



The Joint workshop of the 6th Asia-Pacific GAW on GHGs/ the 5th WMO GAW Experts on VOCs

Oct. 20-22, 2014 / Daejeon, Republic of Korea
Hosted by **KMA, KRISS and WMO GAW**



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The 6th Asia-Pacific GAW Workshop on Greenhouse Gases

Program

20 Oct (Monday)	
9:00~10:00	Registration
10:00~12:00	Opening speech (10 mins) <ul style="list-style-type: none"> • Hee-Dong Yoo, Director Genral of Climate Scienc Bureau/KMA
	Welcome speech (10 mins) <ul style="list-style-type: none"> • Jin-Seog Kim, Vice President of KRISS
	Photo time (10 mins)
10:00~12:00	Keynote speech (each 30 mins) <ul style="list-style-type: none"> • Oksana Tarasova (WMO AER/RES Chief) Title: Global Atmosphere Watch Programme: 25 years of global atmospheric composition observations and analysis • Ed Dlugokencky (WMO GAW SAG Chairman on GHGs, NOAA, USA) Title: Observational Constraints on the Global Methane Budget • Ally Lewis (WMO GAW SAG on VOCs, University of York, UK) Title: Progress towards creating a VOC capcability within WMO-GAW
12:00~13:00	Lunch
13:00~15:00	Session 1 GHGs monitoring activities in Asia-Pacific regions (Chair: Marcel van der Schoot) (each 20 mins) <ul style="list-style-type: none"> • GAW Activities in Korea, Chulkyu Lee(KMA, Korea) • The 6th WMO/IAEA Round Robin Comparison Experiment & Outline of the China Greenhouse Gas Bulletin, Lingxi Zhou(CAMS/CMA, China) • A new JMA program of operational aircraft observation for atmospheric CO₂, CH₄, CO and N₂O in the mid-troposphere, Masaomi Takahashi(JMA, Japan) • Influence of monsoons on atmospheric CO₂ spatial variability and ground-based monitoring over India, Yogesh K. Tiwari(India Institue of Tropical Meteorology, India) • A decade of greenhouse gas monitoring activity at the Global GAW Station Bukit Kototabang, Indonesia, Alberth C. Nahas(Global Atmosphere Watch Station Bukit Kototabang, Indonesia) • An Introduction to a New S. E. Asian Monitoring Station in Malaysia for Regional and Local Observations: The Universiti Malaya Bachok Atmospheric Research Laboratory, M. I. Mead(University of Malaya, Malaysia)
15:00~15:30	Coffee breaks
15:30~17:30	Session 2 GHGs monitoring activities in Asia-Pacific regions (Chair: Chulkyu Lee) (each 20 mins) <ul style="list-style-type: none"> • Evaluation of new technology in-situ greenhouse gas analyzers for CSIRO Atmospheric Observation Network, Marcel van der Schoot(CSIRO, Austrailia) • Introduction of greenhouse gases in Viet Nam, Trinh Lan Phuong(NHMS, Viet Nam) • Characteristics and EEMD analysis of CO₂ and CH₄ at Lulin Atmospheric Background Station (LABS), Taiwan, Chang-Feng Ou-Yang(National Central University, Taiwan) • Comparison of instruments for atmospheric CO₂ observations at Baring Head, New Zealand, Gordon Brailsford(NIWA, New Zealand) • A brief introduction to the UK GAUGE and MAMM projects (University of Manchester, UK) • Intoriduction of Anmyeondo FTS station as a New TCCON site, Taeyoung Goo(NIMR/KMA, Korea)
18:00~21:00	Banquet (Hotel)

Program

21 Oct (Tuesday)	
8:30-9:00	Coffee break
9:00-10:20	<p>Session 3 WCC activities (Chair: Ed J. Dlugokencky) (each 20 mins)</p> <ul style="list-style-type: none"> • Why standard gases? : WCC-SF₆ activities at the AMY station in Korea, Haeyoung Lee(KMA, Korea) • Toward improving precision of SF₆ measurement: comparison of various analytical methods using GC-ECD, Jeong-Sik Lim(KRISS, Korea) • The challenge of achieving Data Quality Objectives in the WMO-GAW N₂O network, Rainer Steinbrecher(KIT, Germany) • Recent Developments at the World Calibration Centre WCC-Empa, Christoph Zellweger(EMPA, Switzerland)
10:20-12:00	<p>Session 4 Data QA/QC and its application (Chair: Hiroshi Koide) (each 20 mins)</p> <ul style="list-style-type: none"> • Quality Control and Quality Assurance from WDCGG viewpoint, Hiroshi Koide(JMA, Japan) • A Statistical Approach for the Background CO₂ Concentration Measurement at the Korea GAW Center, Young-Seop Lee(Dongguk University, Korea) • A new statistical method for determining regional baseline concentrations of atmospheric trace gases, Sun-Young Park(Kyungpook National University) • Asian greenhouse gases budget assessment, Prabir K. Patra(JAMSTEC, Japan) • Carbon Tracker-Asia: A tool to quantify CO₂ uptake/release, Chun-Ho Cho(NIMR/KMA, Korea)
12:00-13:00	Lunch
13:00-18:00	Discussion session

22 Oct (Wednesday)	
9:00-11:00	KRISS Lab tour
11:00-12:00	Lunch
12:00-14:00	KRISS to KGAWC(Bus)
14:00-16:00	Technical tour in KAGWC(Anmyeondo station)
14:00-16:00	KGAWC to Hotel(Bus)

The 5th WMO GAW Experts workshop on VOCs

Program

20 Oct (Monday)	
9:00-10:00	Registration
10:00-12:00	Opening speech (10 mins) <ul style="list-style-type: none"> • Hee-Dong Yoo, Director Genral of Climate Scienc Bureau/KMA
	Welcome speech (10 mins) <ul style="list-style-type: none"> • Jin-Seog Kim, Vice President of KRISS
	Photo time (10 mins) Keynote speech (each 30 mins) <ul style="list-style-type: none"> • Oksana Tarasova (WMO AER/RES Chief) Title: Global Atmosphere Watch Programme: 25 years of global atmospheric composition observations and analysis • Ed Dlugokencky (WMO GAW SAG Chairman on GHGs, NOAA, USA) Title: Observational Constraints on the Global Methane Budget • Ally Lewis (WMO GAW SAG on VOCs, University of York, UK) Title: Progress towards creating a VOC capcability within WMO-GAW
12:00-13:00	Lunch
Session 1. Observations and analysis (Chair: O. Tarasova)	
13:00-13:20	<ul style="list-style-type: none"> • Twenty years of VOC monitoring in EMEP(Kjetil Torseth, NILU)
13:20-13:40	<ul style="list-style-type: none"> • A seven-year (2006-2013) record of non-methane hydrocarbons (NMHCs) in the subtropical marine boundary layer at the Cape Verde Atmospheric Observatory(Ally.C. Lewis, Uni York)
13:40-14:00	<ul style="list-style-type: none"> • Further developments in background VOC monitoring at CSIRO Marine and Atmospheric Research(Ian Galbally, CSIRO)
14:00-14:20	<ul style="list-style-type: none"> • Ten Year Anniversary of the Global Atmospheric Volatile Organic Compound Network(Detlev Helmig, INSTAAR)
14:20-14:40	<ul style="list-style-type: none"> • Analysis of 10 Years online C₂-C₁₁ NMHC Measurements close to the Gulf of Mexico(Bernhard Rappenglück, University of Houston)
14:40-15:00	<ul style="list-style-type: none"> • Field observations of anthropogenic and natural VOCs in East Asia by PTR-MS(Hiroshi Tanimoto, NIES)
15:00-15:30	Coffee breaks
15:30-15:50	<ul style="list-style-type: none"> • Global Network Volatile Organic Compound Data for Evaluation of Impacts of Oil and Gas Development (Detlev Helmig, INSTAAR)
Session 2. Quality Assurance (Chair: Detlev Helmig)	
15:50-16:20	<ul style="list-style-type: none"> • VOC Measurement Guidelines – from ACTRIS Drafts to GAW Recommendations(Stefan Reimann, EMPA)
16:20-17:30	<ul style="list-style-type: none"> • Discussion on the VOC MGs
17:30-18:00	Move to Hotel
18:00-21:00	Banquet (Hotel)

