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Newsletter

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The CSIRO/CAWCR Australian Tropical Atmospheric Research Station (ATARS)

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Australia's Centre for Australian Weather and Climate Research (CAWCR), at CSIRO Marine and Atmospheric Research, has recently established a pilot Australian Tropical Atmospheric Research Station (ATARS) at the Gunn Point Radar Facility, in Australia's Northern Territory (12.25°S, 131.05°E). The radar facility is operated by the Australian Bureau of Meteorology/CAWCR. The research station is integrated into the CSIRO/CAWCR collaborative global greenhouse gas (GHG) observation network, which is based on the collection of flask air samples and also *in-situ* measurements techniques. The Gunn Point research station is also part of the World Meteorological Organisation (WMO) Global Atmospheric Watch (GAW) network (site code "GPA").

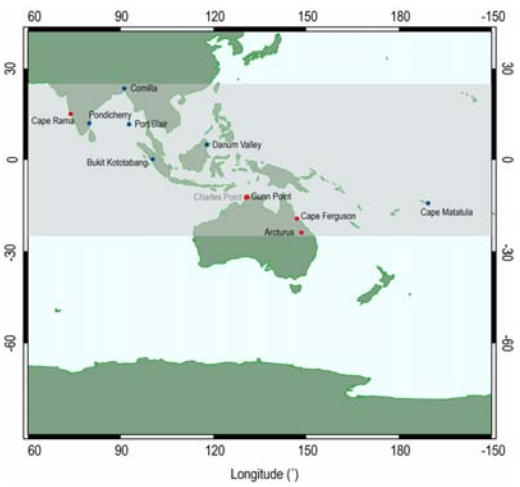


Figure 1. Atmospheric GHG research sites in the Southeast Asian-Australian tropics

Austalian-Southeast Asia Regional Atmospheric Observation Network

The introduction of the Gunn Point ATARS is expected to be an important addition to the sparse atmospheric observation network operating in the Australian-Southeast Asian tropical region, and the global tropical regions in general. Existing ground based atmospheric measurement sites operating in this region are shown in Fig. 1.

Table 1. Australian tropical atmospheric sampling sites ("NT"=Northern Territory, "QLD"=Queensland)

Air sampling location	Period of operation
Gunn Point, NT	2010 -
Arcturus, QLD	2010 -
Cape Ferguson, QLD	Dec 1989 -
Great Barrier Reef, QLD	Jun 1986 - Dec 1988 (sporadic)
Charles Point, NT	Sep 1990 - Dec 1990, Oct 1992 - Dec 1998
Jabiru, NT	Jan 1987 - May 1991
Myilly Point, NT	Aug 1990 - Mar 1993 (sporadic)

In the Australian tropical region, there has been a paucity of high quality atmospheric GHG observations. Attempts have been made to establish GHG observation programs in this region, as summarised in Table 1. Recently, two stations have been developed at Gunn Point and Arcturus (Queensland) with *in-situ* continuous carbon dioxide (CO_2) and methane (CH_4) measurement programs. Apart from these two stations, however, the other sites have been restricted to air sample collection programs (bi-weekly flasks). Prior to 1991/1992 the trace gas species analysed in these flasks were CO_2, CH_4 and carbon monoxide (CO). Following 1991/1992 the trace gas species also included hydrogen (H_2), nitrous oxide (N_2O) and isotopes of CO_2. Of particular relevance to the Gunn Point station was an air sampling site at nearby Charles Point, situated across the harbour to the west of the city of Darwin, which was operated for most of the 1990's. Logistics for sampling at this site were difficult and data from this site indicated frequent contamination from local anthropogenic GHG sources associated with city of Darwin (Refer Fig. 2).

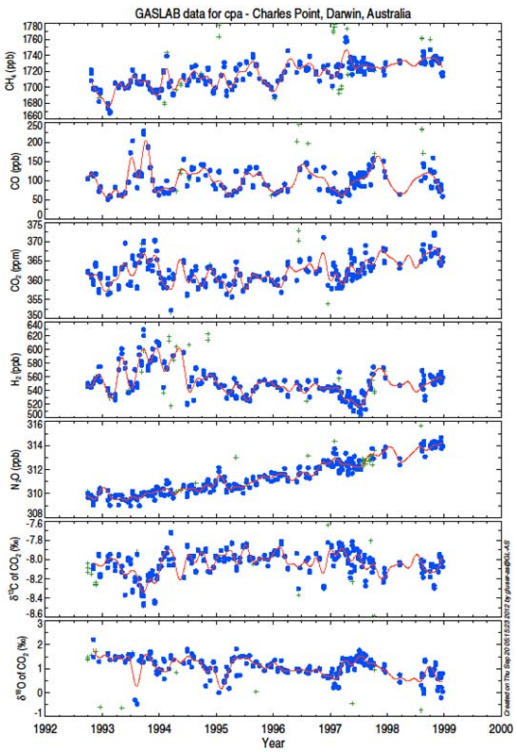


Figure 2. Charles Point (Darwin) flask air samples trace gas time series (1991-1998) (CSIRO/CAWCR GASLAB)

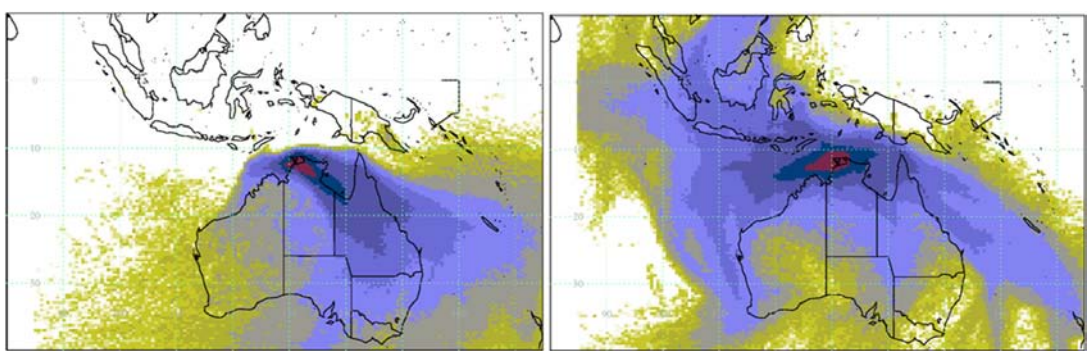


Figure 3. Gunn Pt. "NAME" Lagrangian dispersion model air mass origin maps (courtesy A. Manning, UK Met Office) (left panel: 2007 average dry season, right panel: 2007 average wet season)

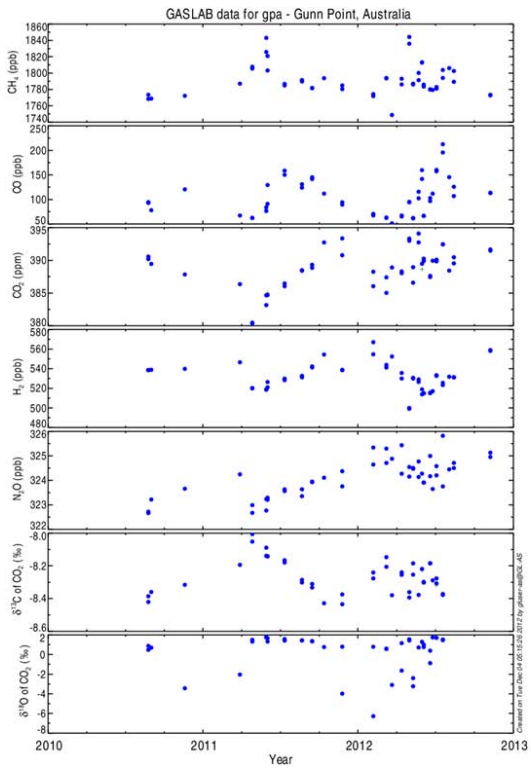
The prevailing dry season (Austral winter) meteorology at the Gunn Point station exposes the site to air masses derived predominantly from tropical northern Australia (northern Queensland and Northern Territory), as shown in Fig. 3 (left panel). Importantly, these synoptic easterlies would entrain strong biomass burning signals from continental Australia (savannah). During the wet season (Austral summer), the Gunn Point site is exposed to air masses from the significant GHG source and sink regions of Southeast Asia, including: the Timor Sea, Indonesian 'warm pool', Timor-Leste, Java, Sumatra, Borneo and Malaysia, as shown in Fig. 3 (right panel).

The current atmospheric research program for the tropical observatory at Gunn Point is shown in Table 2. A second laboratory container space has recently been installed at the site and will be instrumented with aerosol and particle analytical instrumentation in early-mid 2013.

The processed trace gas datasets from the flask air sampling program at the Australian tropical sampling sites at Gunn Pt. and Cape Ferguson is shown in Fig. 4. From the limited number of air samples collected so far from Gunn Pt., the site shows strong seasonality with influences from the monsoon clearly showing elevated atmospheric CH_4 and significant draw down of atmospheric CO_2 in March/ April, following wet season inundations (Refer Figs. 5 and 6). It must be noted in Fig. 4 the isotopic data $\Delta^{18}O$ of CO_2 at Gunn Pt. has been corrupted by the high humidity of the air samples at the time of sample collection. This is being rectified with a modified air sampling protocol to commence in 2013. In addition, N_2O data from Cape Ferguson (Fig. 4) has been compromised since 2003 from the particular chemical desiccant being used at the site. This will also be rectified in early 2013.

