|-------------------|-------|
| Peak height | 6.883 | 5.553 | 6.854 | 6.700 | 6.910 | 6.631 | 6.907 |
| Response ratio [*] | / | 0.8085 | / | 0.9735 | / | 0.9599 | / |
| Gas mixture | STD ₆ | WS | STD_{10} | WS | WS | STD ₁₂ | WS |
| Peak height | 4.982 | 6.909 | 8.062 | 6.857 | 6.836 | 9.877 | 6.868 |
| Response ratio | 0.7212 | / | 1.1713 | / | / | 1.4414 | / |

Table 1. Response ratios of standard and sample gases against the working standard gas

* Response ratio of SPs and STDs = $2 \times SP(or STD) / (WS + WS')$

As shown in Figure 2, the GC/ μ ECD used in WCC-SF₆ has a non-linear response curve in the corresponding range. So it would be ideal to calibrate the GC using more than four standard gases at every measurement, but it consumed too much time and could be affected by unexpected instrumental drift during the measurement. Therefore, we would like to suggest the best

calibration method by calculating the



Figure 2. Response curve of GC used at WCC-SF₆

concentration of one sample (SP_B) gas in difference calibration situations. SF₆ concentration of sample B (SP_B) which applies multi-point calibration (multi_{4p}) using four standard gas mixtures was 7.854 ppt. This value was used as a reference value to compare each concentration value from various calibration situations. As shown in Table 2, as expected, any values calculated using STD₈ showed good results. Single point calibrations using STD₆ or STD₁₀ were all valid as well. In some cases which apply single point calibration using STD₁₂ and two point calibration using STD₆ and STD₁₂ showed big biases in the SP_B measurement. Based on this result, the two-point calibration method was applied to this experiment to obtain accurate measurement results.

Table 3 shows the measurement result from WCC-SF₆ for the intercomparison. Duplicate measurements by two-point calibration method (STD₆ and STD₈) were performed, and a multi-point calibration method (using four standard gases from 6 ppt to 12 ppt) was applied to only one result (the third measurement). As shown in the table, SF₆ concentrations measured by WCC and CCL were agreed well within 0.034 ppt. This difference is slightly higher than the WMO recommended measurement target for SF₆, but these two measured value were within their measurement uncertainty (standard deviation) each other.

| | Standard gas | STD_6 | STD_8 | STD_{10} | STD_{12} | |
|-------------|--|-------------------------------------|--------------------------------------|--|--------------------------------------|--|
| calibration | SF_6 concentration of SP_B | 7.879 | 7.861 | 7.863 | 7.916 | |
| canoration | Difference (Single-Multi _{4p}) | 0.025 | 0.007 | STD10 7.863 0.009 STD6, STD10 8.869 0.015 STD8, STD9 7.8 0.00 | 0.062 | |
| Two-point | Standard gas | STD ₆ , STD ₈ | STD ₈ , STD ₁₀ | STD ₆ , STD ₁₀ | STD ₈ , STD ₁₂ | |
| | SF_6 concentration of SP_B | 7.861 | 7.860 | 8.869 | 7.898 | |
| canoration | Difference (Two-Multi _{4p}) | 0.007 | 0.006 | 7.863 0.009 STD ₆ , STD ₁₀ 8.869 0.015 STD ₈ , STD 7. 0.015 | 0.044 | |
| Three-point | Standard gas | STD_6 , STD_8 , and STD_{10} | | STD ₈ , STD ₁₀ , and STD ₁₂ | | |
| | SF_6 concentration of SP_B | 7.861 | | 7.862 | | |
| canoration | Difference (Multi _{3p} -Multi _{4p}) | 0.0 | 007 | 0.0 | 008 | |

Table 2. Calculated SF₆ concentration of sample B from difference calibration situations (unit: ppt)

| Sample | Number of measurements | | | | WCC | CCL | Difference | |
|--------|------------------------|-------|-------|-------|-------|------------------|------------------|-----------|
| | 1 | 2 | 3 | 4 | 5 | [SD*] | [SD] | (WCC-CCL) |
| SPA | 6.651 | 6.649 | 6.629 | 6.636 | 6.612 | 6.635 [0.016] | 6.633 [0.012] | +0.002 |
| SP_B | 7.841 | 7.833 | 7.851 | 7.828 | 7.901 | 7.851 [0.029] | 7.885 [0.019] | -0.034 |

Table 3. Measurement result of two sample gases for the intercomparison



* SD: Standard Deviation

Based on these well established infrastructures and advanced measurement techniques for SF_6 , WCC-SF₆ will implement several long-term plans, such as to prepare operation procedures to maintain laboratory standard gases traceable to the WMO reference scale; to develop the measurement guideline for SF₆ observation in cooperation with KRISS; to provide the technical training course for GAW stations to enhance their capability building for SF₆ observation; to conduct intercomparison campaigns and system and performance audits for stations to improve the quality of observation data; and to expand the SF₆ observation network including the *in-situ* and/or flask sampling analysis supported by several funding sources.

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