Program

21 Oct (Tuesday)	
8:30-9:00	Coffee break
Session 3. GAS standards (Chair: Christian Plass-Dulmer)	
9:00-9:20	<ul style="list-style-type: none"> Review and progress on standards for the measurements of biogenic and anthropogenic VOCs in the atmosphere(Marivon Corbel, NPL)
9:20-9:40	<ul style="list-style-type: none"> Monoterpene Gas Standard Developments at NIST(Jerry Rhoderick, NIST)
9:40-10:00	<ul style="list-style-type: none"> Development of Standard Gas Mixtures for Dimethyl Sulfide (DMS) and Acetonitrile at KRISS(Sangil Lee, KRISS)
10:00-10:20	<ul style="list-style-type: none"> Progress on both dynamic and static formaldehyde standards at the $\mu\text{mol mol}^{-1}$ level(Joele Viallon, BIPM)
10:20-10:40	<ul style="list-style-type: none"> KEY-VOCs project: Metrology for VOC indicators for air pollution and climate change(Annarita Baldan, VSL)
10:40-11:00	Discussion : need for VOC gas standards in GAW(Review of the gas standards table)
Session 4. Quality Assurance part 2 (Chair: Stefan Reimann)	
11:00-11:20	<ul style="list-style-type: none"> The challenge of preparing ambient air standards for calibrating VOC analysis systems(Rainer Steinbrecher, KIT)
11:20-11:40	<ul style="list-style-type: none"> VOC Round-Robin Exercise for VOCs in the framework of the European Infrastructure project ACTRIS – results and suggestions for implementation(Stefan Reimann, EMPA)
11:40-12:00	<ul style="list-style-type: none"> Side-by-side Intercomparison for OVOC in the framework of ACTRIS(Christian Plass-Dulmer, DWD)
12:00-13:00	Lunch
13:00-15:00	General Discussion session(including further discussions on Measurement Guidelines) (Chair Ally Lewis)
15:00-16:00	Coffee break
16:00-18:00	No official schedule (buffer)
18:00-20:00	Dinner (restaurant next to hotel)

22 Oct (Wednesday)	
9:00-11:00	KRISS Lab tour
11:00-12:00	Lunch
12:00-14:00	KRISS to KGAWC(Bus)
14:00-16:00	Technical tour in AMY station
16:00-18:00	AMY to Hotel(Bus)

The 6th
Asia-Pacific
GAW Workshop on
Greenhouse Gases

Observational Constraints on the Global Methane Budget

Ed Dlugokencky*, Andrew Croftwell, Patricia Lang, Ken Masarie

NOAA Earth System Research Laboratory, Global Monitoring Division

The atmospheric burden of CH₄ has increased by a factor of 2.5 since 1750, contributing 0.5 W m⁻² to total radiative forcing by long-lived greenhouse gases (2.90 W m⁻² in 2013), while its atmospheric chemistry affects background air quality and contributes an additional ~0.2 W m⁻² indirect forcing through production of tropospheric O₃ and stratospheric H₂O. Because atmospheric CH₄ has a relatively short life time, ~9 yr, reducing its emissions is considered a potential approach to slowing the rate of increasing radiative forcing. In fact, reductions in emissions from many anthropogenic sources would be cost-effective. But, the effectiveness of emissions mitigation may be over-estimated by bottom-up inventories, so emission reductions must be verified through atmospheric observations. Also, reductions in anthropogenic emissions may be canceled by increased emissions from natural sources such as Arctic wetlands as they respond to changing climate.

NOAA has been measuring the global distribution of atmospheric CH₄ since 1983. The data provide important constraints on methane's global budget and how it is changing with time. An observed decrease in CH₄ growth rate from 1983 to 2006 suggests that, if the CH₄ lifetime has been approximately constant, then atmospheric CH₄ is approaching steady state with no long-term trend in total global emissions through 2006. Super-imposed on this long-term picture is significant interannual variability in CH₄ growth rate, including an increasing atmospheric CH₄ burden since 2007. Inherent in the spatial patterns of this variability is information about processes that emit or destroy CH₄. In this presentation, I will review some key findings determined from NOAA CH₄ measurements with particular focus on the renewed increase in atmospheric CH₄ since 2007 and the potential contribution of climate feedbacks in the Arctic. While this presentation is focusses on NOAA data, it will emphasize the importance of long-term in situ measurements by GAW partners in constraining the CH₄ budget at global and regional scales.

GAW Activities in Korea

Chulkyu Lee, Bok-Haeng Heo, Homan Lee, Haeyoung Lee, Heejong Yoo, Sangsup Park, Jegyu Yu, Yungseok Yoo, Hyuk-Je Lee, Dong-Bong Yu, Tawgyun Jeong, Han-Cheol Lim, Hongwoo Choi, Eunsil Kim, Seyoung Moon, Miyoung Ko

Korea Global Atmosphere Watch Center, Korea Meteorological Administration, Republic of Korea

Korea Meteorological Administration (KMA) operates three main measurement stations, which are located in the west (at Anmyeon), south (at Gosan), and east (at Ulleungdo) of Korea, in aim of monitoring of transportation of the atmospheric substances and variation in the atmospheric composition over the Korean Peninsula. It also has the auxiliary stations at Seoul, Pohang, Gwangju, Mokpo, Uljin, Gangneung, and Jeju to collect more specific data, e.g. radioactivity (Radon), ozone sonde, and UV. From the measurement stations, KMA collects and provides reliable scientific data and information on the chemical composition of the atmosphere, its natural and anthropogenic change to help improve the understanding on climate change. KMA collects the atmospheric observation data of 37 components in the fields of greenhouse gases, aerosols, reactive gases, ozone, atmospheric radiation including ultraviolet (UV) radiation, and precipitation chemistry in the Korean Peninsula, in accordance with the measurement recommendations of the Global Atmosphere Watch (GAW) program. In the fields of greenhouse gases, the abundance of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbons (CFCs), and sulfur hexafluoride (SF₆) has been measured with high accuracy and precision. Physical, chemical, and optical characteristics of aerosols, widely acknowledged as one of the most significant and uncertain aspects of climate change projections, have been measured with in-situ instruments, including their vertical profiles retrieved using a ground-based LIDAR. The reactive gases such as carbon monoxide (CO), surface ozone (O₃), nitrogen oxides (NO_x), and sulfur dioxide (SO₂) have been measured because the compounds play a role in the chemistry of the atmosphere and the formation of aerosols. Regarding to the stratospheric ozone, total column ozone is measured using the Brewer spectrometers, together with UV and solar and terrestrial radiation. Precipitation chemistry observations focus on the acidity, conductivity, and major 9 ions. New parameters and methodologies are also secured and applied, e.g. greenhouse gas isotopes, aerosol chemical species, and volatile organic compounds (VOCs). To enhance the effectiveness and application of the long-term measurements within GAW, KMA cooperates with the atmospheric measurement networks worldwide along with focusing on the quality assurance and control. World Calibration Center for SF₆ (WCC-SF₆) was designated to be established in KMA in 2012, and has been operated since 2013. WCC-SF₆ conducts the missions for the traceability and compatibility of the SF₆ measurement for the GAW stations. The Asia-Pacific GAW Workshop on Greenhouse Gases has annually been held by KMA since 2009. It provides a good opportunity to share our knowledge on greenhouse gases measurements in the Asia and Pacific region.

The 6th WMO/IAEA Round Robin Comparison Experiment & Outline of the China Greenhouse Gas Bulletin

Lingxi Zhou^{1*}, Pieter Tans², Duane Kitzis², Ken Masarie², James Butler²,
Shuangxi Fang¹, Lixin Liu¹, Bo Yao¹, Gen Zhang¹, and Siyang Cheng¹

¹*Chinese Academy of Meteorological Sciences, China Meteorological Administration*

²*NOAA Earth System Research Laboratory, Boulder, Colorado, USA*

The primary goal of the WMO/IAEA Round Robin Comparison Experiment is to assess the level to which participating laboratories maintain their link to the WMO mole fraction scales using normal operating procedures. Maintaining a direct link to the WMO/IAEA scales and successfully propagating the scales to working laboratory scales are fundamental to the measurement process. The primary focus of the Round Robin experiment is comparison of CO₂ scales. Many participating labs are also able to make measurements of other greenhouse gas and related tracers including CH₄, CO, H₂, N₂O, SF₆, O₂/N₂, and δ¹³C and δ¹⁸O of CO₂. Participating labs are encouraged to make these additional measurements provided the effort does not extend beyond the allotted time. Results from the periodic Round Robin experiments have proven useful to understanding the cause(s) when measurement differences between laboratories are observed. A WMO/CCL is responsible for maintaining and distributing the WMO Mole Fraction scale for a specified gas in air. NOAA/ESRL/GMD in the USA is the WMO CCL for CO₂, CH₄, N₂O, SF₆, and CO. MPI-BGC laboratory in Jena Germany is the CCL for H₂ and for the stable isotopes of CO₂. The 6th Round Robin is currently underway [started: January 2014] <http://www.esrl.noaa.gov/gmd/ccgg/wmorr>.