Table 2. Current atmospheric measurement program for Gunn Point ATARS

Atmospheric species	Analytical method	Research group
In-situ CO_2 & $^{13}CO_2/^{12}CO_2$	CRDS (Picarro)	CMAR
In-situ CH_4	CRDS (Picarro)	CMAR
CO_2, $^{13}CO_2/^{12}CO_2$, $CO^{13}O$, CH_4, N_2O, H_2, CO	Flask air sampling (GC-FID, GC-ECD, MS)	CMAR
Short-lived halocarbons, C_4-C_{12} HCs	GC-ECD/FID/PDD	CMAR /University of Cambridge, UK
O_3	UV spectrometry	CMAR
CO	NDIR	CMAR
NO/NO_x	Chemiluminescence	CMAR
Radon	Dual flow loop two filter radon detector	Australian Nuclear Science & Technology Organization



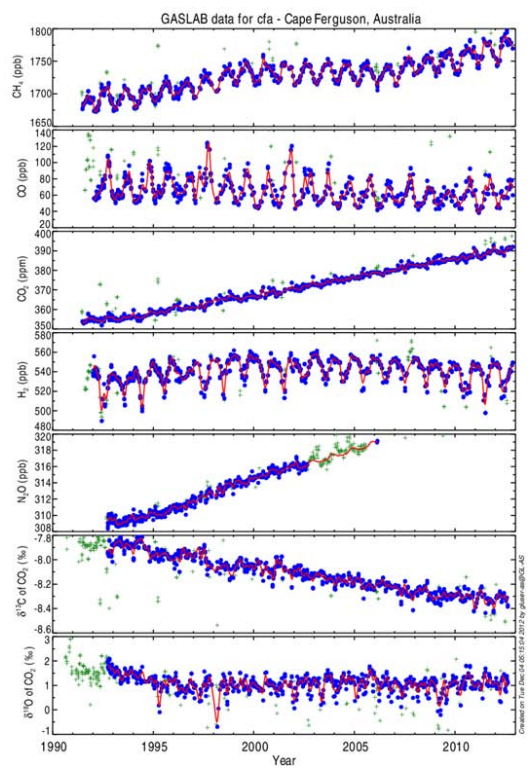


Figure 4. Flask air samples trace gas time series for Gunn Point (left panel) and Cape Ferguson (right panel) tropical sites (CSIRO/CAWCR GASLAB)

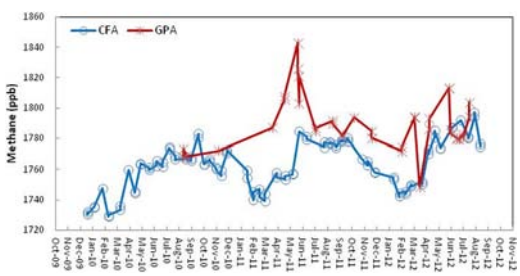


Figure 5. Flask air samples methane time series for Gunn Point ("GPA") and Cape Ferguson ("CFA") (CSIRO/CAWCR GASLAB)

Figure 6. Flask air samples carbon dioxide time series for Gunn Point ("GPA") and Cape Ferguson ("CFA") (CSIRO/CAWCR GASLAB)

GHG observation programs in India

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We have developed a gas chromatograph (GC) system capable of measuring atmospheric Carbon Dioxide (CO_2), Methane (CH_4), and Nitrous Oxide (N_2O) concentrations in air samples at the Centre for Climate Change Research, Indian Institute of Tropical Meteorology, Pune India. All the species are measured with single gas chromatograph having two detectors Flame Ionization Detector (FID) and Electron Capture Detector (ECD). Air samples collected at weekly interval in a pair of glass flasks of one liter capacity through automatic air sampler. Magnesium per chlorate is used as drying agent to dry air samples. After analysis flasks are evacuated and heated simultaneously in an oven to dry out any moisture content inside the flasks. Reference cylinders provided by GMD/NOAA/ESRL Boulder Colorado U.S.A are used for analysis and a target gas for quality control. The GC system described in this study is in use since November 2009 at our Institute laboratory at Pune, India as well as glass flask air sampling program at our remote site Sinhagad (SNG) located near Pune India (73.75° E, 18.35° N, 1600 m a.s.l.).

Background

Most of the observed temperature increase since the mid-20th century can probably be attributed to the observed increase of anthropogenic greenhouse gas mixing ratios (IPCC, 2007). The Carbon Dioxide Information Analysis Center (CDIAC), U.S.A, 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 (Boden, *et al.*, 2010). Some of these emissions might have compensated by vegetation uptake (Lal *et al.*, 2000; Patra *et al.*, 2011). Quantifying the carbon balance between the emissions of industry and transport, and the ecosystem uptake in India is an important step towards the design of effective greenhouse gas mitigation strategies in this subcontinent. Over India, till to date, monitoring of atmospheric CO_2 concentration is very little (Tiwari *et al.*, 2011b).

In recent years, the thrust of TransCom (The Atmospheric Tracer Transport Model Intercomparison Project) and carbon cycle research community has shifted to investigate the interannual

variability of fluxes (Baker *et al.*, 2006) rather than long-term means because these estimates believed to be more robust than the mean estimates. While this may be true in general, the scarcity of Indian continental surface CO_2 concentrations observations is unforgiving and large uncertainties continue to plague the CO_2 sources and sinks estimates especially in India. The only station Cape Rama Goa in India which operated for 10 years has been discontinued since 2002 (revived in July 2009, ref. WDCGG). International collaborations could help in starting some monitoring activities in India in 2006. LSCE (Paris, France) in collaboration with CMMACS (Centre for Mathematical Modeling and Computer Simulation, Bangalore, India) and IIA (Indian Institute of Astrophysics, Bangalore, India) have established few sites in India (Indira *et al.*, 2011). LSCE provided all its expertise and taken responsibility for doing routine analysis of glass flasks air samples collected weekly over these sites, through its gas chromatograph lab at Paris, France (Indira *et al.*, 2011). Similarly, other institutions in India like ARIES (Aryabhatta Research Institute of Observational Sciences, Nanital, India) have established a new station in collaboration with NIES Japan and weekly air samples are routinely analyzed at NIES lab in Japan (Scientist at ARIES and NIES- personnel communication). Therefore the ability to analyze glass flask samples to the precision required for inversion has been limited to a few international labs such as LSCE, NIES, NOAA, CSIRO, KMA, etc. With several new stations being planned for the future in India, it is imperative that India also contribute to the analysis at the precision required by using WMO prescribed NOAA/ESRL calibration standards to achieve high accuracy capability similar to other international labs in the world.

Assessing above, we have developed a facility for measuring ambient mixing ratios of the three most important long-lived greenhouse gases CO_2, CH_4, and N_2O in India. An analysis lab has been established, with high precision gas chromatograph analytical system, automatic air sampling, high quality glass flasks, conditioning facility for glass flasks, at the Centre for Climate Change Research, Indian Institute of Topical Meteorology, Pune, India. Pair of glass flasks are sampled on weekly interval at a remote site called Singhagad (SNG) near Pune India.

In this study we present detailed description of glass flask air sample collection, air sample analysis through gas chromatograph, comparisons of results with other sites, etc.

Monitoring site

Air samples collected at a top of 10 meter tower at a remote site called Singahad (SNG) (73°45'E, 18°21'N, 1600 m a.s.l.), located on a mountain top approx 40 km southwest of Pune India. Its top is flat with an area about 0.5 km^2. The site is free of any major vegetation over a scale 500 m from one side (south east) where the inlet of sampling tube installed. On the other side's sparse and short (less than 3 m) vegetation is available in the vicinity of 20 meter of the monitoring tower (Fig. 1).

Meteorological data at Sinhagad site show that zonal wind direction is south and south-east during afternoon hrs. Wind speed during afternoon is very calm and temperature varies between 25-30 ℃. The mean wind speed, during summer and winter months, at the time of sampling is about 0.5 to 1 ms^{-1}. Therefore samples mostly represent a vast area free from any dense vegetation. The site receives maritime as well as continental air masses during the year.

Figure 1. Sinhagad (SNG) observational site, Pune, India. Container (top left), tower (top right), and site view from tower (bottom left & right). Site is free from any major vegetation.

During Indian summer monsoon months (JJAS) it is mostly dominated by maritime air masses and during winter months (DJF) it receives continental air masses.

Samples are collected at a weekly interval on every Friday between 12:00 to 12:30 hrs in the afternoon. It is assumed that airmases are well mixed in the afternoon and site is not biased towards any local signal. Chemical drying agent 'magnesium per chlorate' is used as a moister drier in the air sampler system. Magnesium per chlorate is changed every week before sampling starts. In order to detect sample contamination, flasks are sampled in pair. When the concentration in a pair of flasks differs by more than a certain threshold, the measurement is flagged. Sampling starts with fitting of the flasks to the air sampler. Once flasks are fitted leak test is done on the flasks. Any leak may contaminate air sample in the glass flasks, leak proof fitting undergoes for glass flask flushing for 10 minutes. Samples are collected after pressurizing flasks. After the sampling, flasks are detached and sent to Gas Chromatograph lab at the Indian Institute of Tropical Meteorology, Pune, India for GHG analysis. Samples are analyzed within a week it sampled.

Automatic air sampler used for air sample collection in glass flasks are manufactured and tested at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Paris, France. Flasks are manufactured at a company called Normag Labor-und Prozesstechnik GmbH located at Jena Germany. Similar flasks are tested at the Max Planck Institute for Biogeochemistry (MPI-BGC) at Jena Germany for alterations of trace gas mixing ratio via diffusive loss during the flask storage. Storage tests have not indicated loss of CO_2 or N_2O since more than one year. Flasks are conditioned before re-sending to measurement site. Each flask is tested for valve leak, evacuated down to 10^{-3} and heated at 60 ℃ continuously up to 72 hrs in a conditioning unit. Conditioning unit is developed here and has automatic time and temperature controller.

Sample analysis

Analytical system is based on a commercially available Thermo Scientific Trace GC Ultra Gas Chromatograph (GC) manufactured by Thermo Milan Italy which was modified to our purposes. A chromatographic run starts with flushing sample gas through the two sample loops. The sample is transported with a carrier gas and led through a chromatographic column where separation of the gases takes place. The effectiveness of this separation is very sensitive to the gas flow,

the temperature of the column and the type of the column used. Finally, the individual components (gases) are analyzed by a detector.

