

Pressure broadening effects of inert gases on CO₂ and CH₄ measurement using a wave scan-cavity ring down spectrometer

H. Nara, H. Tanimoto, Y. Nojiri, H. Mukai, K. Katsumata, Y. Tohjima, T. Machida

National Institute for Environmental Studies
16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

nara.hideki@nies.go.jp

A wavelength-scanned cavity ring-down spectrometer (CRDS, available from PICARRO, Inc., Santa Clara, CA) is a rapidly spreading observation instrument which can detect atmospheric CO₂, CH₄, and H₂O simultaneously based on the principle of laser absorption technique (Crosson, 2008). Chen et al. (2010) made airborne observations of CO₂ and CH₄ over the Amazonian rain forest using a CRDS and evaluated its performance for CO₂ measurement in comparison to NDIR. These investigators reported that CO₂ mixing ratios from both CRDS and NDIR instruments showed good agreement, except that the CRDS measurements were affected by the variations in inert gaseous species (N₂, O₂, and Ar) due to pressure broadening effects on absorption spectrum of CO₂ and CH₄. However, the magnitudes of the pressure broadening effects were not tested. In this work we have evaluated the pressure broadening effects through laboratory experiments. Figure 1 shows pressure broadening effects of the inert gases on the measurement of CO₂ and CH₄, expressed as a function of inert gas mixing ratio added. The pressure broadening of N₂ shows negative effect on CO₂ and CH₄ while the effects of O₂ and Ar are positive, suggesting the largest impact of N₂. Take into account that the typical analytical precision of the CRDS is ± 0.03 ppm for CO₂ and ± 0.3 ppb for CH₄, we found that pressure broadening effects are not negligible when the N₂ increases more than 0.1% for CO₂ and 0.9% for CH₄ from the original mixing ratio. These results imply possible biases in atmospheric CO₂ and CH₄ measurements using the CRDS when synthetic gas standards are used as a reference gas.

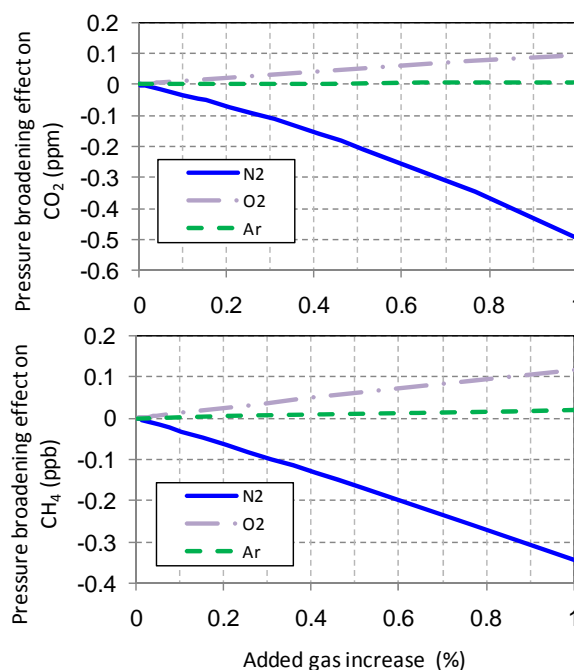


Figure 1. An example of estimated CRDS (model G1301) responses of CO₂ (top) and CH₄ (bottom) against N₂ (solid line), O₂ (dashed line), and Ar (dotted dashed line) added in the compressed natural air.

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A Multi-Year Record of Airborne Continuous CO₂ in the U.S. Southern Great Plains

Sébastien C. Biraud¹, William J. Riley¹, Margaret S. Torn¹, James R. Smith²

¹ Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California

² Atmospheric Observing Systems, Inc., Boulder, Colorado

SCBiraud@lbl.gov

We report on three years of airborne measurements of continuous atmospheric CO₂ concentrations over the Atmospheric Radiation Measurement Program (ARM) Climate Research Facility (ACRF) in the U.S. Southern Great Plains. These continuous measurements are collected weekly from a small aircraft (Cessna 206) on a series of horizontal legs ranging from 17,500 feet down to 1,500 feet above sea level. The continuous CO₂ observations are measured using a CO₂ analyzer built by Atmospheric Observing System Inc., based in Boulder, Colorado. The analyzer has non-imaging optics and negligible sensitivity to motion of platform. The NDIR Analyzer is the core element of the system. Accuracy, including bias, is approximately 0.1 ppm of CO₂ DMF at 1 Hz. Each flight lasts between 2.5 and 3 hours, yielding about 10,000 CO₂ measurements per flight. Since November 2007, more than 300 continuous CO₂ vertical profiles have been collected, along with NOAA/ESRL 12-flask (carbon cycle gases and isotopes) packages for validation. Comparison between the continuous and flask CO₂ measurements indicates a no systematic difference.

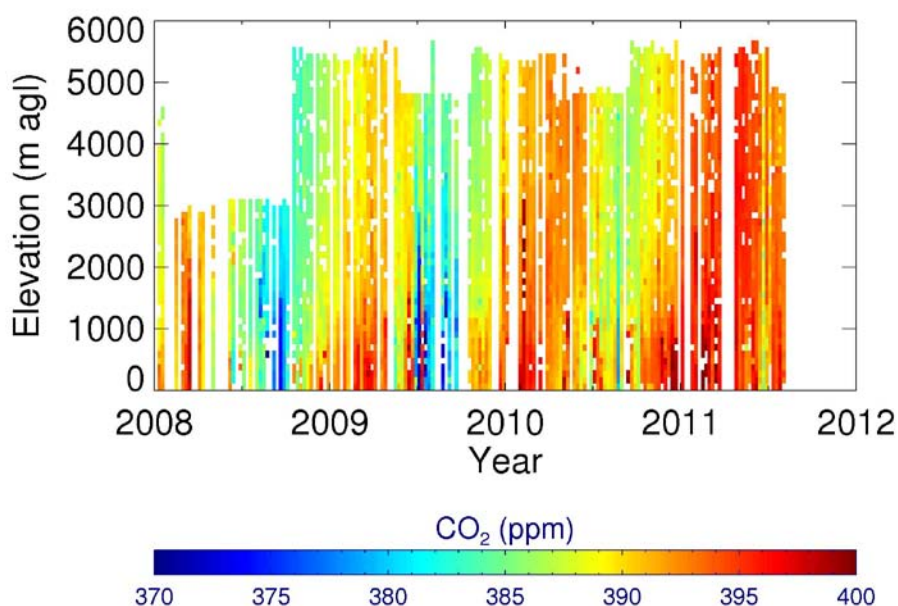


Figure 1. Weekly average continuous CO₂ concentrations collected in the U.S. Southern Great Plains since Jan. 2008.

Detection of combusted methane emissions for the city of Bern (Switzerland) by analysis of high-resolution O₂ and CO₂ observations.

S. van der Laan, I.T. van der Laan-Luijkx, M. Haeberli, M. Leuenberger

University of Bern, Physics Institute, Climate and Environmental Physics, Sidlerstrasse 5, CH-3012 Bern, Switzerland

svanderlaan@climate.unibe.ch

Anthropogenic CO₂ emissions are widely considered to be the main cause of enhanced global warming since the 18th century¹. Although the CO₂ fluxes on the global scale are relatively well understood, little is still known about the spatial and temporal variation in CO₂ fluxes on regional to local scales.

This project aims at quantifying one of the largest contributors of CO₂ emissions in the city of Bern, Switzerland: combusted methane. Natural gas accounts for more than 20% of the annual energy consumption as it is used for heating and cooking purposes by the approx. 124.000 inhabitants. Since the year 2007 the University of Bern measures semi-continuously ambient CO₂ and O₂ concentrations at the roof of the university building in the centre of Bern. A clear diurnal pattern is observed with rapid increases in the CO₂ concentration from the background concentration and concurrent decreases in the O₂ concentration. These so-called events typically last for about 8-12 hours and are caused by a combination of regional CO₂ sources and changes in atmospheric stability (i.e. lack of turbulence). Often, these events have smaller events superimposed on them with a typical duration in the order of 2-4 hours, representing local CO₂ sources. The events are selected with an automated FFT-filter. A regression plot is made for each event between CO₂ and the concurrent O₂ to determine the stoichiometric ratio^{2,3}. A stoichiometric ratio of -2 mol O₂/mol CO₂ indicates combusted methane. To determine the surface fluxes for these events we use the ²²²Rn-tracer method^{4,5,6}. Accompanying measurements of ¹³CO₂ are used to determine the δ¹³C signature of the local natural gas mix. At the meeting we will show our first results and outline our future perspectives.

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Developing high precision CO₂ monitoring technique in India: preliminary results

Yogesh K. Tiwari, K. Ravi Kumar, Aparna Krishnamurthy

Indian Institute of Tropical Meteorology, Pune, India

yktiwari@gmail.com

Developing countries account for ~73% of the global emissions CO₂ [Raupach *et al.*, 2007]. According to the Energy Information Administration (EIA), the CO₂ emissions are expected to increase by 1.8 percent annually between 2004 and 2030. The Carbon Dioxide Information Analysis Center (CDIAC) estimates the total fossil fuel CO₂ emissions from India as 189 TgC in 1990, 324 TgC in 2000, 385 TgC in 2005 & 508 TgC in 2009, and the annual rate of increase is ~7% per year during 2005-2009 [Boden *et al.*, 2010]. Most of the models that participated in the Transcom programme [Gurney *et al.*, 2004] show large uncertainties over regions of poor data coverage. The number of stations taking regular measurements of atmospheric CO₂ in India are on the order of one or two. There have been very little monitoring of atmospheric CO₂ concentration over India to date [Bhattacharya *et al.*, 2009]. To provide regular data of atmospheric CO₂, it is strongly agreed that there ought to be a network of stations [Tiwari *et al.*, 2011a]. In order to do so, we have started an observing site at Sinhagad (SNG) located near the west coast of India and about 1600 m above sea level. Regular sampling at SNG (lat=18.35, lon=73.75) started in November 2009, with air samples being collected weekly. SNG receives marine air during Indian summer monsoon months (JJA) and terrestrial air during winter months (DJF). We have established a Gas Chromatograph (GC) lab at the Indian Institute of Tropical Meteorology Pune India [Tiwari *et al.*, 2011b] with two detectors Electron capture detector (ECD) and flame ionization detector (FID). We present CO₂ concentration data and compare them with those obtained from model simulations.

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Experimental estimation of line broadening of Carbon dioxide monitoring

Jeongsoon Lee¹, Jin Bok Lee¹, Dong Min Moon¹, Jin Seog Kim¹

¹Korea Research Institute of Standards and Science (KRISS), Division of Metrology for Quality Life,
P.O.Box 102, Yusong, Daejeon, Republic of Korea

Email: leejs@kriss.re.kr

The global warming requires an observation of green house gases accurately and precisely. It is well known that the carbon dioxide (CO₂) is the green house gas which contributes highly global warming. (IPCC 2007). Currently, Non-Dispersive Infra-Red(NDIR) analyzer is used for monitoring the background CO₂ atmosphere. The analyzer has excellent stability and repeatability compared to others. However it requires at least 4 points calibration and 4 standard mixtures. Therefore, the application of a Cavity Ring-Down Spectroscopy(CRDS) increases recently. A CRDS analysis has several advantages of excellent linearity and reproducibility of a level(0.1 μmol/mol) as well as outstanding stability.

In this work it is studied the CRDS measurement of CO₂. Its repeatability, linearity, and reproducibility were investigated. For the purpose of investigating the line broadening effects, we have prepared 6 standard gases. A group of cylinders among them were prepared with the gravimetric method and another group of cylinders were prepared by way of air sampling. As a result, it was found that CRDS should be calibrated the mixtures with the same composition of air to monitor ambient CO₂ accurately. Consequently this study provide an effective estimation of absorption line broadening of Carbon dioxide monitoring with CRDS.

Tower-based CRDS greenhouse gas measurements in an urban environment: Calibration, field tests, and results from the INFLUX project.

Natasha Miles¹, Scott Richardson¹, Thomas Lauvaux¹, Laura McGowan¹,
Daniel Sarmiento¹, Kenneth Davis¹, Jocelyn Turnbull², Colm Sweeney²,
Kevin Gurney³, Maria Cambaliza⁴, Paul Shepson⁴

¹The Pennsylvania State University

²NOAA ESRL GMD / University of Colorado

³Arizona State University

⁴Purdue University

nmiles@met.psu.edu

Independent verification of anthropogenic greenhouse gas emissions is an emerging need as legislation to regulate greenhouse gas emissions becomes increasingly likely. However, relatively few atmospheric measurements using towers above the surface layer have been attempted in urban environments. As part of the INFLUX project, CO₂, CH₄ and CO mixing ratios are measured using wavelength-scanned cavity ringdown spectroscopy (Picarro, Inc.) at two towers separated by 40 km in Indianapolis, Indiana, USA, with ten additional instruments to be deployed in Fall 2011. We first describe calibration, laboratory, and field testing of the instruments, including an 11-day drift test and a 3-month comparison of co-located instruments. We then present case studies of multi-species data, with comparison to forward modelling results. For April – July 2011, histograms of the inter-site differences in CO₂, CH₄, and CO mixing ratios, measured at > 100 m AGL, are shown in Fig. 1. While CH₄ is evenly distributed about zero, both CO₂ and CO are preferentially higher at the urban site, with median inter-site differences of 2.4 ppm and 8.1 ppb, respectively.

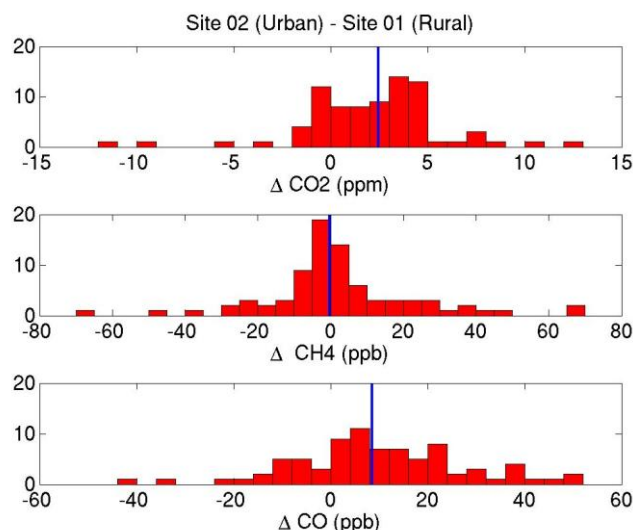


Figure 1. Histograms of daily inter-site differences in mixing ratios at 3 - 4 pm LST. Vertical lines indicate the medians. The sites are the initial two tower sites of the INFLUX project: Site 01 is southwest of Indianapolis in a rural area, whereas Site 02 is on the western edge of the city.