Since the 1980s, the China Meteorological Administration has put in place seven atmospheric background stations-Waliguan in Qinghai (WLG), Shangdianzi in Beijing (SDZ), Lin'an in Zhejiang (LAN), Longfengshan in Heilongjiang (LFS), Shangri-La in Yunnan (XGL), Jinsha in Hubei (JSA) and Akedala in Xinjiang (AKD), which represent a number of typical climatic, ecological and economic zones in China. GHGs and related tracers have been observed by network stations in a standard and consistent routine. In particular, the WLG GAW Global station has engaged in flask air sampling analysis since 1990 and in-situ observation since 1994, in collaboration with international colleagues. The greater than 20-year history of observations has yielded the longest time series of atmospheric CO₂ and CH₄ mixing ratio records in China. The flask air sampling analysis and the in-situ observations were launched from other background stations beginning in 2006. Echo to the WMO Greenhouse Gas Bulletin No.8 (2012), No.9 (2013) and No.10 (2014 Climate Summit Edition), the CMA is responsible for the China Greenhouse Gas Bulletin No.1 (2012), No.2 (2013) and No.3 (2014) based on observational datasets that are traceable to the World Reference Scales. These scientifically defensible data sets are produced with an approach consistent with WMO guidelines and recognized QA/QC procedures (They are regularly updated and periodically revised by small amounts should the international calibration scales be adjusted).

A new JMA program of operational aircraft observation for atmospheric CO₂, CH₄, CO and N₂O in the mid-troposphere

Masaomi Takahashi^{1*}, Yuji Esaki¹, Yukio Fukuyama¹, Shinya Takatsuji¹, Hiroaki Fujiwara¹, Tomoki Okuda¹, Kohshiro Dehara¹, Yoki Mori¹, Hidekazu Matsueda², Yousuke Sawa², Kazuhiro Tsuboi², Yosuke Niwa²

¹*Japan Meteorological Agency*

²*Meteorological Research Institute*

In order to better understand the spatial and temporal variations of the greenhouse gas fluxes in Asia and their contributions to the global carbon cycle, the Japan Meteorological Agency (JMA) has carried out an operational aircraft observation as a new atmospheric monitoring activity since 2011.

By using a cargo aircraft which flies from the suburbs of Tokyo to Minamitorishima once a month, flask samplings are conducted during a cruising section at about 6 km over the western North Pacific as well as during a descending section to Minamitorishima. After a flight, mole fractions of four trace gases (CO₂, CH₄, CO and N₂O) in the flasks are measured at the JMA headquarters in Tokyo. An automated measurement system was newly developed by a collaborative work of Meteorological Research Institute and JMA to achieve high-precision measurements for all trace gases. This system consists of the following four analyzers: NDIR analyzer (LI-COR, LI-7000) for CO₂, CRDS analyzer (Picarro, G2301) for CH₄, VURF analyzer (Aero-Laser, AL5002-AIR) for CO and off-axis ICOS analyzer (Los Gatos, DLT100) for N₂O. The traceability of measurements to the WMO mole fraction scale for each trace gas is ensured because the multi-species working standard gases used for the aircraft sample measurements are calibrated by the JMA primary standard gases, of which scales are propagated from the NOAA/CCL.

Over Minamitorishima, the observation results showed that the CH₄ vertical profile varied seasonally. Specifically, the CH₄ mole fraction decreases with the increase of altitude during winter–spring, but it increases as the altitude increase during summer–autumn. This result strongly suggests that the air masses of the Asian continental outflows over the western North Pacific were influenced by anthropogenic emissions in winter-spring, while by increased biogenic sources such as rice paddies and wetlands in summer-autumn.

In the presentation, the outline of the JMA aircraft observation and its unique observed results will be introduced.

Influence of monsoons on atmospheric CO₂ spatial variability and ground-based monitoring over India

Yogesh K. Tiwari^{1*}, Ramesh K. Vellore¹, Ravi Kumar², Marcel van der Schoot³, Chun-Ho Cho⁴

¹ *Centre for Climate Change Research, Indian Institute of Tropical Meteorology*

² *Centre for Climate Change Research, Indian Institute of Tropical Meteorology, Pune, India*

³ *Centre for Australian Weather and Climate Research, CSIRO Marine & Atmospheric Research*

⁴ *National Institute of Meteorological Research*

This study examines the role of Asian monsoons on transport and spatial variability of atmospheric CO₂ over the Indian subcontinent, using transport modeling tools and available surface observations from two atmospheric CO₂ monitoring sites Sinhagad (SNG) and Cape Rama (CRI) in the western part of peninsular India. The regional source contributions to these sites arise from the horizontal flow in conduits within the planetary boundary layer. Greater CO₂ variability, greater than 15 ppm, is observed during winter while it is reduced nearly by half during summer. The SNG air sampling site is more susceptible to narrow regional terrestrial fluxes transported from the Indo-Gangetic Plains in January, and to wider upwind marine source regions from the Arabian Sea in July. The Western Ghats mountains appears to play a role in the seasonal variability at SNG by trapping polluted air masses associated with weak monsoonal winds. A Lagrangian back-trajectory analysis further suggests that the horizontal extent of regional sensitivity increases from north to south over the Indian subcontinent in January (Boreal winter).

A decade of greenhouse gas monitoring activity at the Global GAW Station Bukit Kototabang, Indonesia

Alberth C. Nahas

Global GAW Station Bukit Kototabang, BMKG

As of the end of 2013, the greenhouse gas monitoring activity at the GAW Station Bukit Kototabang has reached a ten-year period of observation. During the course of this period, mole fractions of the three major greenhouse gases, CO₂, CH₄ and N₂O, have indicated an incremental trend by 6.2%, 1.8% and 2.5%, respectively. These increasing percentages, however, are overwhelmingly surpassed by a 51.5% rise of SF₆ mole fractions, indicating the fastest growth of all greenhouse gases.

Meanwhile, all gases have reached the newest highs in 2013, with the annual mole fractions of CO₂ at 392.1 ppm, CH₄ at 1839.3 ppb, N₂O at 327.1 ppb and SF₆ at 8.2 ppt. Moreover, last year is also marked by the highest increase of year-on-year CO₂ mole fractions; between the period of 2012 and 2013, CO₂ has increased by 1.7%, which is slightly more than four times larger than its annually averaged growth rate during the period 2004-2012. This significance increase can be related to extensive peat and forest fire episodes over a number of areas in Sumatra, occurred in February-March and in June-August 2013. It has been suggested that besides the health and environmental impacts, wildfires also contributed to a considerable amount of CO₂ emissions, which can be counted for a massive release of the gas in a short period.

References

- [1] Langmann, Barbel. "The Impact of Vegetation and Peat Fire Emissions in Indonesia on Air Pollution and Global Climate." *Asian Journal of Water, Environment and Pollution* 11.1 (2014): 3-11.
- [2] Marlier, Miriam E., et al. "Future fire emissions associated with projected land use change in Sumatra." *Global change biology* (2014).
- [3] Vadrevu, Krishna Prasad, et al. "Analysis of Southeast Asian pollution episode during June 2013 using satellite remote sensing datasets." *Environmental Pollution* (2014).