Sample air gets introduced through magnesium per chlorate tube into the GC system by entering a 10-port, electrically driven valco valve controlled via external events output connector of the GC, and flushed through two sample loops. For analysis of CO_2 and CH_4 5 mL sample loop is used and 2 mL sample loop is used for N_2O. Both sample loops are temperature stabilized in valve oven at 90 ℃. Sample loops are flushed and injected onto the respective pre-column using 10 port valco valves. Columns are used for separating individual components from the air samples. They are temperature stabilized at 70 ℃. Following the separation of the air sample, the species are analyzed with the detectors FID and the ECD. All the gases such as carrier gas, zero air, hydrogen are led through individual purifier (28864-U, Sigma-Aldrich) in order to ensure stable baseline conditions.

For calibration of chromatograms of unknown air samples, reference cylinders with known mixing ratios are used. These reference scales are provided by the National Oceanic and Atmospheric Administration / Earth System Research Laboratory / Global Monitoring Division (NOAA/ESRL/GMD, Boulder, Colorado, USA). Reference cylinders contains high (H), mid (M), and low (L) mixing ratios. Mixing ratios H and L are high- and low of the current ambient mixing ratio whereas M is at about the current ambient mixing ratio. A separate tank is used as target gas to check instrument stability on day to day basis.

Results

Air samples collected in one liter glass flasks at Sinhagad (SNG) Pune India site were analyzed at the Centre for Climate Change Research, Indian Institute of Tropical Meteorology Pune India (Tiwari, *et al.*, 2011a). On the other hand, air samples collected by CSIRO Australia at Cape Rama (CRI) Goa site located at the west coast of India, were analyzed by GASLAB at the Centre for Australian Weather and Climate Research, CSIRO Marine and Atmospheric Research, Aspendale, Australia (Francey *et al.* 2003). CRI is a coastal site (50 m asl) whereas SNG is a mountain site (1600 m asl), both located at western part of India (Fig. 2). Sinhagad (SNG) has a flat top with an area about 0.5 km^2. It receives maritime as well as continental air masses during the year. During South West monsoon months (JJAS) it is mostly dominated by maritime air masses from Arabian Sea and during rest of the months it receives

Figure 2. Locations of GHG monitoring sites in India. Sinhagad (SNG) and Cape Rama (CRI) monitoring sites are marked in yellow color font in this map.

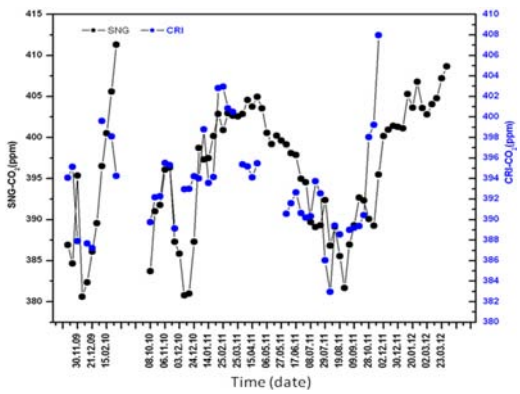

Figure 3. CO_2 observations at Sinhagad (SNG) site India (black color) compared with CO_2 observations by CSIRO at Cape Rama (CRI) India (blue color).

continental air masses. Cape Rama (CRI) is a unique site which experiences a seasonal reversal of wind pattern. During South West monsoon months (JJAS) it receives air masses having marine signatures while during remaining period it receives typical west coast region (continental India) characteristics. Air sample collection at SNG started in November 2009, whereas CRI site revived by CSIRO in July 2009. Here we compare CO_2 mixing ratio observed at both of these sites (Fig. 3). CO_2 (ppm) observed at CRI show seasonal amplitude of approx 18 ppm whereas SNG seasonal amplitude is 25 ppm.

Being a mountainous site SNG contains sparse biosphere in the visible vicinity and gets regulated by the nature. Whereas CRI being a coastal site almost has no biosphere in visible vicinity therefore it gets regulated by the coastal winds. Therefore, it can be assumed that local orography at these sites are playing an important role and regulating CO_2 seasonal amplitude shown in Fig. 3. There was some instrument failure at SNG site only so were no observations during May 2010 to Sept 2010, period. Observations at SNG revived in October 2010. For simplicity in comparison we have chosen CRI CO_2 data as same time as SNG CO_2. CO_2 observed at CRI show maxima (minima) in March (August) whereas SNG show CO_2 maxima (minima) in April (September). Other greenhouse gases observed at these sites show understandable variability (figure not shown here). As

above are preliminary data during first few years of observing period, long term observations will be required to understand many un-answered questions in carbon cycle research over this region.

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Greenhouse Gases Monitoring Activities at Global GAW Station Bukit Kototabang, Indonesia

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Introduction

Global Atmosphere Watch Station Bukit Kototabang is located in the island of Sumatra, Indonesia. This station is situated just in equatorial region and is surrounded by tropical rainforest as the main biome. This station has fully operated since late 1995 and is equipped with several devices and instruments for the purpose of air quality and climate change parameters measurement. With regards to climate change, this station has measured ground level ozone since 1999, followed with the other gases, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and sulfur hexafluoride (SF_6), as part of GMDL NOAA network, which was started in 2004. Unfortunately, this program has been terminated in March 2011. In 2009, the station added another instrument to measure CO_2 and CH_4. This measurement is a near real time device, with supports from MeteoSwiss and Empa Switzerland for calibration and maintenance.

Figure 1. Global Atmosphere Watch Station Bukit Kototabang, Sumatra - Indonesia.

Measurement Highlights

Carbon dioxide (CO_2)

Fig. 2 shows CO_2 concentration measured at Bukit Kototabang in the period of 2004-2011. As depicted beside, CO_2 concentration is on the positive trend, with the seasonal variations slightly observed during the period, even though these variations are not very clear. A huge spike in concentration can be seen in early 2005, as the influence of major peat fires in Sumatra. Between 2004 and 2011

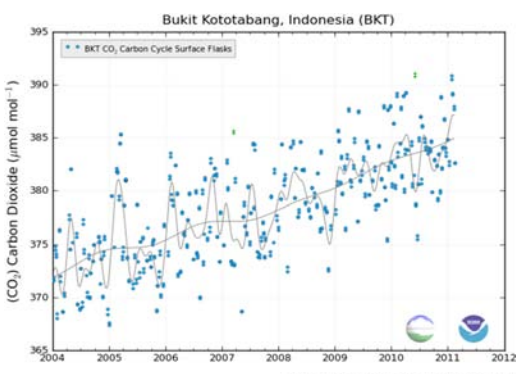

Figure 2. Trend of CO_2 concentration at Bukit Kototabang in 2004-2011.

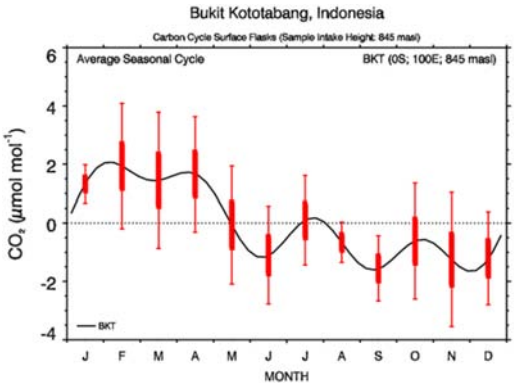

Figure 3. Average seasonal cycle of CO_2 concentration at Bukit Kototabang.

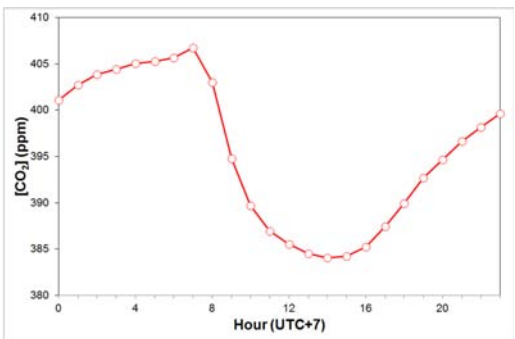

Figure 4. CO_2 hourly average concentration at Bukit Kototabang.

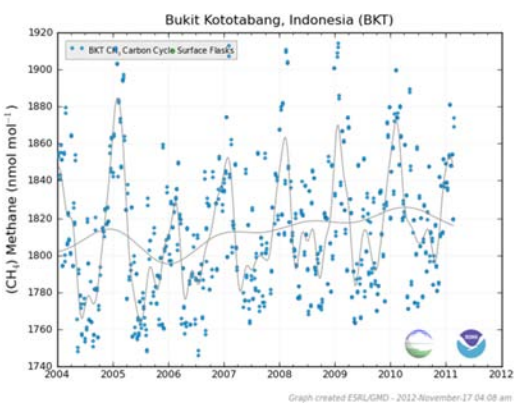

Figure 5. Trend of CH_4 concentration at Bukit Kototabang in 2004-2011.

CO_2 concentration has increased at the rate of 1.8 ppm/year.

Seasonality concentration of CO_2 is shown on Fig. 3. CO_2 is well higher than its monthly average on the first four months of the year and also in July. While the anomaly in July is rather unclear, higher concentration on January to April is very likely related to predominant air mass from the northern hemisphere, bringing CO_2-rich air to the station.

CO_2 hourly average concentration is illustrated on Fig. 4. During the day time, CO_2 is relatively low, reaching the lowest at 14.00 local time, when the air mass is well-mixed. Meanwhile, on the night and just after the sunrise, CO_2 concentration is increasing by approximately 20 ppm and at its maximum on 07.00 in the morning. This trend is resulted as the response of the effect of respiration process by vegetation and lower inversion level.

Methane (CH_4)

CH_4 concentration measured at Bukit Kototabang is slightly increasing, as can be seen from Fig. 5. This increasing trend is observed since 2008, with the growth rate is at the level of 3.1 ppb/year. Meanwhile, in line with the positive trend, monthly average concentration (Fig. 6) has indicated the CH_4 concentration is higher than its observational average by 30-100 ppb. Similar to CO_2, CH_4 concentration is higher when the prevailing air mass comes from the northern hemisphere.

Diurnal variation of CH_4 concentration is shown on Fig. 7. From midnight to around 07.00 local time, CH_4 concentration increases gradually. Then, the concentration rapidly decrease and reaches the lowest at noon. Between noon and midnight, small increase is observed.