JMA aircraft observation using a cargo aircraft C-130H

Yousuke Sawa¹, K. Tsuboi¹, H. Matsueda¹, Y. Niwa¹,
M. Nakamura², D. Kuboike², K. Saito², H. Oomori², S. Iwatsubo²,
H. Nishi², Y. Hanamiya², K. Tsuji², and Y. Baba²

¹ MRI, 1-1 Nagamine, Tsukuba, 305-0052 Japan

² JMA, 1-3-4 Ohtemachi, Chiyoda-ku, Tokyo, 100-8122 Japan

Corresponding author: ysawa@mri-jma.go.jp

Japan Meteorological Agency (JMA) started an operational aircraft observation of greenhouse gases as a new atmospheric monitoring activity in 2011. A cargo aircraft C-130H in Japan Ministry of Defence is used for the flask sampling observation during a regular flight between Tokyo and Minamitorishima (MNM) once a month. The air samples are collected during a cruising flight at about 6 km over the western North Pacific as well as a descending to MNM. After the flight, we measure 4 trace gas concentrations of carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO), and nitrous oxide (N₂O). In collaboration with Meteorological Research Institute (MRI), test flights using the C-130H were made in 2010 to establish a flask sampling procedure on board the aircraft. In addition, a high-precision measuring system for the trace gas analyses was newly developed. In this presentation, the details of sampling and analysis instrumentations for the JMA aircraft observation and their performances are introduced.

Sample air in the C-130H was taken from an air-conditioning blowing nozzle upstream of the recirculation fan to avoid the contamination of cabin air. We prepared a 1.7-L titanium flask of which internal surface is coated by silicon. Air samples are pressurized into the flasks by a manual diaphragm pump to an absolute pressure of about 0.4MPa. The storage tests for the flask samples during several days were repeated to ensure the stability of trace gases until analyses. Specially coordinated flights at a low altitude of 1000ft over MNM were made using the C-130H to compare with the ground-based measurements from the MNM monitoring system in JMA. It was confirmed that our aircraft sampling procedure was suitable for the precise measurements of trace gases.

The JMA/MRI developed the automated measuring system consisting of a NDIR analyzer (Licor, LI-7000) for CO₂ as well as recently advanced spectroscopy instruments of WS-CRDS analyzer (Picarro, G2301) for CO₂ and CH₄, VURF analyzer (Aero-Laser, AL5002-AIR) for CO, and off-axis ICOS analyzer (Los Gatos, N₂O/CO Analyzer) for N₂O and CO. High-precision analyses of our system were estimated by the experiments using standard gases and natural air. In addition, our measurements were evaluated from comparison exercises with the conventional GC methods to ensure the consistency of other observational datasets from the JMA monitoring activities.

Measuring CO₂ and H₂O Fluxes from Fast Mixing Ratio without a Need for Density Corrections

George Burba¹, Andres Schmidt², Russell Scott³, Taro Nakai⁴, James Kathilankal¹, Gerardo Fratini¹, Chad Hanson², Beverly Law², Dayle McDermitt¹, and Robert Eckles¹

¹ LI-COR Biosciences, Lincoln, NE, United States

² Oregon State University, Corvallis, OR, United States

³ Agricultural Research Service, USDA, Tucson, AZ, United States

⁴University of Alaska, Fairbanks, AK, United States

george.burba@licor.com

Enclosed gas analyzer with short intake tube is a blend of a traditional long-tube closed-path design and a traditional open-path design. Analogous to closed-path, the enclosed design leads to minimal data loss during precipitation events and icing, and it does not have surface heating issues. Analogous to the open-path design, the enclosed design has good frequency response due to the short intake tube, does not require frequent calibration, needs minimal maintenance, and could be low power when used with short intake tube.

In addition to these advantages, enclosed design could provide measurement of fast mixing ratio, or dry mole fraction, because native density measurements can be converted to mixing ratio units using fast measurements of temperature, water vapor and pressure inside the sampling cell. Fast mixing ratio implies that the thermal expansion and water dilution of the sampled air have been accounted for in such a conversion. Thus, no density corrections are required to compute fluxes when the fast mixing ratio is used. Such a way of calculating fluxes has been used frequently with traditional closed-path analyzers (*e.g.*, LI-6262 and LI-7000), because fast fluctuations in the air temperature of the sample were attenuated in the long intake tube, and because water vapour was simultaneously measured and dry mole fraction was output from the instrument. In an enclosed design, such as the LI-7200 used with short tube, most but not all of the fast temperature fluctuations are attenuated, so calculating fluxes using the mixing ratio output of such an instrument requires validation.

The CO₂ and H₂O Eddy Covariance fluxes of from nine experiments with new LI-7200 enclosed analyzer were examined here: six deployments of the Ameriflux Roving Intercomparison Station in California, Arizona, New Mexico and Oregon; one deployment at a USDA flux site in Arizona; one deployment in University of Alaska-Fairbanks site in Alaska, and one deployment at the LI-COR flux test facility in Nebraska. Fluxes were computed in two ways: (i) via the traditional way using the density corrections, and (ii) via a mixing ratio output from the instrument without applying the density corrections. The results of these comparisons have important implications for future gas flux measurements, because avoiding half-hourly or hourly density corrections could help to minimize at least two kinds of uncertainties: (i) the uncertainties associated with correcting the product of fast covariances of gas density using sensible and latent heat flux calculated over half-hour or an hour; and (ii) the uncertainties in the magnitudes of the sensible and latent heat fluxes used in correcting gas flux.

A level one ICOS atmospheric station in Eastern France

Marc Delmotte¹, Olivier Laurent¹, Sébastien Conil², Olivier Corpacé³, Stephan Baum⁴, Lynn Hazan¹, Ingeborg Levin⁵, Michel Ramonet¹, Martina Schmidt¹, Cyrille Vuillemin¹ and Philippe Ciais¹

¹ Laboratoire des Sciences du Climat et de l'Environnement, Gif sur Yvette, France

² OPE, ANDRA, Bure, France

³ IRFU, CEA, Gif sur Yvette, France

⁴ MPI-BGC, Jena, Germany

⁵ University of Heidelberg, Heidelberg, Germany

marc.delmotte@lsce.ipsl.fr

Within the framework of the ICOS (Integrated Carbon Observation System) project, a new atmospheric continuous monitoring station has been set up in Eastern part of France (Houdelaincourt, 48.33° N, 5.30° E, 392 m a.s.l) in cooperation with ANDRA. A 120 meter tower has been erected on site and measurements are conducted on three levels (120, 50 and 10m) for greenhouse gases (CO₂, CH₄, N₂O) and meteorological parameters (wind speed and direction, temperature, relative humidity as well as atmospheric pressure). Additional useful parameters such as ¹⁴C of CO₂, CO, Radon, CO₂ flux measurements and planetary boundary layer height (from Lidar) are also recorded for a full data interpretation while flask samples are collected for quality control of the continuous analysers and additional compounds measurement (O₂/N₂, H₂, SF₆ and CO₂ stable isotopes). With its complete set of instrumentation, the OPE station is nowadays the unique level one ICOS station. The whole set of instrumentation has been integrated by LSCE and IRFU in an automatic air sampling, calibration and supervision system which is foreseen as the model for the future ICOS “labelled” atmospheric station. Since May 2011, the OPE station is taking part in the ICOS demonstration experiment.

In the present work we will present the new station as well as the integrated system and show the first results obtained during the first months of the demonstration experiment.

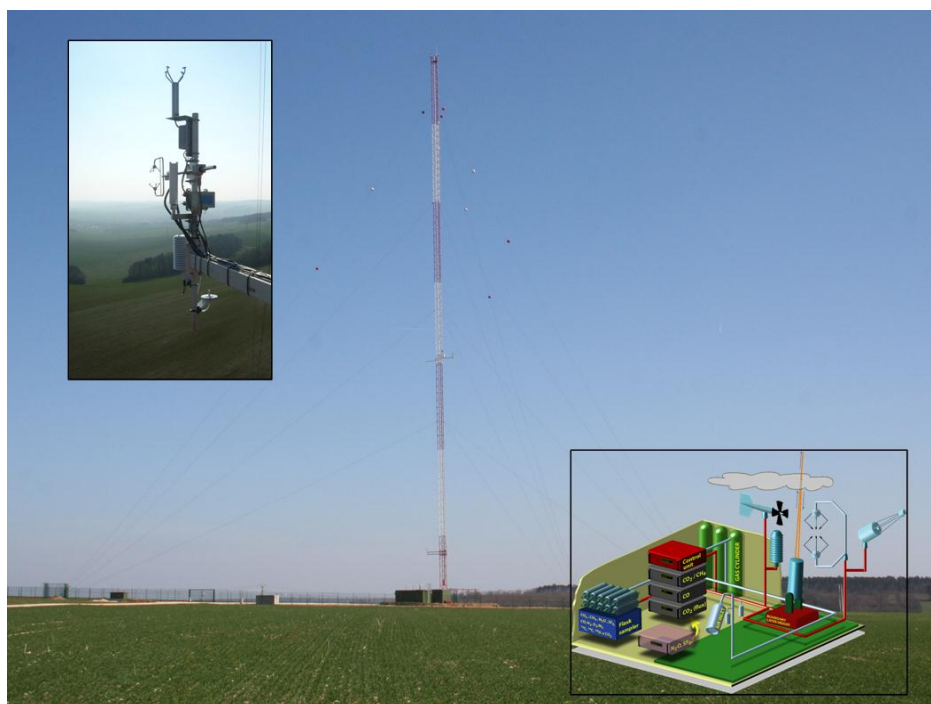


Figure 1: The OPE ICOS level one atmospheric station.

Four years of *in situ* atmospheric O₂ and CO₂ data from Weybourne Atmospheric Observatory, Norfolk, United Kingdom

Philip A. Wilson, Andrew C. Manning, Michael Patecki, Alex J. Etchells and Andrew J. Macdonald

School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

p.wilson1@uea.ac.uk

We present a four year data record of atmospheric measurements of oxygen (O₂) and carbon dioxide (CO₂) collected at Weybourne Atmospheric Observatory (WAO) on the north Norfolk coast (52.95°N, 1.12°E) in the UK. *In situ*, continuous measurements cover the period from the system's inception in October 2007 to the present day.

CO₂ measurements are made using a commercially available NDIR CO₂ analyser, a Siemens 'Ultramat 6E'. O₂ measurements are made utilising an electrolytic reaction on the surface of lead fuel cells in an 'Oxzilla II' analyser from Sable Systems. A gas handling system similar to that used by Stephens *et al.*[2007] is employed to draw air in from an aspirated inlet at the top of a 10 m a.g.l. tower and then controls flow rate and pressure before the sample air reaches the two analysers in series. A rigorous calibration regime similar to that described by Keeling *et al.*[1998] is used to maintain the accuracy and precision of the data collected and WAO participates in both the 'Cucumber' and WMO round robin intercomparison programmes to ensure the compatibility of our data compared to other global stations.

We present the 4 year record of our data for both species and that for Atmospheric Potential Oxygen (APO), which combines the signals for O₂ and CO₂ in such a manner that APO is insensitive to terrestrial processes and thus illustrates, for the most part, only influences due to oceanic processes.. We discuss the seasonal cycle observed at the station, inter-annual variability, and some interesting synoptic events.

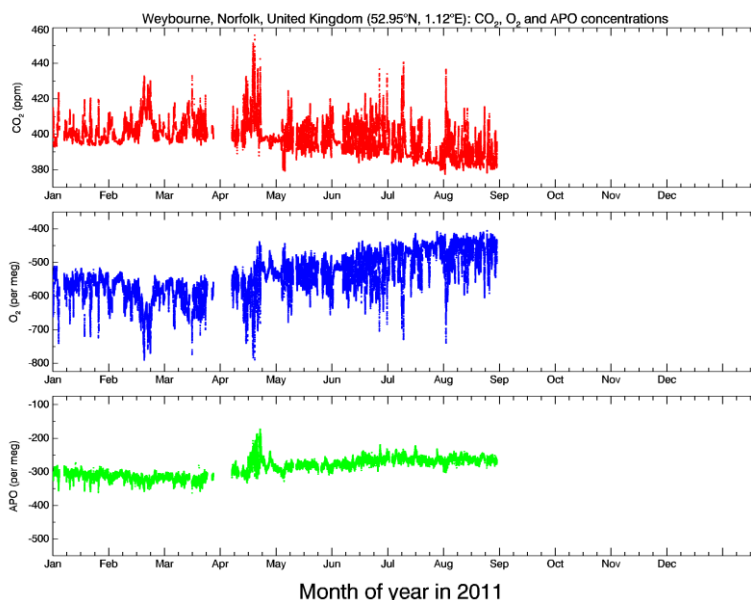


Figure 1. Atmospheric CO₂ (top; in ppm), O₂ (middle; in per meg) and APO (bottom; in per meg) concentrations as measured at WAO in 2011. Y-axis scales have been adjusted so that molar variations are visually comparable for all these species.

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New improvements in the Izaña (Tenerife, Spain) global GAW station in-situ greenhouse gases measurement program.

A.J. Gomez-Pelaez¹, R. Ramos¹, V. Gomez-Trueba^{1,2}, R. Campo-Hernandez¹, E. Dlugokencky³, and T. Conway³

¹ Izaña Atmospheric Research Center, Meteorological State Agency of Spain (AEMET)

² Air Liquide Canarias

³ NOAA-ERSL-GMD

agomezp@aemet.es

We present the main improvements in the in-situ Izaña (Global GAW station) greenhouse gases (GHGs) measurement program during the last few years. First, we present the calibration schemes for the GC-ECD used to measure atmospheric N₂O and SF₆, their calibration processing and statistics, and the software developed for ambient data processing taking into account the hierarchy of calibrations. Also, the in-situ Izaña N₂O and SF₆ series (from June 2007 till July 2011) are showed. Second, we present the software developed to compare in-situ Izaña GHG measurements with co-located NOAA flasks, and summarizes the results of such comparisons for CO₂, CH₄, N₂O and SF₆. Third, some novelties concerning the in-situ Izaña CH₄ measurements are detailed. Finally, updates of the in-situ CO₂ and CH₄ Izaña time series are showed.

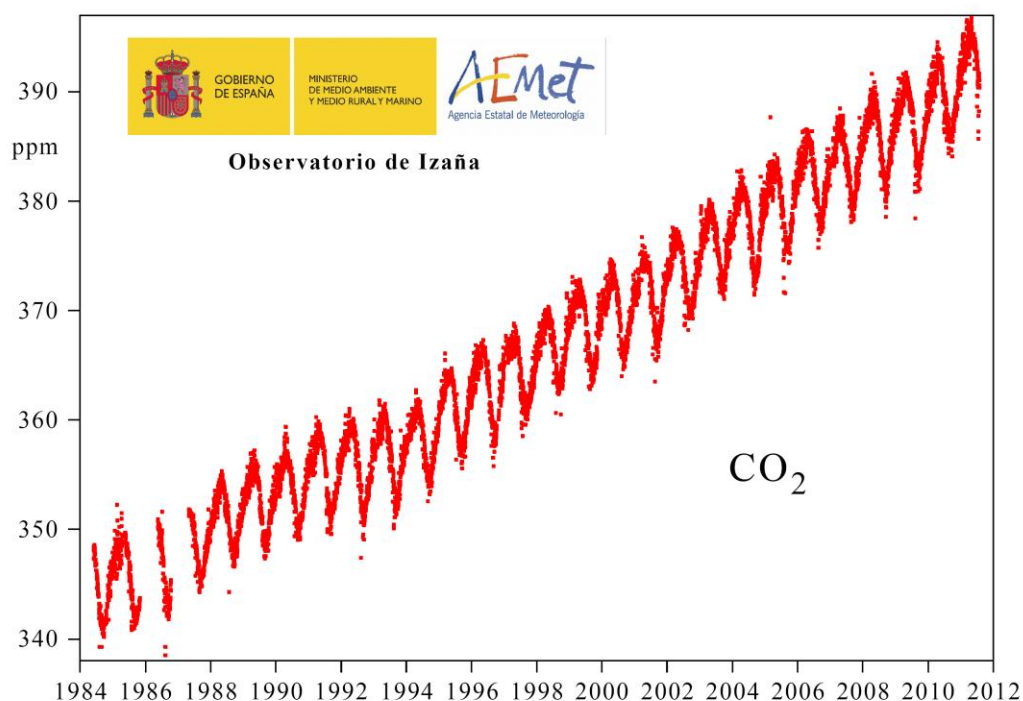


Figure 1. Daily night means (20:00-08:00 UTC) of Izaña in-situ carbon dioxide measurements.

