

GAW Report No. 213

17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013)

(Beijing, China, 10-13 June 2013)

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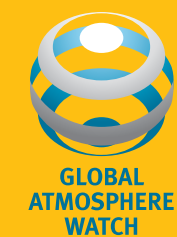
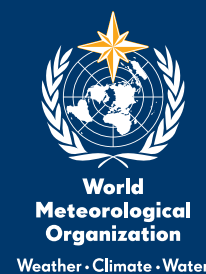
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WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH

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17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013)

(Beijing, China, 10 - 13 June 2013)

Edited by Pieter Tans and Christoph Zellweger



**World
Meteorological
Organization**

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**GLOBAL
ATMOSPHERE
WATCH**

July 2014

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第17届二氧化碳等温室气体及相关微量成分测量技术专家会议
17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2013)
10-14 June 2013, Beijing, China



Participants attending the 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2013) in Beijing, China, 10-13 June 2013
(<http://ggmt-2013.cma.gov.cn/dct/page/1>)

EXECUTIVE SUMMARY

Understanding the global carbon cycle and role of greenhouse gases for climate change to be able to take balanced and scientifically founded actions on emissions control requires well-established integrated global greenhouse gas observing systems. The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) provides a framework for the development and implementation of integrated greenhouse gas (GHG) observations. Measurements of greenhouse gases come from flask sampling and continuous measurement sites, while aircraft and satellite observations provide vertical components of observations integrated into the global fields via modelling. As part of this GHG programme, WMO organizes biennially with the International Atomic Energy Agency (IAEA) a meeting to review the scientific understanding of greenhouse gas sources and sinks, and to examine data quality objectives and measurement techniques.

The 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2013) took place from 10 to 13 June 2013 at China Meteorological Administration in Beijing, China. This was the first GGMT meeting organized in a developing country with a rapidly expanding greenhouse gas measurement programme following the recommendation made at the previous GGMT-2011. The meeting reviewed current WMO data quality objectives and observation scales, covering such topics as carbon dioxide and other greenhouse gases, stable isotopes, radiocarbon in greenhouse gas measurements, calibration, quality control, data management and archiving. The workshop also discussed new and emerging technologies, including measurements of greenhouse gases with high-precision spectroscopic methods.

The group made several recommendations on the WMO data quality objectives, as well as on the development of the GAW Programme infrastructure. These recommendations are summarized in the first part of the meeting report. A number of reports presented at the meeting are included in this report on DVD.

WMO has provided the framework for all carbon dioxide experts meetings since 1975. IAEA in Vienna joined WMO as a co-organizer in 1997 due to the increased use of carbon isotopes in studying the carbon cycle.

SUMMARY OF PURPOSE: WHY WE NEED HIGH ACCURACY ATMOSPHERIC GREENHOUSE GAS MEASUREMENTS

The United Nations Framework Convention on Climate Change (UNFCCC), which has been signed by nearly all nations, requires signatories to assess greenhouse gas emissions. Three main objectives justify atmospheric observations:

1. To monitor atmospheric greenhouse gas burdens.
2. To quantify natural and anthropogenic emissions and removals of greenhouse gases (GHG), including attribution by region and by process, and to understand the controlling processes.
3. To provide the basis for an independent "top-down" audit of the "bottom-up" UNFCCC emissions inventories.

The changing global burden can be quantified most accurately and effectively by making well-calibrated in-situ measurements and by collecting air samples at carefully chosen "baseline" (or "background") sites. These are places with access to air that can represent large areas and where short-term variability due to nearby emissions/removals (also called sources/sinks) is minimal. Objectives 2 and 3 require a combination of high precision measurement, which includes both in-situ instrumentation and flask samples, as well as remote sensing from the ground and perhaps also from satellite platforms, at many more locations.

Long-term, high-quality in-situ observations at the surface, on tall towers, aircraft, and balloons, are indispensable for reliable detection and quantification of long-term changes in GHG emissions and sinks. Modelling studies utilizing these in-situ measurements provide local, regional and global assessment of atmospheric emissions and removals by season, source type and location. These studies are further strengthened by remote sensing estimates of the total column by ground based spectrometers that measure absorption of solar radiation by specific gases. However, these complementing remote sensing GHG measurements again rely on high-quality, traceable and calibrated in-situ measurements because a direct calibration of those measurements is not possible. This is related to the fact that one cannot control the sample in the optical path, nor potential interferences. It was e.g. shown by Karion et al. (2010) that the TCCON (Total Column Carbon Observatory Network) measurements should be regularly validated with calibrated in-situ measurements on aircraft of the partial column and with balloon launched AirCore flights, which collect a vertically resolved in-situ sample, also measured on calibrated instruments, through ~99% of the total column. TCCON also plays a crucial role in the validation of satellite-based remote sensing studies that are as yet developmental and of low precision, lack long-term continuity, and are subject to a number of biases, some known and probably several as yet unknown. They do not cover with sufficient accuracy the full suite of GHG and associated tracers defined by the Global

Atmosphere Watch Programme of the World Meteorological Organization (WMO/GAW), but they offer the prospect of dense global measurements, especially in the still-poorly measured tropical regions, which could greatly help global understanding.

The scientific priorities for GHG study in WMO/GAW are thus to sustain and enhance the global in-situ measurement network, and simultaneously use it to improve and ground-truth developing satellite coverage (in collaboration with TCCON) by allowing on-going diagnosis and elimination of biases in the measurements and retrieval algorithms. In fact, without a considerable expansion of the GAW network this task will be nearly impossible after the largest biases (~ 1ppm or larger for CO₂) have been addressed, while sub-ppm biases are very likely to still cause large errors in inferred emissions for individual nations and regions. To illustrate this point, a simple mass balance for typical meteorological conditions shows that a 1 GtonC/year carbon source in the U.S. causes the full column-integrated CO₂ mole fraction to increase by only ~0.5 ppm on average. If we want to use atmospheric soundings to determine such a source magnitude to 20% uncertainty, a column-average measurement precision, after averaging over an appropriate number of samples, of ~0.1 ppm is required. Stated differently, space and time dependent biases need to be eliminated to a relative precision of one part in 4000 in ambient atmospheric CO₂. This is more demanding than any trace gas measurement ever performed from space by more than a factor of ten. Similar requirements apply to other long-lived greenhouse gases, such as methane and nitrous oxide.

All calibrated and quality-controlled results can then be integrated into local, regional and global data assimilation systems and modelling. Models have their own biases, and a comprehensive set of calibrated measurements will be needed to diagnose and minimize such biases. The results will provide an independent assessment of GHG emissions and trends, at local, regional (e.g. national) and global scales, as needed by the public and by policymakers. Systematic observations of GHG concentrations in the atmosphere and oceans and linked process-oriented carbon cycle observations also bring great benefit in purely scientific terms, improving our understanding of the workings of the carbon cycle and how it responds to climate change, possibly as a positive feedback to climate forcing.

Two major regional programmes are acting to improve atmospheric trace gas observations in GAW in North America (North American Carbon Program, NACP: <http://www.nacarbon.org/nacp/>) and Europe (Integrated Carbon Observation System, ICOS: <http://icos-infrastructure.eu>). It is important that those regional programmes remain tightly linked to the international WMO/GAW effort and produce regional data sets that can be merged safely into an enhanced global picture of GHG budgets. Building expertise in developing countries including the establishment of high-quality measurement capabilities remains a critical issue for achieving

adequate spatial coverage of the globe in the coming decade. WMO and IAEA can make large contributions here.

Global society needs better information to address the problem of rising greenhouse gases in the atmosphere. Solid and trusted facts are indispensable to successful international treaties, national policies, and regional strategies for emission reductions, efficiency improvements, and emissions offsets. Independent, globally coherent information is essential. The closest thing the world has to a globally consistent greenhouse gas observation network is the WMO's Global Atmosphere Watch. However, providing coherent, regional-scale information requires not only enhanced observations, but also improved modelling and ensemble reanalysis. WMO/GAW needs both to sustain the high-quality programme of open-access atmospheric observation, and to encourage multiple independent modelling studies to analyse the measurements.

EXPERT GROUP RECOMMENDATIONS

EXPERT GROUP RECOMMENDATIONS FOR MEASUREMENTS OF CARBON DIOXIDE, OTHER GREENHOUSE GASES, AND RELATED MEASUREMENT TECHNIQUES

The scientists present at the 17th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (abbreviated as GGMT-2013), 10-13 June 2013, in Beijing, China, recommend the following procedures and actions, to achieve the adopted WMO goals for GAW network compatibility among laboratories and central facilities as summarised in Table 1. These goals are motivated from the perspective of the required data quality and compatibility for interpretation of global or continental scale atmospheric data, obtained from different laboratories, and for example joint use in atmospheric transport model inversion studies. These compatibility goals should be reached in the respective specified mole fraction ranges observed in the global background troposphere and where calibration scales are well defined by the WMO/GAW Central Calibration Laboratories.

The use of terminology is based on standardized definitions as released by ISO (International Organization for Standardization; www.iso.org), in particular the Joint Committee for Guides in Metrology (JCGM) (for details see: <http://www.iso.org/sites/JCGM/JCGM-introduction.htm>), and has been requested by GAW since WMO/GAW Report No. 142 (2001), "Strategy for the Implementation of the Global Atmosphere Watch Programme (2001 – 2007)" and highlighted further in the WMO/GAW Strategic Plan: 2008-2015 (WMO/GAW Report No. 172) and its Addendum (WMO/GAW Report No. 197).

Currently, some of the terms related to measurements as well as to Quality Assurance & Quality Control (QA/QC) in atmospheric science are used with different meanings and/or on the basis of different definitions. Since WMO is a signatory to the International Committee for Weights and Measures (CIPM) Mutual Recognition Arrangement (MRA) (<http://www.bipm.org/en/cipm-mra/>) the use of accepted terminology within GAW has become even more important.

A special explanation can be helpful here in the context of the transition from "comparability" to "compatibility". "Comparability" means that results (of different labs) are comparable i.e. can be compared. In a metrological sense this simply means that results have to be on the same scale to be compared. By consistent use of the same scale for the same compound (in all steps such as measurements, determination of corrections etc.), one will have comparability of results. "Compatibility", a property of a set of measurement results, means that results are compatible, within a specified numerical value. Metrologically this means (an oversimplification): the absolute value of the difference between any pair of measured values from two different measurement results is within a chosen value which does not have to be the same as

the total combined uncertainty. For instance, the total combined uncertainty in two labs might be ± 0.1 permil (for example) and still results can be compatible within 0.01 permil.

Definitions of terms concerning recommended ISO terminology are given in the 3rd edition of the VIM (<http://www.bipm.org/en/publications/guides/vim.html>). The reader is also referred to the ISO publication "Guide to the Expression of Uncertainty in Measurement" (GUM, 1995, and at <http://www.bipm.org/en/publications/guides/gum.html>). More explanations, particularly with respect to the transition from VIM2 to VIM3, are given in *De Bièvre* (2008). All GAW participants are strongly encouraged to take note of the ISO documents and consult the GAW glossary on Quality Assurance and Quality Control terms at <http://gaw.empa.ch/glossary/glossary.html>.

The following definitions and units are used throughout this document:

Mole fractions of substances in dry air (dry air includes ALL gaseous species except water):

ppm = $\mu\text{mol/mol} = 10^{-6}$ mole of trace substance per mole of dry air

ppb = $\text{nmol/mol} = 10^{-9}$ mole of trace substance per mole of dry air

ppt = $\text{pmol/mol} = 10^{-12}$ mole of trace substance per mole of dry air

The organizations participating in WMO/GAW agree that they will only use the above notation (that is, ppb or nmol/mol, etc.) in their data distribution and scientific publications, thus discontinuing the use of ambiguous terms such as ppmv, ppbv, and pptv. In communicating with the general public it is advisable to continue using the term "concentration" instead of "mole fraction" because the latter is an unknown term for most people.

Isotopic or molecular ratios:

Isotopic ratio data are expressed as deviations from an agreed-upon reference standard using the delta notation:

$\delta = (R_{\text{sample}}/R_{\text{reference}} - 1)$, with $R = [\text{heavy isotope}]/[\text{light isotope}]$.

δ -Values are expressed in multiples of 0.001 (‰; per mil 'units').

The international reference scale for $\delta^{13}\text{C}$ is VPDB. NBS 19 calcite and LSVEC lithium carbonate are the primary international standard reference materials defining the VPDB scale. NBS 19 has a defined $\delta^{13}\text{C}$ value of +1.95‰ versus the VPDB scale origin. LSVEC defines the second anchor point at $\delta^{13}\text{C} = -46.6\text{‰}$ versus VPDB. All reported $\delta^{13}\text{C}$ data, including air- CO_2 isotopic values, are to be normalized to the NBS 19 – LSVEC isotopic distance (*Coplen et al.*, 2006).

For $\delta^{18}\text{O}$, multiple scales are in use (VPDB, VSMOW, air- O_2). For CO_2 in air samples, the common scale is the VPDB- CO_2 scale (*Brand et al.*, 2010), which includes the isotopic fractionation ($\sim +10.25\%$) from the calcite to the gas. Although the VPDB- CO_2 scale is linked to the VSMOW scale, which includes the 2-point VSMOW-SLAP normalisation, this normalisation cannot be applied to air- CO_2 $\delta^{18}\text{O}$ data for practical reasons. Instead, standardisation of the carbonate- H_3PO_4 digestion reaction is of highest importance (*Wendeberg et al.*, 2011).

For all hydrogen isotope measurements, the common scale is the VSMOW/SLAP scale, realised through the VSMOW-SLAP data normalisation.

Delta notation is also used to express relative abundance variations of O_2/N_2 (and Ar/N_2) ratios in air:

$$\delta(\text{O}_2/\text{N}_2) = (R_{\text{sample}}/R_{\text{standard}} - 1) \text{ with } R = \text{O}_2/\text{N}_2 \text{ (see Section 5)}$$

$\delta(\text{O}_2/\text{N}_2)$ values are expressed in multiples of 10^{-6} or **per meg** 'units'.

The respective international air standard is not established, yet. The Scripps Institution of Oceanography (SIO) local O_2/N_2 scale, based on a set of cylinders filled at the Scripps Pier is the most widely used scale.

Table 1- Recommended compatibility of measurements within the scope of GGMT

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO_2	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm	250 – 520 ppm
CH_4	± 2 ppb	± 5 ppb	1700 – 2100 ppb	300 – 2600 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	20 -500 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb	260 – 370 ppb
SF_6	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt	1.1 – 9.8 ppt
H_2	± 2 ppb	± 5 ppb	450 – 600 ppb	140 – 1200 ppb
$\delta^{13}\text{C}-\text{CO}_2$	$\pm 0.01\%$	$\pm 0.1\%$	-7.5 to -9‰ vs. VPDB	
$\delta^{18}\text{O}-\text{CO}_2$	$\pm 0.05\%$	$\pm 0.1\%$	-2 to +2‰ vs. VPDB	
$\Delta^{14}\text{C}-\text{CO}_2$	$\pm 0.5\%$	$\pm 3\%$	0-70‰	
$\Delta^{14}\text{C}-\text{CH}_4$	$\pm 0.5\%$		50-350‰	
$\Delta^{14}\text{C}-\text{CO}$	± 2 molecules cm^{-3}		0-25 molecules cm^{-3}	
$\delta^{13}\text{C}-\text{CH}_4$	$\pm 0.02\%$	$\pm 0.2\%$		
$\delta\text{D}-\text{CH}_4$	$\pm 1\%$	$\pm 5\%$		
O_2/N_2	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

Values given in Table 1, column 2, are the scientifically desirable level of compatibility for well mixed background air. They may not be the currently achievable minimal measurement uncertainty (1 sigma) for individual analyses of most species. As a guideline for many other studies in which the highest precision is not required, for example a regionally focused study with large local fluxes, column 3 is provided with an extended compatibility goal, in many cases useful for meaningful measurements.

There is no international WMO/GAW Central Calibration Laboratory for O₂/N₂ measurements. Current international comparisons of O₂/N₂ indicate that the compatibility between any two laboratories is not better than ± 5 per meg. For $\Delta^{14}\text{CO}_2$ analyses there is little experience on long-term compatibility of different laboratories, but for global as well as regional applications the desired reproducibility of individual measurements should be better than $\pm 3\%$.

Requirements for regional greenhouse gas networks

Besides national GHG reduction and mitigations programs, several states/provinces, cities and communities have set their own, often more ambitious emission reduction targets for the future, and expanded efforts can be anticipated in the future. Estimates of emissions based on atmospheric measurements using so-called top-down methodologies may play an essential role in supporting these efforts.

The desire for mitigation has led to increasing interest in regional greenhouse gas studies in academic research, by regulatory agencies as well as projects driven by commercial interest. Their focus is often on quantifying GHG emission using continuous or campaign-based atmospheric observations. *In regional studies, measurement and calibration requirements may differ from those in the unpolluted troposphere*, particularly for polluted regions where signals are large. Site selection for regional studies should include consideration of the footprint of the sampling location(s). The determination of background concentrations must also be addressed, and the appropriate background may differ from the global baseline. Compatibility between individual laboratories is of lesser importance, but compatibility between instruments within a regional network is necessary over the often large measurement ranges. Of central importance is the ability to quantify the local excesses in GHG concentration relative to the background, which requires methods for establishing the relevant background (from surrounding baseline or regional measurements) as well as the accurate measurements of the enhancements caused by the regional emissions.

Requirements will vary with the sampling locations and intended application of the measurements. In general, we recommend that measurements should be made with an absolute accuracy of 5% or better of the enhancement over background. At this level, measurement

uncertainties will be small relative to other sources of uncertainty in calculated fluxes based on imperfect knowledge of atmospheric transport. If enhancements over background are small, the 5% requirement may require high compatibility with WMO scales for concentrations that are near background values. If enhancements are large, the requirement of 5% accuracy will require reference standards over a much wider range than for background measurements that are compatible with the WMO scales near ambient values. Thus we recommend that regional measurements still adhere to WMO guidelines for concentrations that are near background levels, but we recognize that compatibility requirements for elevated measurements are far less stringent.

$\Delta^{14}\text{C}$ in CO_2 represents a special case where reproducibility of 30-50% for individual measurements of the regional $\Delta^{14}\text{C}$ offset over background may be sufficient to be useful, although precision of 5% or better is ultimately desirable.

1. CALIBRATION OF GAW MEASUREMENTS

1.1 Background

Round-robin comparisons of laboratory standards and comparisons of field measurements and samples over the last decades have regularly shown differences in trace gas measurements larger than the target compatibility for merging data from different field sites (see Table 1). These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements. The WMO/GAW Central Calibration Laboratories (CCL) for important greenhouse and trace gases therefore remain one of the fundamental components of the WMO/GAW Programme (WMO/GAW Reports No. 172 and 197) to achieve and maintain compatibility of global observations from different laboratories.

WMO/GAW CCLs currently exist for: carbon dioxide (CO_2 , at NOAA/ESRL), methane (CH_4 , at NOAA/ESRL), nitrous oxide (N_2O , at NOAA/ESRL), carbon monoxide (CO , at NOAA/ESRL), sulphur hexafluoride (SF_6 , at NOAA/ESRL), stable isotopes in CO_2 (only for CO_2 -in-air measurements, at Max-Planck Institute for Biogeochemistry (MPI-BGC)), and hydrogen (H_2 , at MPI-BGC).

In this section, the general requirements for WMO/GAW CCLs and general issues to maintain calibration of observations by GAW laboratories are discussed. Additional trace gas-specific needs are dealt with separately in subsequent sections.

1.2 General requirements for Central Calibration Laboratories

- a) CCLs maintain the WMO Mole Fraction Scale for each species in air by carrying out regular determinations of the primary scales with primary methods linking them to fundamental quantities (SI). Each scale is embodied in an adequate set of gas mixtures-in-air in high-pressure cylinders (called “WMO Primary Standards”). Isotopic ratios should be reported on the existing accepted scales, such as VPDB, VSMOW. In this case the CCL maintains a common “Scale Anchor” to the accepted scales, in order for us to achieve more stringent compatibility between laboratories.
- b) The CCL carries out comparisons with independent primary scales, established either through gravimetric, manometric, or other means. For the stable isotope scale of CO₂ in air, the CCL establishes the link to the respective international stable isotope scales (e.g. VPDB for δ¹³C).
- c) While the WMO scale for each trace gas is defined and maintained by an operational, designated CCL, WMO and IAEA strive for all monitoring systems to be formally traceable to Primary Reference Materials or Fundamental Constants (SI) through National Metrology Institutes (NMI) and the International Bureau of Weights and Measures (BIPM). This is an essential pre-requisite for an internationally recognized and homogeneous monitoring system of in-situ chemical measurements.
- d) The CCL will participate in Key Comparisons of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) if it is entitled to do so. When a CCL without a mandate to participate in CCQM activities wants to participate in Key Comparisons, it should request WMO for a signature of the side letter to the official WMO- CIPM agreement.
- e) This Expert Group and the Scientific Advisory Group for GHG undertake the responsibility for the evaluation of the effectiveness of CCL procedures and for recommending modifications to existing protocols.
- f) The CCL will update its scale when warranted, as the gas mole fractions of the WMO Primary Standards may become better known over time through repeated primary reference measurement procedures and comparisons. Revisions of the WMO Scale by the WMO/GAW CCL must be distinguished by name, such as WMO CO₂ X2007, and the appropriate version number should be included in each standard calibration report. The CCL archives all earlier versions of the WMO scale.
- g) The current scales are (as of September 2013):

WMO CO₂ X2007

WMO CH₄ X2004

WMO CO X2004¹

¹ In the course of this report preparation a new CO scale, namely WMO CO X2014 has been released.

WMO N₂O X2006A

WMO SF₆ X2006

WMO H₂ X2009

The “X” stands for mole fraction.

Names for isotopic scale anchors could be, for example, WMO isoCO₂ 2012, etc.

- h) The CCL provides complete and prompt disclosure of all relevant data pertaining to the maintenance and transfer of the primary scale, such as manometric calibration procedures and results, and an estimate of the expected uncertainty introduced by the calibration transfer procedure to each individual standard. The CCL maintains a record of traceability of each standard to the Primary scale, which could include intermediate secondary standards.
- i) The CCL provides calibrated reference gas mixtures (gas mixtures-in-natural air, called “transfer standards”) at the lowest possible cost.
- j) In view of different specific sensitivities of various instrumentation to the isotopic composition of the analytes, the isotopic composition of the analyte (CO₂, CH₄, N₂O, others) in transfer standards should be close to atmospheric levels. If the preparation of the standard gas involves the addition of the analyte, the CCL provides information on the isotopic composition of the addition and the approximate fraction of this admixture to the total analyte in air.
- k) The CCL provides for a backup to the embodiment of the primary scale (e.g. a suite of calibrated Primary cylinders) in case a catastrophic event occurs.
- l) The CCL, or a designated WMO/GAW World Calibration Centre (for the list please consult WMO/GAW Report No. 197, p. 4), organizes round-robin comparisons of laboratory calibrations by distributing sets of high-pressure cylinders to be measured by participating laboratories. The round-robin comparisons are to be used for an assessment of how well the laboratories are maintaining their link to the WMO Mole Fraction Scale, or to a WMO Scale Anchor for isotopic ratios. They are not to be used for re-defining laboratory calibration scales, because that would effectively establish two or more traceable paths to the primary scale instead of a single hierarchical path. It is recommended that round-robins are repeated once every two years. However, experience shows that comparisons of reference gases by themselves are not sufficient to ensure that atmospheric measurements are compatible to the degree that is required.
- m) To maximize the usefulness of round-robin results, every participating laboratory has to complete its analyses within two to four weeks (depending on the number of species measured) and then to immediately send the cylinders to the next participant. The circulation of the cylinders is discontinued after two years at the latest, and results are evaluated even if all labs were not able to analyse the tanks. A new round-robin will then be started with the labs that had not been included to be first in line. Tracking tank circulation and data submission will be more rigorous than in earlier round-robins with the status of tank circulation and data submission being posted online on a web page to be installed and maintained by the laboratory organizing the round-robin. Analysis of CO₂ mole fractions has

the highest priority in the round-robins, but laboratories are encouraged to measure multiple species if time and air consumption allow for. By accepting the round robin cylinders in their laboratory, each participating laboratory agrees to complete the measurements within the applicable time limit of 2-4 weeks.

1.3 General requirements for World Calibration Centres

- a) A World Calibration Centre (WCC) performs audits of participating GAW laboratories and field stations as well as organizes round-robin comparisons (as per 1.2.i). More general terms of reference for WCC can be found in WMO/GAW Report No. 172 (p. 16).
- b) Each World Calibration Centre must have in-house standards re-calibrated by the CCL every two years. Longer re-calibration intervals might be acceptable only for compounds with proven long-term stability (e.g. SF₆, CH₄). The WCC calibration strategy should avoid unnecessary levels in the calibration hierarchy while keeping its highest level standards for many years so that a calibration history can be built for each of them. In that case they could then also serve as de-facto additional long-term “surveillance cylinders” providing information on the stability of the WMO Mole Fraction Scales maintained by the CCLs.
- c) Reference gas standards and travelling standards should be in natural air and when trace gases, in particular CO₂, are adjusted in reference air mixtures, the isotopic composition of the cylinder trace gas should remain close to that in air to minimize the influence of isotopic composition on calibrations (same as 1.2.h and j above).
- d) GAW World Calibration Centres are encouraged to assist laboratories in improving their procedures when it becomes apparent from comparison programmes that those laboratories are operating well outside of WMO compatibility goals. The comparisons include the round robins and various comparisons of flask samples and continuous analyser systems.
- e) The World Calibration Centre for CO₂, CH₄, and CO (EMPA) has demonstrated the benefits of using a travelling instrument for GAW station audits. It is very desirable that the air intake is included in the testing process. This practice is encouraged whenever possible. The benefit of using a “travelling” CO₂ measurement system for a period of weeks and in parallel to existing station systems to evaluate the system performance has also been demonstrated by the ICOS development team (*Hammer et al.*, 2012).

1.4 Maintenance of calibration by GAW measurement laboratories

- a) All laboratories that participate in the GAW Programme must calibrate and report measurements relative to a single carefully maintained scale, the WMO Mole Fraction Scale for gas mole fractions in dry air, including its version number, or relative to the appropriate isotopic ratio scales. Each GAW measurement laboratory must actively maintain direct traceability to the WMO Scales, preferably obtaining a sufficient number and range of laboratory standards from the respective WMO/GAW CCL and transferring those

calibrations to working and field standards. Laboratory standards should be regularly calibrated directly by the CCL or else by a World Calibration Centre. The data management system in use should allow for easy reprocessing and easy propagation of scale changes from laboratory standards to final measurement results.

- b) It is recommended that each WMO/GAW measurement laboratory maintains a strictly hierarchical scheme of transferring the calibration of its in-house tertiary standards to working standards, and from working standards to atmospheric measurements. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retro-active changes) in the assigned values of higher-level standards all the way to measured values for atmospheric air.
- c) To minimise the risk of creating offsets that are coherent among laboratories within the same region, each laboratory should maintain the shortest feasible direct link to the WMO Primary Standards, and/or engage in appropriate on-going comparison activities to verify that the recommended WMO compatibility targets (Table 1) are being reached.
- d) Laboratories should, when they find inconsistencies between calibration gas mixtures received from the CCL, bring those results to the attention of the CCL.
- e) A rule of thumb for internal reproducibility goals is one half the compatibility goals given in Table 1. Internal reproducibility incorporates not only instrumental imprecision, but also uncertainties in transferring the calibration scale from the highest level of standards to working standards and other uncertainties, for example related to gas handling, at the field station or laboratory.
- f) Calibration and working standards should be contained in high pressure aluminium cylinders where the interior wall is aluminium alloy 6061. Other aluminium alloys may be acceptable, but this is presently unknown. Steel cylinders are not recommended except for H₂ in which case stainless steel is recommended. Cylinder head valves should be packless, brass valves with PCTFE or metal seats, for H₂ the respective valve type made from steel or brass are appropriate.
- g) When prepared, calibration and working standards should be dried to a dewpoint of at most -70°C (at atmospheric pressure), corresponding to 2.6 ppm or less water vapour content.
- h) In the case of CO₂ the calibration standards should be replaced once the cylinder pressure has decreased to 20 bar. The maximum acceptable initial pressure for calibration standards is unclear, but is at least 140 bar, with little experience within the community at higher pressures.
- i) Cylinder regulators are a critical component of all analysis systems and a poor choice of regulator can significantly impact accuracy and precision. 'High purity' regulators should be used, and those with relatively small internal volume are preferred. In most applications two-stage regulators are ideal, as these ensure constant delivery pressure even as the cylinder pressure drops – particularly important at remote field stations. Brass or nickel-plated brass regulators (with metal diaphragms) have been found to give more stable results for CO₂ measurement in some cases than stainless steel. The selection of a specific

regulator model should be based on experimental evidence of its suitability for the purpose of delivering unchanged standard gases.

- j) Flushing times: Tests must be performed to ensure that cylinder regulators are sufficiently flushed during a measurement period. Regulator flushing times depend on regulator type, flow rate, and length of stagnation time since the regulator was last in use. When a regulator is first installed on a cylinder, it should be 'pressure-flushed' a minimum of four times, that is, draining the regulator from the cylinder pressure to ambient.
- k) We recommend the use of natural air for laboratory and working standards. If trace gas mole fractions are adjusted in reference air mixtures, in particular CO₂, the isotopic composition of the cylinder trace gas should remain unchanged to minimize the influence of isotopic composition on calibrations. The composition of the leading isotopologues of CO₂ standards should be analysed and provided with the mole fraction of CO₂.
- l) It is not possible to recommend a definitive number of calibration standards since this depends on the characteristics of specific instruments used for the air measurements. For example, an ideal suite of standards would include:
 - i. Enough standards used in 'routine' instrument calibrations to define the r^2 ('goodness of fit') parameter from a least squares fit of the instrument response (e.g. if the instrument response is fit to a quadratic function, then at least four standards are needed).
 - ii. For instruments with relatively variable baseline response, a so-called 'zero tank' (ZT) standard may be required to periodically adjust the offset of the baseline response.
- m) Calibration standards should bracket the range of observed mole fractions at the field station, and anticipate long-term trends in background atmospheric mole fraction.
- n) Frequency of calibration also depends on the instrument used, and control of the instrument environment, and thus specific recommendations cannot be given. Calibration frequency for a given instrument at a given location should be determined based upon:
 - i. Consideration of instrument drifts in baseline (zero), span and non-linearity (dependent on both the instrument and ambient environmental conditions). The calibration scheme should correct for such drifts. As a rule of thumb, we recommend frequency of calibration to define each of zero, span and non-linearity of the instrument to be half the time it typically takes for drift in these parameters to lead to a bias outside of the WMO compatibility requirements (Table 1).
 - ii. Consideration of results from initial 'target tank' (TT) analyses at the field station (see below). Variability in TT results should be about the same or less than the internal reproducibility goals.
 - iii. Prior experience or advice from experienced practitioners in the field.
- o) Any calibration analysis made at daily or lower frequency should be run at varying times of day to detect potential diurnal aliasing.
- p) Calibration analyses involving two or more standards should sometimes be run in opposite order to examine for incomplete flushing characteristics. (This requirement is unnecessary for measurement protocols where every sample or calibration measurement is bracketed by

a working standard, but in this case incomplete flushing must be diagnosed through other means, for example by varying the duration of calibration measurements).

- q) Each analysis system must include at least one 'target tank' (TT; sometimes called 'surveillance tank'), which is a very important quality control tool for *in-situ* measurement. Two TTs spanning a range in mole fraction for the measured species are preferred. Frequency of TT measurement should be once or twice a day, with the measurement time of day varying. An ideal analysis system allows the TT gas to pass through the same pumps, dryers and switching valves as the sample air, or less ideally, to be introduced to the instrument via the same path as calibration standards. As with calibration standards, the TT should be contained in a high pressure aluminium cylinder, must contain natural dry air, including trace gases and isotopic ratios to the extent possible, must be dried to a dew point of at most -70°C (at atmospheric pressure), and should be replaced once the pressure decreases to 20 bar.
- r) Care should be taken to maintain a single line of traceability of the calibration (see 1.4b above). The use of target tanks, or other additional standards, should not be used to define a second, optional, path of traceability. That only would create confusion and introduce an element of arbitrariness. Target gases function as a warning that there might be a problem that needs attention.

1.5 General recommendations for the quality control of atmospheric trace gas measurements

To achieve the required levels of compatibility (see Table 1) it is important to understand and carefully consider the design of the whole analysis system including instrument, gas handling, calibration and data management. No single instrument type is recommended. Many can be used with equal success and none are fool proof when poor choices are made with gas handling or data management. A trade-off in instrument stability and complexity versus cost must often be balanced according to the needs, resources and challenges of the measurement programme.