An Introduction to a New S. E. Asian Monitoring Station in Malaysia for Regional and Local Observations: The Universiti Malaya Bachok Atmospheric Research Laboratory

M. I. Mead^{1,2}, P. Siew Moi², A. Abu Samah^{2,3}, W. Sturges⁴, D. Oram^{4,5}, G. Forster^{4,5}, B. Bandy⁴, C. Reeves⁴, A. Manning⁴, N. Harris⁶, A. Robinson⁶, J. Pyle^{6,5}, J. Hamilton⁷, R. Holmes⁷, R Lister⁷, E Nisbet⁸, R Brownlow⁸, M. T. Latif⁹, K. Kreher^{10,11}, P. Johnston¹¹, M. Vanderschoot¹²

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⁴ *Centre for Ocean and Atmospheric Sciences (COAS). University of East Anglia. Norwich. UK*

⁵ *National Centre for Atmospheric Sciences (NCAS). UK.*

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¹¹ *Bodeker Scientific. Otago. New Zealand*

¹² *Commonwealth Scientific and Industrial Research Organisation (CSIRO). Melbourne. Australia.*

A new atmospheric research station has been developed by the Institute of Ocean and Earth Sciences (IOES, Universiti Malaya), located on the East coast of peninsular Malaysia. The station is on the South China Sea and has the potential to provide information on both local and regional atmospheric composition.

The Bachok tower station was developed in 2014 and incorporates instrumentation to provide information on atmospheric composition, pollutant transport, land-sea exchange processes and local meteorology. The instrument suite at the station is focused on selected key areas and incorporates instrumentation for the measurement of trace pollutants, greenhouse gas species, aerosol and meteorological parameters. The site aims to help investigate both transport and emissions of key climate and pollutant species in tropical South East Asia as well as help to better constrain flow of these species into and out of this under analysed but globally important region.

In January/February 2014 the observational program at the station was initiated with a month long demonstration activity with partners from Malaysia, UK Universities, UK NCAS, CSIRO and NIWA. Instrumentation was deployed for an intensive observational program over this period which included parameters such as O₃, NO_x, SO₂, CO, H₂, CO₂, CH₄, VOCs, OVOCs, HCHO, selected halocarbons and δ¹³CH₄. This activity was coincident with the dry period at the end of the Asian winter monsoon to investigate local emissions as well as regional scale transport associated with the “Tropical Cold Surge” phenomenon (potential rapid outflow from seasonal Siberian high pressure systems into Southern Asia with associated transport of anthropogenically polluted, processed air from China and the Indochinese peninsula into areas of dominantly biogenic emissions or into clean background regions).

This activity demonstrated the potential of the site for both targeted campaigns as well as long term observational programs based on global chemistry-climate interactions and transport in the heterogeneous and source rich, dynamically variable, tropical Asian environment.

Evaluation of New Technology in-situ Greenhouse Gas Analyzers for CSIRO Atmospheric Observation Network

Marcel van der Schoot*, Darren Spencer

CSIRO

CSIRO is continuing to expand the Australian Greenhouse Gas Observation Network (AGGON), an important Southern Hemisphere observation capability in the WMO/GAW global network. The Cape Grim Baseline Air Pollution Station (CGBAPS) is the hub of AGGON, acting as the central reference observation site.

In addition to an expanding terrestrial observing network, Australia now has a new purpose-built Marine National Facility research vessel, the “RV Investigator”, with a purpose-built atmospheric research capability, previously not available to the Australian research community. This capability also offers a unique opportunity for international collaborators to engage with Australian collaborators to conduct atmospheric research related to the Southern Hemisphere oceans and coastal regions, including Asian tropical oceanic regions.

In this presentation results from the current state of instrumental evaluation (for greenhouse gases), in addition to the key operational, instrumental and calibration strategies for this expanding Australian atmospheric research capability will be discussed.

In addition, developments at the Australian pilot tropical atmospheric observation site established at Gunn Point in Australia’s Northern Territory (12.249S, 131.045E, elevation 25 metres) will also be presented, with a recent successfully completed early dry season biomass burning measurement campaign being completed in June/July 2014. This site incorporates high precision in-situ measurement and flask air sample collection programs for a range of greenhouse gases (GHGs) and related trace gas species.

Introduction of Green House Gases in Viet Nam

Trinh Lan Phuong^{1*}, Duong Hoang Long²

¹ *National Hydro-Meteorological Service, Center for Hydro – Meteorological and Environment Station Network (HYMENET), NHMS, MONRE*

² *Science, Technology and International Cooperation Department, NHMS, MONRE*

Nowadays, the developing countries like Vietnam strike to implement sufficiently its role while participating in the Kyoto Protocol by specific activities: building a National Activities Program focusing on Climate change, building the Climate change scenarios for Viet Nam, implementing the National Greenhouse gases (GHGs) inventory programs.

The monitoring of meteorological, environmental factors and the greenhouse gases are located in the global climate monitoring, contributing to the deal with of weather forecasting, disaster warning, monitoring variables climate change and environmental protection.

Currently, the network of automatic air quality monitoring stations in Viet Nam includes 10 stations of the National Hydro-Meteorological Service (NHMS) of Viet Nam, 11 stations of Viet Nam Environment Administration (VEA) and Provincial Departments of Natural Resources and Environment. In addition, the Project: "Capacity Building and Twinning for Climate Observing Systems (CATCOS)" funded by the Swiss Agency for Development and Cooperation and coordinated by the Federal Office of Meteorology and Climatology MeteoSwiss is in charge of establishing greenhouse gas measurement capabilities in Viet Nam. The equipment was installed in collaboration with NHMS at Pha Din station (21.57degN, 103.52degE, 1466 m asl), a rural site in a hilly forested area in Northern Viet Nam. It enables the continuous in-situ ground-based observation of carbon dioxide, methane, carbon monoxide, water vapor and ozone next to the new monitoring of optical properties of aerosols. So far, Pha Din station was accepted as a GAW regional station by the World Meteorological Organization.

The presentation will give a comprehensive overview of the network of automatic air quality monitoring stations in Viet Nam especially introduction of new station Pha Din.

References

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Characteristics and EEMD analysis of CO₂ and CH₄ at Lulin Atmospheric Background Station (LABS), Taiwan

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As many efforts have indicated, the Asian Continental Outflow may significantly influence the regional air quality and atmospheric chemistry over the western Pacific, even as far as North America. Taiwan, situated on the rim of the East Asia, is at an ideal location to monitor the activities of biomass burning and anthropogenic air pollution coincided with air masses originating from the Southeast Asia and Asian continent. A high-elevation baseline station, Luling Atmospheric Background Station (LABS; 23.47°N, 120.87°E; 2,862 m a.s.l.), was therefore established to study the atmospheric behaviors and transport patterns in the lower free troposphere in April, 2006.

The measurements of greenhouse gases (GHGs), i.e. CO₂ and CH₄, were started at the LABS since 2011. An increasing trend of CO₂ and CH₄ was found during the past 3 years. The annual maxima and minima of CH₄ at LABS were observed in March and July, respectively, as well as other air pollutants such as CO and PM₁₀. The springtime maximum of these air pollutants was most likely caused by the long-range transport of air masses from Southeast Asia, where biomass-burning emission was intense in spring. In contrast, vegetation growth in spring drew down the CO₂ concentrations at LABS until late fall. In general, a daily minimum of CO₂ with a larger standard deviation was observed during daytime when photosynthesis was active. The diurnal patterns of CH₄, CO, and PM₁₀ were similar, which was presumably sculptured by the mountain-valley circulations at LABS. In this study, EEMD analysis (Ensemble Empirical Mode Decomposition, so-called Hilbert Huang transformation) was performed in order to resolve the respective intrinsic components of the two GHGs in the long-term measurements.

Comparison of instruments for atmospheric CO₂ observations at Baring Head, New Zealand

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NIWA

The observation of atmospheric carbon dioxide (CO₂) requires precise measurement of both air and calibrated reference gases. For the observations to inform and assist in quantifying natural and anthropogenic emissions a compatibility between laboratories in the Southern Hemisphere established by GAW guidelines is 0.05 ppm (WMO, 2014). The requirement for the comparison between instruments at the same site is greater than this and rigorous comparisons must be undertaken as new instruments are introduced to ensure the validity of the record at a site. NIWA have operated non-dispersive infra-red (NDIR) instrument (Siemens, Ultramat 3) at Baring Head for many years (Brailsford, Stephens et al. 2012) and are currently assessing the cavity ring down spectrometer (Picarro, G2301) to make the CO₂ measurements.

The two analysers have been in operation utilising the same air intake, and calibration gases. Analyses of the instrument responses are presented with comparison of known calibration gases, and whole air. Data rates from the instruments differ however the interpretations are conducted over the same time intervals. For the purposes of the comparisons to date, the larger cell, slower responding NDIR is used as the master instrument dictating the selection of gases and the determination of jog stability for both instruments. The effect of isotopic composition for the calibration gases is investigated in an attempt to understand small differences between the two instruments.