Update on the continuous CO₂/CH₄ measurement at Zotino Tall Tower Observatory (ZOTTO) in Central Siberia

Jan Winderlich¹, Jošt V. Lavrič¹, Huilin Chen^{1,2}, Christoph Gerbig¹, Alexey V. Panov³, and Martin Heimann¹

¹ Max Planck Institute for Biogeochemistry, Jena, Germany

² NOAA Earth System Research Laboratory, Boulder, CO, USA

³ Sukachev Institute of Forest, SB RAS, Krasnoyarsk, Russian Federation

Email: jan.winderlich@bgc-jena.mpg.de, jost.lavric@bgc-jena.mpg.de

The Zotino Tall Tower Observatory (ZOTTO, www.zottoproject.org), located in central Siberia next to the Yenisei River (60°N, 90°E), was equipped with a cavity ring-down spectroscopy CO₂/CH₄/H₂O analyzer in April 2009. Assessing the quality through regular target tank measurements prove the system to be remarkably stable over two years continuous operation (Figure 1).

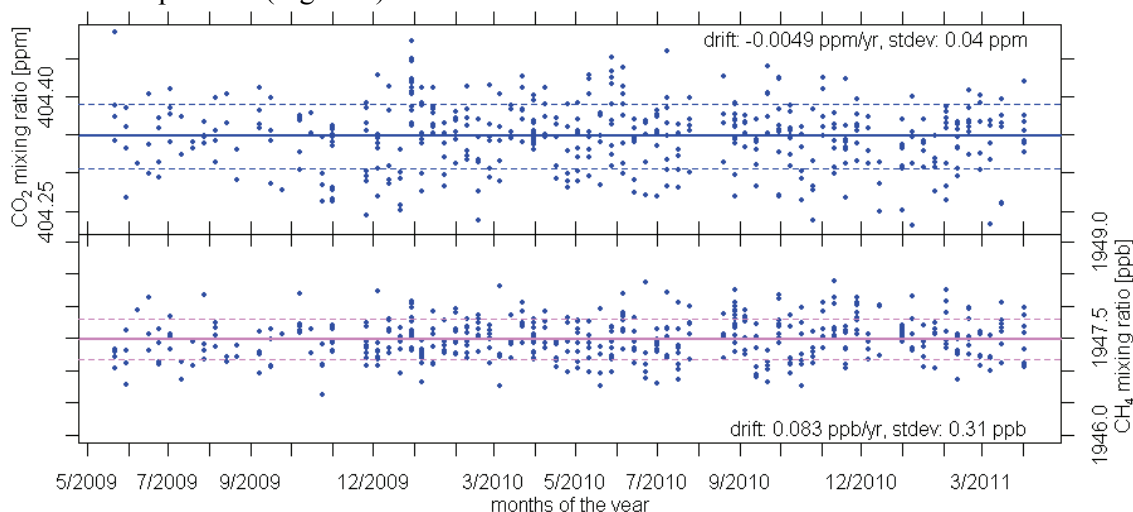


Figure 1. Target tank time series; the solid (dashed) lines indicate the means (standard deviations)

The installation of air buffer volumes in each sample line allows the continuous measurement of six tower levels from 4 m to 301 m height with only one analyzer. The measurement system requires no drying of the sample air. Instead, the simultaneous water vapor measurements are used to correct the dilution and pressure-broadening effects with a repeatability of 0.03 ppm for CO₂ (0.3 ppb for CH₄). The applied correction algorithms have been shown to remain stable over time. Taking into account the measurement uncertainty of the target gas, the calibration gases, and the water correction, the system has a measurement precision (accuracy) of 0.04 ppm (0.09 ppm) for CO₂ and 0.3 ppb (1.5 ppb) for CH₄, which is compliant with the WMO recommendations. Despite the remote location of the system, the maintenance time adds up to only 3.7 % of the operation time.

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Atmospheric Observation Network for New Zealand

Gordon Brailsford, T. Bromley, K Currie, M. Evans, M. Harvey, M. Kotkamp, K. Lassey, J. McGregor, R. Martin, R. Moss, S. Mikaloff-Fletcher, S. Nichol, J. Robinson, V Sherlock, D Smale, K Riedel and A Gomez².

1 National Institute of Water and Atmospheric Research

PO Box 14901, Wellington, New Zealand

2 Victoria University, Wellington New Zealand

g.brailsford@niwa.co.nz

Atmospheric observations have been a key component of research at NIWA, the first observations starting in 1954 with Atmospheric ¹⁴CO₂, and followed later with the first southern hemisphere continuous CO₂ measurement programme at Makara, Wellington in 1969 and relocated to Baring Head, Wellington in 1972. The programme has now expanded to include non-CO₂ greenhouse gases and other tracers that assist in understanding both the carbon cycle and atmospheric chemistry. In recent years the observation network has been expanded to include total column and in situ observations at Lauder in Central Otago, a surface pCO₂ time series out to the Sub Antarctic Surface Waters off Dunedin. Antarctic observations are made routinely at Arrival Heights and periodic transects are collected across the Pacific between New Zealand and the USA and more recently to Japan. The current scope of observations and the future directions will be discussed

Towards a UK-ICOS programme: Existing and underway atmospheric observations on the UK mainland, South Atlantic and Arctic

David Lowry¹, Andrew C. Manning², John B. Moncrieff³, Rebecca E. Fisher¹, Mathias Lanoisellé¹, Philip A. Wilson² and Euan G. Nisbet¹

¹ Royal Holloway, University Of London, Egham TW20 0EX, UK

² School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

³ School of Geosciences, University of Edinburgh, Edinburgh, EH9 3JN, UK

d.lowry@es.rhul.ac.uk

The United Kingdom is working towards a programme which will significantly contribute to the European Union's Integrated Carbon Observation System (ICOS). The UK's Natural Environment Research Council (NERC) is calling for a new £8M consortium proposal, and a £2M measurement project has been recently funded by the UK Government's Department of Energy and Climate Change (DECC). ICOS aims to provide the long-term observations required to understand the present state and predict future behaviour of the global carbon cycle and greenhouse gas emissions in Europe and adjacent regions, and to monitor and assess carbon sequestration and greenhouse gas emission reduction activities, including attribution of sources and sinks by region and sector.

UK infrastructure and ongoing projects in atmospheric greenhouse gas observation includes four atmospheric stations on the UK mainland measuring *in situ* CO₂ concentrations: Angus, Dundee (56.56°N, 2.99°W; UEDIN); Egham, London (51.43°N, 0.56°W; RHUL); Weybourne, Norfolk (52.95°N, 1.12°E; UEA); and Barra, Scottish Hebrides (57.00°N, 07.47°W). These stations have CO₂ records varying in length up to sixteen years, and each also measures a suite of additional greenhouse and greenhouse-related atmospheric species. In addition, RHUL runs remote high precision CRDS-equipped stations on East Falkland Island (51.72°S, 57.85°W) and Ascension Island (7.97°S, 14.40°W). Flask samples are also collected from these stations, as well as from Spitsbergen and Cyprus, and from Cape Point, South Africa (34.35°S, 18.49°E), the latter in collaboration with the South African Weather Service. In 2012, we will initiate flask sampling from Falklands and Ascension for a wider range of species, and *in situ* measurement from Teriberka, Russia (69.2°N, 35.1°E), the latter in collaboration with Main Geophysical Observatory, St. Petersburg.

Laboratory infrastructure for atmospheric greenhouse gas measurement includes the Greenhouse Gas Laboratory at RHUL and the Carbon Related Atmospheric Measurement (CRAM) Laboratory at UEA. RHUL has two Trace Gas CF-IRMS instruments for rapid high-precision $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ analysis, continuous CRDS measurement for CO₂ and CH₄, and PP1 measurement of CO and H₂, as well as older NDIR, GC-FID and RGA systems. Records date from mid-1990s. The CRAM Laboratory is equipped with an NDIR CO₂ analyser, vacuum ultraviolet O₂ analyser, gas chromatograph with FID (CH₄ and CO) and ECD (N₂O and SF₆), and a mass spectrometer (Ar/N₂ ratios). In addition, UEA runs the Calibration Cylinder Filling Facility (CFF) which can prepare dry working and reference standards at sub- and above-ambient concentration for a range of species, at pressures up to 300 bar.

Campaign work is carried out at locations such as Hong Kong, aircraft sampling above the UK, and Arctic locations in Canada, Finland and Russia. These campaigns involve collecting air samples in flasks or bags for subsequent laboratory analysis of atmospheric concentrations (CO₂, CH₄, N₂O, SF₆, CO, H₂, Rn, O₂, and Ar/N₂) and isotopic ratios ($\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$).

Towards continuous measurements of CO and N₂O at Cape Grim

L. Paul Steele, Zoë M. Loh, Rebecca Gregory, Darren A. Spencer, and Paul B. Krummel

Centre for Australian Weather and Climate Research / CSIRO Marine & Atmospheric
Research, Private Bag No. 1, Aspendale, Victoria 3195 Australia

paul.steele@csiro.au

Gas chromatography with electron capture detection (GC/ECD) has been the mainstay analytical technique for studying the trends, seasonal cycles, and distribution of atmospheric nitrous oxide (N₂O). Much has been learned about the atmospheric budget of N₂O by the analysis of such measurements (see, for example Nevison et al., 2011, and references therein). But the uncertainties in the global budget of atmospheric N₂O remain stubbornly large. Fast response, continuous, and highly precise measurements of N₂O based on the use of a quantum cascade laser (QCL)-based instrument (eg. McManus et al., 2008) flown on a research aircraft, have recently revealed compelling new evidence for strong tropical emissions of N₂O (Kort et al., 2011).

Gas chromatography with a heated mercuric oxide detector has been a major technique in the study of tropospheric carbon monoxide (CO), especially in remote, clean air locations. But the nature of the non-linear instrument response has made this technique difficult to maintain in the long-term. Again, a QCL-based instrument can offer fast response, truly continuous, and very precise measurements of CO, with very low detection limits, and a very wide measurement range. The advantages of using such a technique at Cape Grim will be described, as well as some results from our initial experiments with such an instrument.

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China National Report

Ling-Xi Zhou* and Colleagues

Chinese Academy of Meteorological Sciences (CAMS), China Meteorological Administration (CMA), 46 Zhongguancun Nandajie, Beijing 100081, China

zhoulx@cma.gov.cn, zhoulx2007@gmail.com

CMA represents the WMO Commission for Atmospheric Sciences in China and is deeply involved in the GAW programme of the WMO. The CMA initiate/run a Central GHG & Tracers Lab in Beijing and a number of background monitoring stations in China, for example Mt. Waliguan in remote western China (one of the 28 GAW baseline stations) and the long greenhouse gas record contribute to the WDCGG and the Globalview data products. The CMA has strong working relationship with global measurement community within the GAW and has long-term bilateral cooperation with the NOAA/ESRL and other National Meteorological and Hydrological Services (NMHSs) and partners. To serve the needs of the expanding Chinese measurement communities and better contribute to the global network, one of the CMA's capability and effort is to set up a National CCL with linkage to the WMO CCLs. Since 2009, in-situ high accuracy measurement of atmospheric CO₂ and CH₄ mixing ratios by custom designed systems using CRDS technique has been carried out at the five background stations in China. The data was well calibrated relative to international standard scale, which is essential to the integrated database and inverse flux estimations.

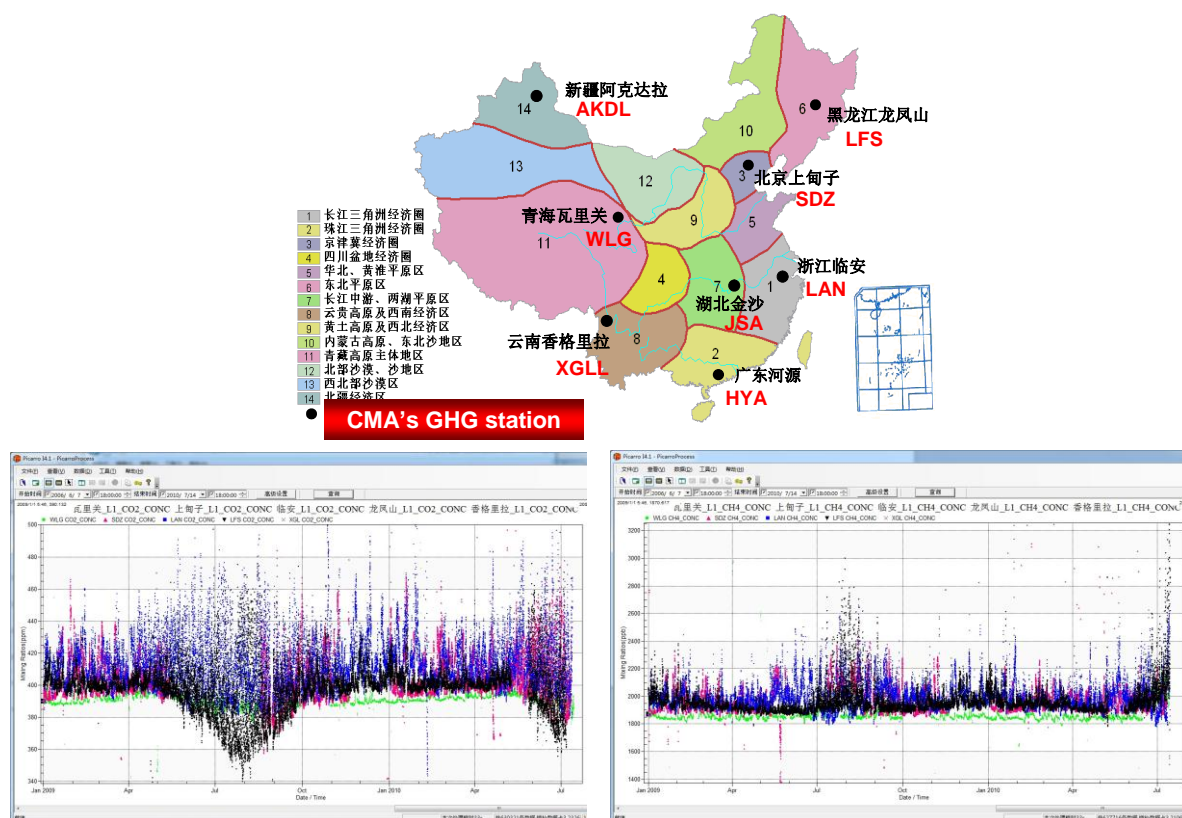


Figure 1. Atmospheric CO₂ (left) and CH₄ (right) record by in-situ CRDS at the five Chinese GAW stations (WLG, SDZ, LAN, LFS and XGL) began in January 2009.