For a more comprehensive discussion of recommendations and guidelines for best practice for *in-situ* measurement, the reader is referred to Measurement Guidelines for CH_4 and N_2O (GAW Report 185, 2009) and for CO (GAW Report 192, 2010), both available at <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>.

The following list of best practices is specifically for CO_2 measurement, however many of these practices also apply to the measurement of other gas species discussed in these recommendations.

- a) Investigators must report uncertainty estimates for their data that include all potential sources of error, including collection and treatment of the air before it enters the instrument. In addition, investigators are encouraged to include with their data an estimate of inter-

laboratory measurement compatibility based on results from on-going comparison of atmospheric measurements. Details of how these estimates are calculated and what activities are used to verify them need to be provided. ISO nomenclature (see details in introduction) shall be used for uncertainty estimates and compatibility discussions.

- b) It is important to ensure that the gas handling design and components used do not unintentionally affect the composition of the air sample or the calibration standards. For any novel design or component that has not previously proven acceptable in the published literature, tests must be carried out.
- c) We recommend further thorough elimination of leaks, minimization of thermal gradients, and horizontal storage of cylinders to minimize the risk of fractionation between the gas components in the cylinder.
- d) With respect to drying air samples:
 - i. Water vapour must either be removed from the sample gas stream, or its influence on the mole fraction determination must be carefully quantified (see 1.5 e below). Furthermore, water vapour and adsorbed water in the entire air intake line, as well as the possibility of accumulation of condensed water in low points, must be considered.
 - ii. Prior to analysis, sample air should be dried to a dew point of at most -50°C (corresponding to at most 39 ppm water vapour content). If a cold trap is used the temperature should also be kept above -78°C to prevent losing a small fraction of CO_2 . These requirements are to ensure that WMO/GAW compatibility goals can be met. Water vapour effects influencing accurate mole fraction determination include spectroscopic interference, pressure broadening, mole fraction dilution, and transient surface effects from wetting and drying tubing walls. Note that drying to a dew point of -40°C (127 ppm water vapour) leads to a 0.05 ppm dilution offset in a CO_2 mole fraction of 380 ppm, if uncorrected. However, if recommendation iv is followed, especially with the use of Nafion[®], then the reference gas is humidified to almost the same humidity level as the sample, which will relax the drying requirements somewhat. The Nafion[®] will dry out as the dry reference gas flows through so that its ability to humidify diminishes over time.
 - iii. Tests must be carried out to ensure that the residence time of sample air in the drying vessel is sufficient to achieve the anticipated level of drying, and that in the case of cryogenic drying ice crystals are not removed from the trap by large air flows.
 - iv. To prevent CO_2 mole fraction offsets between very dry calibration standards and sample air, we recommend passing both calibration standards and sample air through the same drying vessel immediately prior to analysis (this will have the effect of 'wetting' the calibration standard).
 - v. The preferred method of drying is cryogenic, typically via a 'cold trap' immersed in an ethanol bath. Most chemical drying agents can absorb CO_2 and are unsuitable. Magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) can be used, but only under conditions of constant flow and pressure. Nafion[®] membrane dryers may be used, but also only under conditions of constant flow and pressure.

- e) Using water vapour measurements to correct measured CO₂ mole fraction: Studies with Cavity Ring Down Spectroscopy (CRDS) instruments showed that correction functions can be used (*Rella et al.*, 2013). However, the correction functions must be determined for each individual instrument. Furthermore, additional testing and verification studies are needed. These include, but are not limited to: side-by side comparisons of two instruments, one with comprehensive drying of inlet air streams, the other with no drying and using water vapour correction factors. Side-by side studies should take place for several months and under a variety of conditions, for example at locations with poor room temperature stability, on airborne or shipboard platforms, and at locations with very high ambient humidity. Studies should also be carried out with partial drying and correcting for the residual water vapour. Studies should be carried out with different instrument models and instruments from different vendors.
- f) Flushing times: Flow rates should be fast enough and long enough to allow complete flushing of the instrument sensor cell after switching between different sample inlets or calibration standards. Elimination of “dead volumes” is essential for lowering the flushing requirement, which consumes valuable reference and sample gas.
- g) If instrument sensor cell pressure is not actively controlled, then cell pressure should be measured, and the pressure sensitivity of the instrument and its concentration dependence should be routinely determined.
- h) Where possible, instruments should be located in a stable temperature environment. If temperature of the room or immediate environs of the instrument is not actively controlled, then it should be measured, and the temperature sensitivity of the instrument and its concentration dependence should be routinely determined.
- i) Results from direct comparison of atmospheric data derived from different laboratories or using different techniques are valuable to assess the full uncertainty budget. In addition to participation in the WMO/IAEA round-robin comparisons, investigators are required to participate in more frequent and on-going comparison activities between pairs of laboratories, which incorporate the analyses of actual air samples. Comparisons of measurements from co-located in-situ instruments and co-located discrete samples and in-situ instruments are also strongly recommended. Atmospheric air comparison experiments at a single site by multiple laboratories such as those conducted at Alert, Cape Grim, and Mauna Loa are very valuable. The benefit of on-going same-air comparisons has been demonstrated (*Masarie et al.*, 2001). Mutual exchange of air in glass flasks is encouraged as a means to detect experimental deficiencies. Results from comparison activities are used only to expose measurement inconsistencies. Measurements should not be adjusted by WMO participants based on comparison results, but only when the cause of a measurement bias is understood and quantified. Regular comparison of data from various stations at similar settings (altitude, latitude, remoteness) can also help to timely identify instrumental issues with a particular measurement.

- j) Laboratories participating in on-going comparison experiments must make comparison data electronically available to each other within a month after completion of the measurements. It is understood these data are preliminary and may contain undetected errors. Timely review of comparison results increases the likelihood of detecting experimental problems shortly after they develop. The main reason for sharing preliminary data is early detection of problems.
- k) Data comparisons require sufficient metadata to identify methodology differences that potentially influence quantitative comparisons. These metadata should be provided by the participants in the comparison programs (ICP) to allow independent quantification of bias, and assumptions in comparisons should be specifically stated.
- l) To better understand the effectiveness of various comparison strategies, laboratories with on-going comparison experiments are encouraged to report at GGMT meetings what they have learned, how the comparison has affected measurement quality and compatibility and the benefit of redundant or complementary comparisons. This will be needed to develop a comprehensive quality control strategy.
- m) Flask sampling programmes should be implemented where possible at observational sites making continuous measurements. This will provide on-going quality control, help determine measurement uncertainty and allow the joint use of data sets from different laboratories. The Integrated Carbon Observation System (ICOS) will assess the benefit of having a “buffered” or time-integrated flask collection system to increase the representativeness of the flask sample as well as the precision of the comparison.
- n) Clear protocols and reports of experience gained in comparison projects should be provided. Results should be published and be made readily accessible via internet. The evaluation of such activities and recommendations for refinement, co-ordination and expansion of such activities has been accepted as a key responsibility of future GGMT meetings.
- o) Engaging the remote sensing community in validation with ground-based measurements is essential for ensuring that trace gas retrievals can be used in high resolution analyses without introducing spatial and temporal biases. Such engagement should not be limited to the CCLs or WCCs alone, as individual scientists or research groups making vertical profile measurements can contribute significantly to this effort.
- p) Deviations from recommendations: We recognize the value of innovation and experimentation with new approaches. However, we stress that deviations from established practices should be fully tested to confirm that the new approach does not introduce bias into the measurements. The results of such experimentation should be reported at future GGMT meetings and similar venues, and published in the peer-reviewed literature whenever possible.
- q) Data management protocols for *in-situ* measurement closely follow those given in section 12 below for WMO/GAW laboratories. In particular, because of the typically larger volumes of data collected, we emphasise the necessity for automated routines both to produce mole

fraction results from raw data and to retrospectively recalculate mole fraction data owing to any revisions made to either the *in-situ* calibration scale or the externally defined calibration standard mole fractions. Automated routines must also exist to provide frequent system diagnostic and quality control checks, and to alert the investigator to problems.

- r) A logbook, preferably in electronic form, must be maintained, documenting all problems that occur with the measurement system, downtimes, upgrades, routine maintenance, replacement of calibration standards, and any unusual local activity that might compromise the in situ sample measurements.
- s) For an atmospheric monitoring field station, a good practical setup is to measure at least one or two atmospheric species continuously in situ, complemented with meteorological data, whilst datasets of other species are obtained via flask sample collection.

1.6 Recommendations for the assessment of new in situ measurement technologies and/or instruments

An overarching and on-going objective is to simplify all steps of the measurement process, by making operations routine and increasing standardisation, so that carrying out measurements is more accessible to a wider group of scientists, while reducing costs – both start-up and on-going.

The following topics require further research before recommendations for best practice can be defined or revised. We strongly encourage the community to investigate these topics and report their findings at subsequent WMO/GAW GGMT meetings.

- a) We encourage the development of new or improved techniques that would lead to improvements in precision and reproducibility, which includes methods that reduce the consumption of calibration gas. Experience and results obtained with new techniques should be shared with the community through web-based discussion groups or scientific publications.
- b) We recommend that new analytical technologies (e.g., laser-based optical analysers, closed-cell Fourier Transform spectrometers) are tested (e.g., *Hammer et al., 2012*). New techniques should meet the scientific requirements of accuracy and precision as stated in GAW reports. Specific areas that need to be investigated are calibration frequency and ability to correct for water vapour dilution or interference with other trace substances, and other artefacts besides sample drying. Manufacturers are encouraged to offer detailed training, perhaps through the GAW Training and Education Centre (GAWTEC, www.gawtec.de). The community should identify species for which new technologies are needed and formulate desired specifications for instruments that can measure new observables.
- c) *Instrument Characterization*: The goal of these tests is to perform a basic assessment of the suitability of the instrumentation for the application, as well as to provide input for constructing an appropriate calibration strategy for the instrument. The following parameters should be characterized using controlled test conditions.

- Noise: Instrument noise should be measured using known dry air from cylinders, under the following conditions. The total time period for this test should extend to well beyond the expected time period between *in-situ* instrument calibrations or target tank measurements. Regular calibrations should be performed during this test. Allan variance plots can then be constructed with or without (a subset of) the calibrations, so that the plots are informative for the choice of an optimal calibration strategy.
 - Linearity: the linearity of the instrument should be assessed, with traceability to the WMO or other standard scales. Three standards well separated from each other is the minimum number to establish linearity.
 - Response time: The response of the instrument to step function changes of the input gas mole fraction should be quantified with dry gas mixtures. This test establishes the effective time constant of the instrument at a given flow rate, and is relevant for how standards are introduced. The response of the instrument should also be characterized in response to step function changes in a) humidity, and b) inlet pressure, c) flow rate.
 - Environmental conditions: Potential systematic biases associated with the instrument response to environmental temperature, pressure, and humidity changes should be evaluated over the range of environmental conditions expected during deployment.
 - Interfering species: The systematic bias of the instrument response to the introduction of interfering atmospheric species to the gas inlet should be assessed. A complete assessment is not practical, but interferences from the principal atmospheric constituents should be measured. Each technology and application will suffer from different potential interference, so likely candidates should be selected and prioritized from the following list, with technical input from the manufacturer of the instrument.
 - o Water vapour
 - o Carbon dioxide
 - o Methane
 - o Composition of main air components N₂, O₂, Ar
 - o Nitrous oxide
 - o Isotopes of the primary concentration measurement or potential interfering species
 - o Other trace species
- d) *In-situ Application Validation:* The instrument should be located at the measurement site or at an appropriate proxy site for long term monitoring. Drift of the instrument response function should be quantified over a long period, preferably six months or more, using known reference standard mixtures. The time between individual standard measurements should be at most 1 week (< 1 day preferred) to capture more rapid variability. A ~10 day subset of this time should be sampled at a higher frequency (several times per day) to capture diurnal systematic errors in instrument performance. The instrument should be evaluated hourly (or other time interval suitable to the application) against 1) another well-validated *in-situ* monitoring technology AND 2) co-sampled flasks that are analyzed at an

established laboratory using proven methodology. With increasing duration of the validation period, additional confidence is gained in the performance of the new technology. A target comparison period of 1 year or greater should be the goal, but the interim results provide a very valuable initial assessment. For a full assessment of the uncertainty of the measurement system the air sample inlet and air preparation, such as drying, needs to be included in the evaluation.

- e) *Communication:* Those involved with instrument validation and testing are encouraged to publish their findings in a peer-reviewed publication for dissemination to the wider community and to provide a reference for citation.

2. SPECIFIC REQUIREMENTS FOR CO₂ CALIBRATION

2.1 Background

The general goals for compatibility of measurements of CO₂ in air are stated above in Table 1. The target of 0.1 ppm for the Northern and 0.05 ppm for the Southern Hemisphere is intended to address small, globally significant gradients over large spatial scales (for example Southern Ocean fluxes). However, in polluted or vegetated continental regions, the annual-mean fluxes of interest leave small imprints on mole fraction gradients in the free troposphere, especially on an annual mean basis in the highly-variable boundary layer so that a target of 0.1 ppm is still needed. However, for certain local, for example urban, studies the extended compatibility goal of Table 1 may be appropriate.

NOAA/ESRL serves as CCL for CO₂ for the GAW Programme. The current (September 2013) version of the WMO mole fraction scale for carbon dioxide is WMO CO₂ X2007.

The range of the WMO CO₂ X2007 scale is from 250 to 520 ppm, but the CCL has cylinders that have been measured several times manometrically ranging from 70 ppm (covering atmospheric values in ice cores) to 3000 ppm (covering CO₂ partial pressures in the oceans). The WMO scale is currently embodied in a set of 15 CO₂-in-air mixtures in large high-pressure cylinders covering the ambient range 250-520 ppm, while another 20 cylinders provide both a backup and a much larger range.

2.2 Recommendations for CO₂ calibration and comparison activities

- a) Since the WMO scale was maintained until 1995 by Scripps Institution of Oceanography (SIO), comparisons with SIO are especially relevant. It is recommended that remaining uncertainties associated with the SIO pre-1995 WMO scale and its transfer to NOAA are resolved.

- b) The CO₂ isotopic composition of distributed reference standards should anticipate the evolution of CO₂ and its isotopic ratios in background air when the standards are intended to be kept for decades, in order to avoid isotopic measurement bias during instrument calibration. The isotopic composition of distributed standard gases should be reported by the CCL as information values, at the precision required to minimize potential biases of total CO₂ calibrations well below WMO compatibility goals (0.03 ppm, see 2.2.d). These information values are thus not isotopic calibration values.
- c) The CCL is encouraged to make available on its web site calibration results of all GAW laboratory standards based on the current scale in a format that can be accessed and used by automated data processing routines.
- d) To make possible a level of compatibility of ±0.03 ppm or less among the CO₂ calibration scales of laboratories participating in the WMO/GAW Programme, the CCL shall aim to transfer the CO₂ scale to secondary and tertiary standards at that level of consistency.
- e) Each WMO/GAW measurement laboratory must actively maintain its link to the WMO Scale by having a subset of its in-house highest level standards for CO₂ (covering the measurement range) re-calibrated by the CCL at least every three years. A network calibration centre of GAW partners must do the same, as standard procedure, except at least every two years (see 1.3b).

3. SPECIFIC REQUIREMENTS FOR STABLE ISOTOPE CALIBRATION

The target values for compatibility of stable isotope measurement results of CO₂ and CH₄ in air are presented in Table 1 above. These targets are required to achieve reasonable signal/noise ratios when addressing small yet globally significant gradients over large spatial scales, for example, Southern Ocean isotopic disequilibrium fluxes.

Given that ecological or biogeochemical studies of predominantly local or regional significance deal with larger signals in time and space, the compatibility goals for such studies can be relaxed and a coarser measurement precision can be tolerated (Table 1). Precision and compatibility values tolerated for local studies are intended to scale with the magnitude of the gradients studied. (See section above: Requirements for regional greenhouse gas networks).

3.1 Background

MPI-BGC serves as CCL for the stable isotopes of CO₂ in air for the GAW Programme. The CCL activity is based on work performed at the MPI-BGC in Jena (Germany) in collaboration with EC (Canada) and NIES (Japan) since 2001. As a result, MPI-BGC offers the scale realization in the form of CO₂ in reference air (Jena Reference Air Set, JRAS), with the aim to reach the scale realization compatibility of ± 0.01‰ for δ¹³C and ± 0.025‰ for δ¹⁸O. This CO₂ isotope scale realization is named as JRAS-06.

Following the 15th WMO/IAEA Meeting (GGMT-2009), a number of laboratories have implemented JRAS as their scale anchor for stable isotope measurements of CO₂ in air. In order to reach the compatibility targets (Table1), this process needs to be completed in the near future.

Analysis of the first data obtained during an inter-comparison exercise using JRAS sets (Wendeberg et al., 2011) has reiterated the need for consistent application of the ¹⁷O correction. Further, the above inter-comparison based on JRAS has revealed differences in the anchoring of laboratory scales to VPDB and has quantified instrument-dependent scale contraction issues (Wendeberg et al., 2011). This, along with results from on-going inter-laboratory comparison programmes, has led to an extension of the service provided by the Central Calibration Laboratory for stable isotopes of CO₂ in air. In addition to the provision of reference materials in the form of JRAS sets in 5-L glass flasks (carbonate-CO₂ in air, with δ¹³C close to +1.9‰ and dry ambient air with δ¹³C close to -8‰), MPI-BGC in Jena will continue to perform isotopic calibration of high pressure air tanks provided by participating laboratories. These materials with different δ¹³C values represent the JRAS-2006 scale realisation. As air-flasks or tank air have δ¹³C values close to actual samples, these are intended to be used as the immediate calibrator for the VPDB-CO₂ scale. The JRAS flasks with CO₂ from calcites can be used as measurement quality checks, in order to test instrument performance (specific effects such as scale contraction 'η'-effect, extraction effects etc.) and potentially to quantify corrections. As all measurements at MPI-BGC comply with the NBS19 – LSVEC normalization on the δ¹³C VPDB scale, the calibration scheme as given above is consistent with this scale.

Estimating the total combined uncertainty of measurement results and traceability to the VPDB-scale, the corresponding data for each JRAS flask and air tank calibrated on the JRAS-2006 scale are key points and need to be provided by the CCL. Hence, further efforts by the CCL (MPI-BGC) and the participating laboratories are necessary. The practical realisation and future steps are discussed further below.

3.2 Current calibration and comparison activities of the stable isotopes of CO₂

The major difficulties in harmonizing stable isotope ratio results for CO₂ in air have been identified:

- a) Scale contraction ('η'-effect) during calibration of mass spectrometric measurements. While this affects both δ¹³C and δ¹⁸O measurements, where measurements are referred directly to the scale origin (defined by NBS-19) the greatest impact is on δ¹³C of CO₂, as in ambient air this is 10‰ away from the reference. δ¹⁸O is generally less than 4‰ different from the scale origin. Ion source materials as well as ion source flushing times (idle time) are major parameters responsible for this effect (*Verkouteren et al.*, 2003a; *Verkouteren et al.*, 2003b).

- b) For $\delta^{18}\text{O}$, exchange with water during sample storage and inconsistent scales between laboratories seem to be the main culprits.
- c) Further inconsistencies between laboratories arise from different algorithms and/or parameterizations of the necessary corrections for ^{17}O and N_2O .
- d) Failure to report assignment uncertainties in the isotopic composition of gas used as a reference.
- e) Failure to estimate and report total combined uncertainty of the data as traced to the VPDB-scale and also failure to assemble the uncertainty budget.

Most of these problems have been fully recognized and documented (*Brand et al.*, 2009; *Coplen et al.*, 2006; *Verkouteren et al.*, 2003a; *Verkouteren et al.*, 2003b; *Wendeberg et al.*, 2011; *Wendeberg et al.*, 2013). It is agreed that progress in this area requires the availability of whole-air standards reliably calibrated on the VPDB- CO_2 scale by the Central Calibration Laboratory. The CCL makes such “anchor” gases available in glass flasks as well as in high-pressure cylinders, as distribution of calibrated pure CO_2 alone will not be able to resolve the issues. Tests aimed to quantify the magnitude of memory or cross contamination (*Ghosh et al.*, 2005; *Verkouteren et al.*, 2003a; *Verkouteren et al.*, 2003b) performed locally may prove more efficient when aspects of sample extraction and mass spectrometric measurement can be studied separately.

For a reliable compatibility assessment between laboratories and reliable uncertainty estimation, generation and maintenance of the full measurement traceability chain to the primary (VPDB) scale is necessary and should be provided. For this purpose, the CCL should provide a measurement traceability chain on the VPDB scale for all calibration measurements as well as the full error budget of all materials given out by the CCL; these should also be made available on the JRAS web site.

Participating laboratories can base their measurement traceability chain on the material calibrated by the CCL and include all corrections required locally. The uncertainty propagation should include all uncertainty sources such as the uncertainty assigned to the calibration material, uncertainties of all measurement steps involved as well as the combined uncertainties of all corrections. The carbonate-based CO_2 JRAS flasks should be used as a measurement quality check and not be included in the uncertainty estimation.

Furthermore, progress in the compatibility assessment is visualized by the results of various inter-laboratory comparison programmes.

3.3 Central Calibration Laboratory for stable isotopes of CO_2 in air

In addition to supplying the community with JRAS gases, the MPI-BGC has been asked to perform calibration for high-pressure cylinders from interested laboratories. These cylinders are intended to provide a working standard (or calibration gas) to individual laboratories.

Further, support from participating laboratories to provide a limited number of cylinders containing clean air will be given, preferably with dry marine Southern Hemisphere air. These can serve as a suite of quasi-primaries inside the CCL, calibrated by the MPI-BGC at air-isotope values and marking the ambient atmosphere range independent of availability of other, solid reference materials and associated procedures.

3.4 Recommendations for CO₂ stable isotope calibration and comparison activities

- a) *Data management*: Data must be archived in a way to facilitate data re-processing, in case such a need will arise from reference gas re-calibration or other corrections to be applied retrospectively.
- b) *¹⁷O-correction*: For removing the ¹²C¹⁶O¹⁷O contribution from the mass spectrometrically measured δ^{45} results, the method described in Assonov and Brenninkmeijer (2003a, b) should be used. A sufficiently accurate linearized version of this method has been proposed by Brand (2010), which will facilitate the transition from any previously used ¹⁷O correction method. Further, to ensure that the effect of the ¹⁷O-correction is kept at a minimum, the use of air references is recommended and the use of reference materials with a large deviation in $\delta^{18}\text{O}$ (e.g. NBS 18) should be avoided. To provide a consistent link to the VPDB–CO₂ scale as defined through NBS 19-CO₂, the CCL is advised to apply corrections based on the Assonov-Brenninkmeijer ratio assumption set exclusively.
- c) *N₂O-correction*: The N₂O correction has been the subject of several publications, which through different experimental approaches lead to a common size for the correction. The CCL is asked to implement the required correction on distributed reference gases and verify its validity over time. With the provision of reference air, ambiguities in the N₂O correction of different laboratories will be extremely small and should not affect compatibility of results and/or scale realisation. As a control measure, the CCL is asked to provide air with varying N₂O mole fractions occasionally (also without N₂O) to the participating laboratories and report the results on its web site.
- d) *JRAS*: For improving data compatibility at air isotopic composition, the Jena Reference Air Set has been expanded to include a reference point at atmospheric CO₂ levels ($\delta^{13}\text{C} \approx -8\text{‰}$). The measurement traceability chain and the uncertainty propagation has to be based on the calibration material with $\delta^{13}\text{C} \approx -8\text{‰}$, with the second material ($\delta^{13}\text{C}$ close to + 2‰ or -4‰) to be used as quality check and test for instrumental effects. In lieu of a calcite with suitable isotope composition, clean air from Jena has been used for this purpose. As a future second air source, a Southern Hemisphere air high-pressure cylinder will be provided by CSIRO Marine and Atmospheric Research, Australia.
- e) *Inter-Laboratory Comparisons*: All laboratories are encouraged to continue their participation in the existing inter-laboratory comparison activities. These are required to evaluate data and scale realisation compatibility values. Inter-laboratory comparison activities should address all possible sources of discrepancies and biases. A

comprehensive comparison activity should include all forms of samples, i.e. flasks as well as low- and high-pressure cylinders or pure CO₂ ampoules like the Narcis sets from NIES. Reported values must be accompanied by estimates of uncertainties, based on a calibration / measurement traceability chain. Laboratories that have long histories of participating in inter-laboratory comparisons are encouraged to re-assess their comparison data in light of present recommendations regarding corrections and ensure compatibility with current inter-laboratory comparisons.

- f) *Instrument-specific scale contraction*: Further investigation of the indications of instrument-specific influences on scale contraction is needed. Specifically it should be investigated whether there is a scale contraction effect, which might be common or typical for certain instrument models or batches of instruments (for example, *Meijer et al.*, 2000; *Verkouteren et al.*, 2003a; *Verkouteren et al.*, 2003b). Operational instrument parameters and analytical protocols to minimise the scale contraction effect, to monitor its magnitude over time, and to correct for it should be implemented locally, following the literature cited above. The information on cross-contamination tests, its magnitude and corrections, if applied, should be provided together with the data in publications, by data centres and on web sites.
- g) *Selection of laboratory working gases*: During isotope ratio mass spectrometer (IRMS) measurements scale contraction and memory effects critically depend on the reference gases in use. More specifically, the results are affected by the isotopic distance between these gases. To minimize such effects, the isotopic composition of the working reference gases should be as close as possible to that of CO₂ in ambient air. In addition, investigators are encouraged to include with their data an estimate of inter-laboratory measurement compatibility based on results from on-going comparison of atmospheric measurements.
- h) *Uncertainty estimates*: Similar to other measurements, investigators are requested to report estimates of total combined uncertainty for the data, including the uncertainty of scale realisation (e.g. calibration material in use) and all potential sources of error such as all instrumental corrections and errors related to the CO₂ extraction. The measurement uncertainty must be reported on the VPDB-scale and be traced (by calibration) to the primary isotope standard, NBS 19. A simplified form of uncertainty propagation for $\delta^{45}\text{R}$ - $\delta^{46}\text{R}$ values measured has been proposed by (*Brand et al.*, 2010), which will also facilitate both the uncertainty propagation and the ¹⁷O correction.
- i) *JRAS-scale realisation*. MPI-BGC is asked to document details of the preparation of JRAS sets and high pressure air tanks and their calibration on the VPDB-scale, including the total uncertainty propagated to the VPDB-scale and the uncertainty budget. The description should be available on the MPI-BGC web-page and revised on a regular basis.

3.5 Isotopic measurements from emerging optical techniques

In recent years, optical analysers that report mole fractions of individual isotopologues have become available and are now in routine use. Many of these instruments can provide isotopic ratios with a precision of around 0.1‰ for $\delta^{13}\text{C}$ of atmospheric CO₂ and are valuable for continuous

measurements. Unlike mass spectrometric techniques, δ values from such instruments are often calculated from the ratio of individual measured mole fractions using tabulated absorption line strengths and are not from direct measurements of a standard material. The reference isotopic abundance is normally taken from a spectral parameter database (typically HITRAN, see JQSRT special issue, 2009) that is used in the analysis, and this does not provide a common scale such as VPDB or JRAS. Some corrections applicable to mass spectrometric methods, such as those for ^{17}O and N_2O are not required, but other corrections, depending on the method used to calculate the isotopic “ δ ” values from individual mole fractions, such as interference from other atmospheric components and instrument fluctuations, may be required. Thereafter, calibration and drift-correction for optical instruments should be done based on CO_2 -in-air characterised by the traditional IRMS method.

Recommendations:

- a) To determine calibrated amounts of individual isotopologues in a sample, both the whole species mole fraction and the isotopic composition of at least all singly-substituted isotopologues must be provided by the CCL for the calibration gases to enable isotopologue-specific calibration of the analyser.
- b) Measured isotopic “ δ ” values must be related to the accepted scales, such as VPDB for CO_2 , normally by calibration against standards of known isotopic composition on the relevant reference scales.
- c) Developers and providers of optical analysers which deliver isotopic analyses should make available and distribute to the user communities all relevant algorithms used in the calculation of calibrated δ values, as well as the relevant primary measurements used to derive isotopologue amounts and calculated δ values. This will ensure comparability across instrument types, manufacturers and measurement laboratories, and allow checks of procedures and corrections. Measurements may include pressures, temperatures, optical path lengths, spectra, absorption line peak heights, areas or widths, as appropriate. Algorithm details should include all relevant calculations and corrections for variations such as those in water vapour and other interfering gases (including O_2 , N_2 , and Ar), pressure and temperature fluctuations and variations in mole fraction of each isotopologue.

3.6 Isotopologues of N_2O and CO

Growing interest in measuring the stable isotopic composition of nitrous oxide and carbon monoxide in air will drive the need for a standardized calibration for these species in ambient air. In collaboration with IAEA, a group will be formed to investigate strategies for providing a calibration of stable isotope ratios, including all isotopologues of these gases in air to the accepted IAEA scales and for preparing and providing secondary standards and/or recommendations on preparation steps to be distributed to capable laboratories.

3.7 Recommendations for CH₄ isotope calibration and comparison activities

The need for a standardized isotopic calibration of methane in air ($\delta^{13}\text{C}$ and δD) has also been recognized. New strategies for preparing isotopically characterized methane in air linked to the accepted IAEA scales (V-SMOW, VPDB) have been presented at GGMT-2013. Chemical preparation of CH₄ using δD -calibrated waters in an Al₄C₃ hydrolysis reaction, followed by mixing the resulting methane into methane-free air has been presented. A similar step might be possible to produce $\delta^{13}\text{C}$ calibrated gas from the primary carbonates. Distribution of CH₄-in-air mixtures aims to improve the δD and $\delta^{13}\text{C}$ data compatibility between institutes.

In order to address the current need to urgently improve $\delta^{13}\text{C}$ calibration of methane as well as understand and quantify instrumental effects and related corrections, NIWA has started to prepare a suite of high pressure cylinders of methane in air and to determine the carbon stable isotopes. Before the cylinders can be circulated as a common reference material, sub-samples of these gases will be sent to participating institutes for an initial isotopic assessment. Further regular comparison of results from flask samples between laboratories (e.g. within the sausage inter-comparison activity) is encouraged.

4. SPECIFIC REQUIREMENTS FOR THE CALIBRATION OF RADIOCARBON IN TRACE GASES

4.1 Background

Standardization of radiocarbon analysis has been well established in the radiocarbon dating community for many years, and Oxalic Acid Standard and the new Oxalic Acid Standard (NIST SRM 4990C) have been agreed upon as the main standard reference materials. Other reference materials of various origin and ¹⁴C activity are available and distributed by IAEA and some other agencies.

Atmospheric ¹⁴CO₂ measurements are usually reported in $\Delta^{14}\text{C}$ notation, the deviation from the absolute radiocarbon reference standard (*Stuiver and Polach, 1977*):

$$\Delta^{14}\text{C} = \left[\left(\frac{R_{sam}}{R_{ref}} \right) \left(\frac{1 + \frac{-25}{1000}}{1 + \frac{\delta^{13}\text{C}_{sam}}{1000}} \right) \exp(\lambda(1950 - t)) \right] - 1$$

with $R = ^{14}\text{C}/\text{C}$, and the corrections are for fractionation and radioactive decay (λ) and reported in per mil (‰). The date used for the decay correction (typically the date of collection) should be reported with the result. $\delta^{13}\text{C}$ should also be reported if it was measured on the original sample (e.g. atmospheric CO₂), along with the $\delta^{13}\text{C}$ measurement method. Note that $\delta^{13}\text{C}$ measured by

AMS may be fractionated from the original sample material and we strongly recommend that this value, although used to calculate $\Delta^{14}\text{C}$, should not be reported.

When $\Delta^{14}\text{C}$ is used to calculate fossil fuel CO_2 content the ^{13}C Suess Effect is neglected, introducing a slight bias. This can be solved by using $\delta^{14}\text{C}$ (*Stuiver and Polach, 1977*) if the original sample $\delta^{13}\text{C}$ is known, but as some sampling strategies preclude measurement of ambient $\delta^{13}\text{C}$, we recommend $\Delta^{14}\text{C}$ be reported to provide consistency amongst laboratories.

For atmospheric measurements of $\Delta^{14}\text{C}$ in CO_2 , two main sampling techniques are used: High-volume CO_2 absorption in basic solution or by molecular sieve and whole-air flask sampling (typically 1.5-5 L flasks). Two methods of analysis are used: conventional radioactive counting and Accelerator Mass Spectrometry (AMS). The current level of measurement uncertainty for $\Delta^{14}\text{C}$ in CO_2 is 1-5‰. As atmospheric gradients in background air are currently very small, a target of 0.5‰ compatibility is recommended (Table 1). We emphasize again that compatibility is a measure of how well measurements from different instruments and laboratories can be compared over the long-term, and is not the individual measurement certainty.