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Introduction of Anmyeondo FTS Station as a New TCCON Site

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The National Institute of Meteorological Research has operated a ground-based FTIR spectrometer (IFS-125HR) since December 2012. The IFS-125HR manufactured by the Bruker was installed at the Korea Global Atmosphere Watch Center at Anmyeondo. Instrument specification is almost same as the Total Carbon Column Observing Network (TCCON) configuration such as a spectrum range of 3,800~16,000 cm^{-1} , a resolution of 1 cm^{-1} , InGaAs and Si-Diode detectors and CaF_2 beamsplitter.

CO_2 retrieval algorithm which is the latest version of GGG released in 2012 was employed. Site-specific input data such as weather parameters (pressure, temperature, wind speed and wind direction) and surface pressure were used and model-related background information was based on NCEP reanalysis which has 17 layers from 1000 to 10 hPa. After cloud filtering to exclude the spectra contaminated by cloud, XCO_2 was retrieved and was validated against ground- and aircraft-based in-situ measurements using the Cavity Ring-Down Spectroscopy analyzer manufactured by Picarro.

The spectrum fitting indicator, %residual, shows a very good agreement between measured and simulated spectra in the range of -0.5 to 0.5. While the ground- and aircraft-based CO_2 measurement have very large variability as a function of time, FTS XCO_2 shows very stable time variation. Small XCO_2 variation is mainly due to the feature of XCO_2 based on total column density. In addition, it should be noted that XCO_2 retrievals of this work is at the preliminary stage and still need some corrections on airmass independency and in-situ measurement such as aircraft observation. It is also found that most XCO_2 retrievals show lower than in-situ measurement.

Acknowledgement

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Why standard gases? : WCC-SF₆ activities at the AMY station in Korea

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The main activity of World Calibration Center is focusing on the quality assurance through organizing comparison and training session, developing the measurement guidelines, providing training and workshops, and assessing the quality of data residing at the World Data Center. Especially, according to the GAW strategic plan for 2012 to 2015, the main task of WCC on greenhouse gases is the maintenance of a catalogue on the relationships between different measurement scales based on comparisons of standard gases from different laboratories.

Amyeondo (AMY) station, one of regional stations in Korea started monitoring of SF₆ from 2007. The air samples collected at AMY were used the standard gas having traceability to KRISS but it has been changed from KRISS to CCL/NOAA since 2013. For data continuity an inter-comparison experiment of standard gases was implemented between CCL and KRISS scale and the offset was 0.022 ppt indicating that it satisfied the extended goal, 0.05 ppt in 2013.

Historically AMY calibrated the GC-ECD for SF₆ with one point standard gas every 4 hours targeting background concentration. To demonstrate its quality assurance, the calibration methods with multi points, two points and one point were compared. The differences between those of two methods, multi - one point and multi - two points were 0.009 ppt (0.12%) and 0.005 ppt (0.06%) respectively indicating one point calibration is reasonable while standard gas is focusing on background concentration. However, when certified value of standard gas was differed from the level of the background concentration or targeting concentration, one point calibration showed a big bias through the result of 5th Round Robin Test which AMY attended with one point standard gas.

For the stations which have their own method to monitor the background SF₆ concentrations, WCC-SF₆ has a plan to suggest how to guarantee quality assurance with the guideline including various methods which are applicable back to in situ stations of SF₆ and technical education courses based on it from this year.

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Toward improving precision of SF₆ measurement: comparison of various analytical methods using GC-ECD

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Various GC analytical methods for SF₆ measurement using Gas Chromatography (GC) coupled with electron capture detector (ECD) will be introduced. Firstly, Activated Alumina F1 as a packing material of separation column was applied with oven temperature ramping. Since the retention time of atmospheric CFCs, which are also sensitive to the ECD detector, is later than SF₆, flushing those analytes staying in early part of the column was achieved in order to avoid peak interference in next injection. Though this method is simple, analytical precision shows less than 0.02%. Second is the heart-cutting and back flush method. Typically, in SF₆/air analysis, dominant injection peak caused by atmospheric O₂ strongly disturbs to separation of SF₆ from long O₂ tail in AA-F1 column. Also it is well known that the appearance of O₂ in detector unstabilizes the signal read-out regardless of the retention time. Therefore, fore-cutting of O₂ peak might help to increase the precision of SF₆ analysis. This is also amenable for N₂O analysis with Porapak Q column. The back flush of later CFCs during SF₆ stream propagation in column vanishes the arrival of CFCs to the detector in order for shortening analysis time, which is crucial to real time monitoring of atmospheric SF₆. Thirdly, preconcentrator was applied to GC-ECD. In this method, SF₆ was preconcentrated around -80 °C to give high signal to noise ratio even and O₂ was washed out in preconcentrator due to lower boiling point of -182 °C in order not to be introduced to GC. Only the repeatability of recovery rate affects to final analytical precision.

The challenge of achieving Data Quality Objectives in the WMO-GAW N₂O network

Rainer Steinbrecher

KIT/IMK-IFU

Compatible data from observation platforms in the WMO GAW network are essential for sound data products and are a key requirement. Thus, an effective quality management frame work (QMF) has been established. GAW launched several Central Facilities as part of the QMF. Central Calibration Laboratories (CCLs) host the measurement scale to which all calibration processes must be linked. GAW World Calibration Centers (WCCs) with its key task of Quality Assurance and Quality Control (QA/QC) of measurements in the network supervise stations. For N₂O, WMO-GAW Report 185 specifies further measurement procedures in ambient air and its QA.

The results of performance audits as part of QA/QC at several GAW Stations over the past years reveal that at present only a few stations meet the data quality objectives (DQOs) of the network. Mostly a bias and a drift is observed in the reported intercomparison data. Thus, achieving the DQOs still remains a challenge. Whether new techniques, e.g. laser-based instruments, reduce the uncertainty in N₂O ambient air analysis is still under investigation. Some real time investigations on repeatability, reproducibility, water dilution and broadening effects with a continuous wave quantum cascade laser (CW-QCL) system are presented and discussed. In principle, a CW-QCL system is able to achieve the same or even better performance as a GC-ECD system, if operated in a temperature controlled environment, regularly calibrations are performed and corrections for water vapor in the sample are applied.

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Recent Developments at the World Calibration Centre WCC-Empa

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Empa operates the World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide (WCC-Empa) since 1996 as a Swiss contribution to the GAW programme. The concept of the performance audits was recently expanded by the addition of parallel measurements with a travelling instrument using an entirely independent inlet system and calibration scheme.

This presentation will highlight the advantages of the new approach based on recent CO₂ and CH₄ comparisons, e.g. at the Danum Valley GAW station in early 2014. Results from various stations acquired with different analytical techniques will be compared. Instrumental aspects such as water vapour interference as well as the influence of the calibration interval, data coverage, and aggregation times will be addressed. The new performance audit approach gives new insight into the full measurement setup of a station. Due to these advantages, WCC-Empa will continue with travelling instrument comparisons during station audits whenever feasible.

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Quality Control and Quality Assurance from WDCGG viewpoint

Hiroshi KOIDE

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In order to provide qualified and compatible data set within the GAW Programme, Quality Control (QC) at each laboratories and Quality Assurance (QA) throughout downstream procedures are both indispensable. From the viewpoint of WMO GAW World Data Centre for Greenhouse Gases (WDCGG), several practical questions are raised.

- What is the best scheme for data flagging and uncertainty information to enrich your data records?
- How you can properly merge the historical time series when you replace your instrument?
- How you can utilize parallel data streams at the same site and for the same parameter, for example, with in situ measurement and flask sampling or by two different instruments?
- How to ensure the propagation of necessary metadata information from data providers to data users?

In the presentation, the QC procedures operated in JMA's GHG measurement team and QA efforts made at the WDCGG are shown, and recent relevant discussions with GAW colleagues along an ongoing WDCGG reform process will be introduced.

A Statistical Approach for the Background CO₂ Concentration Measurement at the Korea GAW Center

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The background concentrations of atmospheric carbon dioxide (CO₂) at the Korea GAW Center (Anmyeondo) are estimated using the measurement from January 2000 to March 2014 by applying the statistical methods. The hourly raw data of CO₂ concentrations are preprocessed and aggregated to diurnal data through the several data quality control steps. We apply the spectral analysis which is one of the most widely used methods for time series data to find not only long-term trend and annual cycle, but also hidden periodic pattern of variation of CO₂ concentrations. In addition, Fast Fourier transform (FFT) algorithm and filtering method were used to find periodic function in this process. The resulting quality controlled data can be used in the improved climate change modeling and for our better understanding of carbon source.