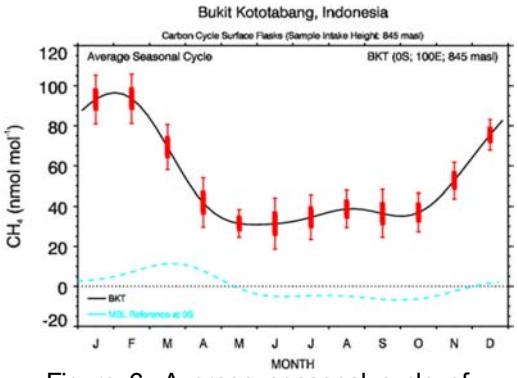

Figure 6. Average seasonal cycle of CO_2 concentration at Bukit Kototabang

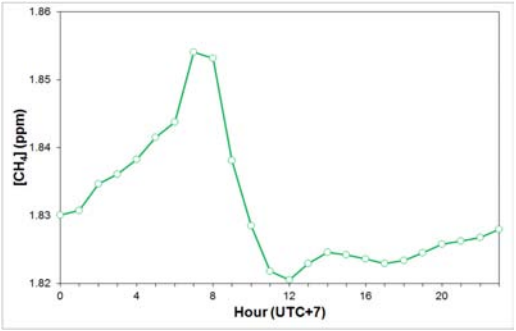

Figure 7. Average diurnal cycle of CH_4 concentration at Bukit Kototabang.

Figure 8. System and performance audit by Empa, November 2011.

System and Performance Audit

In November 2011, a team from Empa-Switzerland came to Bukit Kototabang to perform system and audit performance audit of several measurement parameters. Those parameters are surface ozone, carbon monoxide, carbon dioxide and methane. The audit for CO_2 and CH_4 was conducted for Picarro G1301 by inter-comparing the reading from the instrument to the known concentration of three standard gases. For CH_4, results indicated that the data were within the WMO GAW DQOs by approx. 10 times better compared to single injections of an optimised GC/FID system. As for CO_2, the readings were 0.1 ppm larger than the WMO GAW DQOs for mole fractions below and above the levels of ambient background mole fractions. However, those values were still at the assigned uncertainties of the standards and the repeatability could reach the GAW DQOs requirement (Empa, 2011).

Reference

- EMPA 2011. System and performance audit of surface ozone, methane, carbon monoxide and carbon dioxide at the Global GAW Station Bukit Kototabang - Indonesia, November 2011. WCC-Empa Report 11/4. Empa-Duebendorf, Switzerland.

GAW Activities of Korea Global Atmosphere Watch Center in Anmyeon-do

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Korea Global Atmosphere Watch Center (KGAWC) is located at the Anmyeon-do (36°32'N, 126°19'E), western part of Korean Peninsula (Fig. 1). Altitude of KGAWC is 45.7 m above mean sea level. KGAWC belongs to the regional GAW station. KMA (Korea Meteorological Administration) established weather station at Mt. Soback in 1987. Then it moved into Anmyeon-do, and begins of background atmosphere watch station. Continuous measurement of greenhouse gases (CO_2, CH_4, N_2O, CFC-11, CFC-12) and radiation began in 1998.

Air sampling from the 40 m tower (about 86 m from the sea level) starts from 2003. Beginning of continuous measurement of CFC-113 and SF_6 and aerosol sampling from integrated inlet system began in 2007. Main tasks of KGAWC are as follows: (1) monitoring greenhouse gases, (2) flask air sampling and analysis of special observation, (3) international data exchange with WMO/WDCGG, and (4) participating the International Intercomparison Experiment.

KMA operates two more GAW stations (called Pohang and Gosan). Pohang is located at the eastern part of Korea and Gosan is located at the southern part of Korea.

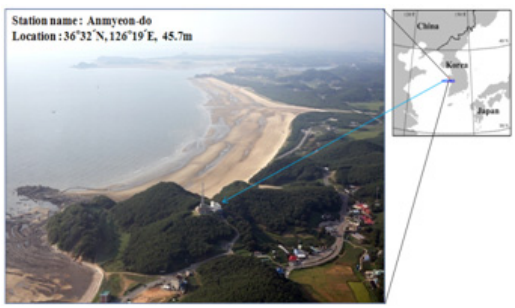

Figure 1. The Korea Global Atmosphere Watch Center is located at the relatively unpolluted western coastal area.

At present, KGAWC (Anmyeon-do) monitoring greenhouse gases, aerosols, reactive gases, ozone and UV, radiation, and precipitation chemistry.

Fig. 2 shows the concentration levels for the greenhouse gas species observed at Anmyeon-do from 1999 to 2011. The CO_2 concentration at Anmyeon-do are higher than the global average and the CH_4 and N_2O concentrations are steadily increasing, while CFC-11 and CFC-12 exhibit a continuously declining trend.

The average CO_2 concentration for the year 2011 recorded 395.7 ppm, an increase of 25.0 ppm (6.7 %) relative to the annual average of 370.7 ppm for 1999, and 5.2 ppm higher than the global average of 390.5 ppm for the same year

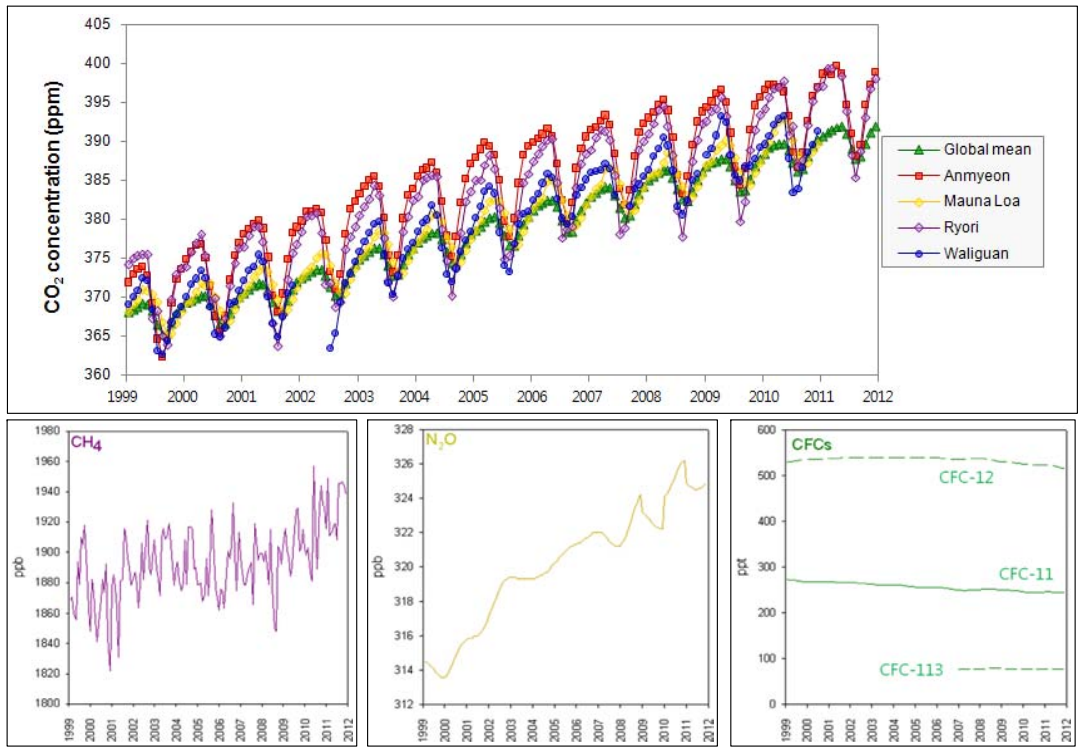

Figure 2. Concentration of greenhouse gases observed at Anmyeon-do from 1999 to 2011.

as documented by NOAA/GMD (Table 1). The annual growth rate of CO_2 for the 13-year period from 1999 through 2011 was 2.2 ppm/year, higher than the global average of 1.9 ppm/year.

The methane (CH_4) concentration in 2011 was 1.929 ppm, an increase of 0.046 ppm (2.4 %) over 1999 (1.883 ppm), resulting in an annual mean growth rate of 0.004 ppm/year (Table 2). The N_2O concentration for 2011 was 324.7 ppb, an increase of 10.7 ppb (3.4 %) over the value recorded in 1999 (314.0 ppb). The annual mean growth rate of N_2O is 0.9 ppb/year, and a persistently increasing trend is evident. All three species of CFCs (CFC-11, CFC-12, CFC-113) are on the declining trend. There was a

Table 1. Anmyeon-do and Global CO_2 concentrations (ppm) and annual mean CO_2 growth rates (ppm/year) for 1999-2011.

Year		1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Anmyeon-do	Concentration	370.7	373.8	376.9	379.7	382.6	384.3	387.2	388.7	389.9	391.4	392.5	394.5	395.7
	Growth rate	+2.9	+3.4	+2.8	+3.2	+2.1	+2.4	+2.1	+1.5	+1.6	+1.2	+0.9	+2.0	+2.0
Global mean	Concentration	367.6	368.8	370.4	372.4	375.0	376.8	378.8	380.9	382.7	384.8	386.3	388.5	390.5
	Growth rate	+1.3	+1.3	+1.8	+2.4	+2.2	+1.6	+2.4	+1.8	+2.1	+1.8	+1.7	+2.4	+2.1

Table 2. Average concentrations for 2011 and annual mean growth rates for the 13-year period from 1999 through 2011 of major GHGs at the Anmyeon-do of the Korean Peninsula.

GHGs	CO_2	CH_4	N_2O	CFC-11	CFC-12
Average concentrations in 2011	395.7 (ppm)	1.929 (ppm)	324.7 (ppb)	245.4 (ppt)	519.9 (ppt)
13-year average growth rates	+2.2 (ppm/year)	+0.004 (ppm/year)	+0.9 (ppb/year)	-2.2 (ppt/year)	-1.2 (ppt/year)

dramatic decrease of 25.0 ppt (-2.2 ppt/year) over 13 years in CFC-11, which fell from 270.4 ppt in 1999 to 245.4 ppt in 2011. CFC-12 decreased by 12.6 ppt, from 532.5 ppt in 1999 to 519.9 ppt in 2011, which is a rather small annual mean decrease of -1.2 ppt/year (Table 2). Concentrations of CFC-113 recorded 76.8 ppt in 2010 and 77.3 ppt in 2011, an increase of 0.5 ppt over one year. The annual mean concentration of SF_6 for 2011 was 8.1 ppt, 0.3 ppt higher than the 2010 average (7.8 ppt), suggesting a slight increase in every year.