Atmospheric $^{14}\text{CH}_4$ measurements are also reported in $\Delta^{14}\text{C}$ notation. Atmospheric ^{14}CO is usually reported in molecules per cubic centimetre. For both species, samples are typically collected into large tanks able to collect sufficient whole air for ^{14}C measurement. For ^{14}CO , extra care is taken to avoid, or account for, in-situ production of ^{14}CO inside the tanks due to thermalized neutrons. The tank material is critical for stability and aluminium is preferred (*Lowe et al., 2002*). The species of interest is extracted from whole air and converted to CO_2 prior to graphitization and AMS measurement.

4.2 Current $^{14}\text{CO}_2$ calibration and comparison activities

The first comparison activity for $\Delta^{14}\text{C}$ in CO_2 was initiated at the 13th WMO/IAEA Meeting of CO_2 Experts in Boulder, Colorado, and is on-going about once per year (*Miller et al., 2013*). Laboratories participated by sending flasks to NOAA/ESRL to be filled with air from two whole-air reference cylinders for CO_2 extraction, target preparation and ^{14}C AMS analysis. Plans for future atmospheric ^{14}C comparison exercises are laid out in the report of the atmospheric $^{14}\text{CO}_2$ workshop at the 21th International Radiocarbon Conference (*Turnbull et al., 2013; Lehman et al., 2013*). Other comparison exercises have been performed on an ad hoc basis: the full $\Delta^{14}\text{C}$ of CO_2 measurement process from sampling method to AMS measurement (*Graven et al., 2013*); comparison of AMS and conventional measurements (*Vogel et al., 2011*).

4.3 Recommendations for $^{14}\text{CO}_2$ calibration and comparison activities

- a) We recommend that laboratories conducting small-volume flask sampling and AMS analysis should use whole air cylinders as a target/surveillance material and, potentially, as a secondary standard.
- b) Reported uncertainties should reflect long-term repeatability of target materials as well as counting statistical uncertainties. A sufficiently detailed description of how the uncertainty was determined should be reported with results.
- c) We recommend continuation of the whole-air comparison at a frequency of once per year or more frequently and expansion of participating laboratories. We recommend adding a second comparison exercise, tied to the existing one, to provide whole air samples to laboratories within China.
- d) We recommend an additional comparison of pure CO_2 , allowing high-volume sampling techniques to be directly compared to AMS measurements.
- e) It is also recommended that laboratories participate in comparison exercises conducted by the wider radiocarbon community (*Scott et al.*, 2010).
- f) Co-located sampling at observation stations should be considered.
- g) We recommend on-going workshops to discuss comparability and standardisation for $\Delta^{14}\text{C}$ in CO_2 measurements.

4.4 Calibration and comparison activities for ^{14}C in other trace gases

No species-specific calibration materials or comparisons for other trace gases ($^{14}\text{CH}_4$, ^{14}CO , others) are currently active. We recommend that members of the radiocarbon community with interest and experience in these species consider developing reference materials and comparison exercises.

5. SPECIFIC REQUIREMENTS FOR O_2/N_2 CALIBRATION

5.1 Background

Measurements of the changes in atmospheric O_2/N_2 ratio are useful for constraining sources and sinks of CO_2 and testing land and ocean biogeochemical models. The relative variations in O_2/N_2 ratio are very small but can now be observed by at least six analytical techniques. These techniques can be grouped into two categories: (1) those which measure O_2/N_2 ratios directly (mass spectrometry and gas chromatography), and (2) those which effectively measure the O_2 mole fraction in dry air (interferometric, paramagnetic, fuel cell, vacuum ultraviolet photometric). A convention has emerged to convert the raw measurement signals, regardless of technique, into equivalent changes in mole ratio of O_2 to N_2 . For mole-fraction type measurements, this requires accounting for dilution due to variations in CO_2 and possibly other gases. If synthetic

air is used as a reference material, corrections may also be needed for differences in Ar/N₂ ratio. By convention, O₂/N₂ ratios are expressed as relative deviations compared to a reference

$$\delta(\text{O}_2/\text{N}_2) = (\text{O}_2/\text{N}_2)_{\text{sample}} / (\text{O}_2/\text{N}_2)_{\text{reference}} - 1$$

in which $\delta(\text{O}_2/\text{N}_2)$ is multiplied by 10⁶ and expressed in “per meg” units. Per meg is a dimensionless unit equivalent to 1 per meg = 0.001 per mil (*Coplen, 2011*). The O₂/N₂ reference is typically tied to natural air delivered from high-pressure gas cylinders. As there is no common source of reference material, each laboratory has employed its own reference. Hence it has not been straightforward to report measurements on a common scale. There is currently no CCL for O₂/N₂. Several laboratories report results on the Scripps scale, but there are no named versions.

There is considerable scientific value to be gained from different laboratories reporting O₂/N₂ measurements on a common scale. The O₂/N₂ measurement community recognizes the Scripps O₂ Scale as the best candidate for a common reference. With a medium-term goal of establishing this as the common scale for reporting and comparing O₂/N₂ measurements, in the near-term we recommend that all O₂/N₂ measuring laboratories participate in the Global Oxygen Laboratories Link Ultra-precise Measurements (GOLLUM) comparison exercise, and we recommend that laboratories begin taking steps to link their internal laboratory scales directly to the Scripps O₂ Scale. In support of this, we recommend that the Scripps O₂ Laboratory continue to provide measurements for other laboratories on a cost-recovery basis, with a targeted turn-around time of 5 weeks for existing tanks, and also continue to provide service for filling and calibration of new tanks with a target turn-around time of 6 months.

The practice of basing O₂/N₂ measurements on natural air stored in high-pressure cylinders appears acceptable for measuring changes in background air, provided the cylinders are handled according to certain best practices, including orienting cylinders horizontally to minimize thermal and gravitational fractionation. Nevertheless, improved understanding of the source of variability of measured O₂/N₂ ratios delivered from high-pressure cylinders is an important need of the community. An independent need is the development of absolute standards for O₂/N₂ calibration scales to the level of 5 per meg or better.

The relationship between changes in O₂/N₂ ratio and equivalent changes in O₂ mole fraction has been discussed in peer-reviewed literature. However, confusion does still exist. Adding 1 μmol of O₂ per mole of dry air increases the O₂/N₂ ratio by 4.77 per meg, which establishes an equivalency of 4.77 per meg per ppm (*Keeling et al., 1998*). The confusion arises because the increase in mole fraction of O₂ caused by this addition is not 1 ppm, but rather 0.79 ppm. The increase in mole fraction is smaller than 1 ppm because the total number of moles has also increased. For a trace gas, in contrast, adding 1 μmol/mol of dry air increases the mole fraction by almost exactly 1 ppm. The factor 4.77 per meg per ppm relates the change in O₂/N₂ ratio to the

equivalent uptake, emission, or change in a trace gas, and is thus the relevant factor for most applications, e.g. estimating changes in O₂/N₂ ratios in an air parcel corresponding to a photosynthetic or respiratory flux of CO₂, or calculating changes in O₂/N₂ ratios resulting from O₂ fluxes in a model that does not account for changes in the total number of moles. The alternative factor of $4.77/0.79 = 6.04$ per meg per ppm can also be relevant in certain applications, however, such as calculating instrument response functions (*Kozlova et al.*, 2008, p. 4).

5.2 Current O₂/N₂ calibration and comparison activities

At the 12th WMO/IAEA Meeting in Toronto (GGMT-2003, WMO/GAW Report No. 161, 2005) the GOLLUM programme was initiated to provide constraints on the offsets between the different laboratory scales and to clarify the requirements for placing measurements on a common scale. There are two components to this programme, each of which has been running since 2005: a “sausage flasks” comparison programme, and a “round-robin cylinder” comparison programme. The sausage flask programme compares the laboratories’ ability to extract and analyse air from a small flask sample, whereas the round-robin cylinder programme compares the laboratories’ calibration scales, and their methods for extracting and analysing air from high-pressure gas cylinders.

Details of the GOLLUM programme can be found in WMO/GAW Report No. 161 (2005) and at a dedicated web site: <http://gollum.uea.ac.uk/>. The programme is coordinated by A. Manning at the University of East Anglia (UEA), with the laboratory of R. Keeling at Scripps Institution of Oceanography (SIO) serving as the point of origin for the round-robin programme and the hub for the sausage-flask programme.

At the time of the 16th WMO/IAEA meeting (GGMT-2011) the two sets of round-robin cylinders were on their fifth global circuit and four sets of sausage flasks had been distributed. The repeated round-robin cylinder analyses at SIO showed the change in the cylinders was zero to within ± 3 per meg, the estimated precision of a trend measurement in the SIO laboratory. All results are shown in detail on the web site.

In addition to preparing cylinders for the GOLLUM programme, the Keeling laboratory at SIO has been preparing high-pressure cylinders for a number of laboratories. These cylinders have provided another means to assess laboratory scale differences and may assist in developing a common scale.

5.3 Recommendations for O₂/N₂ calibration and comparison activities

- a) Continue both, the round-robin cylinder and sausage flask components of the GOLLUM programme for the indefinite future.
- b) Expand the round-robin cylinder programme to include:

- An additional suite of circulating cylinders equipped with “dip-tubes” to minimize influence of thermal fractionation.
 - An additional suite of circulating cylinders that incorporates those field stations making in- situ measurements of atmospheric O₂ and which are not presently included in any O₂ comparison programme.
- c) Sustain the web page for logistical support and for rapid dissemination of results of the GOLLUM programme. Expand the web page by adding results of the sausage flask programme.
 - d) Encourage the timely delivery of comparison results by all participants.
 - e) Encourage SIO to continue to provide reference gases to laboratories on request at reasonable cost.
 - f) Encourage additional comparison efforts, such as overlapping flask sampling from different programmes, to compare O₂/N₂ scales and methods between programmes.
 - g) Encourage the standardisation of existing O₂/N₂ techniques, and particularly to identify and correct weaknesses in laboratories’ current techniques in sample collection, sample analysis, and in defining and propagating calibration scales.
 - h) Encourage laboratories to carry out further research into known issues in O₂ measurement such as developing intake and ‘tee’ designs that do not fractionate O₂ relative to N₂, and to investigate the influence of dip-tubes installed in high pressure cylinders
 - i) It is recommended that an effort be undertaken to produce gravimetric standards for O₂/N₂ to solidify the long-term calibration of O₂/N₂ measurements.
 - j) Encourage efforts by the relevant laboratories to assess the influence on their O₂/N₂ measurements (using different analytical techniques) of variations in CO, H₂, CH₄, N₂O, H₂O, and any other species that are commonly present in air samples with the potential to interfere at the per meg level.
 - k) Produce a list of ‘best practices’ for flask sample collection for subsequent O₂ analysis.

6. SPECIFIC REQUIREMENTS FOR CH₄ CALIBRATION

6.1 Background

NOAA/ESRL serves as the WMO/GAW Central Calibration Laboratory (CCL) for methane. The current (September 2013) version of the WMO mole fraction scale for methane is WMO CH₄ X2004. The calibration scale consists of 16 gravimetrically prepared primary standards which cover the nominal range of 300 to 2600 ppb, so it is suitable to calibrate standards for measurements of air extracted from ice cores and contemporary measurements from GAW sites. This scale results in CH₄ mole fractions that are a factor of 1.0124 greater than the previous scale (now designated CMDL83) in use at NOAA/ESRL (*Dlugokencky et al.*, 2005). The range of secondary transfer standards is nominally 400 to 4100 ppb.

6.2 Recommendations for CH₄ calibration and comparison activities

- a) The CCL will transfer the CH₄ scale to calibrated CH₄-in-air standards with an uncertainty of <2 ppb (95% confidence level, coverage factor k=2).
- b) All laboratories that participate in the GAW Programme must calibrate measurements relative to the WMO CH₄-in-air mole fraction scale and report them to the WMO/GAW World Data Centre for Greenhouse Gases in Japan.
- c) Each GAW measurement laboratory or network calibration centre of GAW partners must actively maintain its link to the WMO Scale by having its highest level standards for CH₄ re-calibrated by the CCL every six years.

7. SPECIFIC REQUIREMENTS FOR N₂O CALIBRATION

7.1 Background

Measurements of nitrous oxide made by GAW partners are used to better understand the sources and sinks of this greenhouse gas. While measurement compatibility is improving, systematic differences among N₂O mole fractions reported by different laboratories are still large compared to atmospheric gradients. The mean interhemispheric difference in N₂O mole fraction is around 1 ppb and the pole-to-pole difference is 2 ppb. These differences are 0.3-0.6% of the recent global mean mole fraction of N₂O in the troposphere. This necessitates not only high measurement precision, but also high consistency among assigned values for standards. Compatibility of measurements from different laboratories of 0.1 ppb is needed.

NOAA/ESRL serves as the CCL for nitrous oxide. The current (September 2013) version of the WMO mole fraction scale for nitrous oxide is WMO N₂O X2006A. The scale consists of 13 gravimetrically-prepared N₂O-in-air Primary Standards covering the range of 260 – 370 ppb (*Hall et al.*, 2007). The reproducibility of NOAA N₂O calibrations is estimated to be 0.18 ppb at the 95% confidence level.

7.2 Recommendations for N₂O calibration and comparison activities

- a) Each GAW measurement laboratory or network calibration centre of GAW partners must actively maintain its link to the WMO Scale by having a subset of its highest level standards for N₂O re-calibrated by the CCL every four years.
- b) The CCL and the WCC (Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research) should work together to establish more frequent comparisons among GAW stations and other key laboratories that measure N₂O. Given the difficulties involved in N₂O measurement, the frequency of current round-robin activities is insufficient for quality control purposes.

- c) The use of a travelling N₂O instrument during e.g. audits by the WCC-N₂O is encouraged. Parallel measurements should be made using an independent sampling system whenever feasible.

8. SPECIFIC REQUIREMENTS FOR SF₆ CALIBRATION

8.1 Background

Sulphur hexafluoride (SF₆) is a long-lived trace gas with strong infrared absorbance. SF₆ is 23900 times more effective as a climate forcing agent than CO₂ on a per-mass basis over a 100-year time scale. The tropospheric mole fraction of SF₆ has increased steadily, with a growth rate of 0.2-0.3 ppt yr⁻¹. The steady growth rate and long lifetime (≈3200 years) make it a useful tracer of atmospheric transport, including stratospheric “age-of-air determination”.

SF₆ is typically measured using gas chromatography with electron capture detection (GC-ECD), similar to N₂O. NOAA/ESRL serves as the WMO/GAW Central Calibration Laboratory (CCL) for atmospheric SF₆. The current (September 2013) version of the WMO mole fraction scale for sulphur hexafluoride is WMO SF₆ X2006. The scale is defined by 16 primary standards over the range 1-10 ppt. Because SF₆ is growing rapidly in the atmosphere, this range will soon be insufficient. An extension of the scale, including investigations at the CCL of the non-linear response of the ECD, is needed.

The Korean Meteorological Administration (KMA), assisted by Korea Research Institute of Standards and Science (KRISS), serves as a World Calibration Centre for SF₆.

8.2 Recommendations for SF₆ calibration and comparison activities

- a) Investigations are encouraged to explore advanced techniques to improve measurement precision.
- b) The CCL should prepare primary standards to extend the range of the scale to 20 ppt.

9. SPECIFIC REQUIREMENTS FOR CO CALIBRATION

9.1 Background

CO is an important component in tropospheric chemistry due to its high reactivity with OH. It is the major chemically active trace gas resulting from biomass burning and fossil fuel combustion, and a precursor gas of tropospheric ozone. Atmospheric measurements are based on collected air samples or in-situ analysis, as well as systematic measurements from satellites, aircraft and surface-based FTIRs. Spectroscopic retrieval of CO principally provides column

abundances; wide geographical coverage of CO with some limited vertical resolution is becoming available from ground-based remote sensing as well as several satellite-based sensors (MOPITT-TERRA, TES-AURA, AIRS-AQUA, GOSAT). The TCCON network of ground-based remote-sensing instruments provides total column information. Differences among reference scales and drift of standards have been a serious problem for these in-situ CO measurements in the past. The present recommendations will, however, pertain to the calibration of in-situ observation only; the validation of remote sensing data is a separate issue not addressed here.

9.2 Current CO calibration and comparison activities

NOAA ESRL is the WMO/GAW CCL for carbon monoxide. The CCL has produced three CO scales during the past 24 years using a similar gravimetric method. The current scale (as of September 2013) is WMO CO X2004². It is traceable back to two primary standards ranging of 330 and 400 ppb prepared gravimetrically in 1999/2000. Two sets of secondary standards, one contained in 29 L aluminium cylinders (350 and 360 ppb), the other one in 43 L cylinders (eight standards from 57-300 ppb) were assigned CO mole fractions using these primaries until 2006 with the Vacuum-UV Resonance Fluorescence technique (VURF). The 29 L secondary standards were used up to 2008 as reference for calibrations performed with the VURF instruments. In later years, tertiary standards in the same type of 29 L cylinders tied to this secondary set were used as reference for the VURF instruments. The set of secondaries in 43 L aluminium cylinders was used to assign CO mole fractions to another set of 10 tertiary standards in 43 L cylinders that forms the reference for measurements done with an Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument since 2011.

The CCL produced two earlier scales (WMO/NOAA CO 1988 and WMO CO X2000) of which only WMO CO X2000 is sometimes still used for comparison purposes. WMO CO X2000 is based upon a larger set of the primary standards made in 1999/2000 using the GC-HgO reduction technique.

Primary standards gravimetrically prepared in 2006 and 2011 ranging from 50-500 ppb and 20 to 1000 ppb, respectively, were compared to the WMO CO X2004 scale. The 1999/2000 primary reference gases containing less than 200 ppb CO are low compared to more recent measurements and have been re-evaluated. In addition, drifts of reference standards that had been in use for calibration have been observed. This necessitates re-assignment of CO mole fractions to all previously calibrated cylinders. As of April 2014, the issue has been resolved through a revision of the reference gases. However, standards with mole fractions above 200 ppb calibrated between 2000 and 2004 and standards with CO > 350 ppb measured during 2008-2011 still need updating. Most standards have been updated to the new scale WMO CO X2014, and

² In April 2014 a transition to new CO scale has started

results are available at http://www.esrl.noaa.gov/gmd/ccl/co_scale.html and at <http://www.esrl.noaa.gov/gmd/ccl/refgas.html>

The CCL has organized round robin comparisons with several GAW laboratories. These have exposed a number of measurement problems including the application of the analytical technique, the calibration approach, drift of reference gases and uncertainties in the reference scale. EMPA, as WCC for CO, has developed an audit system for CO measurements at GAW stations. This has helped the international in-situ CO measurement community enormously, but also exposed some drift and inconsistency in the NOAA/ESRL calibration scale, as well as in the gravimetric technique.

9.3 Recommendations for CO calibration at the WMO/GAW CCL and at GAW stations

- a) The CCL shall aim to propagate the CO scale to ± 1 ppb or 0.5% (whichever is greater, expanded uncertainty, $k=2$). All GAW participants should use standards traceable to the WMO CO X2004 or a revised version of the WMO scale.
- b) The CCL should maintain one set of standards of known stability that defines the WMO scale (see section 1.2a of these recommendations).
- c) The CCL should maintain a strict hierarchy of standards. All intermediate levels of reference standards (secondaries, tertiaries) that are part of this hierarchical calibration chain should be reassigned relative to the scale at appropriate intervals to assure calibration consistency over time. Multiple methods should be used to ensure the CO mole fractions in primary standards are not changing, or are tracked.
- d) The CCL is responsible for documenting the evolution of the WMO CO scale and for communicating all revisions to the stations as well as to WCC at EMPA. This documentation should involve disclosure of gravimetric results for individual primary standards as well as information on the cylinders that carry the scale including their assigned composition.
- e) The replacement of the gas chromatographic technique with HgO reduction and photometric detection at the CCL has resulted in significant improvements of the consistency of CO calibrations. It is strongly recommended that standards that have been calibrated by the CCL before the implementation of the laser-spectroscopic technique are recalibrated. Based on recent assessments of standard drifts a recalibration interval of three years for station standards is recommended.
- f) Evaluation of CO audits by the WCC should be limited to the average range covered by the seasonal variability of daily means.
- g) Within the GAW Programme, regular comparisons and audits by the WCC serve as an independent check of the measurements on-site. Regional round-robins that involve the CCL should be continued.

- h) It is recommended that the CCL pursues activities to expand the CO scale up to 1000 ppb in the near future.

10. SPECIFIC REQUIREMENTS FOR H₂ CALIBRATION

10.1 Background

Molecular hydrogen plays a significant role in global atmospheric chemistry due to its role in CH₄ – CO - OH cycling. The balance of hydrogen could change with the implementation of a new H₂ energy carrier. Therefore, it is important to establish its global budget and atmospheric trend. There is a clear need to get compatible data from independent networks and therefore the propagation of the WMO scale for the GAW network remains a task of high priority. Molecular hydrogen is recognized as an important target variable to be measured in the WMO/GAW global network and specific tasks are outlined for implementation by the global research community (WMO/GAW Report No.197, 2011).

10.2 Current H₂ calibration and comparison activities

MPI-BGC serves as the WMO/GAW Central Calibration Laboratory (CCL) for atmospheric molecular hydrogen. The current scale is WMO H₂ X2009 (formerly the MPI-2009 H₂ scale) consisting of 13 primary standards of hydrogen in air ranging from 140 to 1200 ppb (*Jordan and Steinberg, 2011*). Recently a growing H₂ mole fraction in two of the primary standards has been detected. Experimental results suggest a bias of the scale of 2-3 ppb in the atmospheric range that will induce a revision of the WMO scale in 2014.

10.3 Recommendations for H₂ calibration and comparison activities

- a) It is recommended that the CCL bi-annually produces additional standards that provide a check for the stability of the WMO scale.
- b) Long time series of atmospheric hydrogen have been generated by the NOAA and CSIRO/AGAGE monitoring networks. To enable a collaborative global network for hydrogen measurements the measurement groups are encouraged to establish traceability to the new WMO scale.
- c) In addition, temporal changes of inter-laboratory biases that have not always been related to scale changes, underline the necessity to continue comparison of hydrogen data. These exercises will be a valuable tool to monitor the compatibility of the measurements and shall be continued at regular intervals.
- d) A major problem encountered by most laboratories that measure hydrogen is the stability of their standards. Aluminium cylinders commonly used for other trace gas standard mixtures often show significant growth of hydrogen. Therefore, it is recommended that every laboratory develops a strategy to account for this. To minimize the risk of drift the highest

level standard gas containers of any laboratory should preferably be made of stainless steel. A recalibration by the CCL after two years is recommended.

- e) Appropriate characterization of the detector response in the ambient range is required given the strong non-linear response of the commonly used HgO reduction detectors. Analysis techniques with characteristics (i.e. precision and non-linearity) superior to the common HgO reduction detectors have been described recently and should be considered for new installations.
- f) Due to the strong non-linearity of the HgO reduction detectors it is particularly important for H₂ measurements that the mole fraction of the working standard gas is close to the mean annual H₂ level observed at the site. In contrast, the target standard gases used for quality control purpose are recommended to have H₂ mole fractions that are at the high end of the observed values to provide good diagnostic information.

11. RECOMMENDATIONS FOR GROUND BASED REMOTE SENSING TECHNIQUES

The Total Carbon Column Observing Network (TCCON) was accepted into the GAW network following the 15th GGMT meeting in 2009. TCCON is a ground-based network of Fourier Transform Spectrometers which measure high resolution direct beam solar absorption spectra in the near infrared. Total column amounts of trace gases are inferred from the measured spectra using standardized retrieval procedures. Column average dry air mole fractions are determined by dividing the trace gas total column by the total dry air column derived from the simultaneous retrieval of the total column of O₂. The measured water vapour column is also obtained from the solar spectrum.

TCCON measurements are subject to strict controls on instrumentation and data analysis set out in the TCCON data policy (<https://tcccon-wiki.caltech.edu/>). Adherence to these controls is a necessary condition to contribute to the TCCON database.

TCCON measurements must be linked to WMO mole fraction scales. TCCON total column amounts are validated by simultaneous determination of the partial vertical column amount of relevant trace gases by in-situ measurements during aircraft overflights or by other techniques such as near-total column direct air samples (AirCore) obtained near the location of a TCCON instrument, and measured upon landing by WMO-scale calibrated instruments.

Recommendation: Ground based remote sensing measurements of CO₂, CH₄, N₂O and CO must follow the formal TCCON data protocols and be accepted in the TCCON network to be acceptable to GAW.

12. RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING

12.1 Data management

All GAW measurement laboratories regardless of programme size are required to manage all new and existing atmospheric trace gas and supporting metadata using a database management strategy (DBMS) that meets or exceeds the following criteria:

- a) Demonstrate that mole fractions and isotope ratios can be unambiguously and automatically reproduced, also retrospectively, from raw data at any time in the future.
- b) Demonstrate that revisions to a laboratory's internal calibration scale or to the WMO scale can be efficiently and unambiguously propagated throughout the database.
- c) Support routine and automatic database updates of all measurements and metadata.
- d) Ensure that all data reside locally, in a single location, and are centrally accessible to internal users.
- e) Ensure fast and efficient retrieval of all data.
- f) Maximise users' ability to assess data quality.
- g) Facilitate data and metadata exploration.
- h) Minimise the risk of data loss or corruption due to theft, misuse, or hardware/software failure.
- i) Maximise security of primary data (e.g., data from which all processed data is derived).
- j) Support routine and automatic backup of all data.
- k) Support complete data recovery in the event of catastrophic data loss.

GAW measurement laboratories are encouraged to use WMO/GAW Report No. 150 as a guideline in developing and implementing an atmospheric data management strategy.

Laboratories with demonstrated expertise in data management are encouraged to share their expertise. At the GGMT-2011 meeting in New Zealand, participants expressed interest in a workshop focused on data management and tools and strategies for converting data to a new or updated internal or WMO scale. A post-meeting survey was sent to all participants to assess the level of interest. Fewer than 10 individuals expressed interest in attending such a workshop. About the same number of individuals offered to contribute to the workshop. It was determined the most effective and efficient strategy for sharing knowledge would be to construct a list of those willing to share their expertise with others. In this way, labs or individuals looking to obtain certain skills and capabilities could work directly with those labs that might best meet their needs. Table 2 list those in the WMO/GAW community who have offered to share their expertise. The area of expertise is general; interested researchers are encouraged to e-mail the contact person directly for more detail.

12.2 Data archiving

- a) Laboratories participating in the WMO/GAW Programme must submit their data to the World Data Centre for Greenhouse Gases (WDCGG) (according to WMO/GAW Strategic Plan, WMO/GAW Report No. 172, 2007). A co-ordinated annual submission of data before the end of August of the following year, with clearly identified version number of submitted data and calibration scale, as well as supporting details is strongly recommended. The data obtained in a regional or other national or cooperative network should be submitted through the network centre responsible for data evaluation and archiving. The same recommendation holds to other public-access data archive centres.
- b) The revised WDCGG Data Submission and Dissemination Guide (WMO/GAW Report No. 188, 2009) includes data categories, data submission formats, data submission procedures, and ways of distributing data and products. Adherence to this guide is requested.
- c) The WDCGG distributes data in versions consistent with the annual DVD Report and keeps old versions. To enhance the value of archived data, the WDCGG is encouraged to develop a system of flags for archived data, based on metadata for the measurements, instrument type, precision of measurements, results of comparison activities, and types of comparison activities engaged in collecting data. The SAG GHG should consider working with WDCGG in developing the flags and encouraging contributing groups to provide the additional information needed.
- d) The WDCGG will establish a data user group with the help of Sander Houweling to provide guidance on ways to improve the useability of data distributed by the WDCGG.

12.3 Recommendation

Community agreements are needed on how to archive and report in a more standardized way the various components of measurement uncertainty, metadata, and quality control information such as data flags, keeping in mind the needs of both data providers and users.

12.4 Co-operative data products

All laboratories making high-quality greenhouse gases measurements are strongly encouraged to participate in cooperative data projects. Value-added products such as GLOBALVIEW enhance the value of any one individual measurement record by including it in a much larger cooperative network of observations.

12.5 Data distribution

This community recognizes the need to develop new strategies to improve communication between data providers and data users. The WDCGG and its contributors will work together to explore ways in which this can be achieved including user registration prior to data access and persistent digital identifiers (e.g., Digital Object Identifier (DOI)). We strongly encourage both data

contributors and data users to commit themselves to providing feedback during this development to ensure the needs of all are considered.

Table 2 - WMO GAW members who have offered to share expertise

Name	Contact Email	Lab	Location	Area of Expertise
WDCGG	hkoide@met.kishou.go.jp	JMA	Japan	Data management in WDCGG
Lynn Hazan	lynn.hazan@lsce.ipsl.fr	LSCE	France	Data management
Paul Krummel	paul.krummel@csiro.au	CSIRO	Australia	Quality control, non-CO2 scale conversions, inter-comparisons
NOAA data team	kenneth.masarie@noaa.gov	NOAA	United States	Data management, quality control, scale conversion
Ludwig Ries	ludwig.ries@uba.de	UBA	Germany	Data acquisition, management and quality control. Software solutions available for data acquisition, instrument control, calibration processing, interactive data preparation and validation.
Martin Steinbacher	martin.steinbacher@empa.ch	EMPA	Switzerland	Data acquisition and processing with commercially available and custom-built software
Doug Worthy	Doug.worthy@ec.gc.ca	EC	Canada	Near real-time data processing via GC, NDIR, and CRDS technologies

13. RECOMMENDATIONS FOR THE COOPERATIVE WMO/GAW NETWORK

The WMO Commission for Atmospheric Sciences (CAS) held its 16th Session on 20-26 November 2013 in Antalya, Turkey. CAS considered ten-year future priorities and challenges for research. Among six priorities, CAS included development of an Integrated Greenhouse Gas Information System.

In particular the Commission noted:

“9.3.3 The Commission noted that currently emission reductions are monitored through self-reported inventories, but that it has become increasingly clear that these alone are not enough, as inventories require independent verification. To be useful for verification on policy-relevant scales, independent analyses are best derived with atmospheric inversions (where atmospheric

observations are used to constrain numerical models). Because there are large reservoirs of carbon in the terrestrial and oceanic environment that exchange with the atmosphere, the verification process must be able to separate human from natural influences if it is to inform policy or engineering decisions. Doing this requires an Integrated Greenhouse Gas Information System (IGIS) that is global in scale, but also addresses sub-continental, policy-relevant regions.

9.3.4 The Commission appreciated on-going developments to establish IGIS, including such programmes as the North American Carbon Program (NACP) in the USA, Canada, and Mexico, the Integrated Carbon Observation System (ICOS) in Europe, expansions of observation suites in developing countries such as China and Brazil, cross-cutting initiatives involving commercial aircraft, and even private organizations that can enhance observing system infrastructure and information delivery. The Commission appreciated on-going efforts from TCCON (Total Carbon Column Observing Network) to consolidate a global network that can play a key role in GHG satellite and model validation as well as in model data assimilation. By integrating these and other observations, in particular emerging observations from satellites, through validation, quality control, and analysis, one can deliver robust, sub-continental scale information that is globally coherent.

9.3.5 *The Commission noted that implementations of IGIS requires higher density of the greenhouse gas observational network and increased variety of observations (including isotopic measurements and measurements of co-emitted species), improved complexity and performance of transport models on global, regional and local scales, and better coordination of efforts with developments in other Earth system components (e.g. biosphere and oceans).* The Commission requested Members to undertake the necessary steps in the development of these high-quality observations for them to be compatible with the established GAW network and to improve the modelling tools to implement IGIS.

9.3.6 The Commission agreed that WMO Programmes have a confirmed capacity to develop the atmospheric part of IGIS but it also stressed that full implementation of IGIS would require the established *collaboration with other international organizations and coordination bodies, e.g., working together with GEO-Carbon, GCOS and CEOS.* “

We recommend the following observational strategies:

- 1) Sustain, improve and increase the number of the stations with continuous in-situ measurements in the boundary layer and in the troposphere by aircraft. The WMO/GAW community should make an effort to establish and sustain observations in under-sampled continents/areas. In addition efforts should be made to expand aircraft flights over vegetated areas that are currently not sampled or under-sampled, with priority to tropical South America, Africa, and South East Asia. Station twinning, partnership and collaboration programmes (like CATCOS by MeteoSwiss) should be further encouraged.