GREENHOUSE GASES BACKGROUND STATIONS IN BRAZIL COAST

Viviane F. Borges¹, Luciana V. Gatti¹, Alexandre Martinewski¹, Caio S.C. Correia¹,
Luana S. Basso¹, Lucas G. Domingues¹, Emanuel Gloor², John B. Miller³

¹*Instituto de Pesquisas Energéticas e Nucleares – IPEN/USP, São Paulo, Brazil.*

²*University of Leeds, Leeds, United Kingdom.*

³*National Oceanic and Atmospheric Administration – NOAA, Boulder, Colorado, USA.*

lvgatti@gmail.com and vivianefran.borges@gmail.com

Since Amazonia represent 50% of tropical forest in the world, the absence of measures in the tropics and the Amazon, generate significant uncertainty in the Climate models predictions. Thus were established two locations along the Brazilian coast and these were compared with to NOAA's global stations in the Atlantic Ocean, Ascension Islands (ASC: 8°S, 14°W) in the South Atlantic Ocean (SAO) and Barbados (RBP: 13°N, 59°W) in the North Atlantic Ocean (NAO). The two background Brazil stations are located in northeast coast were Natal, RN (NAT: 5°S, 35°W), and Salinópolis, PA (SAL: 1°S, 47°W). The air sampling was performed on the surface, using a pair of 2.5l glass flasks. Air samples were analyzed in the Laboratory of Atmospheric Chemistry of IPEN. It was calculated back trajectories using HYSPLIT¹ model to determinate the origin and seasonality of air masses that arrive there. Two pairs of flasks are sampled at the same time for IPEN and NOAA, allowing a continuous comparison program.

The Figure 1 (A) shows the study sites along the Brazilian coast, Natal and Salinópolis and the NOAA global stations, Ascension and Barbados, and (B) the CO₂ concentrations found in NAT and SAL (IPEN) and ASC and RPB from NOAA network.

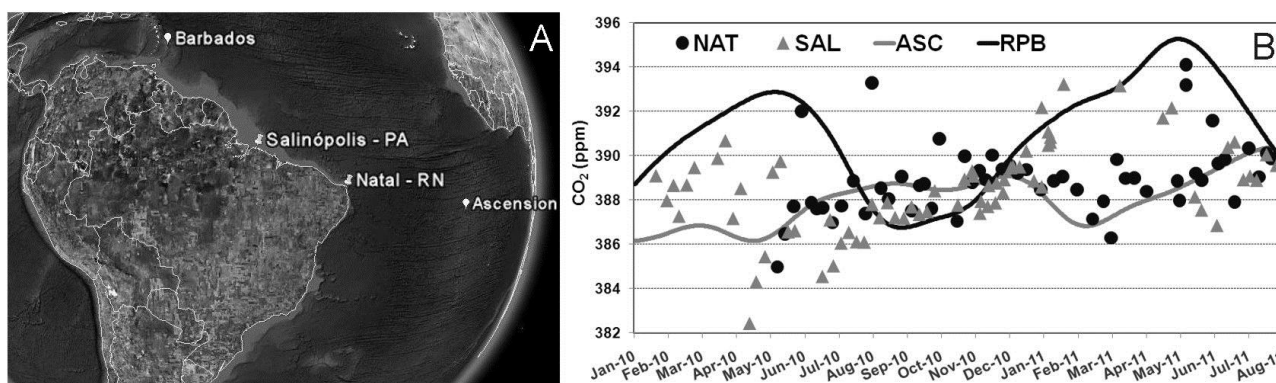


Figure 1: (A) shows the study sites and global stations, and (B) the concentrations for CO₂ found in NAT and SAL, comparing them with the global stations.

The mean concentrations found were: SAL: 388ppm CO₂, 1790ppb CH₄, 98ppb CO, 324ppb N₂O and 7ppt SF₆; and NAT: 389ppm CO₂, 1777ppb CH₄, 78ppb CO, 324ppb N₂O and 7ppt SF₆, generally between the two global stations concentration. CO₂ in NAT presents no seasonality and at SAL follows Barbados seasonality approximately. Observing the concentrations between January to April it is like a average between ASC and RPB. From April to July were lower than the ASC, meteorological studies indicated low wind speed for this period and south origin for the air masses.

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Acknowledgment: IPEN, NERC, NOAA and FAPESP.

ASSESSMENT OF CHEMICAL COMPONENTS PRESENT IN THE ATMOSPHERIC AEROSOL

Sapana Gupta
(IIASA YSSP-2009)
Central Institute of Technology, Raipur CG, India
Email: sapana.gupta02@gmail.com

Key words: Chemical components of PM, Aerosol, Health effects, PCA,

Particulate matter (PM) has been widely studied in recent years due to its potential health impact and need for its control. A study of the atmospheric particulate matter (APM) and associated anions present in aerosol has been carried out for the city of Raipur India using principal component analysis (PCA) and positive matrix factorization (PMF) models. The particulate matter can pass through the natural protective mechanism of human respiratory system and plays an important role in genesis and augmentation of allergic disorders. Sources of air pollution in the area and the unique problem arising out of the emission from the vehicles, industries, etc. have been described. Ambient air quality was monitored along with micrometeorological data and the results are discussed. The status of air pollution in the area has been evaluated and a questionnaire survey was conducted to estimate the allergic symptoms and exposure to assess the respiratory disorders. The data are analysed to evaluate the critical situation arising out of the emission of air pollutants and the impact on human health due to respirable diseases (RDs) to middle class sub-population in the area are assessed. A strategic air quality management plan has been proposed. The particulate matters (PM_{10} and $PM_{2.5}$) in the ambient air at residential site of Raipur city were collected using sequential speciation air sampler (Partisol Model 2300, Thermo Sci., USA) equipped with temperature and humidity sensor. Two types of filters were used for collection of the PM_{10} and $PM_{2.5}$ simultaneously. The teflon and nylon 47-mm filters were used for the collection of the trace elements (i.e. Al, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb) and water soluble ions (i.e. SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+}), respectively. The PCA and PMF models have shown that the central India particulate matters is a six-component system: secondary nitrate, crustal material, long-range transport of regional and marine aerosols, and three anthropogenic sources (metallurgy, coal combustion and cement manufacture). The seasonal evolution of the daily contributions confirmed the interpretations of these sources.

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Atmospheric Carbon Monoxide Measurements at NIWA

Rowena C. Moss¹, Ross J. Martin¹, Gordon W. Brailsford¹

¹ NIWA (National Institute of Water and Atmospheric Research Ltd.),
Private Bag 14901, Wellington 6021, New Zealand.

r.moss@niwa.co.nz

Atmospheric carbon monoxide concentrations have been measured at NIWA since 1989. Recently a Tekran CVAFS (Cold Vapour Atomic Fluorescence Spectrophotometer) mercury detector was installed at the NIWA Gas Lab to replace the old Trace Analytic RGD (Reduction Gas Detector) attached to an HP5890 GC. The CVAFS uses high purity Argon as a carrier on a molecular sieve 5A, 3.x mm OD packed column, and utilises a heated Mercuric Oxide bed to oxidise the CO before the detector. The heated zone for the Mercuric Oxide reaction bed is precisely controlled by the GC inlet control significantly improving baseline stability. Initial issues with interference from the eluting oxygen peak have been avoided by switching the oxygen peak out of the airstream before it reaches the detector.

We have found the CVAFS detector to be significantly more sensitive than the old RGD. The standard deviation of 5 injections of a standard gas (NOAA06 scale CA03825 at 64.4ppb) has reduced from 2 ppb to less than 0.7 ppb and peak heights are an order of magnitude higher.

InGOS - Integrated non-CO₂ Greenhouse Gas Observing System; a new European Infrastructure project

Alex Vermeulen¹ and Ingeborg Levin², Stefan Reimann³, Martina Schmidt⁴, Thomas Bange⁵, Peter Bergamaschi⁶, Albert Bleeker¹, Somon O'Doherty⁷, Arjan Hensen¹, Lynn Hazan⁴, Armin Jordan⁸, Andrew Manning⁹, Ivan Mammarella¹⁰, Eiko Nemitz¹¹, Euan Nisbet¹², Thomas Röckmann¹³, Thorsten Warneke¹⁴

¹ ECN - Energy research Centre of the Netherlands, Petten, Netherlands

² Institut für Umweltp Physik, University of Heidelberg, Germany

³ EMPA, Dübendorf, Switzerland

⁴ Laboratoire des Sciences du Climat et de l'Environnement, France

⁵ IFM-GEOMAR, Kiel, Germany

⁶ JRC - Joint Research Centre, Ispra, Italy

⁷ University of Bristol, United Kingdom

⁸ Max Planck Institute for Biogeochemistry, Germany

⁹ School of Environmental Sciences, University of East Anglia, United Kingdom

¹⁰ University Helsinki, Finland

¹¹ NERC, Edinburgh, United Kingdom

¹² Royal Holloway University of London, United Kingdom

¹³ University of Utrecht, the Netherlands

¹⁴ University of Bremen, Germany

a.vermeulen@ecn.nl

InGOS is a new European infrastructure project that will start in October 2011 and will run for four years. The overall objective of InGOS is to integrate the existing European facilities for monitoring of non-CO₂ greenhouse gases (NCGHGs) in the atmosphere, at ecosystem flux measurement sites and over the ocean, by developing common quality control and quality assurance procedures. Moreover, new measurement techniques and instrumentation will be explored for preparing the integration of NCGHG measurements into ICOS, thus giving these observations an operational, long-term monitoring perspective.

Specific objectives of InGOS are:

- Quality check and harmonize the "historical" NCGHG observations in Europe,
- Standardize measurements by developing common QC/QA procedures, and prepare for integration with the ICOS infrastructure
- Provide near-real time access to the atmospheric CH₄, N₂O, SF₆ and H₂ data, also preparing for integration with the ICOS infrastructure
- Provide access to key field stations and installations such as the calibration facilities and aircraft sampling of flux heterogeneity
- Prepare expansion of the current network with new stations in under sampled regions,
- Improve analysis methods using innovative techniques and strategies,
- Attribute CH₄ source categories by advanced isotope techniques,
- Apply sophisticated, high-resolution inverse models to analyze the measurements made in InGOS and to support further development of the European NCGHG network,
- Link remote sensing data to the in situ network including FTIR XCH₄ observations,

- Improve NCGHG flux measurements and link European flux towers to the atmospheric observational network,
- Stimulate atmospheric science knowledge transfer between experts, and between experts and young scientists,
- Generate a European non-CO₂ GHG observation database, which will be made available to the scientific community and general public via the InGOS Data Centre, in close connection with the ICOS infrastructure methodology and databases.

<http://www.ingos-infrastructure.eu>

Spectroscopic Effects and Eddy Covariance Calculations of Methane Flux

George Burba, Tyler Anderson, Dayle McDermitt, Anatoly Komissarov, Liukang Xu,
Bradley Riensch, Douglas Allyn, and Kevin Ediger

LI-COR Biosciences, Lincoln, NE, United States

george.burba@licor.com

Traditionally, when Eddy Covariance flux is computed, the fast changes in gas density are correlated with fast changes in vertical wind speed. The measured changes in gas density happens due to gas flux itself, due to thermal expansion and contraction of the sampled gas, water vapor dilution, and pressure-related expansion and contraction. These are standard processes described by Ideal Gas Law and by Law of Partial Pressures, and often are called density effects. The gas flux is usually corrected for these density effects using Webb-Pearman-Leuning correction. When gas density is measured by the means of laser spectroscopy, there are also spectroscopic effects affecting measured gas density depending on fluctuations in temperature, water vapor and pressure, in addition to the density effects. The spectroscopic effects are related to changes in the shape of the absorption line due to changes in gas temperature, pressure and presence of water vapour. These effects are specific for each specific absorption line, and the measurement technique.

For closed-path gas analyzers, the majority of density effects and spectroscopic effects could be reduced or eliminated, when: (i) intake tube is very long, (ii) air sample is dry, and (iii) pressure fluctuations are very small. While minimizing uncertainty related to density and spectroscopic effects, use of long intake tubes and drying air sample also lead to significant increase in power demand, and to increased uncertainties due to excess attenuation of the fluctuations of the gas of interest in the drier. Not drying air sample leads to the need for applying density correction for dilution, and spectroscopic corrections for gas absorption due to fast fluctuations in water vapor pressure. For both of these corrections water vapor should be measured accurately at hi-speed inside the closed-path device, which increases measurements costs. In addition, present closed-path analyzers based on laser spectroscopy have to work under significantly reduced pressures, and require powerful pumps and grid power (600-1500 Watts). Power demands may be reasons why these instruments are often deployed at locations with infrastructure and grid power, and not where the gas is produced.

Alternatively, open-path design can be very low-power (*e.g.*, 5-10 Watts) permitting solar-powered deployments, cost-effective permitting an addition of a single new gas measurement to the present array of CO₂ and H₂O measurements, and in-situ avoiding attenuation of gas fluctuations in the intake tube. These features enable long-term deployment of permanent, portable or mobile open-path flux stations at remote locations with high production of the gas of interest. However, open-path density and spectroscopic effects cannot be neglected. Here we propose a new way to account for spectroscopic effects due to fast fluctuations in air temperature, *water vapor and pressure in the same manner as Webb et al.* (1980) proposed a way of accounting for respective density effects. Since both density effects and spectroscopic effects are known from Gas Laws and HITRAN respectively they could be incorporated into WPL correction. We use an example of the fast open-path CH₄ gas analyzer, LI-7700, yet the proposed approach would also apply to any closed-path design where fluctuations in temperature, water vapor and pressure are not fully eliminated.

Three and a half years of atmospheric CO₂ and O₂ data from Ivittuut, Southern Greenland

Marc Delmotte¹, Jean-Louis Bonne¹, Jošt Valentin Lavrič², Andrew C. Manning³, Willi Brand², Martina Schmidt¹ and Victor Kazan¹

¹ Laboratoire des Sciences du Climat et de l'Environnement, Gif sur Yvette, France

² MPI-BGC, Jena, Germany

³ University of East Anglia, Norwich, United Kingdom

marc.delmotte@lsce.ipsl.fr

Since autumn 2007, an atmospheric monitoring station has been running at Ivittuut southern Greenland (61.21°N, 48.17°W). The station is equipped with highly precise analysers that provide continuous CO₂ and O₂ records, and a set of meteorological sensors (temperature, pressure and relative humidity, wind speed and direction). Regular flask sampling allows for additional measurements of CH₄, CO, N₂O, H₂, and SF₆ mixing ratios, and CO₂ isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) as well as for an independent quality control of the continuous records.