KGAWC held the 4th Asian GAW Greenhouse Gases Workshop on September 24th~25th in Ramada Plaza Jeju Hotel in Jeju Island, Republic of Korea. Total 75 people including Maznorizan Mohamad (Malaysia), Yogesh Tiwari (India), Herizal (Indonesia), and Marcel Vale van der Schoot (Australia) participated.

Total 7 presentations are given during the workshop. Speakers and presentation titles are as follows:

Marcel Vale van der Schoot (Australia), The CSIRO/CAWCR Australian tropical atmospheric research station (ATARS); Yogesh Tiwari (India), Monitoring of atmospheric carbon dioxide and other GHG's in India; Herizal (Indonesia), Current status GAW activities in Indonesia; Haeyoung Lee (Korea), Greenhouse gases monitoring activities in Korea Global Atmosphere Watch Center, 2011; Sunyoung Park (Korea), Toward identifying and quantifying emission sources of Halogenated compounds in East Asia: Analysis of atmospheric monitoring data obtained at Gosan, Jeju Island in Korea; Jeongsoon Lee (Korea), Standard gas mixtures of KRISS scale for atmospheric Greenhouse Gas monitoring; Maznorizan Mohamad (Malaysia), The measurement and analysis of the GHG and reactive gases at GAW stations in Danum Valley, Malaysia.

KMA hosted World Calibration Center (WCC) for SF_6 (Sulphur Hexafluoride) and will officially operate beginning of 2013. World Calibration Center (Figs. 3 and 4) is located at the Korea Global Atmosphere Watch Center in Anmyeon-do. As described

(a) Cylinder evacuation system (b) Sampling tower (c) Compressor room (d) Air sampling system

Figure 3. Systems for preparation of compressed dry air in the cylinder

Figure 4. Analytical system (left) and primary standard gases (right) to prepare laboratory and transfer standards traceable to the WMO SF_6 mole fraction scale

in the Box 7 of GAW Report 172, the duties of WCC are as follows:

(1) Assist Members of operating GAW stations to link their observations to the GAW primary standard.
(2) Develop quality control procedures following the recommendations by the SAGs, support the QA of specific measurements and ensure the traceability of these measurements to the corresponding primary standard.
(3) Maintain laboratory and transfer standards that are traceable to the primary standard.
(4) Perform regular calibrations and performance audits at GAW sites using transfer standards in co-operation with the established RCCs.
(5) Provide, in co-operation with the QA/SACs, training and long-term technical help for stations.

The address of WCC homepage is : http://www.climate.go.kr.

Measurements of Natural and Anthropogenic GHGs at Gosan, Jeju Island in Korea and the Emission Estimates in East Asia

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Gosan station has been receiving much attention recently in particular as one of the most important sites to monitor continental outflows from East Asia and thus compliance with international treaties on those important greenhouse gases and/or ozone-depleting substances. Gosan station is located on the south-western tip of Jeju Island, south of the Korean peninsula (126°9' E, 33°17' N, 72 m asl) on a remote hill-top by the coast. As such effects from local contamination can be assumed to be minimal, this allows for monitoring of long-range transport from the surrounding region. The wind patterns at Gosan are typical of the Asian Monsoon pattern, with strong northern winds in winter, and southern influence during summer (Fig. 1(a)). These wind patterns are favorable for monitoring air masses passing through East Asia, especially China and Korea. Clean “baseline” conditions are observed when a clean stream of air flows in directly from northern Siberia (in winter, Fig. 1(b)) and during transport of southerly oceanic winds (in summer). Thus, general wind patterns at Gosan bring air masses from the surrounding areas, allowing the monitoring of both clean baseline and polluted air masses.

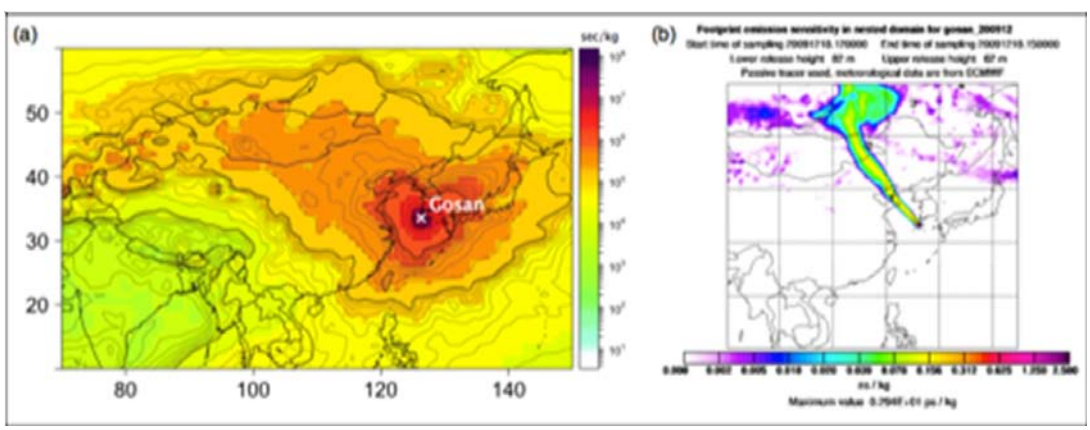

Figure 1. (a) Location of Gosan (Jeju Island, Korea), shown with footprint emission sensitivities calculated using FLEXPART. Larger sensitivities are analogous to greater residence times of air masses arriving at Gosan. (b) Typical air mass back-trajectory during background events.

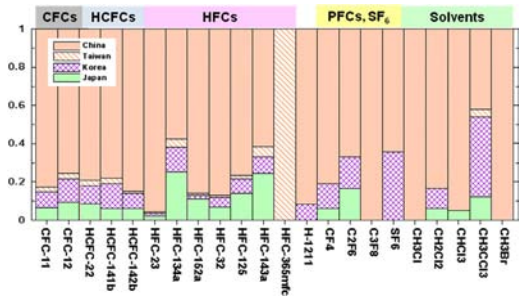

Figure 2. Fractions of each compound to total halocarbons (CFCs, HCFCs, and HFCs) emissions for 2008 in each country.

The measurement systems at Gosan are comprised of (1) flask sampling and measurements of atmospheric CO_2 concentration and $\delta^{13}C$- and $\delta^{18}O$- CO_2 in cooperation with the Scripps Institute, (2) high-frequency measurements of CO_2 concentration using LOFLO CO_2 analyzer, (3) high-frequency monitoring of CH_4 and CO concentrations with FID-GC and NDIR systems, respectively and (4) an in situ GC-MSD system for measuring ~40 halogenated compounds, based on an advanced cryofocusing technique ("Medusa"). The Medusa- GC-MSD system is operated under the Advanced Global Atmospheric Gases Experiment (AGAGE).

Here, we briefly introduce one of our recently reported findings from measurements of a wide range of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6) and other halogenated compounds at Gosan. Due to increased economic growth in East Asia, regional emissions of many anthropogenic halogenated compounds now constitute a substantial fraction of the global totals, and thus it is an urgent issue to quantify the emissions of these species in East Asia. The results of the measurements of halogenated compounds at Gosan can be characterized by frequent pollution events superimposed on the Northern Hemispheric baseline concentrations in the colder months (late fall through early spring), and lower concentrations in summer from the Southern Hemispheric influence brought in by the Asian Monsoon. We calculated the country-based emissions of 24 halogenated compounds using namely a ratio method based on interspecies correlation between measured compounds, in combination with analysis of air mass back-trajectories to separate periods of clear influence from China, Korea, Japan, and Taiwan (Li *et al.*, 2011). The analyses showed that for most compounds emissions from China constituted more than 80% of East Asian emissions. Especially, contributions to HFC-23 emissions from China account for approximately 98% of total emissions from East Asia. For some compounds, however, significant contributions from Korea, Japan and Taiwan were also found; HFC-134a and HFC-143a emissions in Taiwan, Korea, and Japan were equal to approximately two-thirds of Chinese emissions. SF_6 and CH_3CCl_3

were emitted mostly in China and Korea with equal contribution from both countries. In contrast to China's dominant contribution to global emissions, the per-capita emissions were highest in Korea (Fig. 3); especially PFCs and SF_6 are approximately five times higher than global per capita emissions. The per capita emissions for China, Japan, and Taiwan are close to the global per capita emissions for most compounds. These results are very important for the regulation strategies of the compounds, given the fact that CFCs, the most important ozone-depleting substance are now decreasing in concentration under international treaties, but increasing emissions from East Asia of HCFCs and HFCs, which are significant greenhouse gases, may be large enough to negate the CFCs offsets. In summary, high-precision, high-frequency measurements of the natural and anthropogenic GHGs at Gosan should continue to provide new insights of the GHG emission patterns and their recent trends and thus help verify both bottom-up emission inventories and inverse model estimates of these compounds in East Asia.

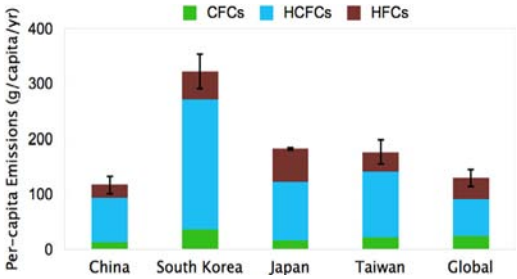

Figure 3. Per-capita emissions of CFCs, HCFCs, and HFCs in China, Korea, Japan and Taiwan for 2008.

Reference

- Li S., Kim J., Kim K-R., Mühle J., Kim S-K., Park M-K., Stohl A., Kang D-J., Arnold T., Harth C.M., Salamek P.K., and Weiss R.F. Emissions of halogenated compounds in east asia determined from measurements at Jeju Island, Korea. *Environ. Sci. Technol.* 2011, 45, 5668-5675.