- 2) Develop and implement long-term total column measurements of Greenhouse Gases at a number of sites within the WMO/GAW Programme and its partners, the Total Carbon Column Observing Network (TCCON) and the Network for the Detection of Atmospheric Composition Change (NDACC), recognizing the need for satellite validation and modelling. Total column measurements should be compared to vertical profiles of calibrated in-situ and AirCore measurements on a regular basis.
- 3) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes ($^{13}\text{CO}_2$, O_2/N_2 , ^{18}OCO , stable isotopes in CH_4 and CO), especially to separate fossil fuel emissions ($^{14}\text{CO}_2$, CO ...) from natural sources/sinks. Further collaboration should be established with the biosphere and the ocean communities to improve source/sink estimates. Ship based observations of both atmospheric and ocean dissolved GHG should be encouraged. Along these lines it is essential that detailed spatially and temporally resolved emissions inventories of fossil fuel CO_2 , CH_4 , and CO are being developed and pursued.
- 4) To achieve the above goals, thorough quality control procedures are necessary to ensure that WMO/GAW data meets the recommended compatibility goals. Data which has not been quality controlled is of very limited value for the scientific community as well as for society.
- 5) WMO encourages and facilitates the development of improved atmospheric tracer transport models. Atmospheric observations should be used to quantify regional sources and sinks by means of improved inverse modelling. Not only model parameterization improvements are important, but also the use of several independently developed models and their frequent comparison, contributes significantly to a more realistic assessment of the uncertainty of the inferred fluxes. Finally, it is important to develop and maintain community models which are numerically efficient, which can run from standard computer platforms with a modest amount of training, and which are made available to the entire scientific community.

14. ORGANIZATION OF GGMT-2015

There was general agreement among all that it would be desirable to convene the next meeting, the 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, at Scripps Institution of Oceanography to celebrate the 40th anniversary of the first meeting in 1975. Dr Ralph Keeling has agreed to organize and host this meeting.

References

- Assonov S.S., C.A.M. Brenninkmeijer (2003a): On the O-17 Correction for CO₂ Mass Spectrometric Isotopic Analysis. *Rapid Comm. Mass Spectrom.* 17, 1007-1016.
- Assonov S.S., C.A.M. Brenninkmeijer (2003b): A Redetermination of Absolute Values for R-17(VPDB-CO₂) and R-17(VSMOW). *Rapid Comm. Mass Spectrom.* 17, 1017-1029.
- De Bièvre, P., (2008): Essential for metrology in chemistry, but not yet achieved: truly internationally understood concepts and associated terms, *Metrologia* 45, 335-341.
- Brand, W.A., S.S. Assonov, and T.B. Coplen (2010):, "Correction for the O-17 interference in delta(C-13) measurements when analyzing CO₂ with stable isotope mass spectrometry (IUPAC Technical Report)," *Pure and Applied Chem*, vol. 82, pp. 1719-1733.
- Brand, W.A., L. Huang, H. Mukai, A. Chivulescu, J. M. Richter, and M. Rothe (2009): "How well do we know VPDB? Variability of delta C-13 and delta O-18 in CO₂ generated from NBS19-calcite," *Rapid Commun. Mass Spectrom.* 23, pp. 915-926, 2009.
- Coplen, T.B., W. A. Brand, M. Gehre, M. Groening, H. A. J. Meijer, B. Toman, and R. M. Verkouteren (2006): High Accuracy Measurements of Carbon Isotopic Reference Materials and Two-Point Anchoring of the VPDB Scale to Improve d¹³C Data. *Anal. Chem.* 78 (7), 2439 -2441.
- Coplen, T. B. (2011): Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Commun. Mass Spectrom.* **25**, 2538-2560.
- Dlugokencky, E.J., R.C. Myers, P.M. Lang, K.A. Masarie, A.M. Croftwell, K.W. Thoning, B.D. Hall, J.W. Elkins and L.P. Steele (2005): Conversion of NOAA CMDL Atmospheric Dry Air CH₄ Mole Fractions to a Gravimetrically Prepared Standard Scale. *J. Geophys. Res.* 110, D18306, doi:10.1029/2005JD006035.
- Ghosh, P., M. Patecki, M. Rothe and W.A. Brand (2005): Calcite-CO₂ Mixed into CO₂-Free Air: A New CO₂-in-Air Stable Isotope Reference Material for the VPDB Scale. *Rapid Comm. Mass Spectrom.* 19, 1097-1119.
- Graven, H. D., X. Xu, T. P. Guilderson, R. F. Keeling, S. E. Trumbore and S. C. Tyler (2013): "Comparison of independent D14CO₂ records at Point Barrow, Alaska." *Radiocarbon* 55(2-3), 1541-1545.
- GUM (1995): ISO Publications, Guide to the Expression of Uncertainty in Measurement, International Organization for Standardization (Geneva, Switzerland), ISBN 92-67-10188-9, 110 p. (The abbreviation of this title is GUM). Equivalent Guide: American National Standard for Calibration - U.S. Guide to the Expression of Uncertainty in Measurement, ANSI/INCSSL Z540-2-1997, NCSL International, Boulder, USA, 101 p. (1997).)
- Hall, B. D., G. S. Dutton, and J. W. Elkins (2007): The NOAA Nitrous Oxide standard Scale for Atmospheric Observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954.
- JQSRT (2009): *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110, no.9-10, June/July 2009, Special issue on HITRAN.
- Jordan, A., and B. Steinberg (2011): Calibration of atmospheric hydrogen measurements, *Atmos. Meas. Techniques*, 4, 509–521, doi:10.5194/amt-4-509-2011

- Karion, A., C. Sweeney, P. Tans, T. Newberger (2010): AirCore: An innovative atmospheric sampling system, *J. Atmos. Oceanic Technology* 27, 1839-1853. doi: 10.1175/2010JTECHA1448.1
- Keeling, R. F., A. C. Manning, E. M. McEvoy, and S. R. Shertz (1998): Methods for measuring changes in atmospheric O₂ concentration and their applications in southern hemisphere air, *J. Geophys. Res. Atmospheres*, 103 (D3), 3381-3397, doi:10.1029/97JD02537.
- Kozlova, E. A., A. C. Manning, Y. Kisilyakhov, T. Seifert, and M. Heimann (2008): Seasonal, synoptic, and diurnal scale variability of biogeochemical trace gases and O₂ from a 300 m tall tower in central Siberia, *Global Biogeochem. Cycles*, 22 (4), doi:10.1029/2008GB003209.
- Lehman, S. J., J. B. Miller, C. Wolak, J. R. Southon, P. P. Tans, S. A. Montzka, C. Sweeney, A. E. Andrews, B. W. LaFranchi, T. P. Guilderson and J. C. Turnbull (2013). "Allocation of terrestrial carbon sources using ¹⁴CO₂: Methods, measurement, and modelling." *Radiocarbon* 55(2-3), 1484-1495.
- Lowe, D. C., V. Levchenko, R. C. Moss, W. Allan, G. Brailsford and A. M. Smith (2002): "Assessment of "storage correction" required for in situ ¹⁴CO production in air sample cylinders." *Geophysical Research Letters* 29(7): 1139.
- Masarie, K.A., R.L. Langenfelds, C.E. Allison, T.J. Conway, E.J. Dlugokencky, R.J. Francey, P.C. Novelli, L.P. Steele, P.P. Tans, B. Vaughn and J.W.C. White (2001): NOAA/CSIRO Flask Air Intercomparison Experiment: A Strategy for Directly Assessing Consistency among Atmospheric Measurements Made by Independent Laboratories. *J. Geophys. Res.* 106, 20445-20464.
- Meijer, H. A. J. Neubert, R. E. M., and Visser, G. H. (2000): Cross contamination in dual inlet isotope ratio mass spectrometers. *Internat. J. Mass Spectrom.*, 198 (1-2), 45-61.
- Miller, J. B., S. J. Lehman, C. Wolak, J. C. Turnbull, G. Dunn, H. D. Graven, R. F. Keeling, H. A. J. Meijer, A. T. Aerts-Bijma, S. W. Palstra, A. M. Smith, C. E. Allison, J. R. Southon, X. Xu, T. Nakazawa, S. Aoki, T. Nakamura, T. P. Guilderson, B. W. LaFranchi, H. Mukai, Y. Terao, M. Uchida and M. Kondo (2013): "Initial results of an inter-comparison of AMS-based atmospheric ¹⁴CO₂ measurements." *Radiocarbon* 55(2-3), 1475-1483.
- Rella, C. W., et al. (2013): High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.*, 6(3), 837-860.
- Scott, E. M., G. T. Cook and P. Naysmith (2010): "A report of phase 2 of the fifth international radiocarbon intercomparison (VIRI)." *Radiocarbon* 52(2-3): 846-858.
- Stuiver, M. and Polach, H. (1977): Discussion: Reporting of ¹⁴C data, *Radiocarbon* 19, 355-363.
- Turnbull, J. C., H. D. Graven, J. B. Miller and S. J. Lehman (2013): "Atmospheric radiocarbon workshop report." *Radiocarbon* 55(2-3), 1470-1474.
- Verkouteren R. M., C.E. Allison, S.A. Studley and K.J. Leckrone (2003a): Isotopic metrology of carbon dioxide. I. Interlaboratory comparison and empirical modelling of inlet equilibration time, inlet pressure, and ion source conductance. *Rapid Communications in Mass Spectrometry* 17(8), 771-776.

- Verkouteren R. M., S. Assonov, D.B. Klinedinst and W.A. Brand (2003b): Isotopic metrology of carbon dioxide. II. Effects of ion source materials, conductance, emission, and accelerating voltage on dual-inlet cross contamination. *Rapid Communications in Mass Spectrometry* **17**(8), 777-782.
- VIM (2008): International vocabulary of metrology. Basic and general concepts and associated terms, 3rd edition, Joint Committee for Guides in Metrology (JCGM),
http://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf.
- Vogel, F., J. Jeschka, B. Kromer, A. Steinhof, S. Hammer and I. Levin (2011): A robust setup for long-term monitoring of fossil fuel CO₂ and other trace gases, and its test against established conventional monitoring in Heidelberg. Expert Group Recommendations from the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracer Measurement Techniques, Jena.
- Wendeberg M., J.M. Richter, M. Rothe and W.A. Brand (2011): delta O-18 anchoring to VPDB: calcite digestion with O-18-adjusted ortho-phosphoric acid. *Rapid Communications in Mass Spectrometry* **25**(7), 851-860.
- Wendeberg M., J.M. Richter, M. Rothe and W.A. Brand (2013): Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO₂ in air. *Atmospheric Measurement Techniques* **6**(3), 817-822.
- WMO, All WMO references below are available from
<http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>
- WMO (2001): Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), A Contribution to the Implementation of the Long-Term Plan, GAW Report No. 142, WMO TD No.1077.
- WMO (2003): Updated Guidelines for Atmospheric Trace Gas Data Management, GAW Report No. 150, WMO TD No. 1149.
- WMO (2005): Global Atmosphere Watch, 12th WMO/IAEA Meeting of Expert on Carbon Dioxide Concentration and Related Tracers Measurements Techniques (Toronto, Canada, 15-18 September 2003) GAW Report No.161, WMO TD No. 1275.
- WMO (2007): Global Atmosphere Watch (GAW) Strategic Plan: 2008-2015, GAW Rep. No. 172, WMO TD NO.1384.
- WMO (2009): Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance, GAW Report No. 185. WMO TD No. 1478.
- WMO (2009): Revision of the World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide, GAW Report No. 188, WMO TD No.1507.
- WMO (2010): Guidelines for the Measurement of Atmospheric Carbon Monoxide, GAW Report No. 192. WMO TD No. 1551.
- WMO (2011): Addendum for the Period 2012 – 2015 to the WMO Global Atmosphere Watch (GAW). Strategic Plan 2008 – 2015, GAW Report No. 197.

ABBREVIATIONS AND ACRONYMS USED IN THIS REPORT

AGAGE	Advanced Global Atmospheric Gases Experiment
AIRS	Atmospheric Infrared Sounder (AIRS) aboard AQUA satellite
AQUA	Earth Science satellite mission of the National Aeronautics and Space Administrations of USA
AURA	Satellite operated by the National Aeronautics and Space Administrations of USA for atmospheric chemistry observations
BIPM	International Bureau of Weights and Measures
CAMS	Chinese Academy of Meteorological Sciences
CATCOS	Capacity Building and Twinning for Climate Observing Systems
CCL	Central Calibration Laboratory
CCQM	Consultative Committee for Amount of Substance – Metrology in Chemistry
CIPM	International Committee for Weights and Measures
CMA	China Meteorological Administration
CMDL	Climate Monitoring and Diagnostics Laboratory, Boulder, CO, USA (now NOAA ESRL GMD)
CRDS	Cavity Ring Down Spectroscopy
CSIRO	Commonwealth Scientific & Industrial Research Organisation
DBMS	Data Base Management Strategy
ECD	Electron Capture Detector
EMPA	Swiss Federal Laboratories for Materials Science and Technology
ESRL	Earth System Research Laboratory (NOAA, Boulder, CO, USA)
GAW	Global Atmosphere Watch (WMO Programme)
GAWTEC	GAW Training and Education Centre
GG or GHG	Greenhouse Gases
GGMT	WMO/IAEA Meetings of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques
GLOBALVIEW	Co-operative Atmospheric Data Integration Project
GMD	Global Monitoring Division (NOAA ESRL, Boulder, CO, USA)
GOLLUM	Global Oxygen Laboratories Link Ultra-precise Measurements
GOSAT	Greenhouse gases Observing SATellite (GOSAT), a joint effort by the Japan Aerospace Exploration Agency (JAXA), the National Institute for Environmental Studies (NIES) and the Ministry of the Environment (MOE)

GUM	Guide to the Expression of Uncertainty in Measurement
IAEA	International Atomic Energy Agency
ICP	Inter-laboratory Comparison Program
ICOS	Integrated Carbon Observation System (EU-funded project)
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JCGM	Joint Committee for Guides in Metrology
JRAS	Jena Reference Air Set
KMA	Korean Meteorological Administration
KRISS	Korea Research Institute of Standards and Science
MOPITT-TERRA	Measurements Of Pollution In The Troposphere
MPI-BGC	Max-Planck Institut für Biogeochemie, Jena, Germany
NACP	North American Carbon Programme
NIES	National Institute for Environmental Studies, Tsukuba, Japan
NIST	National Institute of Standards and Technology
NIWA	National Institute of Water and Atmospheric Research (NZ) NOAA National Oceanic and Atmospheric Administration (USA)
NOAA	National Oceanic and Atmospheric Administration (USA)
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
SAG	Scientific Advisory Group
SIO	Scripps Institution of Oceanography
SRM	Standard Reference Material
TCCON	Total Carbon Column Observing Network
TES-AURA	Tropospheric Emission Spectrometer aboard AURA satellite
UEA	University of East Anglia
UNFCCC	United Nations Framework Convention on Climate Change
VIM	International vocabulary of metrology
VPDB	Vienna Pee Dee Belemnite (Isotope Standard)
VSMOW	Vienna Standard Mean Ocean Water (Isotope Standard)
VURF	Vacuum-UV Resonance Fluorescence
WCC	World Calibration Centre
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization

**17th WMO/IAEA Meeting on
Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013)**

(Beijing, China, 10 - 13 June 2013)

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**17th WMO/IAEA Meeting on
Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013)**

(Beijing, China, 10 - 13 June 2013)

MEETING AGENDA

Sunday, 9 June 2013

Time	Content	Topics & presenters
09:00-17:00	SAG meeting	Meeting Room #603, CAMS Guide from CMA entrance at 08:30 Meeting facilities & Lunch served
18:00-20:00	GGMT-2013 Ice breaker & registration	Guide from CMA entrance at 17:30 Posters can be placed from 17:30

Monday, 10 June 2013

Time	Content (oral+QA)	Topics & presenters
08:00-9:00	Registration	Guide from CMA entrance
09:00-09:40	Opening session	Chair: Panmao ZHAI, CAMS vice president
09:00-09:10	10 min	Heng ZHOU, Director-General, CMA Department of International Cooperation: Welcome remarks
09:10-09:20	10 min	Lingxi Zhou: GGMT-2013 overview & related information
09:20-09:40	Group photo & break	
09:40-10:30	Overview	
09:40-10:00	15+5 mins, WMO/IAEA	Oksana Tarasova: Greenhouse gas observations and analysis in the WMO/GAW Programme
10:00-10:30	25+5 mins, Keynote	Jim Butler: Are the world's measurement systems ready for "prime-time"?
10:30-11:00	Coffee break	
11:00-12:20	Session 1.1	Chair: Lingxi Zhou Topic: Scales, standards and comparisons
11:00-11:20	15+5 mins	Brad Hall: Recent analysis of the WMO CO ₂ primary standards
11:20-11:40	15+5 mins	Ralph Keeling: Assessment of reference gas calibrating system for carbon dioxide in air standards at Scripps
11:40-12:00	15+5 mins	Pieter Tans: Isotopologues of carbon dioxide standards
12:00-12:20	15+5 mins	Britt Stephens: The NCAR O ₂ / CO ₂ calibration facility
12:30-13:30	Lunch	CMA Training Center Canteen, 2nd floor
13:30-15:20	Session 1.2	Chair: Ralph Keeling Topic: Scales, standards and comparisons
13:30-13:50	15+5 mins	Paul Krummel: Trace gas measurement comparison activities at the Cape Grim Baseline Station

13:50-14:10	15+5 mins	Christoph Zellweger: Added value of side-by-side comparisons with a travelling analyzer during WCC-Empa audits
14:10-14:30	15+5 mins	Markus Leuenberger: Comparison of continuous in-situ CO ₂ observations at Jungfraujoch, Switzerland using two different measurement techniques
14:30-14:50	15+5 mins	Lingxi Zhou: Update on the 5 th WMO round-robin
14:50-15:20	<i>Recommendations</i>	Discussion Leaders: Brad Hall & Britt Stephens (Chapter 1 & 2)
15:20-15:40	Coffee break	
15:40-17:50	Session 2	Chair: Luciana Gatti Topic: Integration of observations, data products and policy
15:40-16:00	15+5 mins	Sander Houweling: User perspective on WMO/GAW greenhouse data
16:00-16:20	15+5 mins	Ken Masarie: Data and product distribution: the challenge in meeting the needs of data users and providers
16:20-16:40	15+5 mins	Hiroshi Koide: Reforming WDCGG: strategy and implementation plan
16:40-17:00	15+5 mins	Lynn Hazan: ICOS Atmospheric Data Management
17:00-17:20	15+5 mins	Ludwig Ries: Standardized and automated data quality assurance at GAW Stations: concept, methods and tools
17:20-17:50	<i>Recommendations</i>	Discussion Leaders: Ken Masarie & Hiroshi Koide (Chapter 13)
18:00-19:00	Side meeting 1	Britton Stephens: O ₂ /N ₂ and APO (Chapter 5)

Tuesday, 11 June 2013

Time	Content (oral+QA)	Topics & presenters
08:30-10:20	Session 1.3	Chair: Paul Krummel Topic: Scales, standards and comparisons
08:30-08:50	15+5 mins	Ed Dlugokencky: Extension of the WMO CH ₄ standard scale beyond the background ambient range
08:50-09:10	15+5 mins	Deullae Min: SF ₆ measurement technique for preparing laboratory standards to satisfy the WMO recommended compatibility in WCC-SF ₆
09:10-09:30	15+5 mins	Sanam Vardag: First in-situ comparisons of continuous atmospheric N ₂ O measurements with the InGOS travelling instrument at Mace Head
09:30-09:50	15+5 mins	Huilin Chen: Long-term stability of calibration gases in cylinders for CO ₂ , CH ₄ , CO, N ₂ O, and SF ₆
09:50-10:20	<i>Recommendations</i>	Discussion leader: Ed Dlugokencky (Chapter 6, 7 & 8)
10:20-10:40	Coffee break	
10:40-12:30	Poster session	Poster Session 1, 2, 3 & 4
11:00-12:30	Public Lecture	Pieter Tans, Ken Masarie & Lingxi Zhou Topic: How can we make measurements that are good enough to inform public policy?
12:30-13:30	Lunch	Conference Center of CMA
13:30-15:20	Session 3.1	Chair: Oksana Tarasova Topic: CO₂ observations (measurements techniques and calibration)
13:30-13:50	15+5 mins	Andrew Manning: Progress on the preparations of CO ₂ Measurement Guidelines

13:50-14:10	15+5 mins	James Whetstone: The Los Angeles megacity carbon project: measurement challenges in urban greenhouse gas dome characterization
14:10-14:30	15+5 mins	Martin Kunz: A package for CO ₂ measurements on board unmanned aerial vehicles
14:30-14:50	15+5 mins	Shuangxi Fang: Observation of atmospheric CH ₄ /CO ₂ mixing ratios from different height by Cavity Ring Down Spectroscopy system
14:50-15:20	<i>Recommendations</i>	Discussions Leaders: Andrew Manning & Andrew Crotwell (Chapter 11 & 12)
15:20-15:40	Coffee break	
15:40-17:30	Session 3.2	Chair: Doug Worthy Topic: Non-CO₂ Observations (measurements techniques and calibration)
15:40-16:00	15+5 mins	William Sturges: Measurement of selected halogenated greenhouse gases in very small air volumes
16:00-16:20	15+5 mins	Martin Steinbacher: Long-term field intercomparison of N ₂ O observations with GC-ECD and Cavity Enhanced Absorption Spectroscopy at Jungfrauoch
16:20-16:40	15+5 mins	Luana Basso: Study of SF ₆ concentrations in Amazon basin and Brazilian coast
16:40-17:00	15+5 mins	Jingsong Li: Development of field-deployable QCL sensor for simultaneous detection of atmospheric N ₂ O and CO
17:00-17:30	<i>Recommendations</i>	Discussion Leader: Armin Jordan (Chapter 9 & 10)
18:30-20:30	GGMT-2013 Banquet	Jinfuyanbang Restaurant

Wednesday, 12 June 2013

Time	Content (oral+QA)	Topics & presenters
08:30-10:20	Session 4	Chair: James White Topic: Isotope measurement and calibration
08:30-08:50	15+5 mins	Colin Allison: Integrating a remotely deployed stable isotope Picarro CRDS with a global monitoring network
08:50-09:10	15+5 mins	Chris Rella: Advances in atmospheric d ¹³ CH ₄ analysis in the field using CRDS
09:10-09:30	15+5 mins	Weijian Zhou: A primary study on tracing fossil fuel CO ₂ in the atmosphere in Xi'an using AMS- ¹⁴ C technique
09:30-09:50	15+5 mins	Peter Sperlich: Reference material and analytical developments to measure the isotopic composition of CH ₄ in air with high precision and accuracy
09:50-10:20	<i>Recommendations</i>	Discussion Leader: Willi Brand (Chapter 3 & 4)
10:20-10:40	Coffee break	
10:40-12:30	Session 5.1	Chair: Hitoshi Mukai Topic: Developments of the GHG networks and sites update
10:40-11:00	15+5 mins	Marcel van der Schoot: Revision of the historical Cape Grim atmospheric CO ₂ record and expansion of the Australian regional WMO/GAW network
11:00-11:20	15+5 mins	Gordon Brailsford: Developments in the New Zealand observation network

11:20-11:40	15+5 mins	Ann Stavert: Southern Ocean CO ₂ network: Intercomparison results from multiple measurement platforms
11:40-12:00	15+5 mins	Lixin Liu: Background variations of atmospheric CO ₂ and carbon stable isotopes at Waliguan (WLG) and Shangdianzi (SDZ) stations in China
12:00-12:30	Golden Sponsor's	Eric Crosson: Application Innovation and Technology Development at Picarro
12:30-13:30	Lunch	Conference Center of CMA
13:30-14:30	Side meeting 2	Gloria Jacobson: Trace gas analyzer performance testing standardization
14:30-15:30	Side meeting 3	Doug Worthy: Intercomparison
14:30-15:30	Side meeting 4	Jocelyn Turnbull: radiocarbon in trace gases calibration
14:30-17:30	Lab tour (by groups)	2min by walk from meeting venue to Lab #201 & #217, CAMS
13:30-17:30	Poster session with coffee/tea/snacks	Poster Session 5, 6 & 7
18:30-20:30	Dinner	Invitation by Golden Sponsor

Thursday, 13 June 2013

Time	Content (oral+QA)	Topics & presenters
08:30-09:50	Session 5.2	Chair: Marcel Van der Schoot Topic: Developments of the GHG networks and sites update
08:30-08:50	15+5 mins	David Lowry: Continuous monitoring of greenhouse gases in the South Atlantic and Southern Ocean: contributions from the Equianos network
08:50-09:10	15+5 mins	Markus Leuenberger: First tall tower installation in Switzerland for greenhouse gas concentration monitoring within CarboCount-CH
09:10-09:30	15+5 mins	Jost Lavric: Atmospheric research at the Amazonian Tall Tower Observatory (ATTO)
09:30-09:50	15+5 mins	Luciana Gatti: New improvements in Amazon greenhouse gas measurement program
09:50-10:20	Coffee break	
10:20-12:30	Session 5.3	Chair: Gordon Brailsford Topic: Developments of the GHG networks and sites update
10:20-10:40	15+5 mins	Konstantin Visheratin: Flask sample and total column greenhouse gas measurements at Obninsk and Issyk-Kul stations
10:40-11:00	15+5 mins	Angel Jesus Gomez Pelaez: Izana global GAW station greenhouse-gas measurement program: Novelties and developments during October 2011–May 2013
11:00-11:20	15+5 mins	Yogesh Tiwari: Atmospheric CO ₂ and other greenhouse gases monitoring in India
11:20-11:40	15+5 mins	Lingxi Zhou: China national report on GHGs & related tracers
11:40-12:30	<i>Recommendations</i>	Discussion Leader: Jim Butler Topic: Network extensions and sustainability (Chapter 14 & 15)
12:30-13:30	Lunch	CMA Training Center Canteen, 2nd floor
13:30-15:00	Expert group recommendations update	General coordination: Pieter Tans & Christoph Zellweger Multiple specific leaders

15:00-15:30	Coffee break	
15:30-17:00	Expert group recommendations update	General coordination: Pieter Tans & Christoph Zellweger Multiple specific leaders
17:00-17:30	Closing remarks	WMO/IAEA & LOC

Friday, 14 June 2013

Time	Content	Topics
07:30-18:00	Station visit	Shangdianzi GAW regional station
	Sight-seeing	Jinshanling Great Wall

POSTER LISTING

Session 1: Scales and standards, comparisons	
Marc Delmotte	Update on the ICOS Atmospheric Thematic Center (ATC) and test laboratory results
Masaomi Takahashi	Intercomparison experiments for GHGs Observation (iceGGO) in Japan
Armin Jordan	Evaluation of the MPI-2009 H ₂ calibration scale
Daniel Rzesanke	Construction of the flask and Calibration Laboratory for ICOS (Integrated Carbon Observation System)
Bo Yao	Preparation method of standards for high accuracy CO ₂ /CH ₄ /CO measurement
Jeong Sik Lim	Development of the primary standards of halocarbons and SF ₆ at ambient levels

Session 2: CO₂ observations (measurements techniques and calibration)	
Zou Li	Characteristics of CO ₂ variation in recent 2 years at shangri-la background station
Keiichi Katsumata	Continuous measurement of carbon dioxide, methane and carbon monoxide mole fractions using cavity ring-down spectroscopy at Hateruma Island
Laszlo Haszpra	How well tall tower measurements characterize the mid-PBL CO ₂ mole fraction?
Dan Smale	Furtherance of the CO ₂ measurement error characterization for the prototype in situ FTIR Trace Gas Analyser operated at Lauder, New Zealand
Sebastien Biraud	A multi-year record of airborne CO ₂ observations in the US Southern Great Plains
Markus Leuenberger	Combined CO ₂ and O ₂ measurements at the High Altitude Research Station Jungfraujoch, Switzerland
Guoqing Zhang	Analysis of CO ₂ and other greenhouse gas monitoring data at Mt. WaLiguan
Philip Wilson	Two new automated field systems for continuous measurement of atmospheric oxygen and carbon dioxide

Session 3: Non-CO₂ observations (measurements techniques and calibration)	
Luciana Gatti	Analysis of the influence of CO ₂ concentration and others external factors on the N ₂ O quantification
Elena Kozlova	High-precision long-term atmospheric measurements of CO ₂ , CH ₄ , N ₂ O and CO with Off-Axis Integrated-Cavity Output Spectroscopy
Chris Rella	Measurements of CO ₂ , CH ₄ , and CO in humid gas streams using CRDS
Hideki Nara	Shipboard monitoring system of atmospheric CH ₄ in Southeast Asia and Oceania regions
Lingjun Xia	Study on the in-situ measurement of greenhouse gas by improved FTIR
Andrew Croftwell	Quality control of N ₂ O measurements from the NOAA cooperative air sampling network

Session 4: Isotope measurement and calibration	
David Giffith	¹⁵ N tracer study of N ₂ O emissions from soil using FTIR spectroscopy
Hitoshi Mukai	Isotope analysis for CO ₂ and long-term continuity of the scale in NIES
Gordon Brailsford	Progress on a δ ¹³ CH ₄ comparison suite

Session 5: Developments of the GHG networks and sites update	
Huilin Chen	Atmospheric observations of greenhouse gases and related tracers and isotopes from the Center for Isotope Research (CIO)
Andrew Manning	The Carbon Related Atmospheric Measurement (CRAM) Laboratory: A United Kingdom national report
Jean-Daniel Paris	French observation service of atmospheric greenhouse gases and the Integrated Carbon Observing System
Sung-Bin Park	Continuous CO ₂ /CH ₄ Tall Tower and Eddy Covariance Measurements at Zotino Tall Tower Observatory in Central Siberia – Status Update
Luciana Gatti	3 years greenhouse gases measurements in 2 Brazilian coastal sites

David Griffith	The Total Carbon Column Observing Network (TCCON) – update
Eric Morgan	The Namib Desert Atmospheric Observatory (NDAO), a new background site for continuous measurements of greenhouse gases and related tracers in southern Africa
N.K. Indira	Continuous measurement of GHGs in India
Ernst Brunke & Casper Labuschagne	Cape Point trace gas observations from different analytical systems.

Session 6: Integration of observations, data products and policy

Ludwig Ries	Standardized and automated data quality assurance at GAW Stations
Boru Mai	Application of CarbonTracker in Pearl River Delta region, China
Penelope Pickers	Investigating bias in the application of curve fitting programs to atmospheric time series data
Jingjiao Pu	Estimation of regional background mixing ratio of CO ₂ at Lin'an Station in Yangtze River Delta, China
Hiroshi Koide	Reforming WDCGG: format and metadata

Session 7: Analysis of observations and source identification (poster session only)

Natasha Miles	In-situ tower-based greenhouse gas measurements in an urban environment: Instrument performance, network design and results from INFLUX
Ping Ding	Fossil fuel-derived CO ₂ contribution to the urban atmosphere in Guangzhou, south China by ¹⁴ CO ₂ observation, 2010 – 2011
Weiwei Lv	Study on the variation characteristics of CO ₂ concentration in Urban Atmosphere
Akie Yuba	Analyses for CO ₂ source in the urban area: simultaneous measurement of stable isotope ratio of CO ₂ , isotope ratio of water, and concentrations of CO, NO _x
Fang Zhang	Short-term variations of atmospheric CO ₂ and dominant causes in summer and winter: analysis of 14-year continuous observational data at Waliguan, China

LIST OF RECENT GLOBAL ATMOSPHERE WATCH REPORTS*

120. WMO-UMAP Workshop on Broad-Band UV Radiometers (Garmisch-Partenkirchen, Germany, 22 to 23 April 1996) (WMO TD No. 894).
121. Report of the Eighth WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques (prepared by Thomas Conway) (Boulder, CO, 6-11 July 1995) (WMO TD No. 821).
122. Report of Passive Samplers for Atmospheric Chemistry Measurements and their Role in GAW (prepared by Greg Carmichael) (WMO TD No. 829).
123. Report of WMO Meeting of Experts on GAW Regional Network in RA VI, Budapest, Hungary, 5 to 9 May 1997.
124. Fifth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry, (Geneva, Switzerland, 7-10 April 1997) (WMO TD No. 898).
125. Instruments to Measure Solar Ultraviolet Radiation, Part 1: Spectral Instruments (lead author G. Seckmeyer) (WMO TD No. 1066), 2001.
126. Guidelines for Site Quality Control of UV Monitoring (lead author A.R. Webb) (WMO TD No. 884), 1998.
127. Report of the WMO-WHO Meeting of Experts on Standardization of UV Indices and their Dissemination to the Public (Les Diablerets, Switzerland, 21-25 July 1997) (WMO TD No. 921).
128. The Fourth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting, (Rome, Italy, 22-25 September 1996) (WMO TD No. 918).
129. Guidelines for Atmospheric Trace Gas Data Management (Ken Masarie and Pieter Tans), 1998 (WMO TD No. 907).
130. Jülich Ozone Sonde Intercomparison Experiment (JOSIE, 5 February to 8 March 1996), (H.G.J. Smit and D. Kley) (WMO TD No. 926).
131. WMO Workshop on Regional Transboundary Smoke and Haze in Southeast Asia (Singapore, 2 to 5 June 1998) (Gregory R. Carmichael). Two volumes.
132. Report of the Ninth WMO Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques (Edited by Roger Francey), (Aspendale, Vic., Australia).
133. Workshop on Advanced Statistical Methods and their Application to Air Quality Data Sets (Helsinki, 14-18 September 1998) (WMO TD No. 956).
134. Guide on Sampling and Analysis Techniques for Chemical Constituents and Physical Properties in Air and Precipitation as Applied at Stations of the Global Atmosphere Watch. Carbon Dioxide (WMO TD No. 980).
135. Sixth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Zurich, Switzerland, 8-11 March 1999) (WMO TD No.1002).
136. WMO/EMEP/UNEP Workshop on Modelling of Atmospheric Transport and Deposition of Persistent Organic Pollutants and Heavy Metals (Geneva, Switzerland, 16-19 November 1999) (Volumes I and II) (WMO TD No. 1008).
137. Report and Proceedings of the WMO RA II/RA V GAW Workshop on Urban Environment (Beijing, China, 1-4 November 1999) (WMO-TD. 1014) (Prepared by Greg Carmichael).
138. Reports on WMO International Comparisons of Dobson Spectrophotometers, Parts I – Arosa, Switzerland, 19-31 July 1999, Part II – Buenos Aires, Argentina (29 Nov. – 12 Dec. 1999 and Part III – Pretoria, South Africa (18 March – 10 April 2000) (WMO TD No. 1016).