Key words: Background concentrations, spectral analysis, FFT, filtering

A new statistical method for determining regional baseline concentrations of atmospheric trace gases

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Atmospheric CO₂ concentrations which are observed at many background monitoring stations these days often reflect significant influence of anthropogenic emissions occurring on local and/or regional scales. Determining the underlying baseline or background concentration from non-baseline data can be a difficult task, but is essential to understanding the variations and trends in atmospheric CO₂ and investigating the quantitative contribution of local/regional emissions.

We present a new statistical method based on cyclostationary empirical orthogonal function (CSEOF) analysis[1,2] for determining baseline data of atmospheric trace species, applying the method to the hourly CO₂ records obtained for the period from 1999 to 2012 at the Korea GAW station located in Anmyeon-do. The CO₂ time series are decomposed via CSEOF analysis into periodic components representing variability with given time scales and stochastic components describing time-variant magnitude of the corresponding periodicity, which are called cyclostationary loading vectors (CSLVs) and principal component (PC) time series, respectively. Diurnal variability of CO₂ is extracted by using 24-hour time scale and the resulting PC time series exhibit variability on time scales longer than 24 hours. Thus, the PC time series are further decomposed into seasonal-scale variability to extract the seasonal cycles and their time-variant amplitudes. For the Korean GAW records, the first diurnal variability explained 66.2% of the total variability and the seasonal decomposition explained 23.2% of the first diurnal component. The seasonal cycles decomposed from the short-term variations were shown as baseline data in Figure 1. Year-to year variations in the long-term trend can be represented by time-variant modulation over a longer time span than 365 days. Unlike conventional methods for defining baseline signals (e.g., fitting the data to the sum of a second-order polynomial function and two harmonics), this method is useful for describing temporally evolving pattern of periodic components in the atmospheric trace concentrations.

30-year time series data of global background CO₂ concentration from NOAA observatories at Mauna Loa, Samoa, Barrow, and South Pole were also used to examine whether the seasonal cycles and long-term trends derived by this approach were appropriate. We also applied this method to CO₂, Radon, and COS observations made at Gosan in Jeju Island from 2009 to 2013 to demonstrate how useful it is to identify baseline signals for all other atmospheric trace species having natural variations upon which local and/or regional influences act on.

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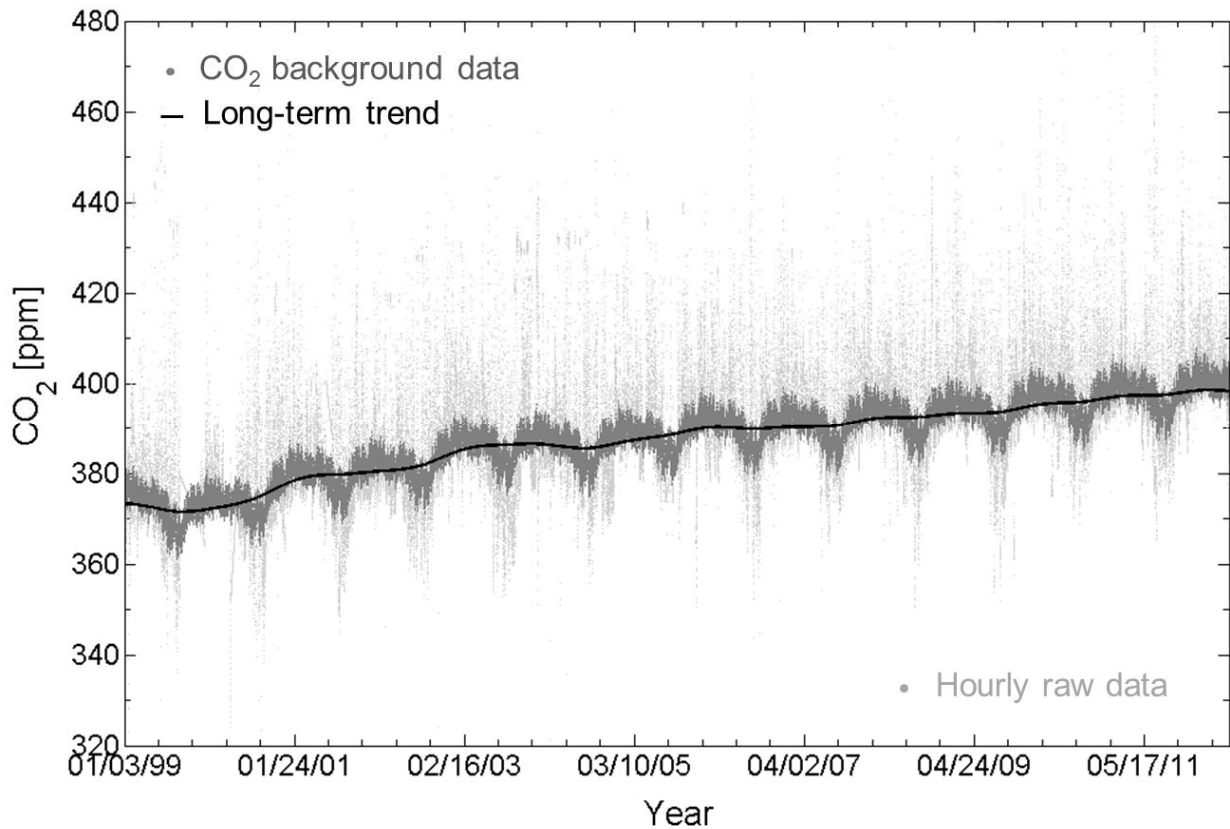


Fig. 1. Hourly raw data of CO₂ affected by regionally polluted air masses (light gray points) at Anmyeon-do station for the 1999–2012 period, background CO₂ concentrations (dark gray points) and a long-term trend (black line) determined by a method newly proposed in this study.

Asian greenhouse gases budget assessment

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As part of a collaborative effort to assess the Asian Greenhouse Gases (GHG) Budget, we are working on top-down estimates using atmospheric inversion models and bottom-up estimates using terrestrial biogeochemical models, remote sensing data, and flux and inventory datasets.

One of main objectives is to evaluate the flux trends in three major GHGs (CO₂, CH₄, and N₂O) and related species (CO, BC) using multiple inverse models over the period 2000-2012 for the South Asia, East Asia and Southeast Asia regions. However, as shown in the earlier assessment reports, these regions have been until very recently largely unconstrained by atmospheric observations (Patra et al., 2013 and Piao et al., 2012). We hope to collaborate with the scientists working on measurements of GHGs in Asia to improve understanding of the regional budgets of GHG sources and sinks.

This budget assessment is a continuation to the REgional Carbon Cycle Assessment and Processes (RECCAP) supported by the Global Carbon Project, which contributed to the IPCC AR5 and funded by the Asia Pacific Network for global change research (APN).

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The 5th
WMO GAW Experts workshop
on VOCs

Twenty years of VOC monitoring in EMEP

Sverre Solberg, Christian Dye, Norbert Schmidbauer and Kjetil Tørseth

NILU/EMEP-CCC

The monitoring of VOCs in EMEP started in the early 1990s and has since then delivered data of NMHC and OVOCs from a few rural European stations on a regular basis – twice/week according to the EMEP recommendation. The original EMEP methodology has been based on manual sampling with its pros and cons, whereas data from automated GCs and PTR-MSs in recent years are seen as a very valuable development of the basic VOC programme. The pros of the traditional manual methods are lower instrument costs and better manual control and overview of the data, whereas the cons are the poor temporal coverage and the need for personnel. Fully automated systems could be more costly but their continuous or semi-continuous data make the interpretation with respect to long-term trends, source regions etc significantly easier and more robust. At EMEP super-sites PTR-MS instruments have the last few years been used to study the role of biogenic vs anthropogenic sources on a campaign basis. The long-term development of C₂-C₈ NMHCs at EMEP sites indicate a gradual decline in concentration the last 10 years.