The Measurement and Analysis of Greenhouse Gases at GAW Station in Danum Valley, Malaysia

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Malaysian Meteorological Department (MMD) has established a baseline or global GAW (Global Atmosphere Watch) station in Danum Valley, Sabah in 2003. The Danum Valley GAW station is located within Class 1 forest conservation area at the northeastern part of Borneo where it is surrounded by the undisturbed tropical rainforest. The Danum Valley GAW station is one of the station located in the equatorial region and 23rd baseline station that are part of the WMO-GAW network. Climatologically, the station's yearly mean temperature is 26.8˚C and the mean annual

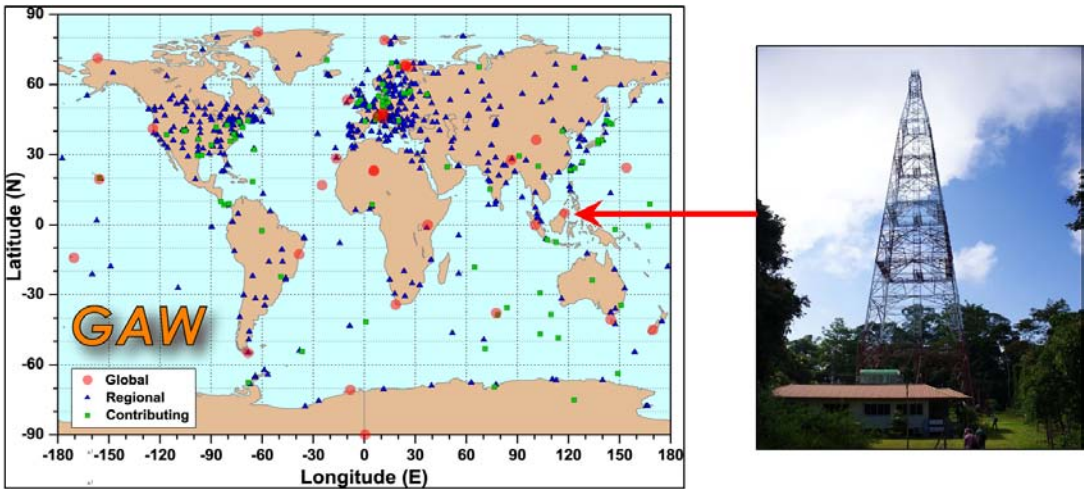
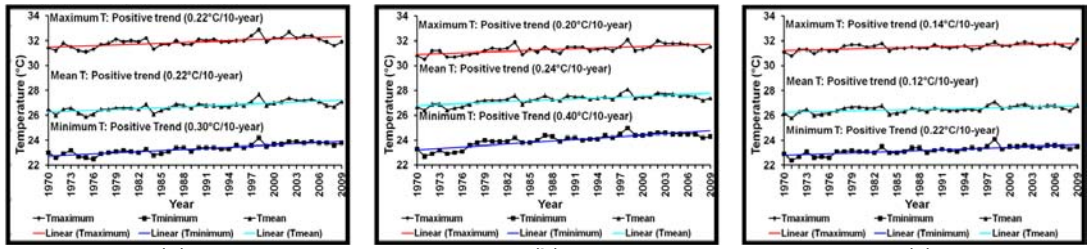


Figure 1. The Danum Valley Global GAW Station located in pristine tropical rainforest in Sabah consists of a laboratory, office, meeting room, rooftop platform and 100 meter sampling tower

Figure 2. View looking from the top of the sampling tower



(a) (b) (c)

Figure 3. Annual temperature trend for: (a) the Peninsular; (b) Sabah; and (c) Sarawak

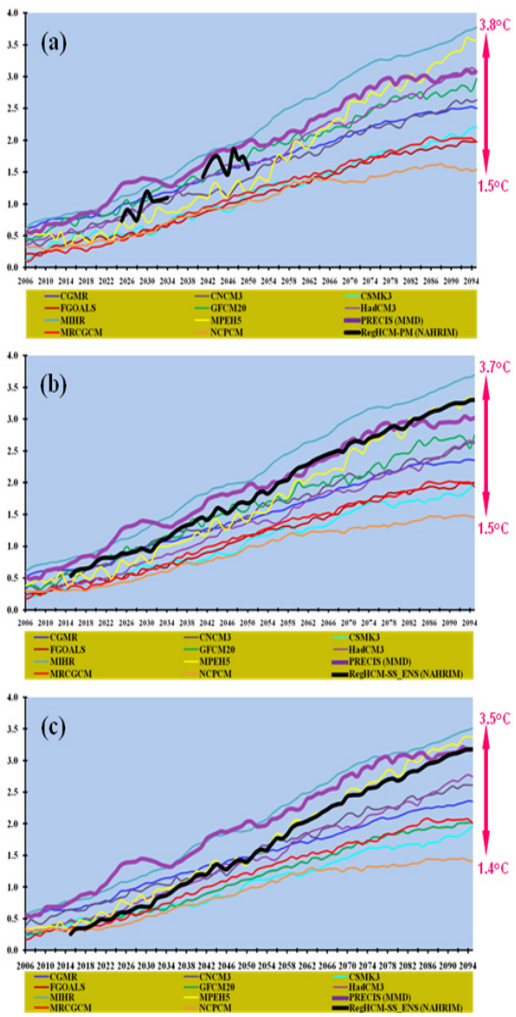


Figure 4. 10 year running mean of projected temperature changes relative to the baseline (1970-1999) for : (a) the Peninsular; (b) Sabah; and (c) Sarawak

precipitation is approximately 2825 mm with January and October recorded as the wettest months and April as the driest month.

Based on the 40 years of record from 1969-2009, the rate of mean surface temperature has increased for Malaysia that include Peninsular, Sabah and Sarawak ranged from 0.6°C to 1.2°C per half century. Similarly, the climate model predicts that the rate of temperature increase during the 30-year period from 2059 to 2090 is projected to generally double the rate of increase simulated for earlier 20-year period from 2029 to 2050. Thus, due to this projected temperature trend in which greenhouse gases (GHG) as a driver to the global warming and climate change contributed significantly, MMD and other relevant agencies continue to monitor closely the concentrations of GHG in the country as to ensure that the emission from these gases will be under control and the projected temperature until the year 2090 will be much lower and the impact of climate change will be very much reduced. The temperature analysis and projection are shown in Fig. 3 and Fig. 4 respectively.

Instrumentation and Measurement

It is known that one of the main contributors to the climate change is the long-lived GHG namely CO_2, CH_4, N_2O and other lesser gases. MMD are aware of the importance in keeping the status of GHG concentration updated, such that an environmental sustainability development could be properly planned and structured. Among activities that MMD prioritized are the GHG and reactive gases monitoring in GAW station in Danum Valley. Since 2004, MMD has collaborated with Commonwealth Scientific and Industrial Research Organisation (CSIRO) in installing a LoFlo Mark II CO_2 Analyzer at the station. At the same time MMD is also collaborating with National Institute of Environmental Studies, Japan (NIES) in monitoring GHG using flask sampling method.

Figure 5. LoFlo Mark II CO_2 Analyzer

Figure 6. Flask Sampling

The LoFlo Analyzer measures carbon dioxide (CO_2) continuously and in order to maintain the accuracy of the instrument and the data quality, the LoFlo Analyzer is calibrated every 4 to 6 weeks.

On the other hand, the flask air samples are collected once a week and after each sixth week the air samples will be packed and sent to NIES for analysis and the data then be shared among the researchers from MMD and NIES.

Results and Analysis

The time series analysis of CO_2 concentrations from June 2009 to June 2012, in which data are measured using LoFlo Analyzer and Flask Sampling at Danum Valley GAW Station is shown in Fig. 7(a). The hourly mean CO_2 concentrations measured using Loflo analyzer ranged from 370 to 420 ppm, while the CO_2 concentrations measure by Flask Sampling ranged from 380 to 410 ppm. The values from both methods are showing quite a comparable value.

As shown in Fig. 7(b) and 7(c), the daily average and monthly average of CO_2 concentration recorded from Nov. 2009 – June 2012 are ranged from 385-398 ppm and 387-395 ppm respectively. On the other hand, Fig. 7(d) is showing the annual average of CO_2 recorded in Danum Valley and Mauna Loa, Hawaii where it is observed that the trend of annual average CO_2 concentration for both Danum Valley and Mauna Loa are quite similar with both are showing an increasing trend of 1.86 ppm/year for Danum Valley and 1.98 ppm/year for Mauna Loa.

Apart from CO_2, the automatic Flask Sampling is also measuring methane (CH_4), nitrous oxide (N_2O), sulphur hexafluoride (SF_6) and carbon monoxide (CO).