* (A full list is available at <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>)

139. The Fifth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Halkidiki, Greece, September 1998)(WMO TD No. 1019).
140. WMO/CEOS Report on a Strategy for Integrating Satellite and Ground-based Observations of Ozone (WMO TD No. 1046).
141. Report of the LAP/COST/WMO Intercomparison of Erythral Radiometers Thessaloniki, Greece, 13-23 September 1999) (WMO TD No. 1051).
142. Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), A Contribution to the Implementation of the Long-Term Plan (WMO TD No.1077).
143. Global Atmosphere Watch Measurements Guide (WMO TD No. 1073).
144. Report of the Seventh Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry and the GAW 2001 Workshop (Geneva, Switzerland, 2 to 5 April 2001) (WMO TD No. 1104).
145. WMO GAW International Comparisons of Dobson Spectrophotometers at the Meteorological Observatory Hohenpeissenberg, Germany (21 May – 10 June 2000, MOHp2000-1), 23 July – 5 August 2000, MOHp2000-2), (10 – 23 June 2001, MOHp2001-1) and (8 to 21 July 2001, MOHp2001-2). Prepared by Ulf Köhler (WMO TD No. 1114).
146. Quality Assurance in monitoring solar ultraviolet radiation: the state of the art. (WMO TD No. 1180), 2003.
147. Workshop on GAW in RA VI (Europe), Riga, Latvia, 27-30 May 2002. (WMO TD No. 1206).
148. Report of the Eleventh WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques (Tokyo, Japan, 25-28 September 2001) (WMO TD No 1138).
149. Comparison of Total Ozone Measurements of Dobson and Brewer Spectrophotometers and Recommended Transfer Functions (prepared by J. Staehelin, J. Kerr, R. Evans and K. Vanicek) (WMO TD No. 1147).
150. Updated Guidelines for Atmospheric Trace Gas Data Management (Prepared by Ken Maserie and Pieter Tans (WMO TD No. 1149).
151. Report of the First CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 18-19 March 2003) (WMO TD No. 1181).
152. Current Activities of the Global Atmosphere Watch Programme (as presented at the 14th World Meteorological Congress, May 2003). (WMO TD No. 1168).
153. WMO/GAW Aerosol Measurement Procedures: Guidelines and Recommendations. (WMO TD No. 1178).
154. WMO/IMEP-15 Trace Elements in Water Laboratory Intercomparison. (WMO TD No. 1195).
155. 1st International Expert Meeting on Sources and Measurements of Natural Radionuclides Applied to Climate and Air Quality Studies (Gif sur Yvette, France, 3-5 June 2003) (WMO TD No. 1201).
156. Addendum for the Period 2005-2007 to the Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), GAW Report No. 142 (WMO TD No. 1209).
157. JOSIE-1998 Performance of EEC Ozone Sondes of SPC-6A and ENSCI-Z Type (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1218).
158. JOSIE-2000 Jülich Ozone Sonde Intercomparison Experiment 2000. The 2000 WMO international intercomparison of operating procedures for ECC-ozone sondes at the environmental simulation facility at Jülich (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1225).
159. IGOS-IGACO Report - September 2004 (WMO TD No. 1235), 68 pp, September 2004.
160. Manual for the GAW Precipitation Chemistry Programme (Guidelines, Data Quality Objectives and Standard Operating Procedures) (WMO TD No. 1251), 186 pp, November 2004.
161. 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Toronto, Canada, 15-18 September 2003), 274 pp, May 2005.

162. WMO/GAW Experts Workshop on a Global Surface-Based Network for Long Term Observations of Column Aerosol Optical Properties, Davos, Switzerland, 8-10 March 2004 (edited by U. Baltensperger, L. Barrie and C. Wehrl) (WMO TD No. 1287), 153 pp, November 2005.
163. World Meteorological Organization Activities in Support of the Vienna Convention on Protection of the Ozone Layer (WMO No. 974), 4 pp, September 2005.
164. Instruments to Measure Solar Ultraviolet Radiation: Part 2: Broadband Instruments Measuring Erythemally Weighted Solar Irradiance (WMO TD No. 1289), 55 pp, July 2008, electronic version 2006.
165. Report of the CAS Working Group on Environmental Pollution and Atmospheric Chemistry and the GAW 2005 Workshop, 14-18 March 2005, Geneva, Switzerland (WMO TD No. 1302), 189 pp, March 2005.
166. Joint WMO-GAW/ACCENT Workshop on The Global Tropospheric Carbon Monoxide Observations System, Quality Assurance and Applications (EMPA, Dübendorf, Switzerland, 24 – 26 October 2005) (edited by J. Klausen) (WMO TD No. 1335), 36 pp, September 2006.
167. The German Contribution to the WMO Global Atmosphere Watch Programme upon the 225th Anniversary of GAW Hohenpeissenberg Observatory (edited by L.A. Barrie, W. Fricke and R. Schleyer) (WMO TD No. 1336), 124 pp, December 2006.
168. 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Boulder, Colorado, USA, 19-22 September 2005) (edited by J.B. Miller) (WMO TD No. 1359), 40 pp, December 2006.
169. Chemical Data Assimilation for the Observation of the Earth's Atmosphere – ACCENT/WMO Expert Workshop in support of IGACO (edited by L.A. Barrie, J.P. Burrows, P. Monks and P. Borrell) (WMO TD No. 1360), 196 pp, December 2006.
170. WMO/GAW Expert Workshop on the Quality and Applications of European GAW Measurements (Tutzing, Germany, 2-5 November 2004) (WMO TD No. 1367).
171. A WMO/GAW Expert Workshop on Global Long-Term Measurements of Volatile Organic Compounds (VOCs) (Geneva, Switzerland, 30 January – 1 February 2006) (WMO TD No. 1373), 36 pp, February 2007.
172. WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015 (WMO TD No. 1384), 108 pp, August 2008.
173. Report of the CAS Joint Scientific Steering Committee on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 11-12 April 2007) (WMO TD No. 1410), 33 pp, June 2008.
174. World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide (WMO TD No. 1416), 50 pp, January 2008.
175. The Ninth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Delft, Netherlands, 31-May – 3 June 2005) (WMO TD No. 1419), 69 pp, March 2008.
176. The Tenth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Northwich, United Kingdom, 4-8 June 2007) (WMO TD No. 1420), 61 pp, March 2008.
177. Joint Report of COST Action 728 and GURME – Overview of Existing Integrated (off-line and on-line) Mesoscale Meteorological and Chemical Transport Modelling in Europe (ISBN 978-1-905313-56-3) (WMO TD No. 1427), 106 pp, May 2008.
178. Plan for the implementation of the GAW Aerosol Lidar Observation Network GALION, (Hamburg, Germany, 27 - 29 March 2007) (WMO TD No. 1443), 52 pp, November 2008.
179. Intercomparison of Global UV Index from Multiband Radiometers: Harmonization of Global UVI and Spectral Irradiance (WMO TD No. 1454), 61 pp, March 2009.
180. Towards a Better Knowledge of Umkehr Measurements: A Detailed Study of Data from Thirteen Dobson Intercomparisons (WMO TD No. 1456), 50 pp, December 2008.
181. Joint Report of COST Action 728 and GURME – Overview of Tools and Methods for Meteorological and Air Pollution Mesoscale Model Evaluation and User Training (WMO TD No. 1457), 121 pp, November 2008.

182. IGACO-Ozone and UV Radiation Implementation Plan (WMO TD No. 1465), 49 pp, April 2009.
183. Operations Handbook – Ozone Observations with a Dobson Spectrophotometer (WMO TD No. 1469), 91 pp, March 2009.
184. Technical Report of Global Analysis Method for Major Greenhouse Gases by the World Data Center for Greenhouse Gases (WMO TD No. 1473), 29 pp, June 2009.
185. Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (WMO TD No. 1478), 49 pp, September 2009.
186. 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Helsinki, Finland, 10-13 September 2007) (WMO TD No. 1487), 31 pp, April 2009.
187. Joint Report of COST Action 728 and GURME – Review of the Capabilities of Meteorological and Chemistry-Transport Models for Describing and Predicting Air Pollution Episodes (ISBN 978-1-905313-77-8) (WMO TD No. 1502), 69 pp, December 2009, electronic version -July 2009.
188. Revision of the World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide (WMO TD No.1507), 55 pp, November 2009.
189. Report of the MACC/GAW Session on the Near-Real-Time Delivery of the GAW Observations of Reactive Gases, Garmisch-Partenkirchen, Germany, 6-8 October 2009, (WMO TD No. 1527), 31 pp. August 2010.
190. Instruments to Measure Solar Ultraviolet Radiation Part 3: Multi-channel filter instruments (lead author: G. Seckmeyer) (WMO TD No. 1537), 55 pp. November 2010.
191. Instruments to Measure Solar Ultraviolet Radiation Part 4: Array Spectroradiometers (lead author: G. Seckmeyer) (WMO TD No. 1538), 43 pp. November 2010.
192. Guidelines for the Measurement of Atmospheric Carbon Monoxide (WMO TD No. 1551), 49 pp, July 2010.
193. Guidelines for Reporting Total Ozone Data in Near Real Time (WMO TD No. 1552), 19 pp, April 2011 (*electronic version only*).
194. 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Jena, Germany, 7-10 September 2009) (WMO TD No. 1553). 330 pp, April 2011.
195. WMO/GAW Expert Workshop on Global Long-term Measurements of Nitrogen Oxides and Recommendations for GAW Nitrogen Oxides Network (Hohenpeissenberg, Germany, 8-9 October 2009) (WMO TD No. 1570), 45 pp, February 2011.
196. Report of the Second Session of the CAS JSC OPAG-EPAC and GAW 2009 Workshop (Geneva, Switzerland, 5-8 May 2009) (WMO TD No. 1577).
197. Addendum for the Period 2012 – 2015 to the WMO Global Atmosphere Watch (GAW) Strategic Plan 2008 – 2015, 57 pp, May 2011.
198. Data Quality Objectives (DQO) for Solar Ultraviolet Radiation Measurements (Part I). Addendum to WMO/GAW Report No. 146 - Quality Assurance in Monitoring Solar Ultraviolet Radiation: State of the Art (*electronic version only*).
199. Second Tropospheric Ozone Workshop. Tropospheric Ozone Changes: observations, state of understanding and model performances (Météo France, Toulouse, France, 11-14 April 2011), 226 pp, September 2011.
200. WMO/GAW Standard Operating Procedures for In-Situ Measurements of Aerosol Mass Concentration, Light Scattering and Light Absorption (Edited by John A. Ogren), 134 pp, October 2011.
201. Quality Assurance and Quality Control for Ozonesonde Measurements in GAW (Prepared by Herman Smit and ASOPOS Panel), 95 pp. January 2013 (*electronic version only*).
202. Workshop on Modelling and Observing the Impacts of Dust Transport/Deposition on Marine Productivity (Sliema, Malta, 7-9 March 2011), 50 pp, November 2011.

203. The Atmospheric Input of Chemicals to the Ocean. Rep. Stud. GESAMP No. 84/GAW Report No. 203. 69 pp. (ISSN: 1020-4873).
204. Standard Operating Procedures (SOPs) for Air Sampling in Stainless Steel Canisters for Non-Methane Hydrocarbons Analysis (Prepared by Rainer Steinbrecher and Elisabeth Weiß), 25 pp. September 2012.
205. WMO/IGAC Impacts of Megacities on Air Pollution and Climate, 309 pp. September 2012 (ISBN: 978-0-9882867-0-2).
206. 16th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2011), Wellington, New Zealand, 25-28 October 2011, 67 pp, October 2012.
207. Recommendations for a Composite Surface-Based Aerosol Network, Emmetten, Switzerland, 28-29 April 2009, 66 pp. November 2012.
208. WMO GURME Workshop on Urban Meteorological Observation Design, (Shanghai, China, 11-14 December 2011).
209. Guidelines for Continuous Measurements of Ozone in the Troposphere (Prepared by Ian E. Galbally and Martin G. Schultz), 80 pp, February 2013 (WMO-No. 1110, ISBN: 978-92-63-11110-4).
210. Report of the Third Session of the CAS Joint Scientific Committee of the Open Programme Area Group on Environmental Pollution and Atmospheric Chemistry (JSC OPAG-EPAC), (Geneva, Switzerland, 27-29 April 2011) (*electronic version only*).
211. Joint Publication of CIE and WMO Technical Report Rationalizing Nomenclature for UV Doses and Effects on Humans.
212. Standard Operating Procedures (SOPs) for Spectral Instruments Measuring Spectral Solar Ultraviolet Irradiance.

INTEGRATING A REMOTELY DEPLOYED STABLE ISOTOPE PICARRO CRDS WITH A GLOBAL MONITORING NETWORK

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CSIRO Marine and Atmospheric Research (CMAR) and Geoscience Australia (GA) have deployed a pair of Picarro cavity ring down spectrometers (CRDS) (one Model G1301, designated CFADS63, and one Model G1101i, designated CFFDS36) at a remote, inland field site Arcturus (ARA: 23.859 °S, 148.475 °E) located near Emerald, Queensland, Australia. The aim of this installation is to establish background concentration measurements of CO₂, CH₄ and H₂O, in addition to the stable carbon isotopic composition ($\delta^{13}\text{C}$) of the CO₂, in an area of interest for both carbon sequestration and storage (CSS) and coal seam gas (CSG) projects. A major task in operating these instruments is calibration to ensure that the measured atmospheric compositions are compatible with the CMAR global monitoring network and that they are reported using internationally accepted scales. To that end, calibration of the CRDS instruments is based on high-pressure cylinders of dry air that have been calibrated in our GASLAB facility [Francey *et al.*, 2003] with checks provided by occasional flask samples collected at the remote site and returned to GASLAB for analysis.

The facility located at ARA is a modified shipping container located in a region where there are several planned CSS and/or CSG projects. The container is supplied with mains power, with limited battery back-up, and air conditioning to provide a relatively stable operating environment for the CRDS systems. To minimize the complexity of the remote installation, the air provided to the Picarro systems is not dried, instead, we rely on the water correction procedures built into the Picarro systems to provide dry air mole fractions of CO₂ and CH₄, and to correct for spectral interferences. The CSIRO Cape Ferguson site (CFA) is located approximately 400 km northwest of ARA and a comparison of CFA data with ARA data shows that they experience similar background air, providing another opportunity to assess the long term records that will be produced from the ARA site.

CO₂, CH₄ and H₂O records have been produced by CFADS63 since 2009; however $\delta^{13}\text{C}$ data from CFFDS36 have been adversely affected by several problems, one of which was the known interference of CH₄ on the $\delta^{13}\text{C}$ measurement [Cunningham, 2011]. CFFDS36 was returned to Picarro in late 2011 for modification; afterwards it was operated in the CMAR GASLAB prior to re-installation at ARA in July 2012.

Calibrations for CFADS63 and CFFDS36 are performed using independent suites of reference tanks, each comprising four high-pressure tanks of marine air. One of the reference tanks in each suite is a tank of clean dry air marine air, with composition of all species close to the background atmospheric composition at ARA (and CFA) in early 2013 that is analyzed daily to provide a constraint on instrument drift. The other three tanks in each suite are modified to provide a range of values encompassing those expected at ARA.

For CFFDS36 we have chosen to perform calibration directly on $\delta^{13}\text{C}$ of CO₂, independent of the specific ¹²CO₂ and ¹³CO₂, until we can verify which of several calibration methods [Wen *et al.*, 2013] is most suitable for our application. Figure 1 summarizes the hourly average results from CFFDS36 for March 2013. The upper panel shows the raw (red) and corrected (blue; corrected for calibration) $\delta^{13}\text{C}$; the calibration occurred over the period 15 - 18 March 2013. The middle panel shows the reported CH₄ from the both CFFDS36 (red) and CFADS63 (blue), and the lower panel shows the reported H₂O from CFFDS36 and CFADS63. Of major concern to us are the large

jumps of $\delta^{13}\text{C}$ visible in both the raw and corrected data that are synchronised with large variations in the CH_4 reported by CFFDS36. CH_4 from CFADS63 does not show these same "jumps" that are clearly unrealistic for atmospheric behaviour. Reported H_2O from both instruments over the period is variable but does not appear to be systematically correlated with the variation of CH_4 or $\delta^{13}\text{C}$ in CFFDS36.

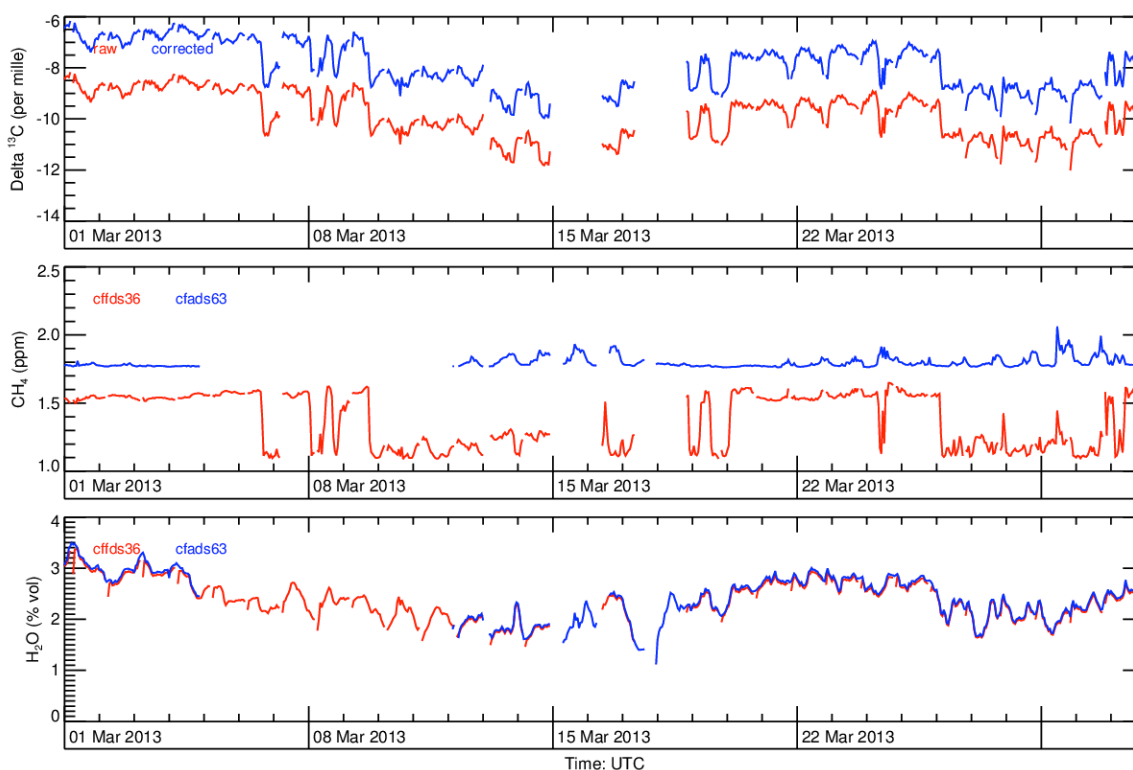


Figure 1 - Hourly average $\delta^{13}\text{C}$, CH_4 and H_2O from ARA for March 2013. The top panel presents raw $\delta^{13}\text{C}$ (red) and corrected (blue) from CFFDS36, (with calibration between 15 and 18 March); the middle panel presents CH_4 data from CFFDS36 (red) and CFADS63 (blue); the bottom panel presents H_2O data from CFFDS36 (red) and CFADS63 (blue). $\delta^{13}\text{C}$ at ARA is expected to be no greater than -8 ‰.

Investigating the relationship between $\delta^{13}\text{C}$ and CH_4 or H_2O for CFFDS36 is difficult due to the variability of atmospheric composition at ARA so we tested the relationship using our laboratory 1101i (CFFDS24) with a tank of very dry air and a water injection system. Using this tank ensured that there was no variation of CO_2 , $\delta^{13}\text{C}$, or CH_4 during the course of the experiment. The results from this test are shown as filled blue diamonds in Figure 2. The reported CH_4 concentration for the tank decreases by 0.7 ppm as H_2O increases from 0 to ~2 %; above this the reported CH_4 "jumps" to the near 0 % H_2O value then decreases slowly as H_2O increases. This bi-modal behaviour is concerning and the transitions are the cause of the jumps in $\delta^{13}\text{C}$ and CH_4 observed in Figure 1.

We discussed these results with the CRDS manufacturer, Picarro Inc., who verified the results on a third instrument in their laboratory, and proceeded to investigate the cause(s) of the problem. After several weeks an error in the routine used to determine the peak shape of CH_4 was identified and a revised peak-fitting procedure was installed on our laboratory instrument. We repeated the H_2O injection test and these results are shown in Figure 2 as filled red circles. The relationship between CH_4 and H_2O is no longer bimodal and appears to be more linear, although we note increased scatter of CH_4 at higher H_2O levels that warrants further investigation.

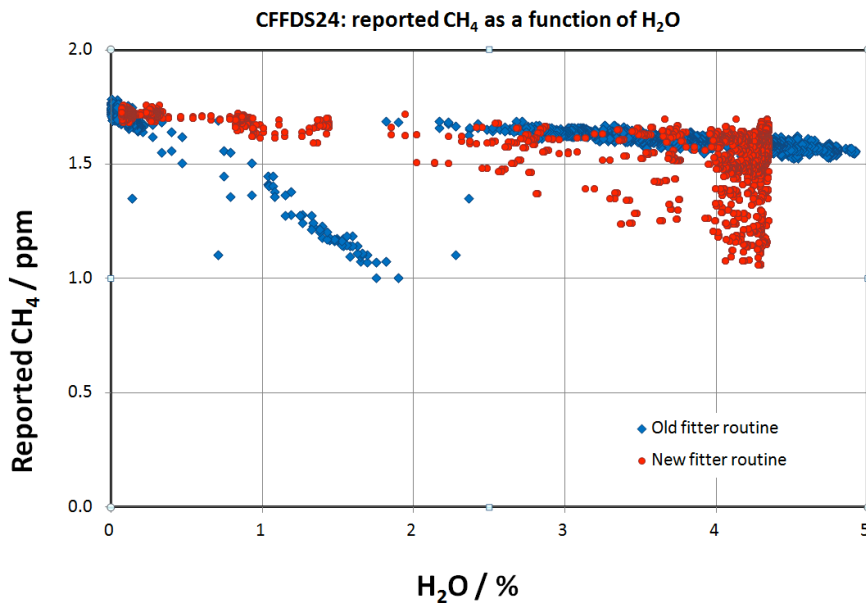


Figure 2 - Plot of CH₄ against H₂O for CFFDS24 tests using tank air

The modified peak fitting procedure was installed on CFFDS36 in September 2013: $\delta^{13}\text{C}$, CH₄ and H₂O for CFFDS36 and CFADS63 for September are shown in Figure 3. The large jumps in both CH₄ and $\delta^{13}\text{C}$ with high H₂O levels are no longer present but the data after 22 September shows decreasing CH₄ with increasing H₂O, in line with expectations from Figure 2. While these variations in CH₄ are unrealistic (and not evident in data from CFADS63) they no longer appear to be causing large jumps in the reported $\delta^{13}\text{C}$. A more complete investigation of this behaviour in both CFFDS24 and CFFDS36 has been initiated.

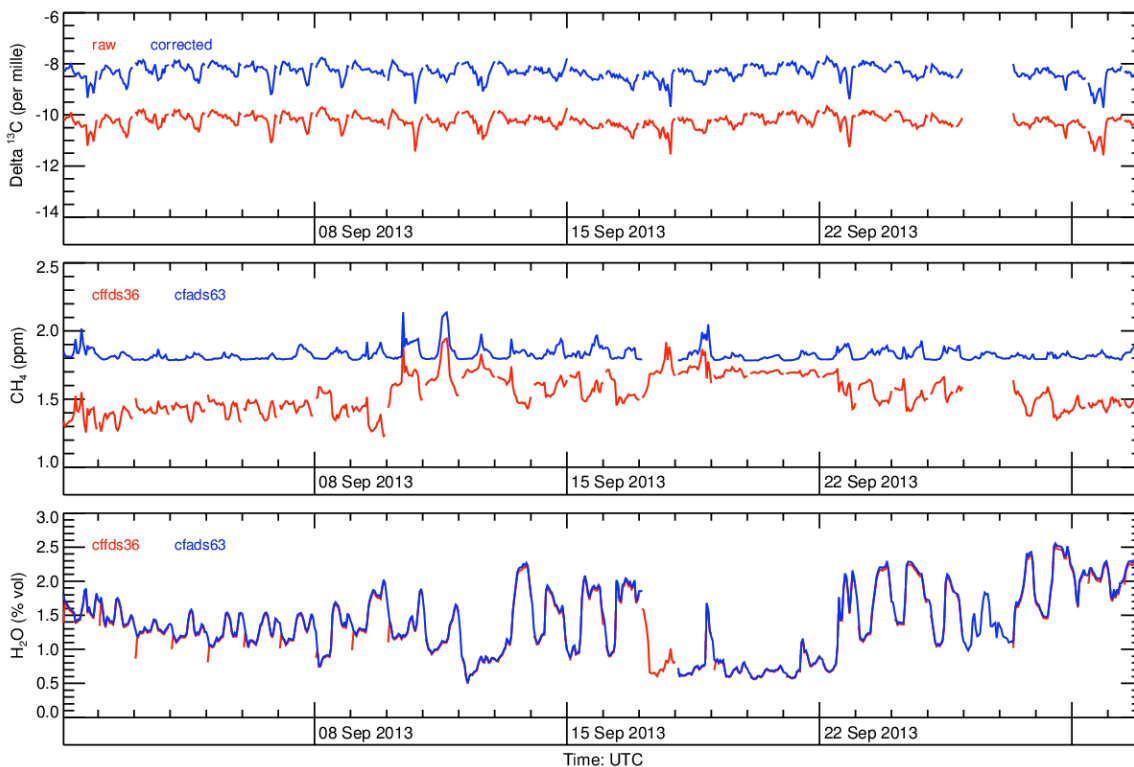


Figure 3 - Hourly average $\delta^{13}\text{C}$, CH₄ and H₂O from ARA for September 2013; details as for Figure 1. The new peak fitting procedure was installed on 10 September 2013. $\delta^{13}\text{C}$ at ARA is expected to be no greater -8 ‰

We have resolved a significant problem with the Picarro 1101i software that was interfering with the reported atmospheric measurements and with instrument calibration but note that there are still unresolved issues with the $\delta^{13}\text{C}$ measurements that are limiting calibration and hence integration with our global network. We are investigating methods for correcting the historical data using the new measurements, and investigating alternatives for removing, or reducing, interference from H_2O on measurements and calibrations at the ARA site.

Acknowledgements

We would like to thank staff at Picarro Inc. for their advice, assistance and perseverance in this study, particularly Chris Rella, Ed Wahl, John Hoffnagle, John Rainwater, Kevin Cunningham, John Heer and Ron Gallegos.

References

- Cunningham, K. (2011): *Isotopic Carbon in CO_2 : Methane Interference*, Picarro Inc.
- Francey, R. J., et al. (2003): *The CSIRO (Australia) measurement of greenhouse gases in the global atmosphere*, in Baseline Atmospheric Program Australia, edited by N. W. Tindale, N. Derek and P. J. Fraser, pp. 42-53, Bureau of Meteorology and CSIRO Atmospheric Research.
- Wen, X. F., Y. Meng, X. Y. Zhang, X. M. Sun, and X. Lee (2013): *Evaluating calibration strategies for isotope ratio infrared spectroscopy for atmospheric $^{13}\text{CO}_2$ / $^{12}\text{CO}_2$ measurement*, Atmos. Meas. Tech., 6(6), 1491-1501.

BARING HEAD CO₂ – FOUR DECADES OF OBSERVATIONS IN NEW ZEALAND

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1. Background

The development of a network of global sites for in situ carbon dioxide (CO₂) observations, and other greenhouse and trace gases started more than 40 years ago. Baring Head in New Zealand became the first in situ station making observations in the Southern Hemisphere and a complement to Mauna Loa in the Northern Hemisphere. Initial observations were aimed at understanding the seasonal nature of the CO₂ cycle in the Southern Hemisphere which had previously been unknown, in more recent times the measurements have been used to inform on the composition of carbon processes. The sources of carbon dioxide (CO₂) emissions are greater in the Northern Hemisphere than in the Southern Hemisphere, resulting in inter-hemispheric differences of atmospheric CO₂ mole fractions. However the trends in the atmospheric CO₂ are comparable between hemispheres due to the fact that the species is long lived and transported to the south. The Southern Hemisphere geographically is dominated by oceans. About 30% of the CO₂ emitted to the atmosphere from fossil fuel burning, land use change and other human activities has been absorbed by Earth's oceans, with the Southern Ocean playing an especially critical role in the carbon cycle. Several critical questions remain unresolved for the carbon cycle that are linked to Southern Hemisphere processes (e.g. trends in the Southern Ocean carbon sink, and uptake by Southern Hemisphere land masses).

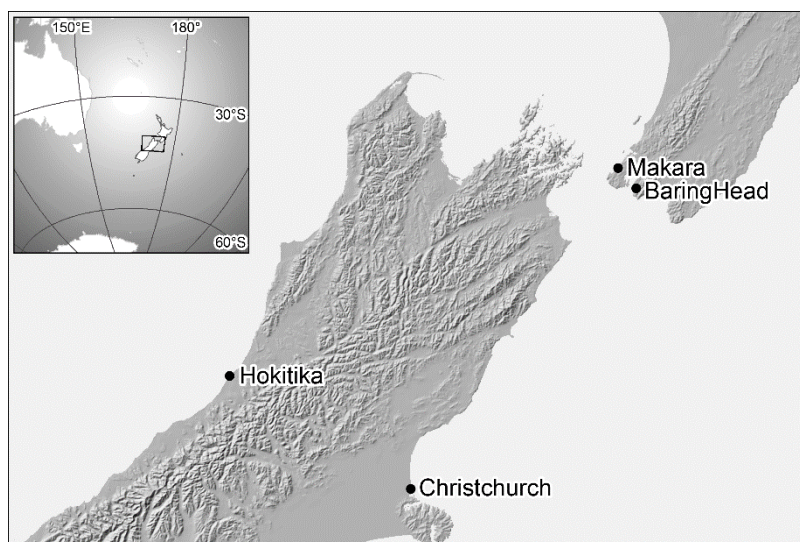


Figure 1 - Baring Head station is located on the southern tip of the North Island (Te Ika-a-Maui), and is frequently exposed to baseline air from the south

2. Baring Head observations

Located on a south facing cliff on the southern coast of the North Island (41.4083° S, 174.8710° E) New Zealand, the NIWA operated Baring Head (BHD) monitoring station began observations of CO_2 in 1972, following a short period at nearby Makara, and is ideally situated to observe air masses that have not been in contact with terrestrial sources for thousands of kilometres and multiple days (Brailsford et al, 2012). Observations have always been made with direct ties to the central calibration laboratories (SIO and now NOAA) to ensure compatibility with observations made elsewhere. Whilst best practice has been used over the forty years of measurements, the community knowledge has advanced with time. For example initial reference gases were prepared using nitrogen as the carrier gas and steel cylinders as the container, whereas now an air matrix is used with aluminium regarded as the most stable cylinders. A site-specific filtering process is used to ensure that local topography and air flows are considered when selecting what is regarded as background, or baseline air representative of mid-latitudes of the Southern Hemisphere. Filtering avoids air that has arrived at the site from the north, and excludes air that has been in contact with the South Island based on pressure differences between the east and west coasts. The full time-series is depicted in Figure 2, in black, and the filtered stable background data are shown in red.