In addition to the LSCE automated data treatment chain handling the CO₂ data, we have now also developed a data treatment chain to process our O₂ raw data

Quality control and filtering procedures applied for this station will be presented with an emphasis on the method applied for O₂ data treatment. We will show the full records for CO₂ and O₂ and discuss the results obtained in terms of inter-annual and seasonal variability with comparison with other high latitude sites, as well as APO (Atmospheric Potential Oxygen). A focus on particular synoptic events will also be presented as “case studies” for air mass origin tracking, using back trajectory models.

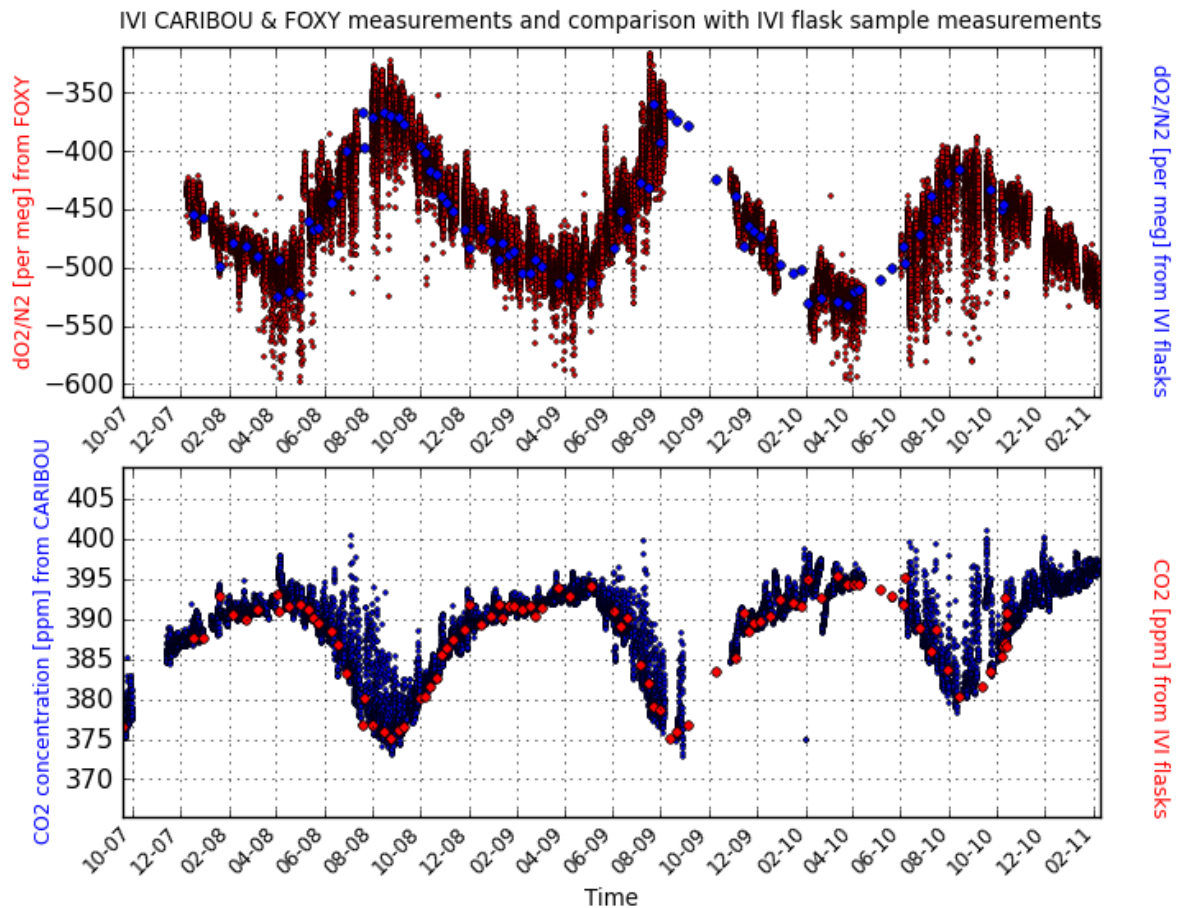


Figure 1: CO₂ and O₂ records at Ivittuut (Southern Greenland)

An accurate CO₂ measurement system for standard gases using NDIR CO₂ analyzer and CRDS ¹³CO₂ analyzer

K. Katsumata, H. Nara, Y. Tohjima, Y. Takahashi, T. Machida, and H. Mukai

National Institute for Environmental Studies (NIES), Tsukuba, Ibaraki, Japan

katsumata.keiichi@nies.go.jp

Non-dispersive infrared CO₂ analyzer (NDIR) is the widely used instruments for measuring atmospheric CO₂ mol fraction because of its high precision, easiness of the operation, and so on. However, because the NDIR measurements are slightly affected by the isotopic composition of CO₂ (Lee et al., 2006, Tohjima et al., 2009), we should evaluate the isotope effect when there are differences in the isotopic compositions of CO₂ between air samples and standard gases. At National Institute for Environmental Studies (NIES), mixtures of pure CO₂ gas derived from burned petroleum and purified air are used as primary standard gases and the their CO₂ isotopic composition ($\delta^{13}\text{C} = -32\text{‰}$) are lighter than the atmospheric value ($\delta^{13}\text{C} = \sim -8\text{‰}$). The isotope effect of our NDIR analyzers, which are calibrated against above primary standard gases, are estimated to be ranging from 0.04 to 0.08 ppm for the measurements of CO₂ in the air samples (Tohjima et al., 2009). In addition to the air samples, we need to determine the CO₂ mole fractions of more than 200 working standard gases used for ground-based measurements, airborne measurements, and shipboard measurements every year. Because these working standard gases, being similar CO₂-in-air mixtures to our CO₂ standard gases, have rather wide range of $\delta^{13}\text{C}$ values from -25 ‰ to -35 ‰, the isotope effects for the NDIR measurements of those standard gases should be evaluated to accurately propagate the CO₂ mole fraction scale. WMO recommends that the isotopic composition of distributed standard gases should be roughly determined (GAW Report 194). For this purpose, we have developed a new CO₂ measurement system, in which the ¹³C isotopic composition is also determined easily and rapidly together with the NDIR CO₂ measurements. We use a wavelength-scanned cavity ring-down spectrometer (G2101-i, Picarro) for the $\delta^{13}\text{C}$ measurements. The analytical precision (1σ) of $\delta^{13}\text{C}$ value is about 0.15 ‰ (5 min average value). This result shows the isotope effect for the NDIR measurements can be corrected with a precision of 0.01 ppm or less.

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Central Calibration Laboratory for Hydrogen:

First Steps

A. Jordan¹, B. Steinberg¹, R.L. Langenfelds², L.P. Steele², P. C. Novelli³, K. Katsumata⁴,
T. Machida⁴

¹ Max Planck Institute for Biogeochemistry, Jena, Germany

² CSIRO Division for Marine and Atmospheric Research, Aspendale, Australia

³ National Oceanic and Atmospheric Administration, ESRL-GMD, Boulder, USA

⁴ National Institute for Environmental Studies, Tsukuba, Japan

ajordan@bgc-jena.mpg.de

At the 15th WMO Experts Meeting the Max-Planck Institute for Biogeochemistry (MPI-BGC) has taken over the role of the WMO-GAW Central Calibration Laboratory for molecular hydrogen (H₂) measurements.

Following the “General Requirements for Central Calibration Laboratories” first activities in this role have been

- a) to carry out comparisons with independent primary scales, namely the CSIRO, the NIES and the NOAA scale
- b) prepare a second set of standards as a backup for the scale
- c) conduct additional experiments to check the stability of the scale
- d) and verify the consistency of the scale using a superior detection technique
- e) provide calibrated reference gas mixtures to measurement groups

A comparison using natural air mixtures in 4.5 L stainless steel containers containing 400 to 670 ppb hydrogen have been circulated between MPI-BGC, NOAA and NIES, and for some samples also CMAR. NOAA and the NIES data were in good agreement showing on average 6 ppb and 7 ppb, respectively, lower results than MPI. CMAR results were 17 ppb lower than MPI data. This latter offset has confirmed a stable inter-laboratory difference observed in multiple other comparisons for several years. CMAR has decided to convert their scale to the MPI-2009 scale.

A backup set of twelve high pressure H₂ in air standards ranging from 200-1200 ppb has been prepared and calibrated. In parallel, some 20 additional mixtures were prepared by diluting a known volume of pure H₂ in hydrogen free air to check the stability of the primary standards. As an additional check of the consistency of the primary calibration standard set these standards have been analysed with a GC-Helium Ionization Pulsed Discharge Detector. The observed absolute residuals are on average below 0.5 ppb.

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Overview on ten years of WCC-N₂O

H.E. Scheel

Karlsruhe Institute of Technology (KIT), IMK-IFU
82467 Garmisch-Partenkirchen, Germany

hans-eckhart.scheel@kit.edu

The World Calibration Centre for N₂O (WCC-N₂O) has been established in 2001 as a central GAW facility according to the requirements of the GAW Strategic Plan 2001–2007 (WMO/GAW Report No. 142). Its overall goal is the improvement of the N₂O data quality and compatibility within the network. The WCC-N₂O is linked to the GAW standard scale maintained by the Central Calibration Laboratory (CCL) for N₂O. The WCC-N₂O (<http://imk.fzk.de/wcc-n2o/>) is hosted by the Karlsruhe Institute of Technology (formerly Forschungszentrum Karlsruhe), IMK-IFU, and its activities are conducted under supervision and through funding by the Quality Assurance/Science Activity Centre (QA/SAC) Germany, operated by the German Environment Agency (UBA). As specified by GAW, the major tasks of the WCC-N₂O comprise the development of quality control procedures, conducting audits at stations and intercomparison experiments as well as providing training and technical advice to GAW station personnel. After ten years of operation of the WCC-N₂O, this presentation gives an overview on its activities and achievements.

During the entire period, the work conducted in the analytical laboratory was related to comparisons of N₂O standards of different levels in the traceability chain and dedicated to different purposes. Presently, eight laboratory standards (range 253 – 358 ppb), recalibrated by the CCL in 2009, establish the link to the GAW N₂O scale. They are used for the calibration and surveillance of a suite of 22 gas mixtures. Five of them serve as scale back-up, while 17 are suitable as travelling standards for audits and intercomparisons, usually comprising sets of five cylinders. Moreover, the WCC-N₂O took part in three international intercomparison experiments.

From the ten system and performance audits conducted since 2002, considerable progress over the years can be noted with respect to network compatibility of N₂O measurements by GAW stations. Thanks to the recommendations of GAW meetings as well as updated measurement guidelines including data quality objectives, and based on the acquisition of CCL-calibrated standards, by several stations the link to the GAW N₂O scale was improved or newly established. On the analytical side, the audits have revealed significant differences in performance for the gas chromatographic systems, even if equipped with similar instrumentation. In conclusion, the fulfilment of the GAW N₂O data quality objectives still remains a challenge. Details on these issues will be discussed. For completeness, a brief summary of other activities of the WCC-N₂O will also be presented.

Automated analysis of $\delta^{13}\text{C}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in CH_4 and CO_2 from air samples in flasks using a new twin cryo-trap / GC / IRMS system

Magnus Wendeborg, Martin Strube , and Willi A. Brand,

Max-Planck-Institute for Biogeochemistry (Beutenberg Campus; Hans-Knoell-Str. 10, 07745 Jena, Germany.

wbrand@bcg-jena.mpg.de

A new system for high precision stable isotopes measurements of carbon and hydrogen in atmospheric methane is being developed at the MPI-BGC in Jena. The design aims utilizing flask samples from existing sampling programs without the need of extra samples for methane analysis. Thus, a frugal use of the sample is an important design criterion. To minimize the total sample volume needed for the analysis, both CO_2 and methane isotopes are measured simultaneously using two Delta V mass spectrometers. One of the mass spectrometers is used for $\delta^{13}\text{C}$ of CO_2 and methane and $\delta^{18}\text{O}$ of CO_2 , while the second MS is dedicated to measure $\delta^2\text{H}$ of methane.

The *iSAAC* system (*'isotopic Analysis of Atmospheric Constituents'*) consists of an inlet carousel – capable of holding 16 sample flasks (1-5 L), from which sample gas is pulled through a series of sample loops mounted within three consecutive Valco 10–port valves. Each 10–port valve takes aliquots from the sample stream, starting with aliquots for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 , followed by $\delta^{13}\text{C}$ of methane and last $\delta^2\text{H}$. In the latter two cases, the CH_4 is pre-concentrated in the respective loops from a larger sample amount (50-100 mL)^{1,2} using a newly designed cryo-trap system operating at variable temperatures down to $-130\text{ }^\circ\text{C}$. The use of 10–port valves allows for a second gas – a precisely calibrated working reference air, to be used in parallel with the sample according to the Principle of Identical Treatment³.

Using these design principles we aim at robust precision levels of $<0.015\text{ }‰$ ($\delta^{13}\text{C}$ of CO_2), $<0.02\text{ }‰$ ($\delta^{18}\text{O}$ of CO_2), $<0.05\text{ }‰$ ($\delta^{13}\text{C}$ of CH_4) and $<1.5\text{ }‰$ ($\delta^2\text{H}$ of CH_4) respectively, at ambient level mixing ratios ($\sim 400\text{ ppm}$ for CO_2 and $\sim 2\text{ ppm}$ for CH_4). These precision levels are planned to hold for future records spanning long time periods (decades).

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A new solution to a standard problem: creating full air standards with precisely referenced isotopic compositions of methane covering the present and past atmospheric variability in $\delta^{13}\text{C}$ -CH₄

Hinrich Schaefer¹ and Myriam Guillevic², Peter Sperlich², Christo Buizert², Theo Jenk²,
Thomas Blunier²

¹ National Institute of Water & Atmospheric Research Ltd, 301 Evans Bay Parade, Greta Point, Wellington 6021, New Zealand

² Niels Bohr Institute, Centre for Ice and Climate, Juliane Maries Vej 30, 2100 Copenhagen, Denmark

h.schaefer@niwa.co.nz, mgllyc@nbi.ku.dk, sperlich@nbi.ku.dk

In order to understand the changes in atmospheric methane concentrations and to identify corresponding biogeochemical mechanisms, studying the isotopic composition of methane from atmospheric or ice cores samples is a promising tool.

An experimental setup to measure isotopes of atmospheric methane requires calibration with reference gases of known isotopic composition. Unlike CO₂ and H₂O measurements, there is no universal standard material or procedure to reference methane isotopes (such as a recommendation by the WMO) [1]. The increasing numbers of laboratories measuring methane isotopes and the high precision level reached emphasizes the need to agree on a universal referencing procedure. In most laboratories, the lack of universal methane standards has been overcome by measuring the samples versus full air standards that have previously been referenced in an external laboratory. These reference procedures are laboratory specific and result in limited amounts of reference material. Both points can limit the agreement of different laboratories measuring the same sample.