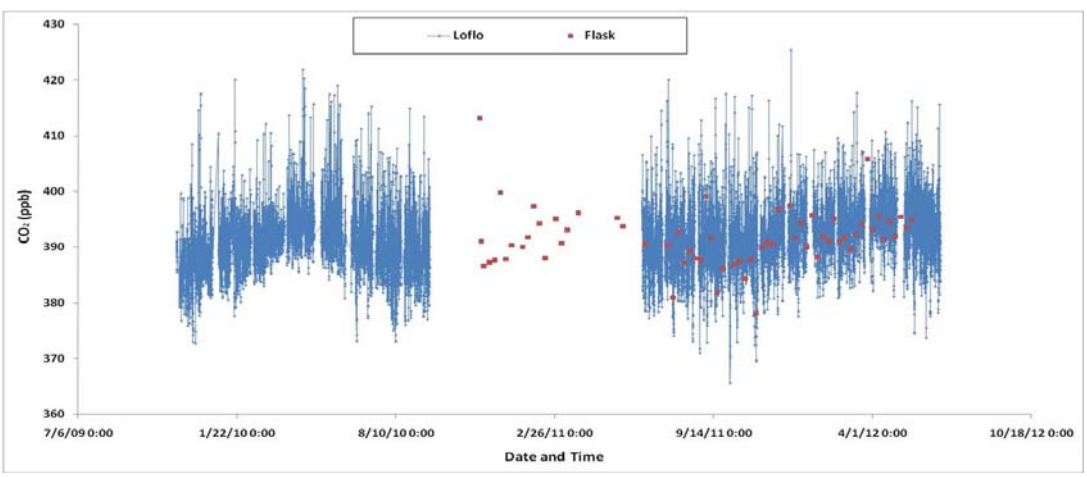


Figure 7(a). CO_2 concentrations measured using LoFlo Analyzer and Flask Sampling

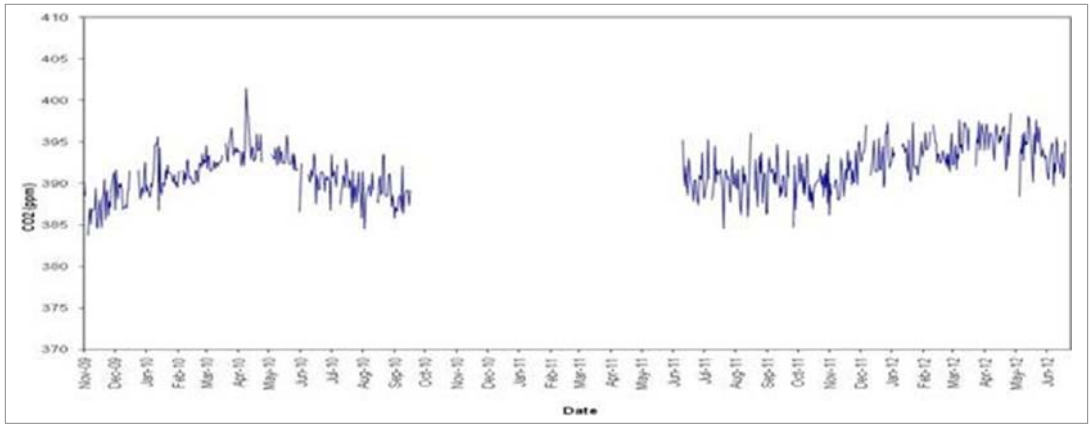


Figure 7(b). The daily average CO_2 measured using LoFlo Analyzer

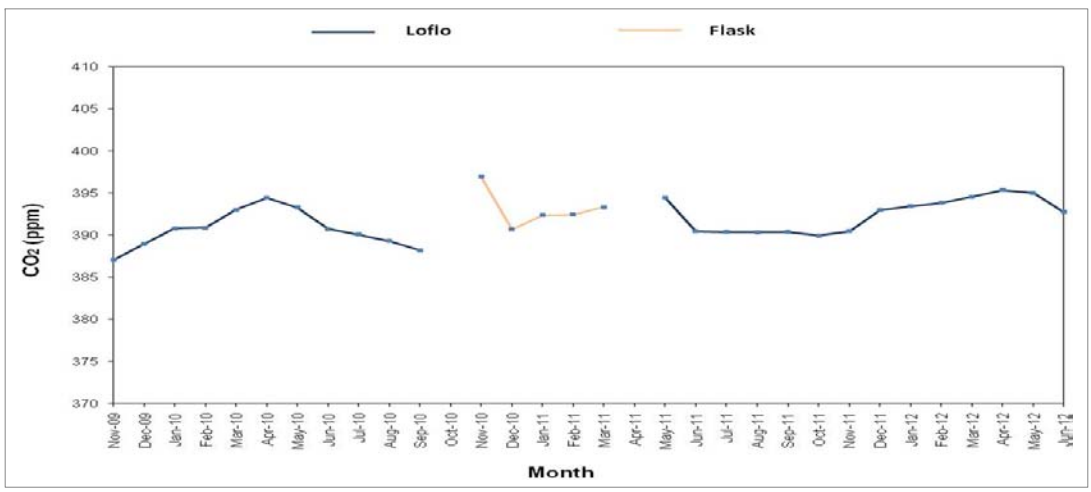


Figure 7(c). The monthly average CO_2 measured using LoFlo Analyzer and Flask Sampling

Fig. 8, 9 and 10 showed the time series analysis of CH_4, N_2O and SF_6. The concentrations of these three GHG, namely CH_4 (1792.35 – 1942.50 ppb), N_2O (322.5 – 326.53 ppb) and SF_6 (6.99 – 7.99 ppt) are comparable with the range of the global average values as issued by the 2010 WMO-GAW Greenhouse Bulletin.

Carbon monoxide (CO) is not a greenhouse gas itself but influences the mole fractions of greenhouse gases by affecting hydroxyl radicals. The CO concentrations in Danum Valley ranged between 73.5 to 207.4 ppb (refer Fig. 11).

The monthly average of N_2O, SF_6, CH_4 and CO is shown in Fig. 12(a) and 12(b). The N_2O and SF_6 shows similar increasing trend whereas CH_4 and CO fluctuates throughout the period from November 2010 to May 2012.

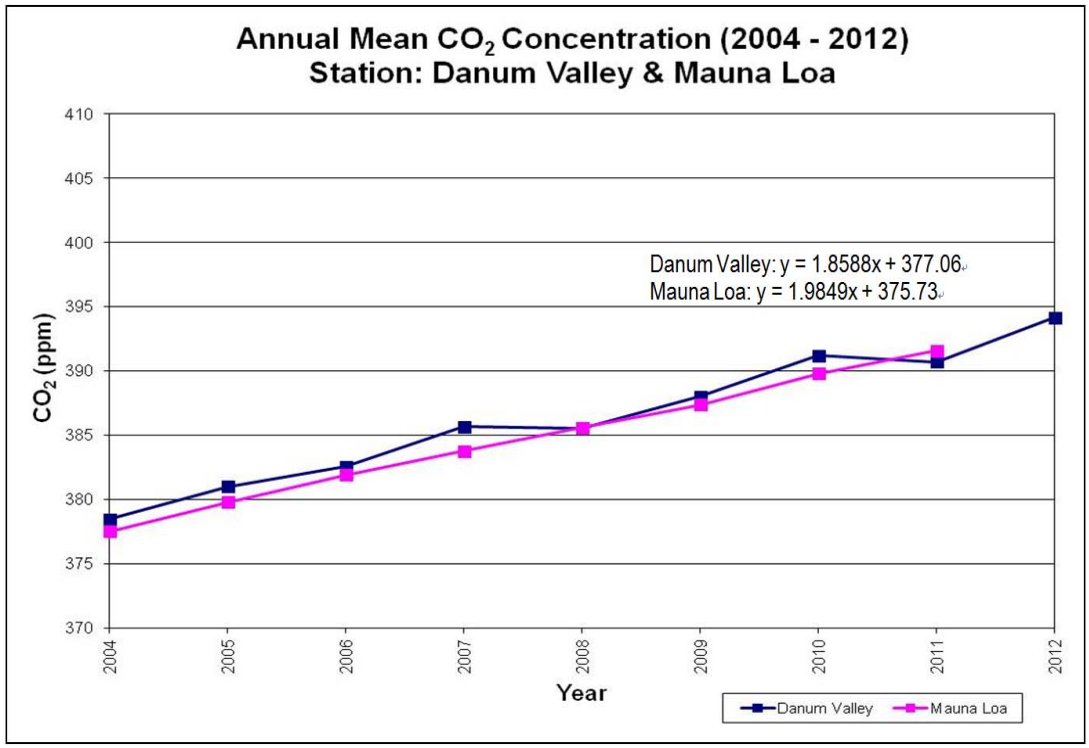


Figure 7(d). The annual average of CO_2 recorded at Danum Valley and Mauna Loa GAW stations

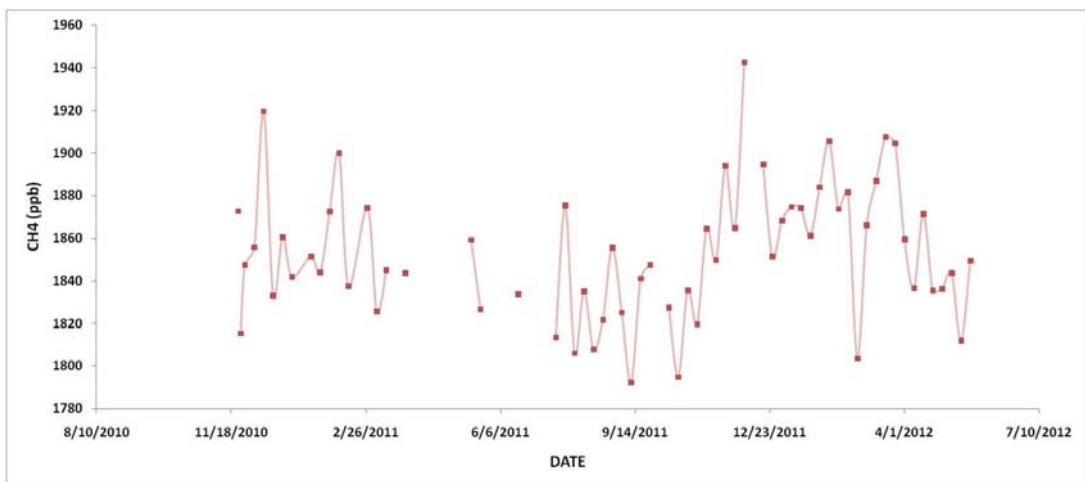


Figure 8. The weekly CH_4 concentrations at Danum Valley GAW Station (Nov 2010 – May 2012)