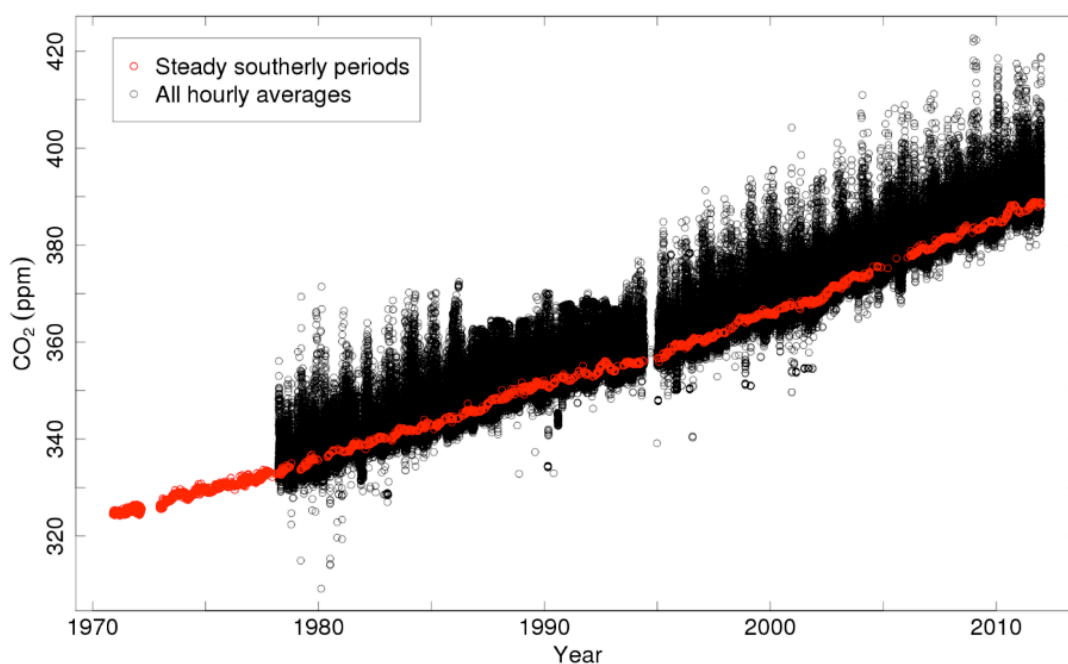


Figure 2 - CO_2 time series from BHD, black points are hourly averages for all directions while red are stable background, steady southerly periods where the variations are less than 0.1 ppm in a 6 hour period

Footprints for the air arriving at Baring Head (Fig. 3) have been estimated using the high-resolution Lagrangian model NAME III (Jones et al., 2007), where particles are released at the site and their trajectories “back in time” are determined using meteorological input from the NIWA (N.Z.) regional forecast model NZLAM-12. Cluster analysis has identified the seven dominant groupings for the released particles. A southerly trajectory is shown to predominantly avoid local land areas, it is air from this cluster that is least perturbed by local effects for CO_2 and forms the majority of the background air data.

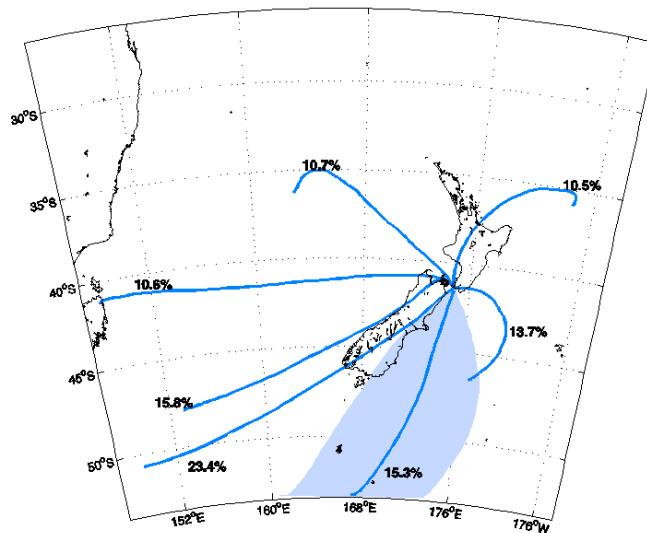


Figure 3 - CO₂ footprint for air arriving at BHD using NAME III over a two-year period. A 1- σ band for the trajectory spread is shown for this southerly cluster

1. Time-series

We employ a seasonal time-series decomposition by Loess (STL) routine (Cleveland et al 1990) to interpret the 40 year time-series, and determine a seasonal amplitude of 0.95 ppm and a long-term growth rate (Fig. 4) of 1.5 ppm yr⁻¹ with an increasing trend with time. During the last decade (2000-2009), we note a difference between BHD and Mauna Loa of -3.03 ppm primarily as a result of fossil fuel usage in the north hemisphere. A difference between BHD and South Pole over the same period of -0.05 ppm is an indication of a greater influence in the recent record of the removal processes of the Southern Ocean on Baring Head compared to than South Pole (Stephens et al, 2013).

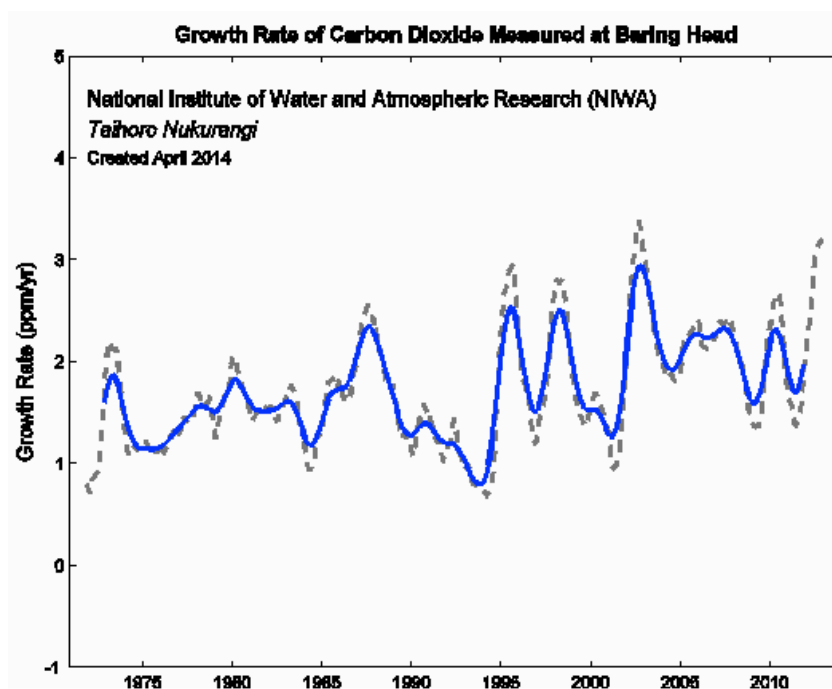


Figure 4 - CO₂ growth rate determined for Baring Head over a 40 year period

By utilizing tagged-tracer simulations from the fine grid version of Transport Model version 3 (TM3) (Heimann and Körner, 2003), we are able to infer source/sink contributions from different geographic regions to the overall seasonal cycle (Stephens et al, 2013). The simulations (Fig. 5) use CarbonTracker-2010 fluxes (Peters et al., 2007) and were run from 2000-2009 with the first three years discarded to allow for spin-up. The atmospheric imprint of the Southern Hemisphere ocean flux at Baring Head has a peak in the autumn (May) and a trough in the early summer (Dec). The Northern Hemisphere terrestrial flux influence at BHD is lagged by about six months due to inter-hemispheric transport time and has a phase and magnitude close to that of the Southern Hemisphere terrestrial flux, with peaks in late winter (Aug-Sep) and troughs in autumn (Mar-Apr).

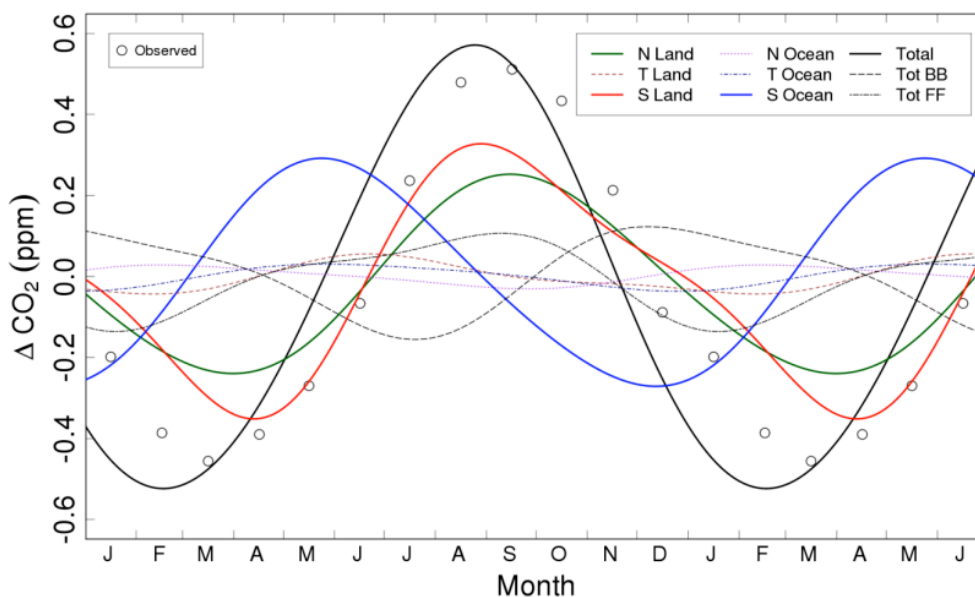


Figure 5 - Output from a tagged tracer experiment were the observations are plotted as circles. The TM3 model “Total” seasonal cycle is of the similar magnitude as the observations however the phase is advanced by one month

2. Summary

A 40 year in situ record of atmospheric CO₂ has been acquired from the Baring Head site, this has proven to be an effective location for the observation of baseline air. When the time-series has been examined a long-term growth rate of 1.5 ppm yr⁻¹ has been determined with a mean peak to peak seasonal amplitude of 0.95 ppm. Air mass origins or footprints have been modelled using NAME and trajectory clusters have demonstrated the effectiveness of the site at observing mid-latitude Southern Hemisphere air. A tagged-tracer model simulation has provided insight into the components contributing to the seasonal cycle and their potential phasing. On-going work will improve knowledge of regional carbon processes whilst maintaining compatibility of observations with other network stations.

References

- Brailsford, G.W., Stephens, B.B., Gomez, A.J., Riedel, K., Mikaloff Fletcher, S.E., Nichol, S.E., Manning, M.R. *Long-term continuous atmospheric CO₂ measurements at Baring Head, New Zealand*. Atmos. Meas. Tech., 5(12): 3109-3117. 10.5194/amt-5-3109-2012, 2012.
- Cleveland, R. B., Cleveland, W. S., McRae, J. E., and Terpenning, I.: *STL: A seasonal-trend decomposition procedure based on loess*, J. Official Statistics, 6, 3–73, 1990.
- Heimann, M. and Körner, S.: *The global atmospheric tracer model TM3*, in Max-Planck-Institut für Biogeochemie (Eds.): Technical Report, Vol. 5, Max-Planck-Institut für Biogeochemie, Jena, Germany, 131 pp., 2003.
- Jones A.R., Thomson D.J., Hort M. and Devenish B.: *'The U.K. Met Office's next-generation atmospheric dispersion model, NAME III'*, in Borrego C. and Norman A.-L. (Eds) Air Pollution Modeling and its Application XVII (Proceedings of the 27th NATO/CCMS International Technical Meeting on Air Pollution Modelling and its Application), Springer, pp. 580-589, 2007.
- Peters, W., Jacobson, A. R., Sweeney, C., Andrews, A. E., Conway, T. J., Masarie, K., Miller, J. B., Bruhwiler, L. M. P., Petron, G., Hirsch, A. I., Worthy, D. E. J., van der Werf, G. R., Randerson, J. T., Wennberg, P. O., Krol, M. C. and Tans, P. P.: *An atmospheric perspective on North American carbon dioxide exchange: CarbonTracker*, Proc. Natl. Acad. Sci. U. S. A., 104, 18925-18930, 2007.
- Stephens, B.B., Brailsford, G.W., Gomez, A.J., Riedel, K., Mikaloff Fletcher, S.E., Nichol, S., Manning, M. *Analysis of a 39-year continuous atmospheric CO₂ record from Baring Head, New Zealand*. Biogeosciences, 10(4): 2683-2697. 10.5194/bg-10-2683-2013, 2013.

IZAÑA GLOBAL GAW STATION GREENHOUSE-GAS MEASUREMENT PROGRAMME. NOVELTIES AND DEVELOPMENTS DURING OCTOBER 2011 – MAY 2013

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1. The Izaña Atmospheric Observatory

The Izaña Atmospheric Observatory (IZO) is run by Izaña Atmospheric Research Center (IARC), which belongs to the Meteorological State Agency of Spain (AEMET). IZO is located on the top of a mountain (28.309° N, 16.499° W, 2373 m a.s.l.) on the island of Tenerife (Canary Islands, Spain), well above a strong subtropical temperature inversion layer. In situ measurements at Izaña are representative of the subtropical Northeast Atlantic free troposphere, especially during the night period. The Izaña Atmospheric Observatory is: a Global GAW station (with many measurement programmes additionally to that for in situ greenhouse gases), a NDACC station, a TCCON station, a BSRN station (radiation), an AERONET/PHOTONS calibration centre and station (aerosols), the GAW Regional Brewer Calibration Centre for Europe... More information about IZO can be obtained visiting its web site: izana.aemet.es



Figure 1 – The Izaña Atmospheric Observatory from two different viewpoints

IARC would like to install also an ICOS (Integrated Carbon Observation System) station at the Izaña observatory. Pursuing this objective, AJGP attended the two Atmospheric ICOS Workshops that held during 2012, and participated in one of the working groups designated in the first of these workshops.

2. In situ greenhouse-gas measurements at the Izaña observatory

IARC (AEMET) measures using in situ analysers at Izaña several atmospheric gases within the greenhouse-gas programme as Table 1 details. Figures 2 and 3 show the time series of daily night-time (20:00 – 08:00 UTC) mean mole fractions measured at Izaña for each gas. See Gomez-Pelaez et al. (2012) and references there in, and Gomez-Pelaez et al. (2013) for details about the measurement systems (these references also are available at the IARC web site izana.aemet.es).

Additionally, as cooperation with other institutions, we have collected weekly flask samples for NOAA-ESRL-GMD-CCGG since 1991, and 2-week integrated samples of $^{14}\text{CO}_2$ for the University of Heidelberg since 1984.

Some recent comparison exercises in which IZO was involved: 1) we perform comparisons between flask (NOAA) and in situ continuous (IARC-AEMET) measurements; 2) IARC participated in the 5th WMO Round Robin; 3) the last GAW GHG audits performed at Izaña were conducted by WCC-N₂O in 2008 and WCC-CH₄-CO in 2009.

Table 1 – Gases measured at Izaña using in situ analysers within the greenhouse-gas programme. The table indicates for each gas: the year in which the measurements started, and the scale and analyser used

GAS	Since year	Scale	Analyser	Model
CO₂	1984	1984-1994: WMO-X87 1995-2006: WMO-X93 2007-present: WMO-X2005	NDIR	Siemens Ultramat 3: (1984-2006) Licor 7000 (2007-present) Licor 6252 (2008-present)
CH₄	1984	WMO-2004	GC-FID	Dani 3800 (1984-present) Varian 3800 (2011-present)
N₂O	2007	WMO-2006	GC-ECD	Varian 3800
SF₆		WMO-2006		
CO	2008	WMO-2004	GC-RGD	Trace Analytical RGA3

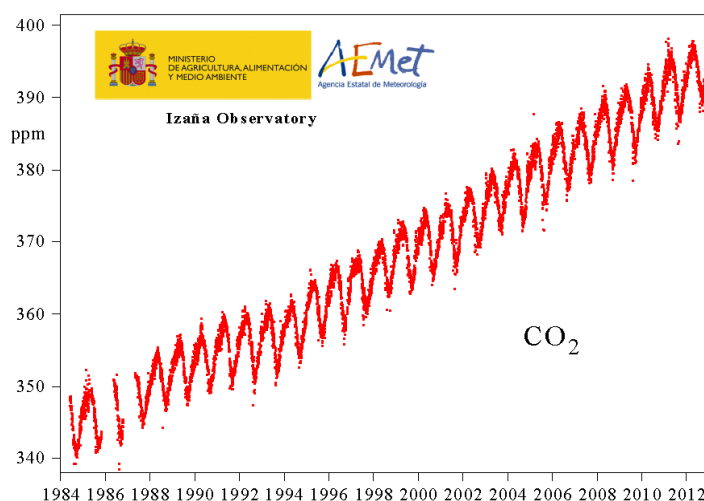


Figure 2 – Daily night-time (20:00 – 08:00 UTC) mean CO₂ mole fractions measured at IZO.

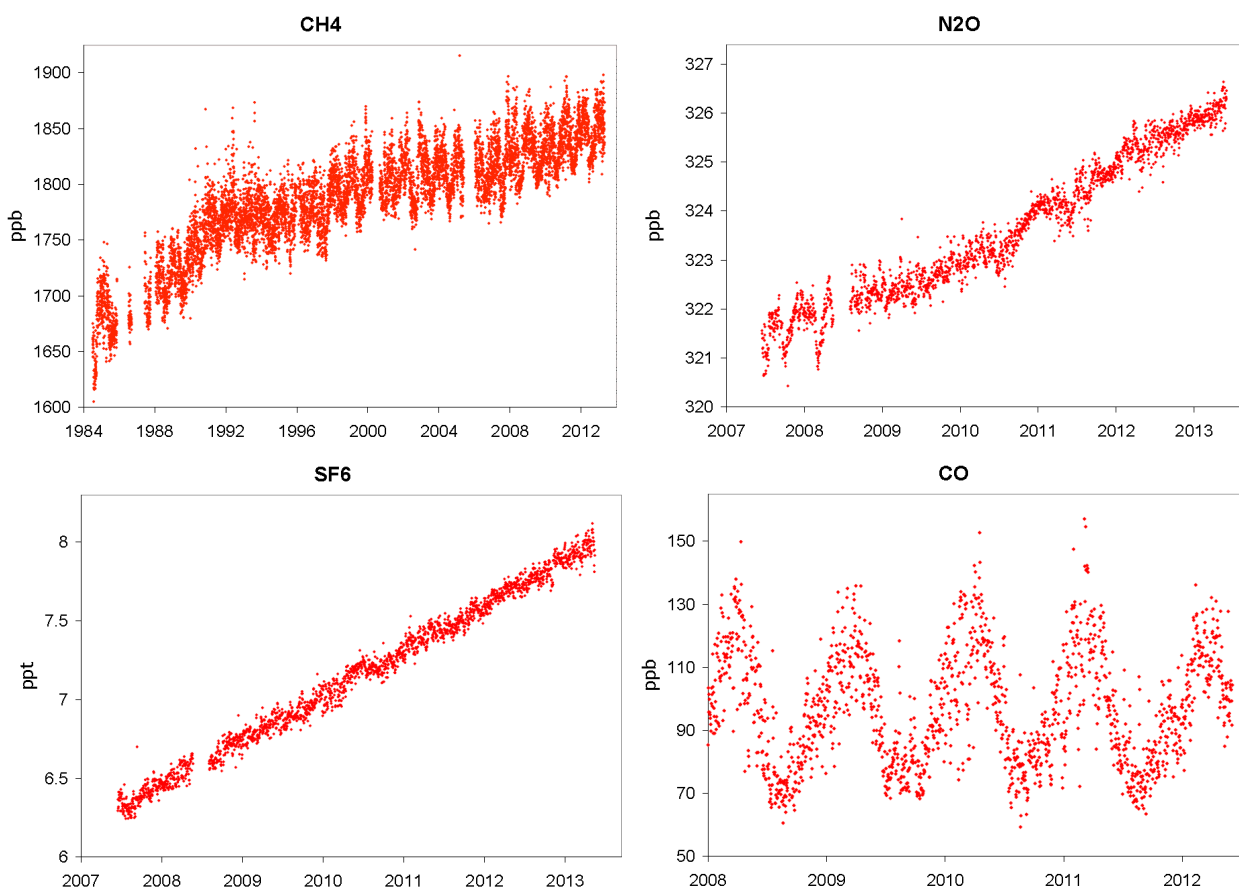


Figure 3 – Daily night-time (20:00 – 08:00 UTC) mean CH₄, N₂O, SF₆ and CO mole fractions measured at IZO.

3. Changes introduced in the GHG measurement systems

In the IZO old GC-FID (Dani 3800), the sample loop always had been out of the column oven. In May 2012 we introduced it inside the oven. In June 2012, we installed a new FID temperature controller, and selected a new FID temperature: 225 °C instead of 110 °C.

In August 2012, we changed slightly the temporal programming of the 3-port-2-position solenoidal valve V4 (which has one inlet for the air to be analysed, and two outlets: one connected to the sample loop of the GC-FID and another one connected to the sample loop of the GC-ECD) of the GC-Varian (see Figure 1 of Gomez-Pelaez&Ramos, 2009) to prevent the potential problem detailed as follows. We realised that when a GC injection valve is in inject position, the sample loop contains carrier gas at a pressure significantly higher than the ambient one. Therefore, when the valve goes to load position, the carrier gas inside the loop expands and partly goes out of the loop. If in this moment the inlet of the loop is not closed at valve V4, perhaps a small amount of the carrier gas might reach the mass flow controller located just upstream of valve V4 and then reach the other sample loop. This seems to be undesirable, especially the possibility that some Ar/CH₄ of the GC-ECD system might reach the loop of the GC-FID system, in spite of the fact that such loop is flushed after such hypothetical event.

Before April 1st, 2013, two NDIRs were working in series at Izaña measuring CO₂. After that date, they were separated completely (see Figure 4), and since then, each one has had its own laboratory standards, working standards and ambient inlet line.

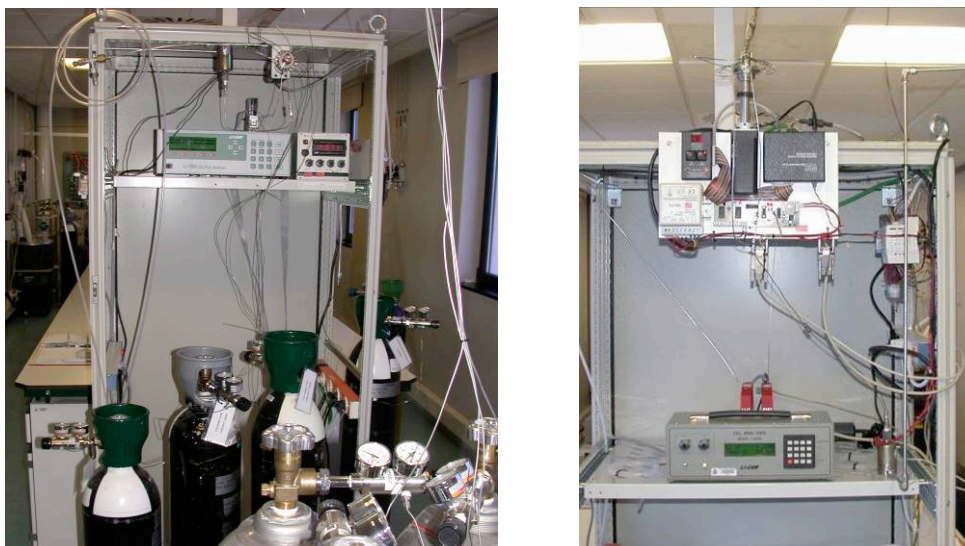


Figure 4 – IZO's Licor-7000 (left picture) and Licor-6252 (right picture) after their complete separation in April 2013

4. Changes introduced in the raw data processing software

IZO submits to the WDCGG hourly, daily and monthly means for all the gases within the greenhouse-gas programme. The daily and monthly means we had been submitting included the 24 hours of every day. In August 2011, we recomputed for all the time series the daily and monthly means using only data from 20:00 to 08:00 UTC (night-time pure background conditions), and resubmitted them to the WDCGG. We have continued submitting data in this new way since then.

For the raw data processing of the CO₂ measured at Izaña with the Licor-7000, we apply F-Snedecor tests to decide if the working standards have drifted in time (see Gomez-Pelaez&Ramos, 2011). We had been requiring a 99% confidence level to reject the hypothesis of no drifting. However, in May 2012, we decided to use a 95% confidence level, and then we reprocessed (and resubmitted to the WDCGG) using this criterion the whole time series measured with this instrument.

The IZO Licor-7000 measures three working gases from minute 30:00 till 39:00 of every hour, whereas the rest of the hour this instrument measures ambient air. We had been discarding only the first minute after minute 39:00 (cell flushing). However, in May 2012, we implemented the rejection of four minutes instead of one for the period January 2007-August 2010, due to a flow transition problem that we identified and solved in September 2010. Then, we reprocessed (and resubmitted to the WDCGG) the time series.

5. Published peer-review article concerning CO measurement uncertainty

In cooperation with Paul Novelli (NOAA-ESRL-GMD-CCGG), we have published the peer-review article Gomez-Pelaez et al. (2013) in AMT (GGMT-2011 special issue). This paper presents mainly a method to rigorously quantify the uncertainty in the CO measurements carried out at the Izaña station using a GC-RGD (RGA). This method could be applied to other GAW stations, not only for CO but also for other GHG measurements (especially if they are carried out using a GC).

We would like to bring to the attention of the reader the paper Sepúlveda et al. (2012), which was prepared by the IARC (O.E. García and E. Sepúlveda) and KIT-IMK FTIR (T. Blumenstock, F. Hase, M. Schneider and S. Dohe) groups in cooperation with the IARC in situ GHG group. This paper uses IZO in situ CH₄ measurements to validate tropospheric column-averaged CH₄ mole fractions obtained by the mid-infrared ground-based FTIR spectrometer which has been in operation at Izaña since 1999.

6. Installation of a system to measure flasks at Izaña

By the end of May 2013, we had almost finished installing at Izaña a system to measure GHG mole fractions in air samples stored in flasks. The system is based on some of the instruments used at IZO to carry out continuous GHG measurements. This means that in situ measurements will not be carried out by these instruments while flasks are being measured. This is not a problem since flask measurements are going to be occasional and only during daytime (background conditions hold at IZO during night-time).

Air samples will be collected mainly on board an aircraft flying near Izaña to get in situ atmospheric vertical profiles of trace gases in the framework of occasional campaigns promoted by financed projects (e.g. MUSICA-AMISOC campaign in July 2013). Additionally to the intrinsic value of the in situ vertical profiles, they will be compared with column measurements carried out by the Izaña FTIR and by the IASI instrument (on board a satellite).

The flasks to be measured are contained in two PFPs (Programmable Flask Packages; see Figure 5). Air sampling will be carried out using a PFP connected in series with a PCP (Programmable Compressor Package). IARC-AEMET purchased at the end of 2011 two PFPs and one PCP. They were designed by NOAA-ESRL-GMD-CCGG and manufactured by HPD.

The system we have implemented to vacuum the PFP manifold, extract air from the flasks and distribute it (see Figure 5) to the instruments is similar to that used in MAGIC (the system that NOAA-ESRL-GMD-CCGG uses to measure flasks). The control software has been created at IARC.

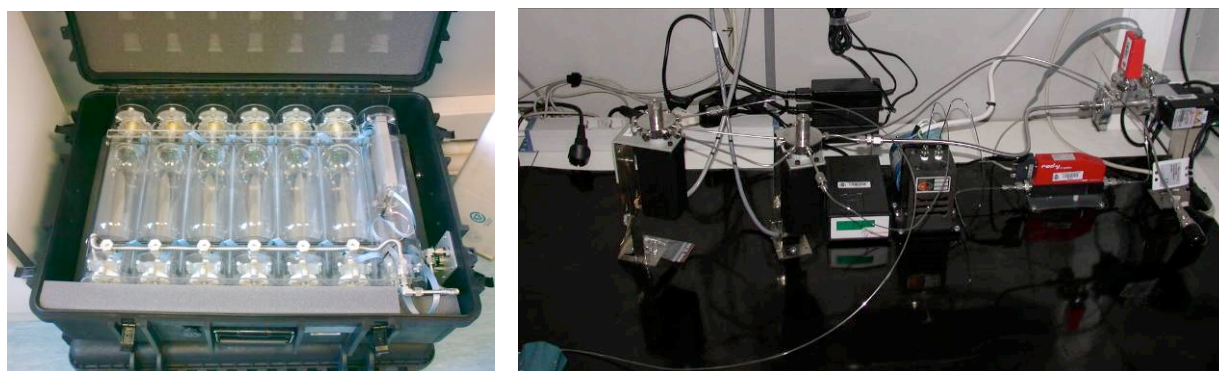


Figure 5 – Left picture: interior of a PFP. Right picture: a part of the system implemented at IZO to vacuum the PFP manifold, extract air from the flasks and distribute it to the instruments

AJGP is grateful to Doug Guenther, Anna Karion and Jack Higgs for providing information about the PFPs and PCPs; and to Andrew Crowell and Tom Conway for providing information about MAGIC (NOAA-ESRL-GMD-CCGG).

References

- Gomez-Pelaez, A.J., Ramos, R., *Installation of a new gas chromatograph at Izaña GAW station (Spain) to measure CH₄, N₂O, and SF₆* in GAW Report (No. 186) of the "14th WMO/IAEA meeting of experts on Carbon dioxide, other greenhouse gases, and related tracers measurement techniques (Helsinki, Finland, 10-13 September 2007)", edited by Tuomas Laurila, World Meteorological Organization (TD No. 1487), Geneva, Switzerland, 55-59, 2009
- Gomez-Pelaez, A.J., Ramos, R., *Improvements in the Carbon Dioxide and Methane Continuous Measurement Programs at Izaña Global GAW Station (Spain) during 2007-2009*, in GAW report (No. 194) of the "15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques (Jena, Germany; September 7-10, 2009)", edited by Willi A. Brand, World Meteorological Organization (TD No. 1553), Geneva, Switzerland, 133-138, 2011
- Gomez-Pelaez, A. J., Ramos, R., Gomez-Trueba, V., Campo-Hernandez, R., Dlugokencky, E., and Conway, T., *New improvements in the Izaña (Tenerife, Spain) global GAW station in-situ greenhouse gases measurement program*, in GAW report (No. 206) of the "16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (Wellington, New Zealand, October 25-28, 2011)", edited by Gordon Brailsford, World Meteorological Organization, Geneva, Switzerland, 76-81, 2012.
- Gomez-Pelaez, A. J., Ramos, R., Gomez-Trueba, V., Novelli, P. C., and Campo-Hernandez, R., *A statistical approach to quantify uncertainty in carbon monoxide measurements at the Izaña global GAW station: 2008–2011*, Atmos. Meas. Tech., 6, 787-799, doi:10.5194/amt-6-787-2013, 2013.
- Sepúlveda, E., Schneider, M., Hase, F., García, O. E., Gomez-Pelaez, A., Dohe, S., Blumenstock, T., and Guerra, J. C., *Long-term validation of tropospheric column-averaged CH₄ mole fractions obtained by mid-infrared ground-based FTIR spectrometry*, Atmos. Meas. Tech., 5, 1425-1441, doi:10.5194/amt-5-1425-2012, 2012.
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RECENT ANALYSIS OF THE WMO CO₂ PRIMARY STANDARDS

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1. Introduction

The WMO CO₂ reference scale is maintained by the NOAA Global Monitoring Division. The core range of the scale is defined by 15 primary standards, consisting of modified natural air in 46.4-L aluminium cylinders. The assigned CO₂ mole fractions are determined from an average of numerous manometric analysis spanning ~16 years. Manometric analysis is performed approximately every two years. Results from “calibration episodes” are also used to determine potential drift. Manometric analysis of the WMO primary standards was performed from Jul. 2012 – Feb. 2013, and is hereafter referred to as the “2012 calibration episode”.