To overcome the referencing problem of methane isotopes, we built a system which enables us to produce full air standards with methane mixtures of precisely referenced $\delta^{13}\text{C}$ and δD isotopes. The central part of the setup is a combustion and trapping system to quantitatively combust pure methane into CO₂ and H₂O and to separately trap these combustion products for consecutive $\delta^{13}\text{C}$ and δD measurement by mass spectrometry. By using methane of two different sources, characterized by two different isotopic compositions, we can mix large amounts of pure methane to any given isotopic value between -40‰ and -52‰ in $\delta^{13}\text{C}$ or between -170‰ and -320‰ in δD . An aliquot of the characterized methane mixture is then mixed with zero air, which was previously purified from any methane content. By varying the amount of methane and zero air in the target mixture, we are able to control methane concentration with well characterized methane isotopes.

References:

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¹⁴CO₂ Processing and Measurement Activities at CU-INSTAAR and NOAA/ESRL

Scott J. Lehman¹, Pieter P. Tans², John B. Miller^{2,3}, Stephen A. Monzka², Colm Sweeney^{2,3}, Arlyn Andrews^{2,3}, Jocelyn C. Turnbull^{2,3,4}, John Southon⁵

¹Institute of Arctic and Alpine Research, University of Colorado, Boulder CO USA

²NOAA Earth System Research Laboratory, Boulder CO USA

³Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder CO USA

⁴now at: Rafter Radiocarbon Laboratory, Lower Hutt NZ

⁵Keck AMS Facility, University of California, Irvine CA USA

Scott.Lehman@Colorado.edu

The small radiocarbon fraction of total CO₂ ($\sim 1:10^{12}$ ¹⁴C:C) has proven to be an ideal tracer for its fossil fuel derived component. Unlike all other contributions to the CO₂ budget, the fossil fuel component is devoid of radiocarbon, so that temporal and spatial gradients in recently added fossil fuel CO₂ can be readily identified as radiocarbon gradients provided there is adequate precision in the measurements. Over large industrialized land areas such as Eurasia and North America, the use of ¹⁴C to isolate the recently added fossil fuel contribution also quantifies (by difference) the change in atmospheric CO₂ due to uptake and release by the terrestrial biosphere. Here we will report on a growing number of ¹⁴CO₂ processing and measurement activities within the NOAA Cooperative Global Air Sampling Network, with a focus on the use of ¹⁴CO₂ to constrain the relative and absolute emissions of a large suite of anthropogenic trace gases measured in the same samples.

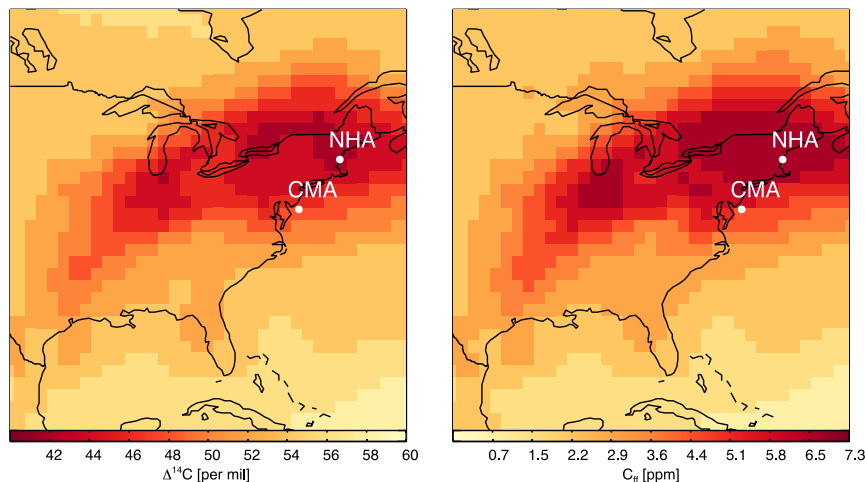


Figure 1: Model representations of annual mean $\Delta^{14}\text{C}$ (right panel) and the fossil fuel component of total CO₂ (left panel) in the atmosphere near the surface over eastern North America, from the TM5 transport model. Color scales are fixed according to the mass balance relationship between $\Delta^{14}\text{C}$ and recently added fossil fuel CO₂ of -2.7 per mil/ppm. Small differences in the color patterns are mostly due to small $\Delta^{14}\text{C}$ gradients arising from the terrestrial disequilibrium flux of ¹⁴C, which can be independently quantified. CMA and NHA denote 2 aircraft sampling sites at which we have been making measurements since 2004.

Atmospheric ^{14}C measurement capability at the Rafter Radiocarbon Laboratory

Jocelyn Turnbull^{1,2}, Troy Baisden¹, Albert Zondervan¹, Christine Prior¹, Gordon Brailsford³, Rowena Moss³

¹Rafter Radiocarbon Laboratory, GNS Science, Lower Hutt, New Zealand

²CIRES, University of Colorado, Boulder, CO, USA

³NIWA, Wellington, New Zealand

jocelyn.turnbull@colorado.edu

The radiocarbon content of atmospheric CO_2 ($\Delta^{14}\text{CO}_2$) is an increasingly important tracer used to quantify the different CO_2 sources. Due to the absence of ^{14}C in fossil fuels, $\Delta^{14}\text{CO}_2$ is perhaps the best way to quantify recently added fossil fuel CO_2 in the atmosphere. The sea-air CO_2 flux also has $\Delta^{14}\text{C}$ different from the atmosphere, so $\Delta^{14}\text{CO}_2$ observations can be used to examine the one-way gross CO_2 flux out of the oceans. Yet $\Delta^{14}\text{CO}_2$ continues to be a challenging measurement, due to the very low abundance of ^{14}C . Single sample uncertainties are currently, at best, about 2‰, and ~2 liters of whole air are needed (the gas counting method requires ~400L of air for similar precision). Measurement capacity is also limited, due to the complex processing and long measurement times required.

The collaboration between NIWA and the Rafter Radiocarbon Laboratory at GNS Science has a long history of atmospheric $\Delta^{14}\text{CO}_2$ measurements, starting in Wellington in 1955. In 2010, the Rafter lab obtained a new accelerator mass spectrometer (AMS) for radiocarbon measurements. A major focus emerging from the upgrade is the opportunity to expand the atmospheric $\Delta^{14}\text{CO}_2$ capability. We will present our progress toward demonstrating that verifiable 2‰ precision can routinely be obtained on this instrument. We will discuss developments in sample preparation and improvements in methodology to obtain this precision on samples of ~1L of whole air. Finally, we will present progress on our immediate goal – a replicated high precision Baring Head $\Delta^{14}\text{CO}_2$ record from archived samples.

Seeking isotopically suitable CO₂ for standard gas

-Production of C isotopic reference gas series from commercially available liquid CO₂-

Hitoshi Mukai, Yumi Osonoi, Yukio Terao, and Yoko Kajita

Center for Global Environmental Research, National Institute for Environmental Studies,
16-2 Onogawa, Tsukuba, Ibaraki 305-5806 Japan

lnmukaih@nies.go.jp

Carbon isotope ratio of CO₂ is important item in terms of C budget study and CO₂ concentration analysis. If our standard gas for CO₂ concentration is produced using commercially available liquid CO₂, C isotopic ratio is very light (-30 - -40 per mil) compared to atmospheric CO₂ (-9 per mil). Sometimes people want to use standard CO₂ gas which has the same isotopic ratio as atmospheric CO₂, because CO₂ analysis by NDIR and CRD technology are known to be affected isotopic composition of standard and sample CO₂.

In general to seek isotopically suitable CO₂ for standard gas is believed to be hard, because industrial liquid CO₂ is usually come from oil chemical process and natural gas (methane) process to produce ammonia. On the other hand, natural CO₂ from volcanic activity is known to have different isotope ratio. We confirmed that hot spring water in Ohita prefecture (JPN) contained high concentration of CO₂, which has -10 permil in C isotope ratio. It must be one of candidates for standard if CO₂ is extracted from it on industrial base.

This time we found that one Japanese liquid CO₂ producer used limestone as a carbon source. This liquid CO₂ has much heavy isotope ratio (about 2 per mil !). Since this CO₂ is commercially available, we have tried to make CO₂ cylinder series of different isotope ratio from -40 to 2 permil (-40, -30, -20, -10, 0, 2 permil) by mixing of usual light CO₂ (A) come from natural gas and this heavy CO₂ (B).

Usually a certain amount of CO₂ is needed as gas cylinder to do experimental works. Therefore, this series must be useful to test isotopic effect on NDIR and CRD, as well as isotopic analysis evaluation.

Table 1. Isotope ratio of liquid CO₂

	Delta 13C (permil vs VPDB)	Delta 18O (permil VPDB-CO ₂)
A	-42.2	-10.9
B	1.8	-12.8

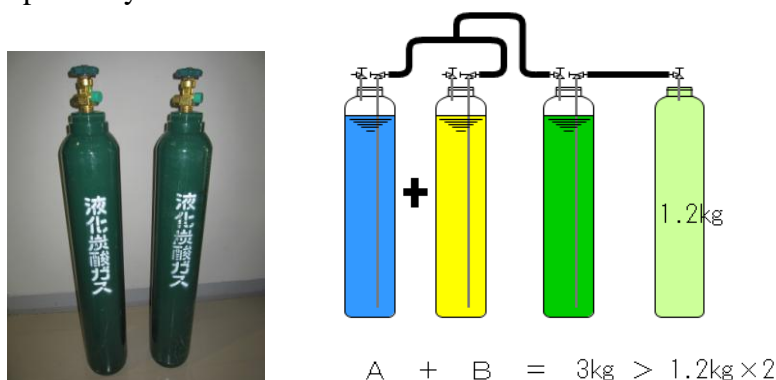


Fig 1 Isotope ratio adjusted CO₂ cylinders and mixing method

Traceability Maintenance in $\delta^{13}\text{C}$ (CO_2) Analysis: applications to continuous measurements via Picarro *G1101-i* Analyzer

Lin Huang, A. Chivulescu, F. Vogel, D. Ernst, D. Worthy, Y.-S. Lee, S. Racki

Climate Research Division (CRD), Atmospheric Sci. & Tech. Directorate (ASTD), STB,
Environment Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4 Canada

lin.huang@ec.gc.ca

A unique traceability pathway for high precision CO_2 isotope measurements has been established and maintained over the last 10 years (2001-2011) in our lab. The stability of the primary anchor, which has been directly calibrated by NBS19- CO_2 and used to link all the individual measurements to the primary scale of VPDB, is shown in the Figure. Taking into account of the uncertainty of the primary anchor, an overall uncertainty of individual measurements in $\delta^{13}\text{C}$ can be estimated.

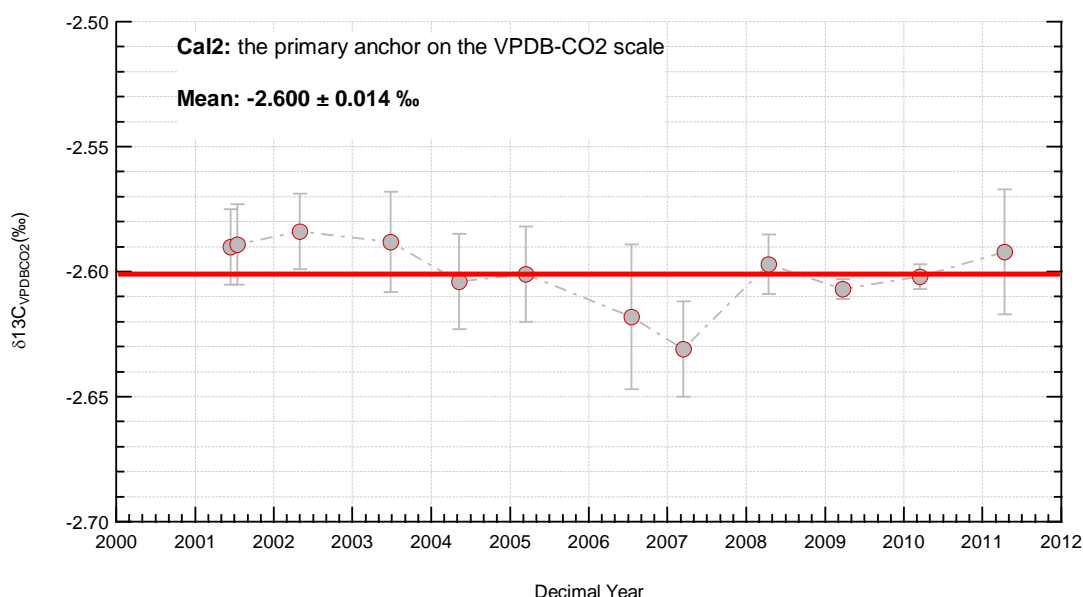


Figure 1. Stability of the primary anchor (i.e., the pure CO_2 evolving from a calcium carbonate powder called “Cal2”) of $\delta^{13}\text{C}$ on VPDB- CO_2 scale during a period of 10 years (2001 to 2011) by the CRD’s stable isotope lab, Environment Canada, in Toronto.

The same principle has been applied to the continuous $\delta^{13}\text{C}$ measurements via CRDS (i.e., *G1101-i* Picarro ^{13}C analyzer, the first generation). Similar to the traditional mass spectrometry measurement, an approach of using frequent injections of Target Working References and Working Standards (from high-pressure air- CO_2 tanks) between sample measurements has been implemented to address the short-term noises (during the period of minutes) and long-term drifts (during the period of hours) of the analyzer. The approach will be presented and discussed, including the traceability pathway, the measurements and calibration schemes. The uncertainty of the measurements will be also estimated.

JRAS–06; an accurate multi-point stable isotope scale anchor for atmospheric CO₂?

Magnus Wendenberg, Michael Rothe, Jürgen M. Richter, and Willi A. Brand

Max-Planck-Institute for Biogeochemistry (Beutenberg Campus; Hans-Knoell-Str. 10, 07745 Jena, Germany.

wbrand@bcg-jena.mpg.de

With the IMECC project^a ending in September this year the time has come to decide about the future use of the JRAS-06^b scale anchor¹⁻⁵. To date the results^c from IMECC clearly show that the JRAS scale anchor is stable; it does not suffer from any significant scale contraction and, because it is based on well-characterized calcite materials, it can be maintained with the required precision and accuracy. With the latest addition of a natural air sample to the JRAS set the number of points for CO₂-in-air scale comparisons has grown to three, covering the full range from the primary VPDB anchor to ambient CO₂-in-air values. Instead of single-point inter-comparisons it has now become possible to directly evaluate entire local scale compatibilities relative to the international (2-anchor) VPDB scale based on the suite of JRAS scale anchors. To evaluate the “whole” scale has turned out to be especially useful for revealing the rather common scale contraction issues (η -effect⁶). It may also serve as a way to re-calculate archived data to the JRAS-06 based VPDB scale.

We would like to thank the laboratories that have participated in the JRAS project and thereby helped us test and improve the JRAS concept.