A seven-year (2006-2013) record of non-methane hydrocarbons (NMHCs) in the subtropical marine boundary layer at the Cape Verde Atmospheric Observatory

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We report observations of light non-methane hydrocarbons (NMHCs), methane (CH₄) and carbon monoxide (CO) measured in the subtropical marine boundary layer at the Cape Verde Atmospheric Observatory (16° 51' N, 24° 52' W) in the east Atlantic Ocean. Presented in Figure 1 is a time series of ethane, propane and CO measured during Oct 2006 - Dec 2013, showing well-defined seasonal cycles with spring maxima and summer minima, consistent with the seasonal variation of the OH radical. Simulations of NMHCs using the CAM-chem model show good agreement with the observations and allow an investigation of source attribution over the time series record. The major sources of ethane are shared with those of methane, and we investigate the relationship between ethane mixing ratios and the methane atmospheric growth rate over the past 7 years. The potential impact of Cl-atom reactions on the atmospheric removal of selected hydrocarbons in the marine atmosphere is also investigated. Oceanic emissions of alkanes may perturb such ratios, obscuring the discrimination of OH from Cl chemistry. Using hydrocarbon variability-OH lifetime relationships, we also show evidence for oceanic emissions of reactive alkenes (ethene and propene).

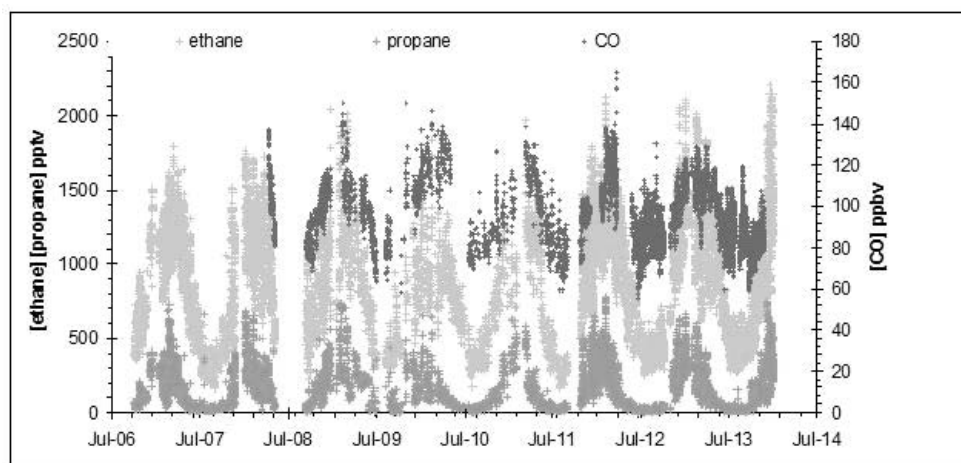


Fig. 1: Time series of ethane, propane and CO during Oct 2006-Dec 2013

Further developments in background VOC monitoring at CSIRO Marine and Atmospheric Research

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Recent work undertaken by CSIRO Marine and Atmospheric Research concerning measurements of reactive VOCs in background air in the southern hemisphere will be presented.

Three measurement techniques are currently in use: PTR-MS, including a Switchable Reagent Ion source; adsorbent tubes with thermal desorption and GC-FID-MS analysis; and DNPH cartridges with HPLC analysis.

Instrument developments include: exploration of the use of PTR-MS with O₂⁺ and NO⁺ ions; optimizing the DNPH method for measuring dicarbonyls; and development of online dual channel thermal desorption GC-FID systems for Cape Grim and the Gunn Point Tropical Atmospheric Observatory.

There have been two recent field campaigns with VOC measurements in background air; the Measurements of Urban, Marine and Biogenic Air (MUMBA) campaign at the University of Wollongong, December 2012 – February 2013, and the dry season campaign at the Gunn Point Tropical Atmospheric Observatory, 2014. There will be VOC measurements during the commissioning trials for Australia's new research vessel the *RV Investigator*, to be conducted in the Southern Ocean in early 2015.

Recent studies will be presented, addressing the emissions and/or precursor distributions and processes that regulate acetonitrile and the dicarbonyls, glyoxal and methylglyoxal in the background atmosphere.

Analysis of 10 Years online C₂-C₁₁ NMHC Measurements close to the Gulf of Mexico

Bernhard Rappenglück

University of Houston

This is an update about online in situ data of speciated C₂-C₁₁ non-methane hydrocarbons (NMHC), which have been measured on an hourly basis at Lake Jackson/TX close to the Gulf of Mexico. Altogether 48 NMHCs, including the GAW NMHC compounds, along with NO, NO₂, NO_x, O₃ have been collected continuously from January 2004-December 2013 under the auspices of the Texas Commission on Environmental Quality.

Data was screened for background conditions representing marine wind sectors. The data set represents a combination of marine air masses mixed with local biogenic emissions. The data analysis addresses photochemical processing of air masses as reflected in the relationship of ln(n-butane/ethane) vs. ln(propane/ethane) and ln(i-butane/ethane) vs. ln(n-butane/ethane). In addition, key NMHC relationships for radical chemistry, e.g. i-butane vs n-butane for OH and Cl chemistry and i-pentane vs. n-pentane for NO₃ chemistry, are discussed. Results are compared to other sites, where available (e.g. GAW site Mace Head).

Seasonal analysis revealed a clear trend with maximum NMHC mixing ratios in winter time and lowest mixing ratios in summer reflecting the impact of photochemical processes in summer. Propene equivalents were highest during summertime, with significant contributions from alkenes, including isoprene. The relation of propane/ethane vs ethane indicates seasonal variation with lowest values (i.e. most aged air masses) in winter.

Contrary to usual GAW NMHC sampling procedures, which at least requires routine daytime samples (e.g. for canister samplings), continuous NMHC data collection allows to analyze nighttime data, which is least impacted by photochemical processes and potentially well-suited for trend analysis. Corresponding trend analysis for the Lake Jackson data suggests an overall slight decrease of selected NMHCs over the 2004-2013 period.

Field observations of anthropogenic and natural VOCs in East Asia by PTR-MS

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Starting in 2006, we have made extensive field work for measuring VOCs in East Asia, including at ground sites of Mt. Tai and in Rudong in China, and onboard R/V Hakuho-maru cruises in the Pacific Ocean. The measurements were mainly made by Proton Transfer Reaction-Mass Spectrometry (PTR-MS), with complementary measurements by Gas Chromatography/Mass Spectrometry/Flame Ionization Detection (GC/MS/FID). The GC analyses were made either on site or in a laboratory at NIES after whole air sampling. The measurements in China focused on VOCs emitted from anthropogenic sources, including alkanes, alkenes, alkynes, aromatics, and oxygenated VOCs. Informal intercomparison with a research group in China was made. The measurements in the Pacific Ocean focused on VOCs emitted from biogenic sources, including dimethyl sulfide, oxygenated VOCs, and isoprene. We paid great attention to gas standards, to assure high quality of the measurements. We will outline our past and ongoing research activities, show major scientific highlights, and discuss issues and future directions.

VOC Measurement Guidelines – from ACTRIS Drafts to GAW Recommendations

S. Reimann, C. Plass-Dülmer, A. Werner, C. Hoerger, and ACTRIS partners

Empa

Measurement Guidelines (MG) are a central part in GAW quality management. As presented in the last VOC Expert meeting in York, a central task of the European infrastructure project ACTRIS is the preparation of a VOC MG. At the last VOC Expert meeting the concept was presented and discussed, and it was agreed on using these draft as a basis for the development of a GAW VOC Measurement Guideline. The final status of the ACTRIS VOC MG will be presented and open issues towards GAW VOC MG are identified, which then should be discussed in the plenum. Things not settled in the discussion are transferred to working groups. A schedule for the finalization of the GAW VOC MG shall be agreed on. (This section shall have 2 x 1.5 hours).

Review and progress on standards for the measurements of biogenic and anthropogenic VOCs in the atmosphere

Marivon Corbel

NPL

Biogenic and anthropogenic Volatile Organic Compounds (VOCs) are present at ppb levels in the ambient atmosphere. They play an important role in the chemical mechanisms that lead to the photochemical generation of ozone and which control the oxidation capacity of the troposphere. Traceability and long term stability of gaseous reference standards are necessary to underpin a rigorous quality assurance and quality control programme for the measurements of biogenic and anthropogenic VOCs in the atmosphere.

A review of the existing standards together with the progress made at NPL towards the development of new standards for oxygenated VOCs and terpenes will be presented. This includes stability trials on a mixture of ethanol, methanol and acetone in nitrogen at 5 $\mu\text{mol/mol}$. The results of a five year stability study will be depicted.