A unique aspect of the 2012 calibration episode is that it followed a personnel change at NOAA/ESRL. Since ~1995, the NOAA manometer was maintained and operated by Conglong Zhao (Zhao and Tans, 2006). Following his retirement those responsibilities were transferred to Duane Kitzis and Brad Hall. The 2012 calibration episode is the first in the NOAA series not conducted by Conglong Zhao. Here we report on the 2012 calibration episode. We compare the 2012 results to previous results and examine possible drift in primary standards.

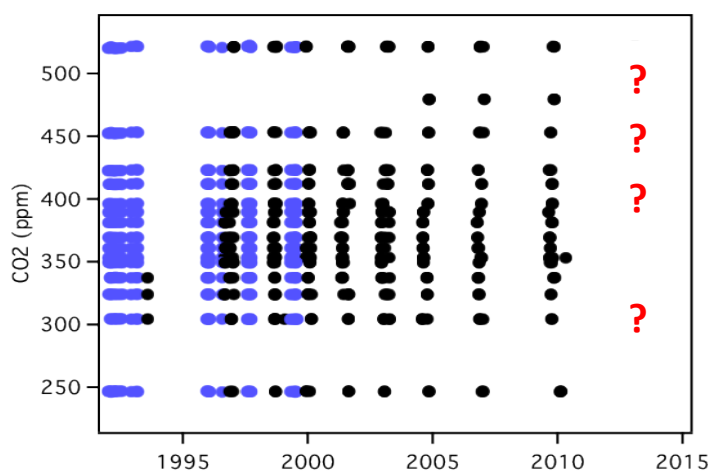


Figure 1 - Calibration history of WMO primary standards prior to the 2012 calibration episode showing SIO results (blue) and NOAA results (black)

2. Traceability

Because the manometer provides an absolute measure of CO₂ mole fraction, traceability to SI must be ensured. The typical steps associated with a primary standard calibration episode include: a) calibration of all critical parameters to ensure traceability to SI (e.g. calibration of devices used to measure pressure and temperature); b) determination of the relevant volumes needed to determine CO₂ mole fractions (hereafter referred to as the “volume ratio (VR)”); c) manometric analysis of each primary standard over multiple days; d) reassessment of traceability and the volume ratio periodically during the period of primary measurement; and e) analysis of all

primary standards by NDIR after manometric determinations are complete. Only steps “a”-“d” will be discussed here. Step “e” had not been completed at the time of the GGMT.

Calibration of temperature sensors is normally performed by an accredited laboratory. The pressure sensor (Paroscientific, 6000-15A) is calibrated in-house using a Ruska 2465A gas piston gauge, which is calibrated by an accredited laboratory. Prior to the CO₂ calibration episode, three platinum resistance thermometers, one thermistor, and a digital interface were calibrated by Fluke (American Fork, Utah). The Ruska 2465A piston gauge was also calibrated by Fluke (Phoenix, Arizona). No significant changes in calibration parameters were noted for either the piston gauge or the temperature devices. Calibration parameters determined by Fluke in 2012 were used throughout the 2012 calibration episode. The Paroscientific pressure sensor was calibrated multiple times from May 2012-Aug. 2012 and again in March 2013 following analysis of all primary CO₂ standards. The same calibration coefficients were used throughout the 2012 episode.

The volume ratio was determined through repeated gas expansion experiments as described by Zhao et al. (1997). Initially, volume ratio experiments showed considerable variability (Fig. 2). What’s more, the volume ratio used in previous calibration episodes could not be reliably verified. It appeared that the volume ratio had changed, but a precise measure of the new VR was not possible due to poor repeatability. We discovered that the baseline (“zero”) of the Paroscientific pressure sensor was drifting upward during the volume ratio experiments. When this drift was accounted for, precision of the volume ratio measurements improved dramatically (Fig. 2).

The volume ratio is a critical element in the manometric determination of CO₂ mole fractions (Zhao and Tans, 2006). The VR determined in 2012 was 897.67 ± 0.02 . The VR ratio used for prior calibration episodes (2004-2010) was 897.3. This difference is significant, and corresponds to 0.16 ppm CO₂ at 395 ppm CO₂.

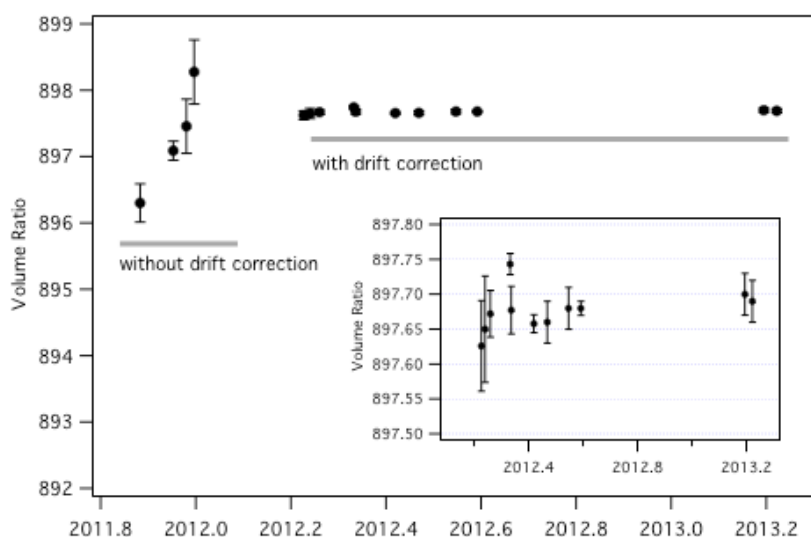


Figure 2 - Results from volume ratio experiments before and after drift correction was implemented. Inset shows all valid experiments used to determine the volume ratio for the 2012 calibration episode

3. Results

Results for primary standards from the 2012 calibration episode are shown in the Table 1. Most of the results are within 0.05 ppm of mole fractions assigned on the WMO-CO₂-X2007 scale. The mean difference among all primary standards is 0.01 ppm. In the ambient CO₂ range, most results show good agreement with X2007. The average difference in the range 360-412 ppm is also 0.01. Note that this mean difference would have been much larger had the previous volume ratio of 897.3 been used.

Table 1 - Results from the 2012 calibration episode, assigned mole fractions on the X2007 scale, and differences between 2012 and X2007. All CO₂ mole fractions are pmol mol⁻¹ (ppm)

Primary	2012 CO2	2012 s.d.	N	X2007 CO2	2012-X2007
AL47-110	246.63	0.11	4	246.65	-0.02
AL47-102	304.38	0.06	5	304.35	0.03
AL47-111	324.05	0.08	6	323.99	0.06
AL47-130	337.32	0.06	3	337.31	0.02
AL47-121	349.47	0.04	4	349.39	0.08
AL47-139	360.92	0.05	4	360.89	0.03
AL47-105	369.38	0.09	5	369.40	-0.02
AL47-136	381.34	0.03	4	381.36	-0.01
AL47-146	389.65	0.06	5	389.55	0.10
AL47-101	396.32	0.05	5	396.32	0.00
AL47-106	412.08	0.05	4	412.11	-0.03
AL47-123	423.04	0.05	3	423.07	-0.02
AL47-107	453.08	0.05	3	453.05	0.02
ND17440	479.51	0.04	3	479.51	0.00
AL47-132	521.38	0.05	4	521.42	-0.04

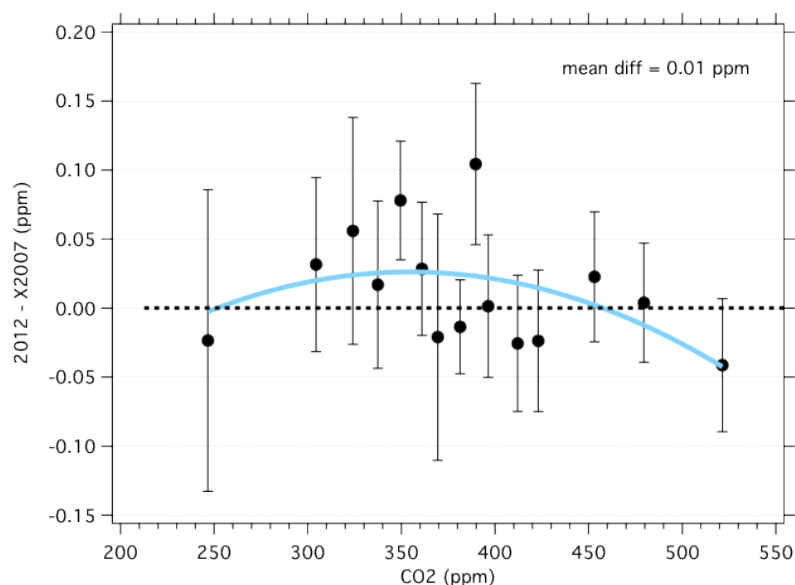


Figure 3 - Differences between results of the 2012 calibration episode and assigned values on the X2007 scale. The blue curve is a polynomial fit to the 2012 residuals

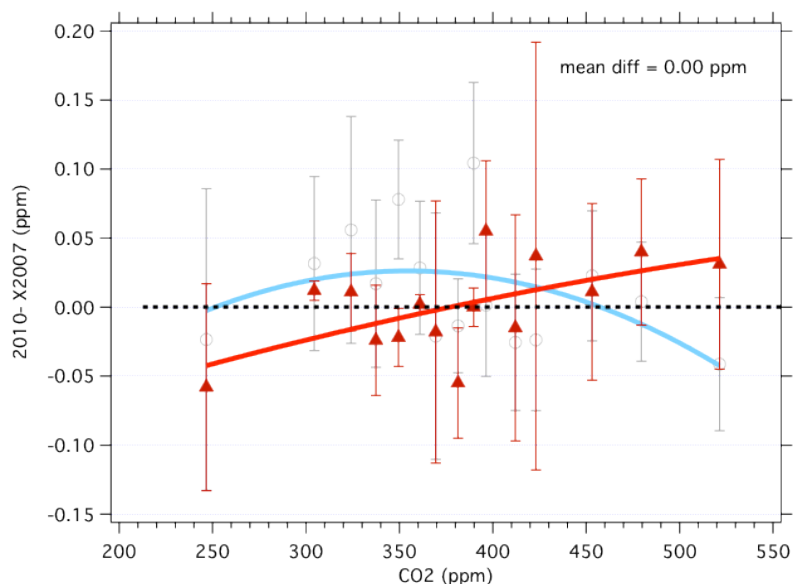


Figure 4 - Same as figure 3 for the 2010 calibration episode. The red line is a linear fit to the 2010 residuals. 2012 results are shown in light gray and blue for comparison

Overall, the 2012 results and level of repeatability are similar to those determined in previous episodes (Fig 4). However, some primary standards showed relative large differences compared to X2007. In 2010, primary AL47-146 was 0.04 ppm higher than X2007. In the 2012 the difference was 0.10 ppm. A statistical analysis of all results for this cylinder indicates a drift rate of $0.007\text{-}0.009 \pm 0.003 \text{ ppm yr}^{-1}$ (Fig. 5). AL47-146 is the only primary standard showing significant drift. Because this drift rate is small, the assigned value has not been updated. We continue to use X2007 assignments, but will reassess AL47-146 following the next calibration episode in 2014. Differences between the 2012 episode and X2007 are sufficiently small for all standards that a scale update is not warranted at this time.

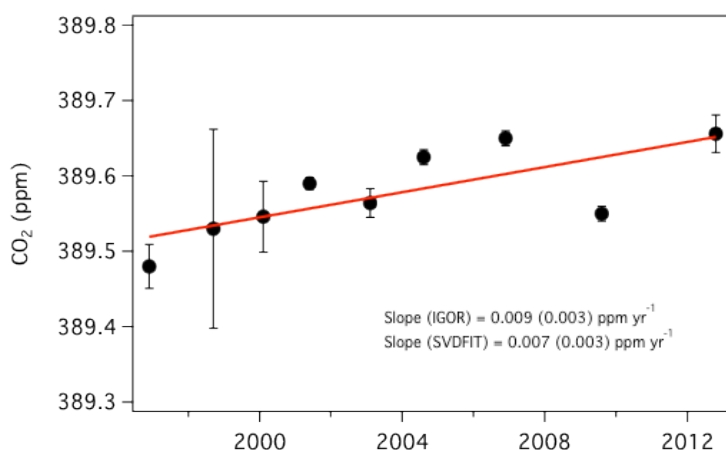


Figure 5 - Calibration history for cylinder AL47-146. A small rate of drift has been detected using two different fitting routines

5. Conclusions

The 2012 CO₂ calibration episode was completed. This marks the first time that the NOAA manometric analysis of the WMO primary standards was performed by someone other than Conglong Zhao. The volume ratio determined in 2012 was 0.04% higher than that used for recent calibration episodes. The reason for the change in the volume ratio is unknown, but we are confident that we can determine the volume ratio with sufficient repeatability should future changes occur.

The mean difference between 2012 results and the X2007 scale is 0.01 ppm. One standard appears to be drifting, although at a very slow rate. Differences between the 2012 episode and X2007 are sufficiently small for all standards that a scale update is not warranted at this time.

References

- Zhao, C. L., P. P. Tans, and K. W. Thoning, (1997), A high precision manometric system for absolute calibrations of CO₂ in dry air, *J. Geophys. Res.*, 102, D5, pp. 5885-5894.
- Zhao, C. L., and P. P. Tans (2006), Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, *J. Geophys. Res.*, 111, D08S09, doi:10.1029/2005JD006003.

HOW WELL DO TALL TOWER MEASUREMENTS CHARACTERIZE THE MID-PBL CO₂ MOLE FRACTION?

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1. Introduction

Mathematical models developed to describe the atmospheric carbon budget need the spatial distribution of carbon dioxide (CO₂) mole fraction as input or for validation. Low-resolution and Lagrangian models use/calculate the carbon dioxide mole fraction for the well-mixed planetary boundary layer (PBL) represented by the middle layer between the surface and the top of the PBL, while more recent, fine resolution ones have several model-layers even within the PBL.

The closer to the ground the measurements are performed the stronger the surface effects (local uptake/release by the vegetation, anthropogenic emission etc.), and the measured CO₂ mole fraction may significantly deviate from that at the middle of the PBL. Introduction of tall towers extending above the directly influenced surface layer offers better estimations. However, the uncertainty with which a tower of a given height estimates the mid-PBL CO₂ mole fraction has not been studied systematically yet.

In this study we estimate the uncertainty with which measurements on a tower characterize the mid-PBL CO₂ mole fraction. In turn, the height of the tower required for a given uncertainty criterion can be determined. The virtual tall tower (VTT) concept is tested whether it can improve the mid-PBL CO₂ mole fraction estimations. For the study the aircraft vertical profiles and tall tower measurements performed at and over a rural Hungarian monitoring site during 2006-2008 are used.

2. Data and methods

CO₂ mole fraction data used in this study derive from a tall tower (115 m) monitoring site located in rural environment in Western Hungary (Hegyhátsál, 46°57'N, 16°39'E, 248 m a.s.l.) above which frequent airborne *in situ* CO₂ measurements were also performed in the early afternoon hours during 2006-2008 (250-3000 m above ground). The tower also hosts an eddy covariance system at 82 m above the ground for the continuous monitoring of the vertical flux of CO₂ and sensible heat. These latter data were used to test the VTT concept first presented by Davis (2005). For the comparability of the data all CO₂ analyzers were calibrated against standards traceable to WMO Central Calibration Laboratory operated by NOAA, U.S.A. Details on the tall tower and airborne measurements can be found in Haszpra et al. (2001; 2010; 2012). Data on the height of the planetary boundary layer were retrieved from the MARS database of the European Centre for Medium-Range Weather Forecasts (ECMWF) and linearly interpolated for the time of the measurements.

As the present study focuses on the mid-PBL, only those airborne profiles could be used when the PBL was at least as high as 300 m and measurement for mid-PBL elevation was available. With these constraints a total of 136 vertical CO₂ profiles were available for the study. VTT concept could be applied only for 75 vertical profiles due to missing data or negative sensible heat flux caused by random error in the measurements.

The airborne *in situ* measurements completed by the tall tower ones record the real vertical distribution of carbon dioxide in the lower troposphere. The airborne *in situ* measurements also give the real value of the mid-PBL CO₂ mole fraction for the time when the aircraft reaches this elevation. This value can be compared with the values measured below the mid-PBL by the aircraft, simulating the top of a hypothetical tall tower, or by the existing tower. This comparison gives information on how well a lower-than-mid-PBL tower could estimate the mid-PBL CO₂ mole fraction. For the calculations the airborne *in situ* measurements were layer-averaged with 25 m vertical resolution from 200 m above the ground up to the middle of the PBL. It was supposed that a tower taller than the actual mid-PBL elevation could always provide the exact mole fraction value for the mid-PBL (zero bias) since it may have an air inlet at that elevation.

3. Results

Figure 1 shows the frequency distribution of the deviations between the measured CO₂ mole fraction in the mid-PBL as the function of the height of the hypothetical tower on the top of which the CO₂ mole fraction could be measured. Taking into account the significantly different surface processes and atmospheric dynamics in different seasons the results are separated for the summer (April-September) and winter (October-March) half years.

In summer the shorter the tower, the higher the underestimation of the mid-PBL mole fraction. It is caused by the fact that usually in summer daytime the surface is a net CO₂ sink due to the uptake by the vegetation. In winter the situation is just the opposite: the surface is a net source due to no or negligible CO₂ uptake by the dormant vegetation, while emission can accumulate close to the surface due to the weak vertical mixing of the atmosphere.

Figure 2 shows the probability with which the bias remains below a given limit as a function of the height of the tower. This figure can be used to determine the height of a tower satisfying a given uncertainty requirement or to evaluate the performance of an existing tower.

In principle, application of the VTT concept might improve the estimation of the mid-PBL CO₂ mole fraction. Figure 3 shows the difference between the biases with which the concentration measurement at a given elevation alone and completed by the VTT method estimates the mid-PBL CO₂ mole fraction. Positive numbers give how much the estimation applying the VTT concept is closer to the real mid-PBL value than the estimation based only on the concentration measurement carried out at the given elevation. Significant improvement in the mid-PBL CO₂ mole fraction estimation can only be achieved in summer in the case of relatively short towers (<100 m) and near-ground monitoring sites.

4. Summary and limitations

The results inform the modelers on the uncertainty of the mid-PBL CO₂ mole fraction estimated from near-ground or tower measurements what they must take into account when the results of the models are evaluated. Application of the VTT concept may improve the performance of the shorter towers, especially in summer. The results are valid for low elevation, continental regions covered by vegetation in the temperate zone.

5. Acknowledgement

The monitoring program at and above Hegyhátsál tall tower site was supported by the 6th R&D Framework Programme of the European Commission (CarboEurope-IP - GOCE-CT-2003-505572, IMECC – RII3 026188), by the Hungarian Ministry of Economy and Transport (GVOP-3.2.1.-2004-04-0107/3.0), as well as by the Hungarian Scientific Research Fund and the National Development Agency (KTIA-OTKA CK77550, OTKA K104816). The authors thank Martin Simon (Air Taxi Ltd.), pilot of the aircraft hired for the airborne measurements, and his crew for operating the *in situ* CO₂ analyzer during the flights.

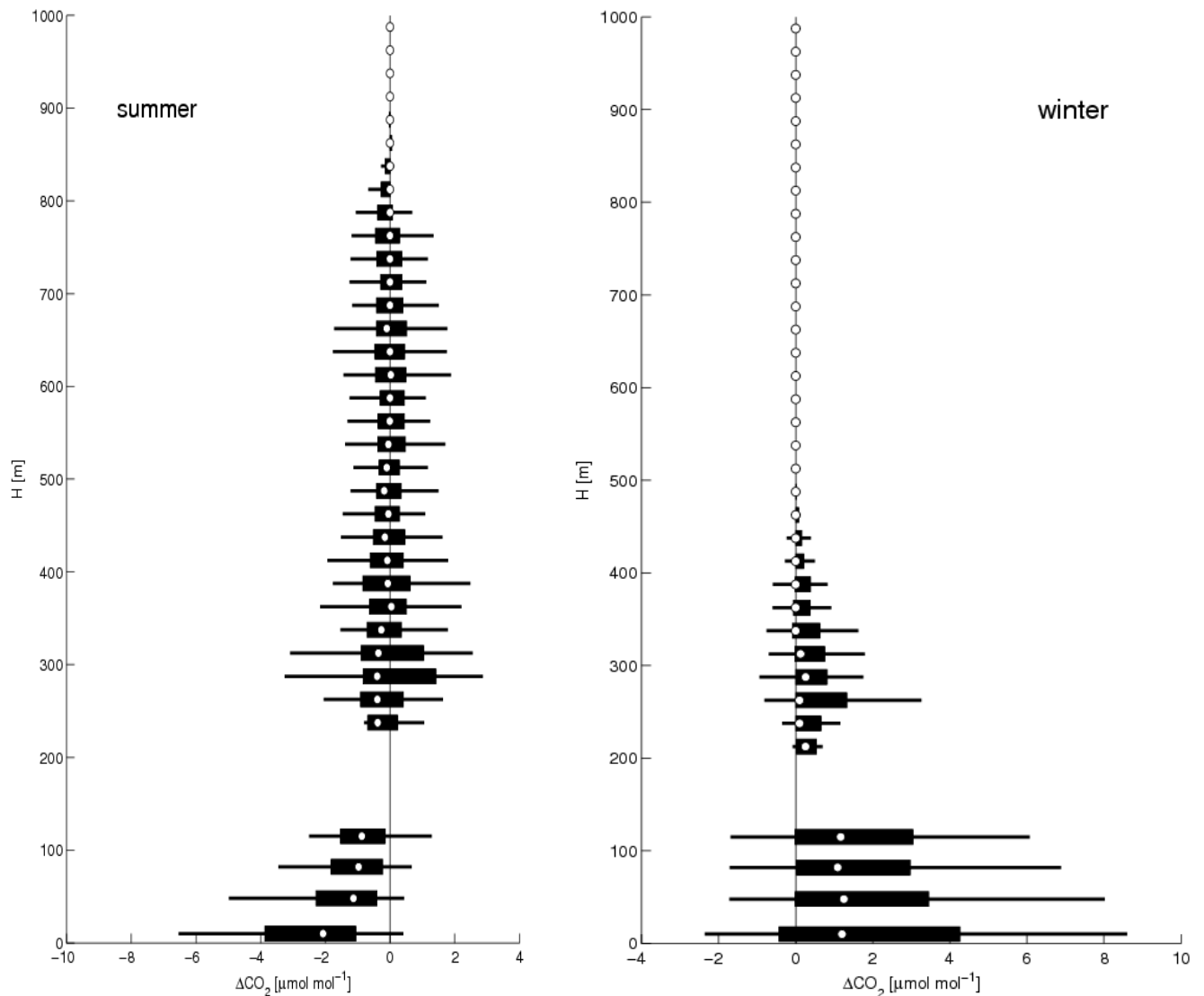


Figure 1 - Empirical frequency distributions of the difference between the CO₂ mole fraction measured at a given height and the mid-PBL CO₂ mole fraction. Whiskers represent the lowest value still within 1.5 interquartile range (IQR) of the lower quartile, and the highest value still within 1.5 IQR of the upper quartile, respectively

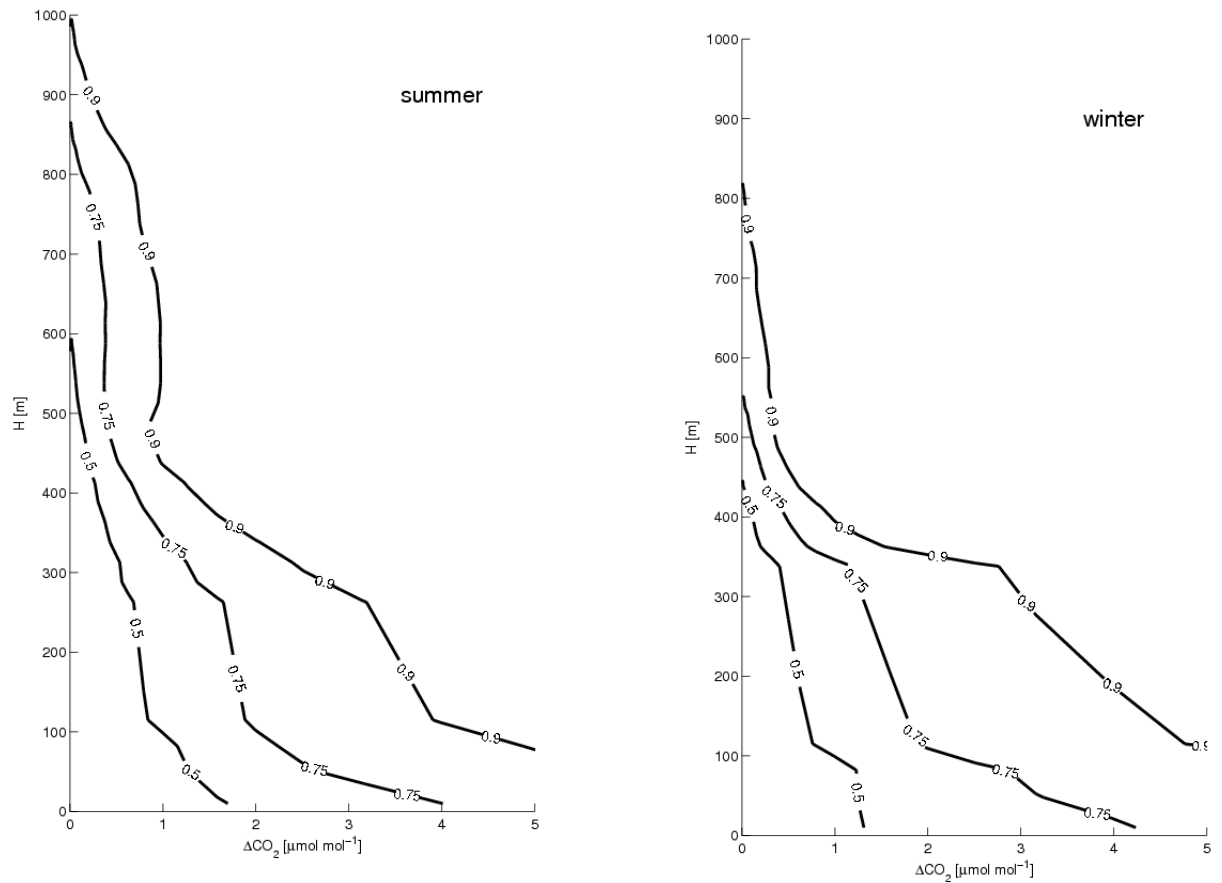


Figure 2 - Empirical probability of the cases when the bias from the mid-PBL CO₂ mole fraction does not exceed a given value at a given elevation

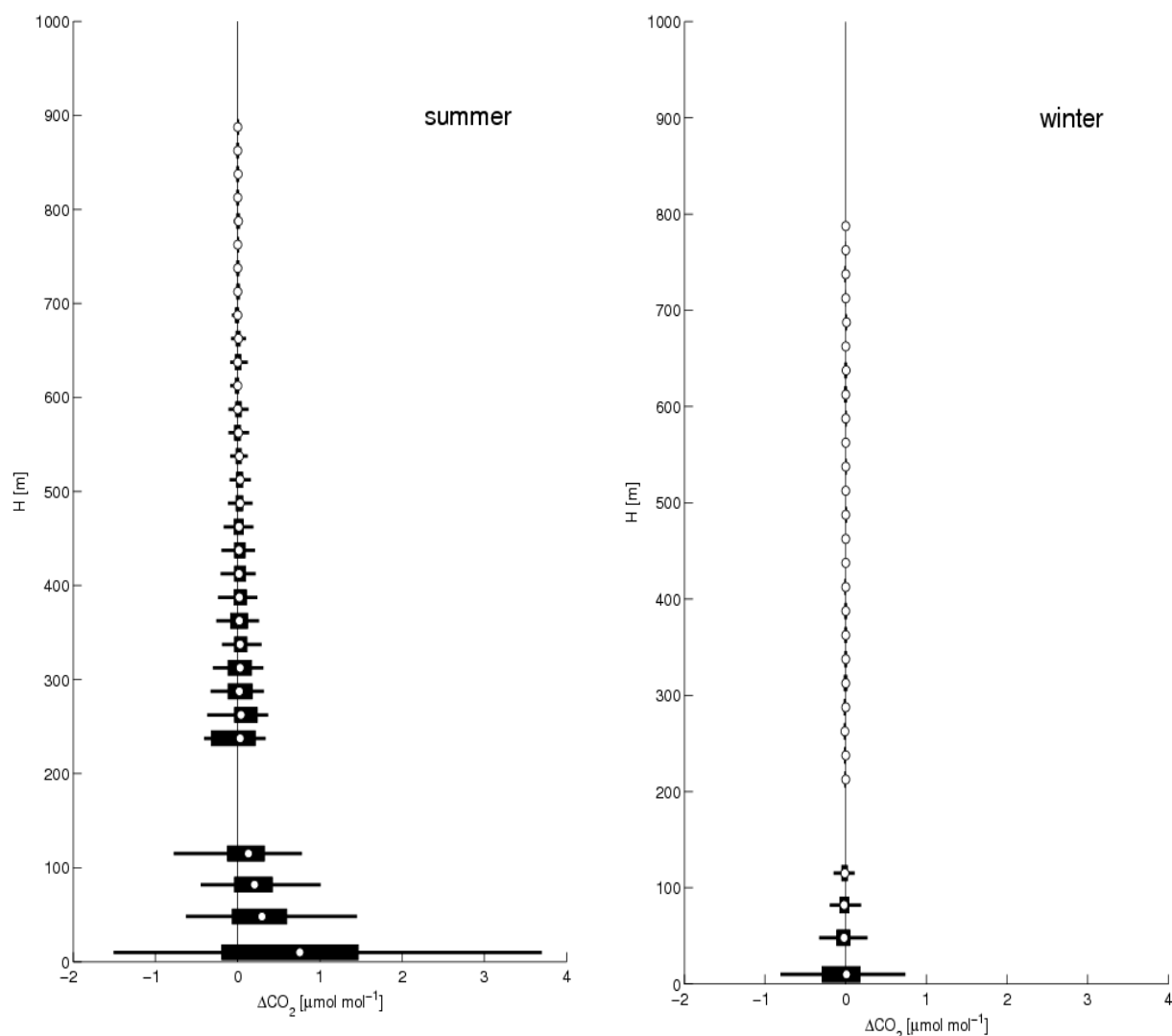


Figure 3 - Empirical frequency distributions of the improvement in the mid-PBL CO₂ mole fraction estimation achieved by means of the application of the VTT concept

References

- Davis, K. J., *Well-calibrated CO₂ mixing ratio measurements at flux towers: The virtual tall towers approach*. In: *WMO GAW Report no. 161 (12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, Toronto, Canada, 15-18 September 2003)*, 101-108, 2005.
- Haszpra, L., Z. Barcza, P.S. Bakwin, B.W. Berger, K.J. Davis and T. Weidinger, *Measuring system for the long-term monitoring of biosphere/atmosphere exchange of carbon dioxide*. *J. of Geophysical Research* 106D, 3057-3070, 2001.
- Haszpra, L., Z. Barcza. and I. Szilágyi, *Atmospheric trends and fluctuations - History and sites of atmospheric greenhouse gas monitoring in Hungary*. In: *Atmospheric Greenhouse Gases: The Hungarian Perspective*, Springer, Dordrecht- Heidelberg - London - New York, 9-23, 2010.
- Haszpra, L., M. Ramonet, M. Schmidt, Z. Barcza, Z. Pátkai, K. Tarczay, C. Yver, J. Tarniewicz and P. Ciais, *Variation of CO₂ mole fraction in the lower free troposphere, in the boundary layer and at the surface*. *Atmospheric Chemistry & Physics* 12, 8865-8875, 2012.

EVALUATION OF THE WMO H₂ CALIBRATION SCALE

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1. WMO Mole Fraction Scale of Molecular Hydrogen

Within the WMO GAW program compatibility goals are set that allow an interpretation of atmospheric measurement data obtained from different laboratories. To produce compatible data these measurements need to be traceable to common calibration scales, the WMO mole fraction scales maintained by the Central Calibration Laboratories. These have to perform regular determinations of the respective WMO scale with primary methods to link it to fundamental quantities (SI) and ensure the stability of the scale.

The WMO scale for molecular hydrogen is based on a series of 53 reference gases that have been produced in 2008 by mixing a constant volume of H₂ with variable amounts of H₂-free air (Jordan and Steinberg, 2011). The cylinders used for the preparation of these reference mixtures have proven in long-term storage tests to slowly produce hydrogen (0.7 ppb/month) prohibiting the use of these gases as primary standards. Therefore, the scale is represented by a set of 13 real air mixtures prepared in 2003-2007 with superior characteristics with respect to maintaining stable trace levels of hydrogen. These 13 primary standards have been assigned hydrogen mole fraction values by being thoroughly analyzed by gas chromatography with a HgO reduction detector that has been calibrated using the 53 reference gases.