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^a <http://imecc.ipsl.jussieu.fr/>

^b JRAS = Jena Reference Air Set

^c http://www.bgc.mpg.de/service/iso_gas_lab/pmwiki/pmwiki.php

Advances in instrumentation for measurements of $^{13}\text{CO}_2$, C^{18}OO and CO_2 in ambient air

Doug Baer,¹ Feng Dong,¹ Manish Gupta,¹ Robert Provencal,¹ Tom Owano¹

¹Los Gatos Research, 67 East Evelyn Avenue, Suite 3, Mountain View, CA 94041
USA

d.baer@LGRinc.com

Fast, precise, and accurate measurement of $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$ in CO_2) and $\delta^{18}\text{O}$ of carbon dioxide is desirable for a number of applications including atmospheric chemistry and carbon sequestering. Recent advances in laser absorption spectroscopy, including cavity enhanced techniques, have enabled field portable instruments which have a number of advantages over traditional, laboratory-based mass spectroscopy systems. We report on the recent developments and improvements of an analyzer, based on a patented laser absorption technique (off-axis integrated cavity output spectroscopy or Off-Axis ICOS), which measures $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO_2 , CO_2 , and H_2O (vapor). The analyzer operates at 1 Hz and can provide a precision for $\delta^{13}\text{C}$ of 0.1‰ (1 σ) and $\delta^{18}\text{O}$ of 1‰ (1 σ) with less than 6 minutes of averaging on mole fractions typically present in ambient air. Higher precision may be reported with higher mole fractions. Besides free-flow (continuous flow) operation, the instrument also can analyze discrete gas samples (via manual injection). For ambient levels of CO_2 (350 ppm to 1000 ppm), the analyzer operates with a gas volume of about 120 mL (standard). With appropriate dilution, smaller sample volumes of higher mole fractions of CO_2 may be analyzed. In the case of pure (100%) CO_2 samples, only 100 microliters of sample is required. In addition, the instrument also reports water vapor mixing ratio to allow the possibility of determining the CO_2 mole fraction and isotopic ratios without removing water vapor (sample drying) for those applications where drying is difficult. Details concerning instrument performance, operation, sample dilution procedure, and calibration will be presented.

Novel instrumentation for measurements of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ in ambient air

Doug Baer,¹Feng Dong,¹ Manish Gupta,¹ Robert Provencal,¹Tom Owano¹

¹Los Gatos Research, 67 East Evelyn Avenue, Suite 3, Mountain View, CA 94041
USA

d.baer@LGRinc.com

Methane is a potent greenhouse gas, whose atmospheric surface mixing ratio has almost doubled compared with preindustrial values. Methane can be produced by biogenic processes, thermogenic processes or biomass, with different isotopic signatures. As a key molecule involved in atmospheric radiative forcing, methane is thus one of the most important molecules linking the biosphere and atmosphere. Therefore precise measurements of mixing ratios and isotopic compositions will help scientists to better understand methane sources and sinks. To date, high precision isotope measurements have been exclusively performed with conventional isotope ratio mass spectrometry, which involves intensive labor and is not field deployable. Optical studies using infrared laser spectroscopy have only recently begun to report isotopic carbon ratios in methane at mixing ratios near ambient levels without preconcentration.

We present characterization of a portable Methane Carbon Isotope Analyzer (MCIA), based on cavity enhanced laser absorption spectroscopy, that provides in-situ measurements of the carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$, $\delta^{13}\text{C}$) and methane mole fraction (CH_4) in ambient air. The gas sample is introduced to the analyzer directly without any requirement for pretreatment or preconcentration. A precision better than 1 per mill ($< 1 \text{ ‰}$) may be achieved in less than 100 seconds (measurement time) in a 1.5-ppm methane sample (or greater) in air. Higher precision may be obtained with longer averaging and with higher mole fractions. The MCIA can report carbon isotope ratio and mole fraction measurements over a range of mole fractions ranging from 1.5 - 100 ppm CH_4 in air. A dynamic dilution system, automatically controlled by the MCIA, may be used to extend the upper range by a factor of 100x to enable measurements up to 1% methane in air. Results of laboratory tests and field measurements will be presented.

Novel instrumentation for direct measurements of $^{15}\text{N}^{14}\text{NO}$ and $^{14}\text{N}^{15}\text{NO}$ in ambient air

Doug Baer,¹Feng Dong,¹ Manish Gupta,¹ Robert Provencal,¹Tom Owano¹

¹Los Gatos Research, 67 East Evelyn Avenue, Suite 3, Mountain View, CA 94041
USA

d.baer@LGRinc.com

The stable isotope composition of atmosphere trace gases provides information of their origin and fate that cannot be determined from their mole fraction measurements alone. Biological source and loss processes, like bacterial production of N_2O , are typically accompanied by isotopic selectivity associated with the kinetics of bond formation and destruction. Due to the relatively low N_2O concentration in ambient air, of the three major biologically mediated greenhouse gases (CO_2 , CH_4 and N_2O), the understanding of N_2O isotopic budget lags behind the other gases.

We report on the development of novel instrumentation for real-time measurements of site-specific isotopic nitrogen ($\delta^{15}\text{N}^a$, $\delta^{15}\text{N}^b$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$) and mixing ratio $[\text{N}_2\text{O}]$ of nitrous oxide over a wide range of mixing ratios. This novel technology, which employs cavity enhanced absorption and a mid-infrared tunable laser and does not require any cryogenic components, has been developed for *in situ* simultaneous measurements of the mixing ratios of main isotopomers – $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{14}\text{N}^{18}\text{O}$, which leads to the nitrogen-isotope ratio ($\delta^{15}\text{N}$) and the ^{15}N site-specific enrichment. A precision of better than 1 per mil may be achieved in ambient air (with 320 ppb N_2O) in less than 100 seconds measurement time. Further details on the operation and performance of the instrument will be presented.

***In situ* observations of atmospheric CH₄ and CO₂ mixing ratios and stable isotopes through the Western Pacific Ocean.**

Tony Bromley, G Brailsford, R. Martin, R. Moss, S. Mikaloff-Fletcher and S. Nichol.

National Institute of Water and Atmospheric Research

PO Box 14901, Wellington, New Zealand

a.bromley@niwa.co.nz

CH₄ and CO₂ mixing ratios were measured using a Picarro CRDS analyser on a voyage of MV Transfuture 5 between Nelson, New Zealand and Osaka, Japan in October/November 2009. In addition large whole air samples were collected for later analysis for ¹³CH₄/¹²CH₄.

Large variations in mixing ratio were recorded in the tropical regions and in the Northern Hemisphere. Changes in the stable isotope composition show evidence of air-mass changes.

These variations are discussed in terms of atmospheric transport from source regions using meteorological data and trajectory analyses.

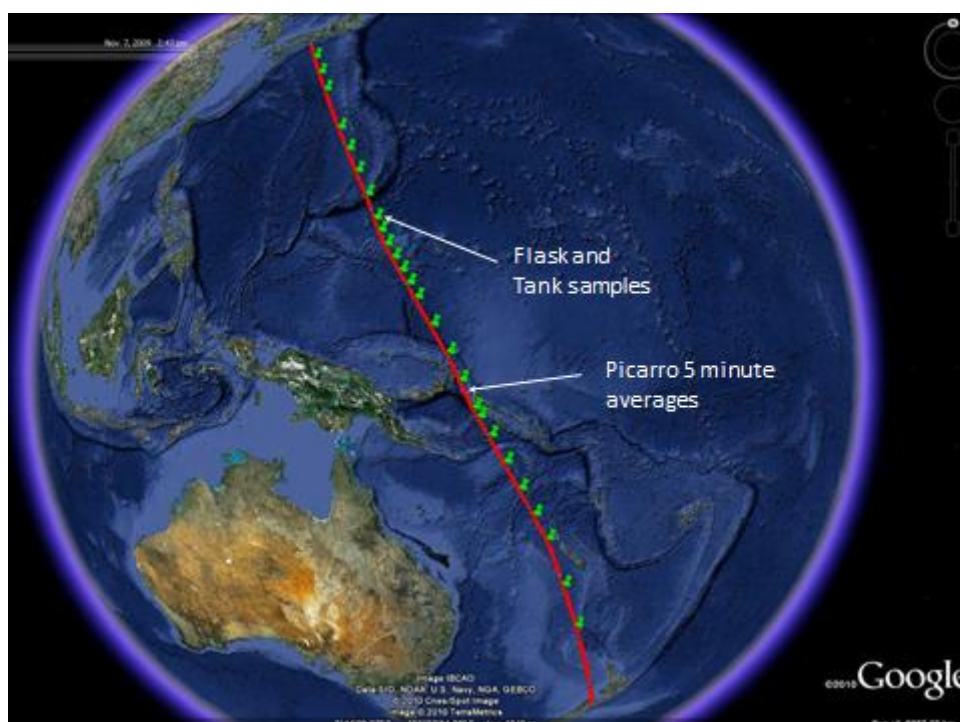


Figure 1. The track of the voyage across the western Pacific.

Using Eddy Covariance Method for Gas and Energy Flux measurements in Disciplines and Applications beyond Micrometeorology

George Burba

LI-COR Biosciences, Lincoln, NE, United States

george.burba@licor.com

The Eddy Covariance method is a micrometeorological technique of high-speed flux measurements of water, gas, heat, and momentum transport within the atmospheric boundary layer, above the soil surface, plant canopy, or industrial and urban terrains. Fluxes, emission and exchange rates could be carefully characterized from a single-point in-situ measurements using the permanent or mobile tower, or moving platforms such as automobile, helicopter, airplane, ship, boat, buoy, *etc.* This technique is widely used by micrometeorologists all over the globe. However, a number of researchers from disciplines outside of micrometeorology may not have been introduced to the information about this method, or may not be familiar enough with it to assess its usefulness within their field. Modern instruments and software can potentially expand the use of this method beyond micrometeorology and prove valuable for plant physiology, hydrology, biology, ecology, entomology, and other non-micrometeorological areas of research, industrial and regulatory applications.

The main challenge of the method for a non-expert is the complexity of system design, implementation, and processing of the large volume of data. In the past several years, efforts of the flux networks (e.g., iLEAPs, FluxNet, ICOS, CarboEurope, Ameriflux, Fluxnet-Canada, Asiaflux, *etc.*) have led to noticeable progress in unification of the terminology and general standardization of processing steps. The methodology itself, however, is difficult to unify, because various experimental sites and different purposes of studies dictate different treatments, and site-, measurement- and purpose-specific approaches. With this in mind, step-by-step instructions were created to introduce a novice to general principles, requirements, applications, and processing steps of the conventional Eddy Covariance technique, to assist in further understanding the method through more advanced references such as textbooks on micrometeorology (Foken, 2008; Montith and Unsworth, 2008; Lee *et al*, 2004; Aria, 2001; Rosenberg *et al*, 1983), network guidelines (ICOS, CarboEurope, Ameriflux, Fluxnet-Canada, Asiaflux, *etc.*), journal and technical papers.

These step-by-step instructions are provided to community in the form of the free electronic resource, a 211-page textbook titled "A Brief Practical Guide to Eddy Covariance Flux Measurements: Principles and Workflow Examples for Scientific and Industrial Applications". The book is based, to a large degree, on frequently asked questions received from new users of the Eddy Covariance method and relevant instrumentation. The explanations are written in a non-technical language to be of practical use to those new to this field. Information is provided on theory of the method (including the state of methodology, basic derivations, practical formulations, major assumptions, sources of errors, error treatment *etc.*), practical workflow (*e.g.*, experimental design, implementation, data processing, and quality control), alternative methods and applications, and the most frequently overlooked details of the field measurements.

Evaluation of new measurement techniques for carbon monoxide

Christoph Zellweger¹, Martin Steinbacher¹, and Brigitte Buchman¹

¹Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution / Environmental Technology, Duebendorf, Switzerland

christoph.zellweger@empa.ch

Experience from station audits conducted by the World Calibration Centre at Empa (WCC-Empa) shows that carbon monoxide (CO) measurement meeting the GAW Data Quality Objectives (DQOs) remains a challenging task for most GAW stations [Buchmann *et al.*, 2009], but it could also be shown that accurate CO measurements are possible using different techniques [Zellweger *et al.*, 2009]. More recently, new analytical techniques such as Cavity Ringdown Spectroscopy (CRDS) and Quantum Cascade Laser (QCL) that have already proven to be adequate for greenhouse gases became also available for CO. Figure 1 shows a comparison of 10-min CO averages of a suburban station using three different analytical techniques. The presentation will give an overview of the performance of these new techniques in comparison to the established measurement techniques.

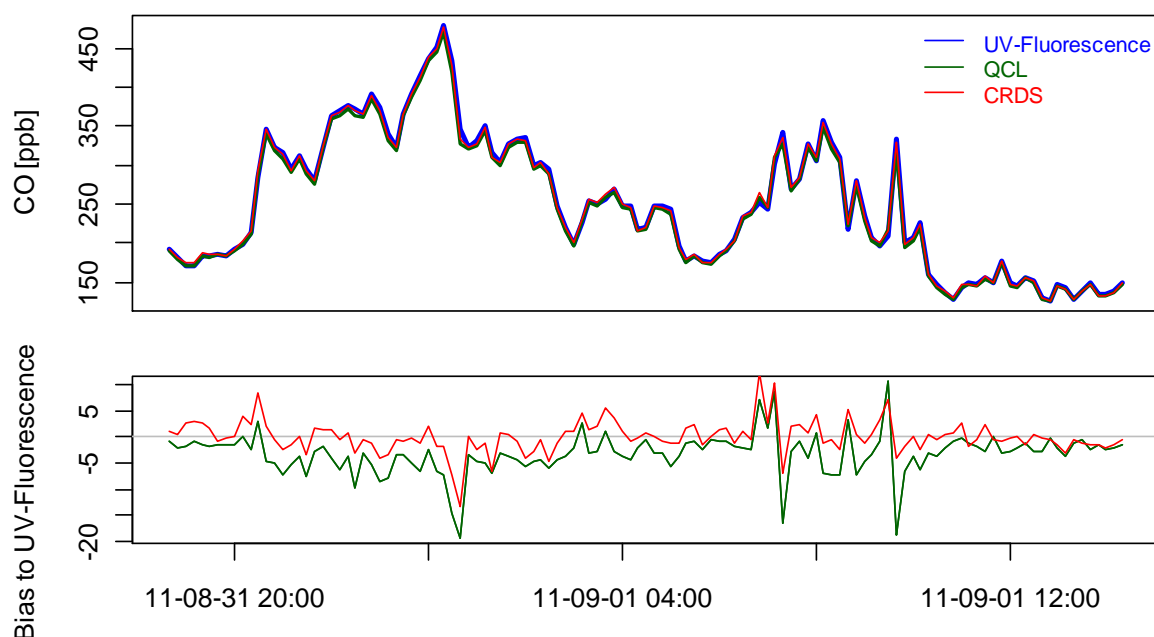


Figure 1. Upper panel: 1-day CO time series using instruments with three different analytical techniques (10-min averages). Lower panel: Difference of the QCL and CRDS instrument to the UV-Fluorescence method.

References:

Buchmann, B., J. Klausen, and C. Zellweger (2009), Traceability of Long-Term Atmospheric Composition Observations across Global Monitoring Networks, *Chimia*, 63(10), 657-660.

Zellweger, C., C. Hüglin, J. Klausen, M. Steinbacher, M. Vollmer, and B. Buchmann (2009), Inter-comparison of four different carbon monoxide measurement techniques and evaluation of the long-term carbon monoxide time series of Jungfraujoch, *Atmos. Chem. Phys.*, 9(11), 3491-3503.