Monoterpene Gas Standard Developments at NIST

Jerry Rhoderick

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The National Institute of Standards and Technology (NIST) have been developing gas standards containing volatile organic compounds (VOCs) in support of the WMO/GAW-VOC community. NIST has been collaborating with other National Metrology Institutes (NMIs) in a group effort to develop standards for several groupings of compounds. As part of this effort, NIST accepted a charge to champion monoterpene gas standards development. NIST has been approved by the WMO as the Central Calibration Laboratory (CCL) for monoterpenes. The latest developments in monoterpene gas standards will be discussed along with data from comparisons of some of the standards between the NMIs. Future developments of these standards and projected key comparisons will be discussed.

Development of Standard Gas Mixtures for Dimethyl Sulfide (DMS) and Acetonitrile at KRISS

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Dimethyl sulfide (DMS) and acetonitrile (ACN) are important reactive gases for understanding atmospheric chemistry and climate change. KRISS agreed with WMO/GAW-VOC group regarding developing standard gas mixtures for DMS and ACN. KRISS has been developing a new method to generate DMS and ACN standard gas mixtures at nmol/mol level. The current status for DMS and ACN standard gas mixtures will be discussed. Future research activities will be also discussed.

Progress on both dynamic and static formaldehyde standards at the $\mu\text{mol mol}^{-1}$ level

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The BIPM and a number of National Metrology Institutes are jointly progressing in their ability to produce, maintain and characterise both dynamic and static formaldehyde in nitrogen standards as will be demonstrated in the upcoming international Key Comparison CCQM-K90, which includes eight participants. Two types of dynamic generation facilities have been developed and are now routinely running: firstly permeation of formaldehyde from a tube containing paraformaldehyde, and the second based on diffusion of trioxane followed by thermal conversion into formaldehyde. The BIPM, in its role of coordinator of the key comparison CCQM-K90, has developed and validated both generation methods using Fourier Transform InfraRed spectroscopy and Cavity Ring Down spectroscopy as analytical techniques. The use of continuous weighing of the formaldehyde source, together with a careful quantification of impurities in the dynamic mixtures allows a relative uncertainty of less than 0.5% to be obtained.

Meanwhile, efforts to produce stable cylinders standards of formaldehyde at the $\mu\text{mol mol}^{-1}$ level using gravimetric techniques are continuing. In that regard the recent one-year stability study performed by the BIPM on a set of cylinders produced by a gas specialty company has been promising, with less than 0.2% loss per month demonstrated.

A set of 14 similar cylinders prepared at $2 \mu\text{mol mol}^{-1}$ were acquired by the BIPM, to be used as transfer standards in the comparison CCQM-K90. They are going to be characterised against the two dynamic generation facilities before being distributed to participating laboratories. The key comparison will benchmark NMIs capabilities in formaldehyde in nitrogen standards at the $\mu\text{mol mol}^{-1}$ level, a first step towards calibration and measurement capabilities at the lower levels required by the GAW program.

KEY-VOCs project: Metrology for VOC indicators for air pollution and climate change

Annarita Baldan

VSL (project coordinator)

In the framework of the European Metrology Research Programme (EMRP) a new project has been granted and it will start in October 2014 and run for three years.

This project focuses on the VOC key compounds that are regulated by European legislation, that are relevant for indoor air monitoring and for air quality and climate monitoring programmes like the VOC programme established by WMO-GAW and the UNECE's European Monitoring and Evaluation Programme (EMEP).

Principle aspects covered by the project are metrological traceability, accuracy and long-term stability in order to achieve and improve the DQOs set for measurement uncertainties by the WMO/GAW and EMEP programmes. This will be achieved by developing ad-hoc gas standards for oxy-VOCs, formaldehyde and terpenes by means of static (gravimetric) and dynamic preparation methods.

A large part of this research will then deal with fundamental issues related to the preparation of VOC gas standards and to the measurement of VOCs in air:

- Evaluation of the adsorption and reaction of VOC with contact material surfaces (both vessels for the storage of standards and sampling lines)
- Obtaining VOC-free zero gas standards (nitrogen and air) to be used for zeroing analysers and for dilution of highly concentrated VOC vapours.

The research related to GAW –VOC activities will be jointly carried out by European National Metrology Institutes and Hohenpeissenberg Observatory.

The presentation will also provide a brief overview of the research activities on the validation of gas sensors for VOCs monitoring and on the preparation of VOC (semi- volatile and polar) gas standards for indoor air measurements.

The challenge of preparing ambient air standards for calibrating VOC analysis systems

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WMO GAW World Calibration Centre for VOC,

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A high compatibility of scientific data from monitoring networks requires regular calibration with traceable standards. For the WMO GAW VOC network now traceable standards for the key target non-methane hydrocarbons as well as key monoterpenes are available and hosted by the corresponding WMO Central Calibration Laboratories (CCL), National Physical Laboratory (NPL, UK) and National Institute of Standards (NIST, USA). A scale for other GAW VOC targets is in preparation. Those standards are generally prepared with nitrogen as balance gas in pressure cylinders for stability reasons (primary and secondary standards). Tertiary standards or laboratory standards (LS) are then used in analytical laboratories to transfer the scale and calibrate the working standards (WS; quaternary standards). As a WS, ambient air filled in a pressure cylinder is often used by the laboratories. Good VOC ambient air standards mimic the characteristic of routine analysis during calibration better than VOC in nitrogen standards. But VOC ambient air standards may drift over time and also may have a different matrix compared to ambient air due to the filling process.. Thus it is crucial for sound ambient air standards to use suited material and devices to ensure stability and purity as demonstrated by some examples. Components of a VOC ambient air standard preparing system may include: (1) oil free air compressor; (2) plastic free humidifying system, pre-treated with VOC free water; (3) stainless steel tubing and stainless steel/Teflon air filter system; (4) special surface treated pressure cylinders.

VOC Round-Robin Exercise for VOCs in the framework of the European Infrastructure project ACTRIS – results and suggestions for implementation

C. Hoerger, **S. Reimann**, C. Plass-Dülmer, A. Werner, and ACTRIS partners

Empa

During 2012, the performance of 20 European laboratories involved in long-term VOCs measurements within the framework of GAW and EMEP was assessed with respect to newly determined ACTRIS data quality objectives (DQOs). Compared to DQOs from GAW the DQOs of ACTRIS are more demanding (deviations of max 5% to a reference value). The participants were asked to measure a ~1 nmol/mol VOC mixture in nitrogen with 30 components (including alkanes, alkenes, alkynes, and aromatic compounds) and compressed ambient air following a standardised operation procedure. For VOCs in nitrogen 61% of the FID- and 51% of the MS-results were within the ACTRIS DQOs. For the ambient air slightly more scatter was observed. The results of the analytical systems are discussed with respect to calibration issues, FID and MS detection, sample matrices, breakthrough, adsorptive losses, and chromatographic resolution.

Side-by-side Intercomparison for OVOC in the framework of ACTRIS

J. Englert, C. Plass-Dülmer, A. Werner and ACTRIS partners

Empa

For high-quality OVOC measurements, the need of a better characterisation of measurement techniques has been identified in GAW VOC Expert meetings. This has been addressed in an OVOC side-by-side intercomparison experiment as part of the EC ACTRIS project. Seven groups with ten different state-of-the-art OVOC instruments (PTR-MS, GC/MS/FID, adsorbent tube sampler and DNPH cartridges) joined at Hohenpeissenberg Meteorological Observatory in October 2013. All instruments were connected to a single manifold which was fed with synthetic air mixtures, zero air, pure and spiked ambient air at controlled ozone and humidity levels. OVOC mixing ratios between ppb and low ppt range were encountered with ozone and water vapour varied up to some 100 ppb and 2%, respectively. Thus, detection limits, linear ranges, and artefacts due to interfering gases and materials of the measuring systems could be investigated. Generally, similar results were obtained by different instruments/techniques, but partly also clear deviations of individual or groups of instruments were seen. These deviations are further analysed with respect to reference concentrations, characteristics of the respective techniques, blank and calibration issues and uncertainties.

Map of KRISS Campus: Workshop Place no. 302. / Restaurant no. 101.



Additional information

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If you need any help, please contact us

Sangil Lee (010-2775-0187, 042-868-5042), Haeyoung Lee (010-4525-0903)

Thanks!