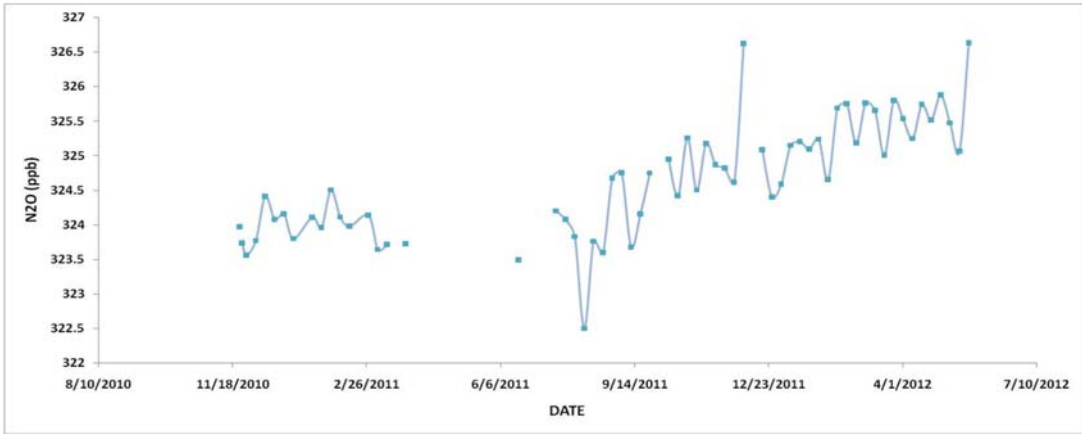


Figure 9. The weekly N_2O concentrations at Danum Valley GAW Station (Nov 2010 – May 2012)

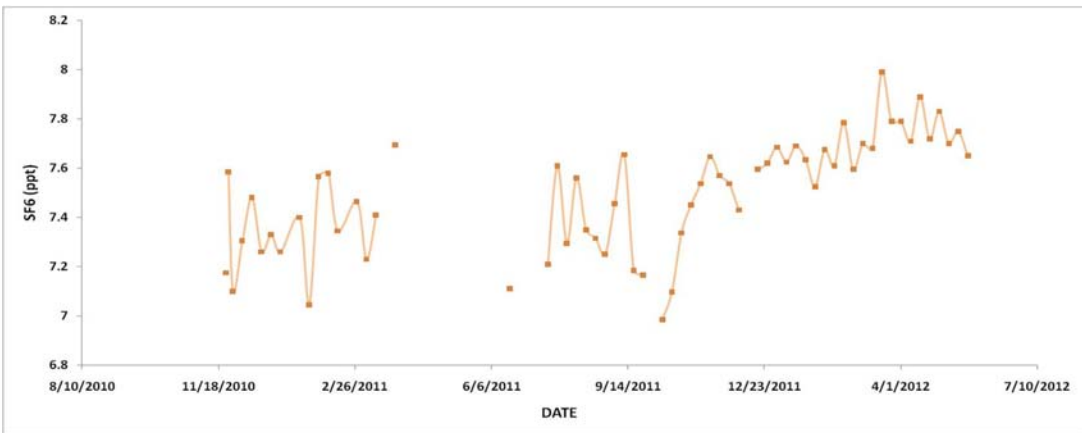


Figure 10. The weekly SF_6 concentrations at Danum Valley GAW Station (Nov 2010 – May 2012)

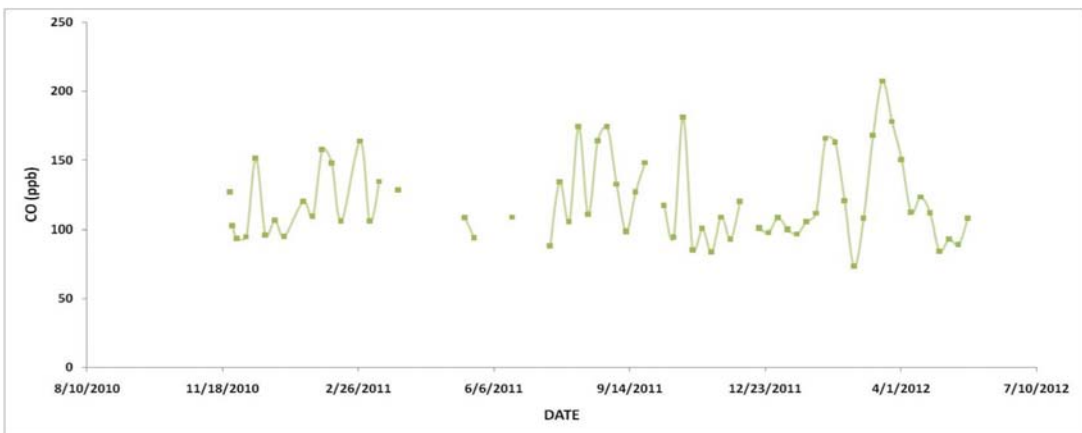


Figure 11. The CO concentrations at Danum Valley GAW Station (Nov 2010 – May 2012)

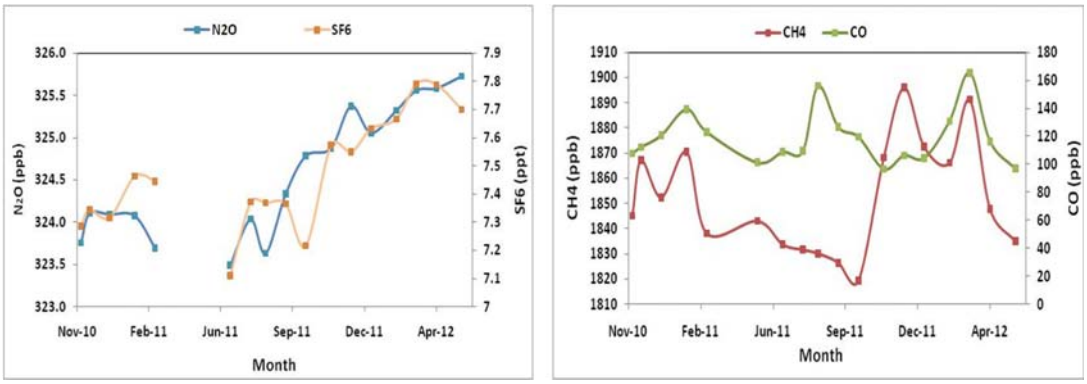


Figure 12. Monthly average concentrations for: (a) N_2O and SF_6; (b) CH_4 and CO

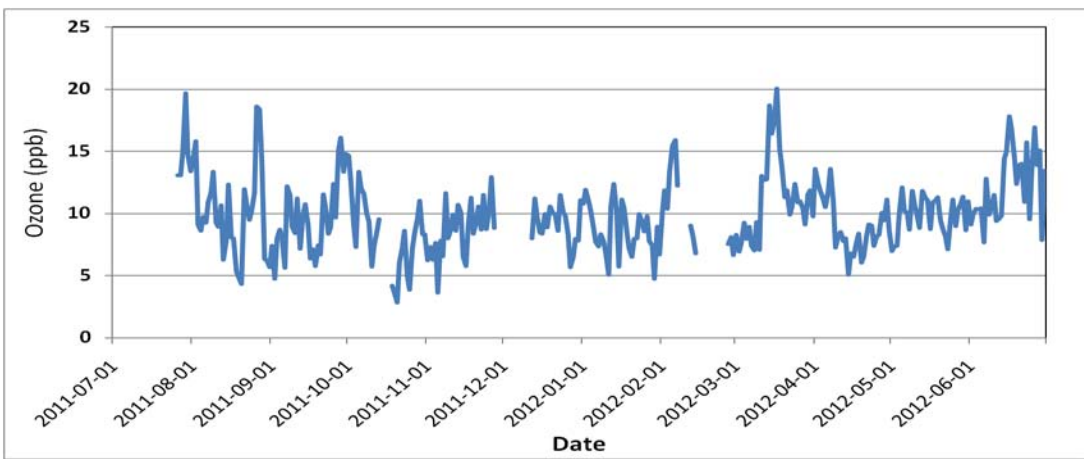


Figure 13(a). The daily average O_3 concentrations at Danum Valley GAW Station (July 2011 – June 2012)

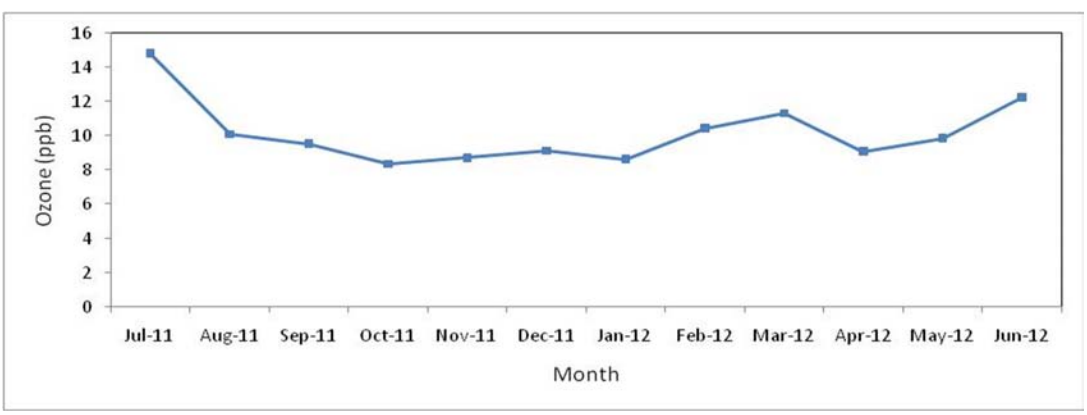


Figure 13(b). The monthly average O_3 concentrations at Danum Valley GAW Station (July 2011 – June 2012)

Surface ozone plays an important role in physical, chemical and radiative process in the troposphere and also contributes to the greenhouse effect. Surface ozone in Danum Valley is measured using the THERMO 49*i* UV Ozone Analyzer. As shown in Fig. 13(a) and 13(b), the daily average and monthly average of ozone concentration recorded from July 2011 – June 2012 are ranged from 2.8 – 20.1 ppb and 8.3 – 14.8 ppb respectively.

From the time series analysis, what is quite evident is that most of the GHG and reactive gases are showing slight increasing trend except for CH_4 and CO and is quite comparable with the global trend. This trend could be contributed to the anthropogenic activities but due to a strict control and enforcement by the Malaysian Government the increment is not that substantial.

Since GHGs are closely linked to anthropogenic activities and have strong interactions with the biosphere and the oceans, thus the GHG measurement program at Danum Valley GAW Station is an important program for background measurement in the tropics and for understanding the critical tropical processes that impact global atmospheric GHG distribution especially in the Southeast Asia region.

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