In-situ FTIR Trace Gas Analyser measurements at Lauder, NZ: Characterisation of CO₂ measurement errors and comparisons with co-located in-situ CO₂ measurements

Dan Smale¹, Vanessa Sherlock¹, Gordon Brailsford¹, David Griffith², Britton Stephens³, Nicholas Deutscher², Mike Kotkamp¹, Rowena Moss¹, Antony Gomez¹, Brian Connor¹

¹ National Institute of Water and Atmospheric Research (NIWA), NZ.

² Centre for Atmospheric Chemistry, University of Wollongong, Australia.

³ National Center for Atmospheric Research (NCAR), USA

d.smale@niwa.co.nz

Prof. David Griffith and co-workers at the University of Wollongong have developed and commercialised a Fourier Transform Infrared (FTIR) trace gas analyser which provides precise, simultaneous measurements of the dry air mole fractions of carbon dioxide (CO₂), methane, nitrous oxide, carbon monoxide and ¹³CO₂ in air samples. The National Institute of Water and Atmospheric Research (NIWA) has been operating a prototype FTIR analyser at Lauder, New Zealand (45.04S, 169.68E) since 2006.

Operational biases and uncertainties in the Lauder analyser measurements have been characterised using internal repeatability tests, calibration tank suites and comparison with other co-located in-situ trace gas measurements. CO₂ measurement repeatability of 0.02-0.04 $\mu\text{mol mol}^{-1}$ is inferred from Allan variance analysis of repeated cell measurements for the operational measurement averaging period of 10 minutes. NIWA primary tanks and EMPA/WCC tanks were measured on the Lauder analyser in April 2010 during the GAW station audit. Results show the FTIR response is linear over the range of concentrations sampled (340-410 $\mu\text{mol mol}^{-1}$) but a zero offset must be accounted for when calibrating FTIR measurements to the WMO scale. If a single working tank is used to make a single-point calibration (the analyser calibration strategy to date), concentration dependent biases result. An analytical expression for the concentration-dependent bias is derived and biases are estimated for the Lauder CO₂ timeseries.

Lauder FTIR analyser measurements are routinely compared to CO₂ measured with an industry standard NDIR LiCor-7000 CO₂ analyser which has been operated at the Lauder site since May 2008, and weekly flask samples acquired at the Lauder site since May 2009. In well-mixed boundary layer conditions the CO₂ measurements from the different systems agree to within 0.25 $\mu\text{mol mol}^{-1}$ RMS difference.

The results of these validation activities demonstrate the FTIR analyser is a promising technology which can and will be further optimized at Lauder to attempt to meet GAW error targets for in situ CO₂ measurements in the Southern Hemisphere (0.05 $\mu\text{mol mol}^{-1}$). Even with current performance the instrument provides useful information on seasonal variations (~several $\mu\text{mol mol}^{-1}$) in regional atmospheric CO₂ concentrations.

Measurements of Carbon Dioxide and Carbon Monoxide at High Spatial and Temporal Resolution in an Urban Environment

Chris Rella, Gloria Jacobson, and Eric Crosson

Picarro Inc., 3105 Patrick Henry Drive, Santa Clara California 94054 USA.

rella@picarro.com

The ability to quantify the sources and sinks of carbon dioxide is essential for understanding the atmospheric drivers to global climate change. “Top down” inversion measurements and models are used to quantify net carbon fluxes into the atmosphere. The overall carbon fluxes are determined by combining remote measurements of carbon dioxide concentrations with complex atmospheric transport models, and these emissions measurements are compared to “bottoms-up” predictions based on detailed inventories of the sources and sinks of carbon, both anthropogenic and biogenic in nature. Atmospheric transport models, which are well understood at a length scale of 100 km, work poorly on urban distance scales. Furthermore, the variability of the emissions sources in space (e.g., factories, highways, residences) and time (rush hours, factory shifts and shutdowns, residential energy usage variability during the day and over the year) complicate the interpretation of the measured signals. Here we present detailed, high spatial- and temporal-resolution greenhouse gas measurements in Silicon Valley, CA. The results of two experimental campaigns are presented: measurements from a 10m urban ‘tower,’ and ground-based mobile mapping measurements. In both campaigns, real-time carbon dioxide data are combined with real-time carbon monoxide measurements to partition the observed CO₂ concentrations between anthropogenic and biogenic sources. Initial interpretation of the data is provided, using simple atmospheric models. These methods show great promise for quantifying and partitioning carbon dioxide emissions in an urban setting.

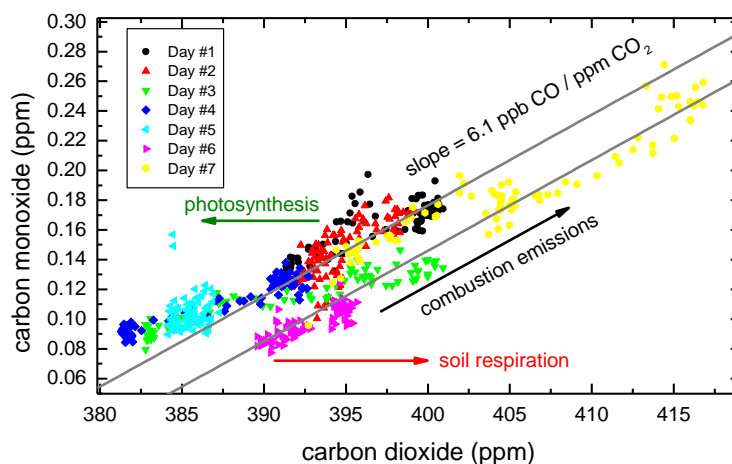


Figure 1: relationship between carbon dioxide and carbon monoxide (measured at a fixed location) during the midday when the atmosphere is well-mixed and when soil respiration is at a minimum. During the day, the overall combustion transit signal is mixed with a photosynthetic signal from the biosphere.

References:

Turnbull, J. C., Karion, A., Fischer, M. L., Faloona, I. C., Guilderson, T. P., Lehman, S. J., Miller, B. R., Miller, J. B., Montzka, S. A., Sherwood, T., Saripalli, S., Sweeney, C., and Tans, P. P.: “Assessment of fossil fuel derived carbon dioxide and other anthropogenic trace gas emissions from airborne measurements over Sacramento, California in spring 2009,” *Atm. Chem. Phys.*, 11, 705-721, 10.5194/acp-11-705-2011, 2011.

Network design assessment for ICOS – EN (Integrated Carbon Observation System – Earth Networks) atmospheric stations

C. Gerbig¹, D. Pillai¹, F.-T. Koch¹, E. Novakovskaia², S. Heckman², F. Chevallier³, P. Ciais³,
A. C. Manning⁴

¹ Max-Planck-Institut für Biogeochemie, Jena, Germany

² Earth Networks, Germantown, USA

³ Laboratoire des Sciences du Climat et l'Environnement, Gif sur Yvette, France

⁴ School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom

cgerbig@bgc-jena.mpg.de

Deriving greenhouse gas balances at regional scales can be done via two approaches: up-scaling of local information such as from inventories for emissions and natural processes (“bottom-up”), or independently via combined atmospheric observations and inverse transport modelling (“top-down”). The European infrastructure project ICOS (Integrated Carbon Observation System), together with Earth Networks (EN), a US based company, will greatly increase the density of the atmospheric network over Europe within the next few years. In total the network will include about 80 existing and planned tall towers and ground stations from ICOS, and a further 25 tall towers from EN. All will be instrumented with continuous measurement equipment for at least CO₂ and CH₄. Such a dense coverage of continuous measurement stations will significantly improve the estimation of surface fluxes, however it is also associated with considerable costs.

To facilitate decision-making with respect to the exact number and ideal location of observing stations to be deployed, a quantitative network design tool is required that allows balancing cost and benefit. Such a tool is currently being developed by the ICOS – EN joint task force, a group recently formed to facilitate the cooperative design and development of the ICOS and EN atmospheric networks. The network design tool requires two principal datasets: locations of towers or structures available for hosting instruments, and detailed emission inventories at high spatial resolution. An initial selection of potential measurement location is made based on the distribution of emissions in the vicinity in relation to regional emissions, resulting in background stations (low near-field emissions) and stations with a potential to better constrain emissions (with low emissions in the immediate vicinity, but higher emissions at distances around 20-80 km). Subsequently, potential networks with different characteristics are chosen, e.g. varying degrees of spatial coverage or targeted sampling of emissions. These potential networks are then assessed using a two-step approach: first, footprints (sensitivities of towers to surface fluxes) for each potential network are computed using various high resolution adjoint transport models and assessed for the spatial and temporal characteristics, and second, a set of full inversion systems is applied to assess each network’s reduction of flux uncertainty. The latter step involves harmonisation of treatment of errors (prior, representation, transport model) in different inversion systems. In addition to the overall strategy, we will present results from the initial tower selection and first results from a footprint analysis.

Tiger Optics Continuous Wave Cavity Ring-Down Spectroscopy Analysers – Commercial Instruments for Greenhouse Gas Analysis and Other Environmental Applications

Graham Leggett¹

¹ Tiger Optics LLC, 250 Titus Avenue, Warrington, PA 18976-2426, USA

gleggett@tigeroptics.com

Tiger Optics introduced the world's first commercial "Continuous Wave Cavity Ring-Down Spectroscopy" (CW CRDS) analyser in 2001. Today, our instruments monitor more than one thousand critical points at semiconductor fabrication plants, LED makers, and gas manufacturers. Our analysers are also at work in thirteen of the world's national metrology institutes, serving as transfer standards for the qualification of calibration gases. Following this success in the industrial and laboratory markets, Tiger Optics is beginning to develop the environmental measurements market for its products. The CW CRDS method is ideally suited to the requirements of numerous environmental measurement applications, where factors such as accuracy, low detection limits, speed of response, long-term stability, low maintenance, and low gas throughput are all essential requirements. This poster begins with an introduction to the CW CRDS method, including an explanation of the calibration-free nature of the approach, followed by descriptions of our current products and applications relevant to the greenhouse gas analysis community and other environmental applications; including long-term greenhouse gas measurements, emissions monitoring, and the determination of key compounds relating to air quality. Finally, the poster describes Tiger Optics' contribution to clean manufacturing in which our instruments are used to optimise production processes with a view to minimising waste and harmful emissions.

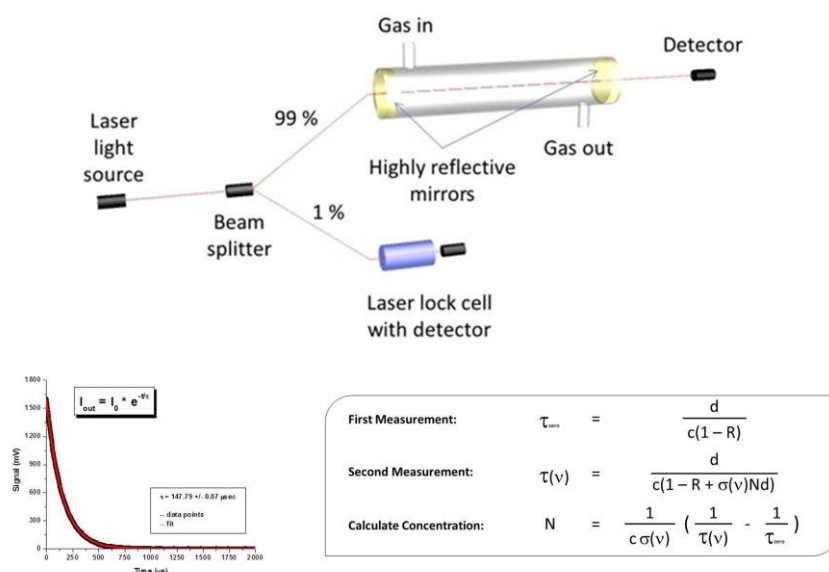


Figure 1. Continuous Wave Cavity Ring-Down Spectroscopy – basic principles of operation.

Atmospheric Data Management at ICOS ATC: Processing, Stewardship, Archiving and Access

Jérôme Tarniewicz¹, L. Hazan¹, L. Rivier¹, T. Laurila², A. Vermeulen³, A. Jordan⁴, O. Laurent¹, M. Schmidt¹, M. Ramonet¹, I. Pison¹, and P. Ciais¹

¹ Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CEA/CNRS/UVSQ, Gif-sur-Yvette, France

² Finnish Meteorological Institute (FMI), Helsinki, Finland

³ Netherlands Energy Research Foundation (ECN), Petten, The Netherlands

⁴ Max Planck Institute for Biogeochemistry, Jena, Germany

jerome.tarniewicz@lsce.ipsl.fr

The Atmospheric Thematic Center (ATC) is one of the four central facilities of ICOS infrastructure. The ATC central facility is needed to ensure that all the data generated by ICOS atmospheric stations are treated harmoniously and properly archived for long term, the atmospheric stations can receive operational-timely support, and to maintain a technological and scientific watch over new measurement techniques. The ATC is currently under construction.

The presentation will describe each step of the data processing at ATC, from data upload from the monitoring station to the web broadcasting. It will focus on data processing, QA/QC, user dedicated tools and applications, and access to measurements and elaborated products.

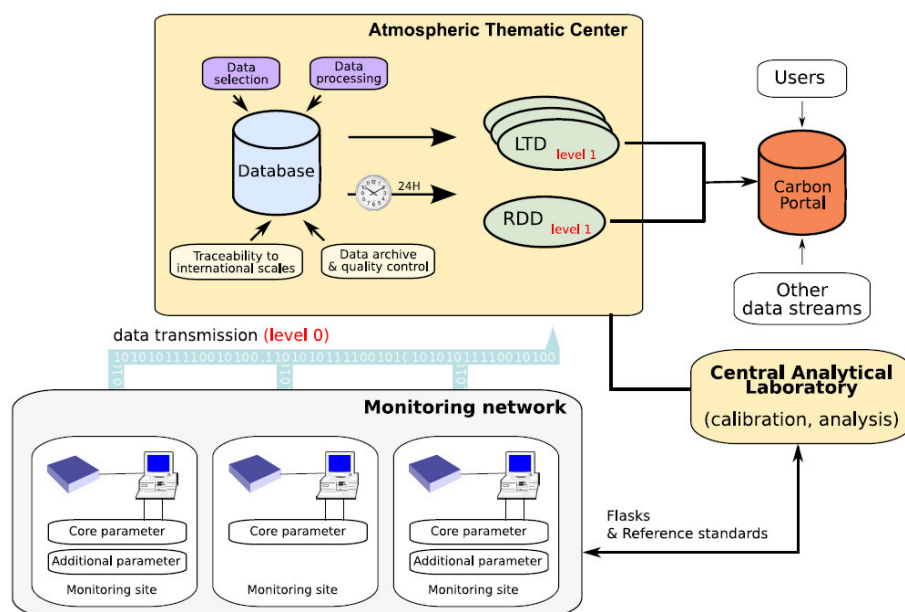


Figure 1. Flow chart for data processing at ICOS ATC. Also presented is the relation between ATC and CAL units.

References:

ICOS infrastructure, <http://www.icos-infrastructure.eu/>

ICOS ATC demo, <https://icos-atc-demo.lsce.ipsl.fr/>