2. Assessment of the scale stability

The entire set of primary standards has been analyzed using a gas chromatograph with helium ionization pulsed discharge detection (GC-HePDD) on twelve occasions between June 2010 and October 2013. A quadratic regression fit is applied to the GC-HePDD data normalized to a working standard. The residuals from this curve fit are displayed in Figure 1. There are consistent long-term residuals that are result of the initial assignment error, the adequacy of the response function and the measurement reproducibility. The stability of the residuals in Figure 1a documents the relative stability of these standards within 0.5 ppb during the three year period. As the primary standard set is contained in five different types of cylinders at different pressures the relative consistency of this large set is providing good evidence for the stability of the scale. However, in Figure 1b the residuals of two standards are depicted that have changed over time indicating a growth of hydrogen at a rate of 0.5 and 0.7 ppb/yr, respectively. Both standards are contained in 27 l stainless steel cylinders at 20 bar. In consequence these standards have been excluded from the set that defines the WMO scale.

In 2011 and 2013 another 14 and 12 mixtures of H₂ in air have been prepared, respectively, ranging from 500-1200 ppb to check the WMO hydrogen scale. In Figure 2 the differences between the GC-HePDD analysis results relative to the mole fractions of these gas mixtures (derived from the measured quantities during the preparation: volume, pressure, temperature, and mass) are displayed. There is a significant offset. However, the data set is still inconclusive whether there is a linear factor (of 0.4% on average) between the recent mixtures and the MPI-2009 scale or whether there is a constant offset of the scale of 2.5 ppb at the low end (<800 ppb) and an increasing deviation at higher mole fractions. This latter difference would be consistent with an undetected H₂ blank in the diluent air used for preparation of the primary standards in 2008 that

would have biased the assignment of the scale standards and an additional assignment error of the highest primary standard. A larger uncertainty in this standard assignment has already been suspected earlier.

There is no evident explanation for the other possibility of a linear deviation of the scale relative to the recent H₂ in air mixtures. To clarify the bias the procedure for preparing new mixtures will be re-assessed, to ensure the validity of this method. If after this examination of the method the next set of new mixtures will confirm the recent offset a scale revision will be made.

The two experimental series made in 2011 and 2013 agree within 0.5 ppb which provides additional evidence that the scale has not drifted over this time period.

References

Jordan, A. and Steinberg, B.: Calibration of atmospheric hydrogen measurements. *Atmos. Meas. Tech.*, 4, 509-521, 2011, doi:10.5194/amt-4-509-2011.

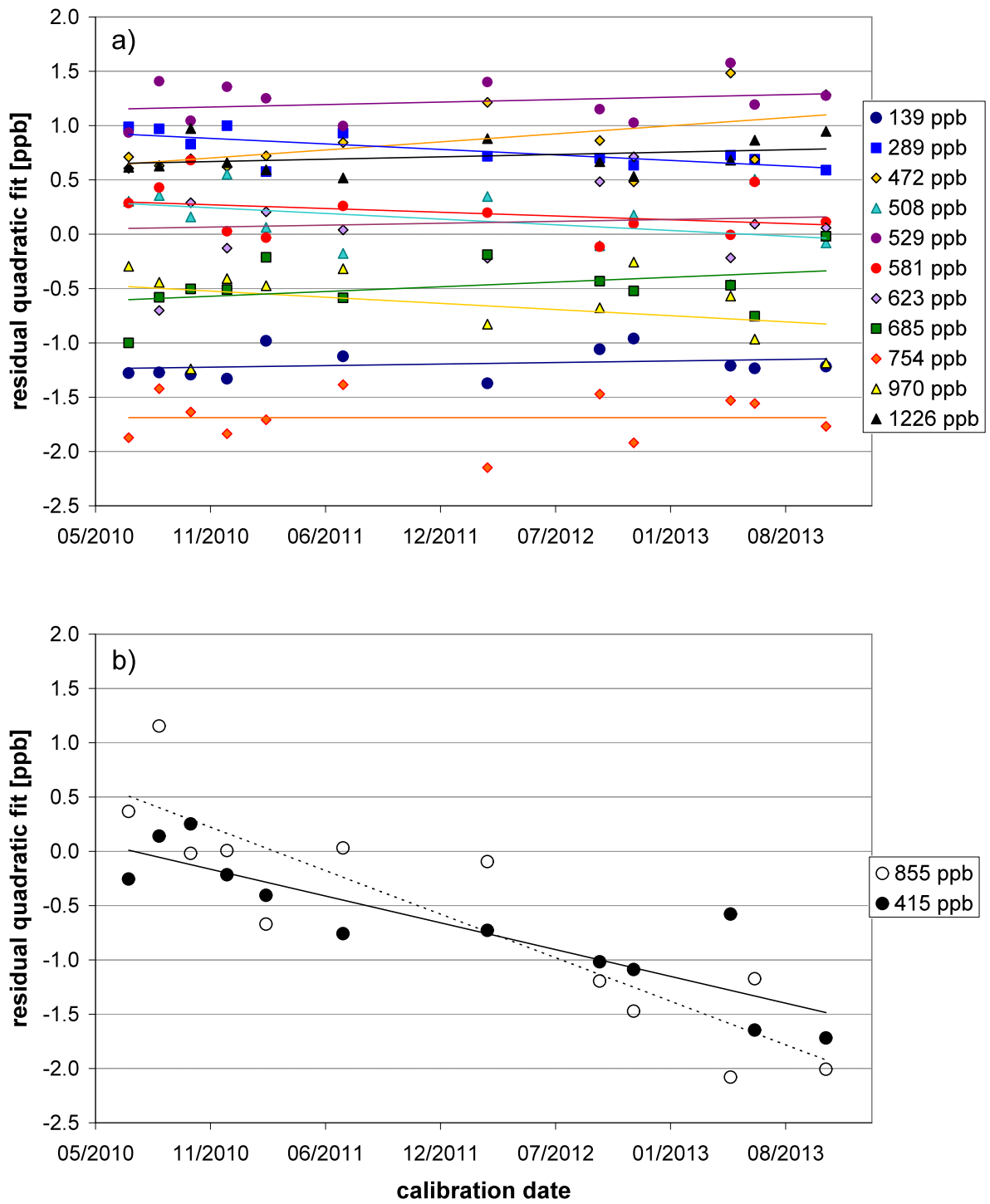


Figure 1 - Residuals of individual primary standards from the quadratic regression fit using the 11 standards with stable H₂ mixing ratios included in Fig. 1a

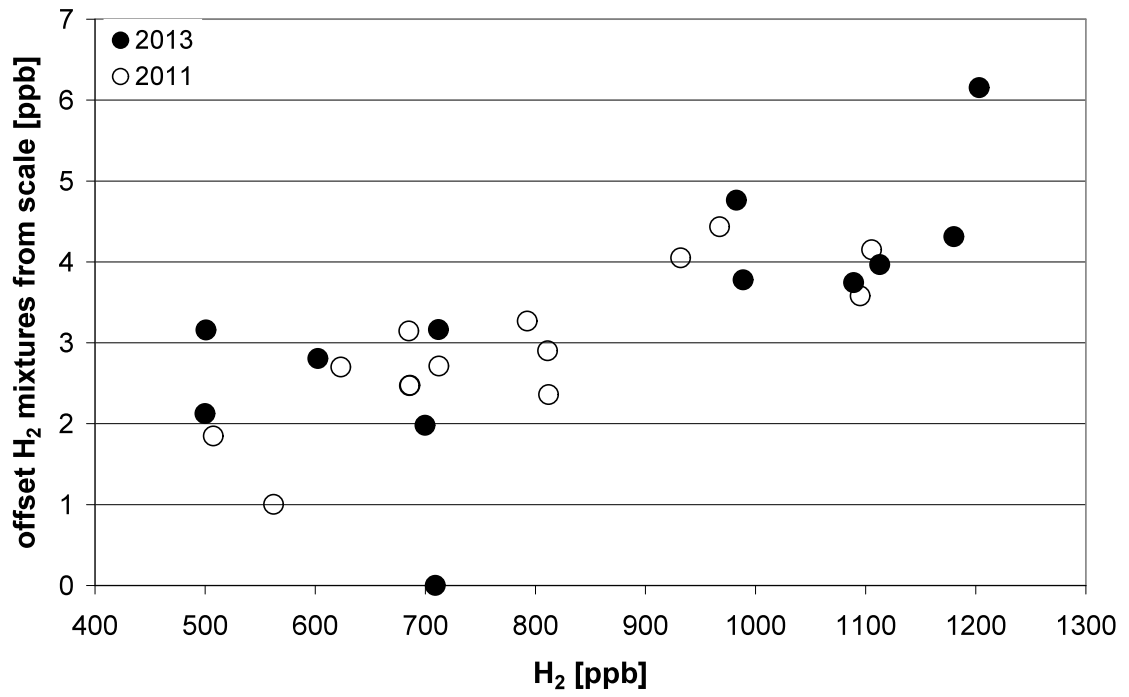


Figure 2 - Difference of the H₂ mixing ratio calculated from the known moles of hydrogen (derived from a pressure, temperature and volume measurement) mixed in known mass of hydrogen free air minus the GC-HePDD analysis result based on the WMO scale

DEVELOPMENT OF FIELD-DEPLOYABLE QCL SENSOR FOR SIMULTANEOUS DETECTION OF ATMOSPHERIC N₂O AND CO

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1. Introduction

Nitrous oxide (N₂O) is one of the anthropogenic greenhouse gases with a global warming potential ~300 times that of carbon dioxide (CO₂) and a long lifetime of ~120 years (Montzka et al., 2011). Primary production of N₂O is by terrestrial and marine microbial communities as a by-product of nitrification and denitrification reaction process. Its major sinks (photolysis and reaction with O(¹D)) occur in the stratosphere, leading to decreasing mixing ratios above the tropopause, while its tropospheric mixing ratio is almost constant at a level of 325 ppbv. Thus N₂O is an ideal tracer for stratospheric air masses. Carbon monoxide (CO) also plays an important role in atmospheric chemistry (Logan et al., 1981), because it is the largest sink for hydroxyl radical (OH). Moreover, carbon monoxide (CO) is an excellent tracer of anthropogenic emissions, with high mixing ratios (>100 ppbv) in the troposphere and low mixing ratios (<50 ppbv) in the stratosphere, making it an ideal tracer for tropospheric air masses. Simultaneous measurements of N₂O and CO allow us to distinguish between stratospheric and tropospheric air masses in the tropopause region. This requires a fast, sensitive and robust measurement technique, capable of airborne operation.

Quantum cascade lasers (QCLs) are relatively new sources of mid-infrared radiation, and are well suited to the application of in-field sensing, being robust, compact, wavelength-versatile, as well as with narrow line width and low power consumption. All that makes laser absorption spectroscopy based on these QCL lasers has become one of the most popular technologies for quantitative chemical detection in a variety of fields including atmospheric monitoring, industrial process control, security or bio-medical studies. In this paper, we report on the development of a field-deployable instrument based on a distributed feed-back (DFB) QCL operating at 4.56 μm for simultaneous, in situ detection of atmospheric trace gases N₂O and CO with high sensitivity, precision and temporal response.

2. Experimental details of CO and N₂O measurement

A complete system diagram illustrating optical and electrical paths is provided in Figure 1. A continuous-wave thermoelectrically-cooled DFB QCL (Aples Lasers) operating at room temperature was employed to probe N₂O and CO around 4.56 μm. A commercial laser temperature and current controller (Tektronix Munich, model ITC110, Karlsfeld, Germany) was modified to set the operation conditions of the QCL for wavelength tuning between 2187.6-2202.1 cm⁻¹ over a temperature range of 243-283 K with power range of 0.1-13.5 mW. The diverging laser beam was guided into an astigmatic Herriott absorption cell (Aerodyne Research, Inc., Model AMAC-36) and a short reference cell (3.5 cm) after being collimated by a series of flat mirrors (M), off-axis ellipsoid (OAE) and off-axis parabolic (OAP) mirrors. Finally both laser beams are focused onto two TE-cooled mercury cadmium telluride (MCT) infrared detectors (PVI-4TE-5, Vigo Systems). A compact cRIO chassis (National Instruments) integrated with two analog to digital converters and two digital to analog converters, was employed for real time processor and Field Programmable Gate Array (FPGA) for laser control, data acquisition and real-time analysis of acquired spectra. Newly developed software written in LabView and a FPGA (field-programmable

gate array) board is used for fully automated instrumentation control, data acquisition and signal analysis (Li et al., 2012).

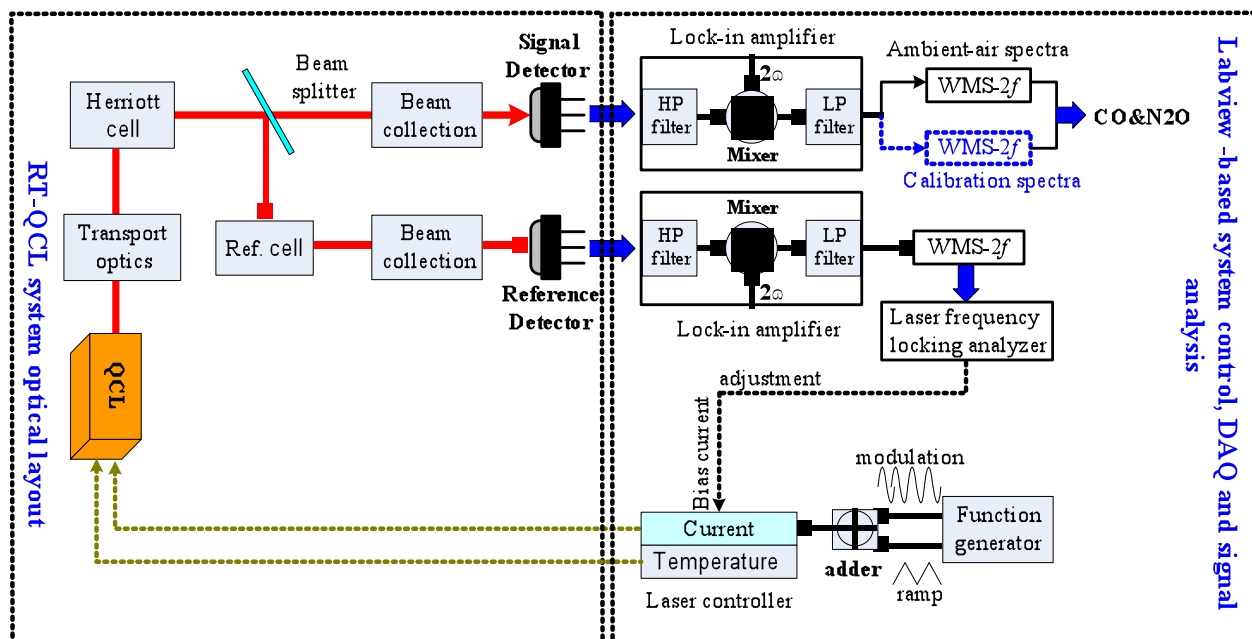


Figure 1 - Diagram of the RT-QCL system

In order to increase the sensitivity of the sensor, wavelength modulation spectroscopy (WMS) with second harmonic ($2f$) detection was employed. The QCL frequency was modulated by adding a 31.25 kHz sinusoidal signal to the injection current, while the laser frequency was tuned across the absorption lines using a triangular wave at a repetitive rate of 30.5 Hz. In WMS, the $2f$ signal was strongly influenced by the laser modulation depth, and maximization of the signal intensity occurs at modulation index of 2.2 (Reid et al., 1981), and thus the largest the SNR. In this study, the selected line pair for CO and N₂O detection was covered within a single current scan of the QCL. The single modulation amplitude can not satisfy modulation optimization for both species synchronously due to different air broadening coefficients (0.0702 cm⁻¹/atm for N₂O and 0.0561 cm⁻¹/atm for CO). To resolve this issue, a dual modulation scheme was developed as shown in Figure 2 (Upper panel). Experimentally the optimal modulation amplitudes were determined for both CO R(12) and N₂O P(35e) transition lines, respectively. The ratio of the optimal modulation amplitudes is in good agreement with the ratio of air broadening coefficients of the selected two transition lines. In addition, the molecule absorption signal intensity profile presents two opposing pressure effects: decreasing spectral line centre intensities due to pressure broadening and an increasing absorber number density with increasing pressure. Figure 2 (Lower panel) shows the simulated optical density at centre position as a function of total pressure. As we can see, the optimum total pressure for the line pairs selected for CO and N₂O detection was found to be around 200 mbar. However, two underlying N₂O lines contribute slightly to the absorption in right wing of the selected N₂O absorption region at high pressure, as shown in the inset. Therefore, the ideal operating pressure of approximately 100 mbar was finally used for simultaneous CO and N₂O detection.

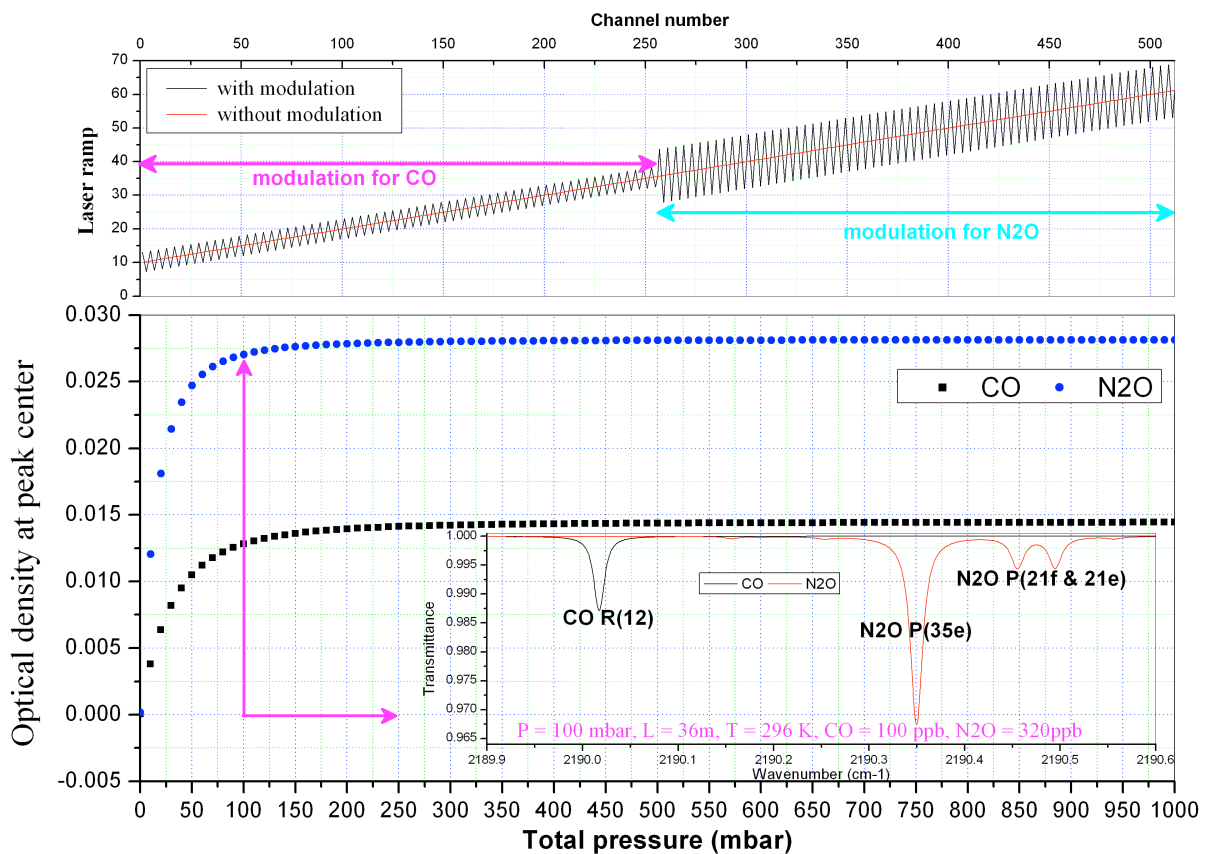


Figure 2 - Upper panel: dual modulation scheme for simultaneous N₂O and CO detection. Lower panel: variation of CO (R(12) transition) and N₂O (R(35e) transition) optical density at peak center with sample pressure

The sensor's performance regarding precision and stability (short-term) was characterized using the Allan variance technique (Werle et al., 1993), based on a 10-min time series of measurements of a certified primary air standards (Scott Marrin Specialty Gases, Inc.) with known CO and N₂O concentrations (as shown in Figure 3). The Allan variance is plotted in a log-log scale versus the averaging time τ , indicating a 1-s measurement precision of 0.64 ppb and 0.85 ppb, and a minimum noise level of 0.14 ppb and 0.16 ppb for CO and N₂O, respectively, at the optimum integration time of ~ 80 s. The long-term stability of the instrument was assessed by performing an unattended periodic measurement of reference sample and ambient air over several days at 1 Hz sampling rate and 1-hourly calibration cycle. The measured CO exhibits a high spatial and temporal variance, while N₂O shows a relatively constant trend. A replicate precision of approximately 1 ppb for N₂O was obtained from the entire dataset.

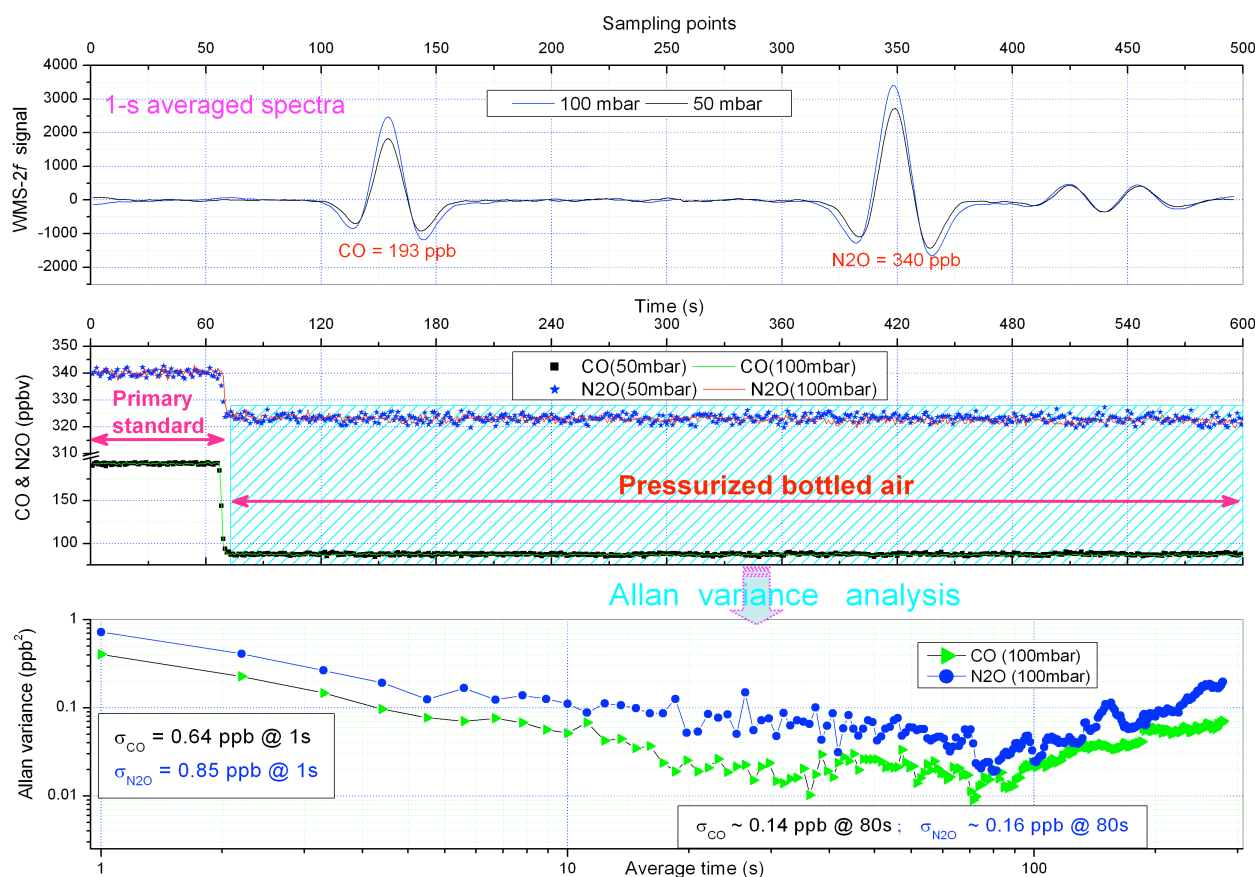


Figure 3 – Typical 1-s averaged WMS-2f signals (Upper panel) , time series CO and N₂O concentration data (Middle panel) measured from air sample tanks and corresponding Allan variance plot (Bottom panel)

3. Conclusions

We have developed a field-deployable QCL sensor for simultaneous detection of the atmospheric trace gases N₂O and CO. Wavelength modulation spectroscopy with second harmonic detection technique in conjunction with a compact multi-pass absorption cell has been employed to demonstrate highly sensitive and precise measurements. The sensor has been demonstrated to have a short-term precision of 0.64 ppbv of CO and 0.85 ppbv of N₂O with 1 Hz sample rate. This completely TE-cooled system shows the capability of long-term, unattended and continuous operation at room temperature without complicated cryogenic cooling.

References

- Li, J.S., U. Parchatka, R. Königstedt, and H. Fischer, *Real-time measurements of atmospheric CO using a continuous-wave room temperature quantum cascade laser based spectrometer*, Opt. Express, 20, 7590-7601 2012.
- Logan, J.A., M.J. Prather, S.C. Wofsy and M.B. McElroy, *Tropospheric chemistry: a global perspective*, J. Geophys. Res., 86, 7210-7254 1981.
- Montzka, S.A., E.J. Dlugokencky and J.H. Butler, *Non-CO₂ greenhouse gases and climate change*, Nature, 476, 43-50 2011.
- Reid, J. and D. Labrie, *Second-harmonic detection with tunable diode lasers-comparison of experiment and theory*, Appl. Phys. B, 26, 203-210 1981.
- Werle, P., R. Mücke and F. Slemr, *The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS)*, Appl. Phys. B, 57, 131-139 1993.

DEVELOPMENT OF THE PRIMARY STANDARDS OF HALOCARBONS AND SF₆ AT AMBIENT LEVEL

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1. Green House Gases containing halogens

Chlorofluorocarbons (CFC-12, CFC-11 and CFC-113) and SF₆ are anthropogenic greenhouse gases, having substantial global warming potential. A precise measurement of those gases is therefore very keen interest due to the regulation to the human-activity driven emission, in accordance with the Kyoto Protocol. As a consequence, the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) serves as an international framework aimed at maintaining the traceability chain for Green House Gases observation going through the Central Calibration Centre (CCL) and World Calibration Centre (WCC). In the meantime, memorandum of understanding (MOU) was signed between the International Bureau of Weights and Measures (BIPM) and WMO in order for ensuring better collaboration and authorisation among national metrology institutes (NMIs) and WMO organizations. Hence, collaborations and comparisons between NMIs and WMO organizations seem to be activated more than before. In a broad sense of BIPM-WMO MOU, for instance, the Korea Research Institute of Standards and Science (KRISS) and the Korea Meteorology Administration (KMA) agreed to host WCC-SF₆ and started to improve the analytical capability of SF₆. [ref. 1] On the other hand, NMI-hosted key Comparison on Atmospheric CFCs and Hydrofluorocarbons (HFCs) is ongoing with the attendance of WMO organizations. Therefore, it is suggested that the phase on the development of primary standards of CFCs and also SF₆ in air should be shifted to the next level for the study of scale comparison.

2. Primary standards developments

2.1 Overview

In this study, we will present our recent achievements on new standards of CFCs gas mixture and SF₆ scale prepared with artificial air matrix. Three CFCs of CFC-12, CFC-11 and CFC-113 in artificial air are mixed in aluminium cylinder. Impurity analysis of pure gases of CFC-11, CFC-12, CFC-113, N₂, O₂ and Ar were performed and every dilution steps are gravimetrically controlled according to ISO 6142. To verify dilution steps, analyses were performed using KRISS-calibrated gas chromatograph with thermal conductivity detector or electron capture detector (GC-TCD and ECD, respectively) according to ISO 6143. For SF₆/air scale, we gravimetrically prepared individual 5 cylinders of which mole fractions are in the range of ambient levels (5~15 ppt). The impurity analyses of the pure gases composing of air, i.e. N₂, O₂ and Ar, were particularly performed with great care. Since the target mole fraction of SF₆ is trace level, precise assignment of SF₆ in pure gases of N₂, O₂ and Ar is very crucial to the control of gravimetric dilution. For this purpose, the preconcentrator-GC-ECD was brought to ensure the SF₆ trace. For the SF₆ scale, we also applied ISO standards correspondingly. Representative analytical conditions are tabulated in Table 1.

Table 1 – Representative analytical condition of analytical system for the verification of gravimetric dilution steps. Typically, CFCs and SF₆ gains sufficient response when using gas chromatograph coupled with electron capture detector. To secure acceptable separations of CFCs, an Resil C column was adapted. In case of ambient level of SF₆, fast retention time and symmetric peak shape of SF₆ was observed by an Activated Alumina F1 column

Representative Analytical Conditions		
	CFCs	SF ₆
Detector	μECD	
Detector temp.	375°C	350 °C
Oven temp.	40°C 7 min 25°C/min 80°C 8.5 min 145°C 5 min	65 °C
Column	Resil C 80/100 24ft	Al-F1 80/100 24ft* 1/8 inch SUS
Carrier gas	P-5, 55.1 psi	P-5, 85 psi
Sample flow	200 ml/min	150 mL/min
Sample loop	5 cc	5 cc

2.2 Primary standard of CFCs mixtures in air

During the impurity analyses, other CFCs impurities in main pure gases of CFC-11, CFC-12 and CFC-113 were rigorously cross-checked. Though, interestingly, significant amount of HFCs were also found due to imperfect purification process, signal interferences were totally disappeared in final chromatograms of primary standard due to very high dilution factor below the limit of detection (LOD) (Figure 1). H₂, O₂+Ar, N₂, CO, CH₄ and H₂O were also assigned for the pure gases of CFC-11, CFC-12 and CFC-113. 6 steps of gravimetric dilutions were performed based on N₂. In the final seventh step, O₂ and Ar were added. Internal consistency of independent dilutions branched to 4 families was verified by the comparison analysis for the mole fractions of CFCs. The resulting mole fractions of CFC-11, CFC-12 and CFC-113 were shown to 529.44 ppt ($U_{rel} = \pm 0.5 \%$, $k = 2$), 239.09 ppt ($U_{rel} = \pm 0.85 \%$, $k = 2$) and 75.10 ppt ($U_{rel} = \pm 1.25 \%$, $k = 2$), respectively, which were mimicked very closely to the ambient levels of KRISS atmosphere.

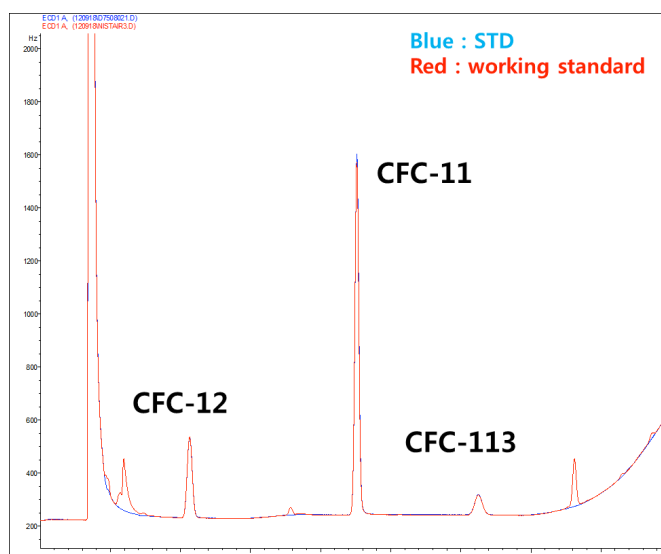


Figure 1 – Chromatograms of KRISS primary standard (blue) and working standard in whole dry air. The mole fractions for CFC-11, CFC-12 and CFC-113 corresponds to 529.44 ppt ($\pm 0.5\%$, $k=2$), 239.09 ppt ($\pm 0.8\%$, $k=2$) and 75.10 ppt ($\pm 1.2\%$, $k=2$), respectively, which are very closed to the ambient levels in Deajeon, South Korea

2.3 SF₆ scale in the range of ambient levels

SF₆ scale in the range of 5 - 15 ppt was gravimetrically prepared. SF₆ gas, of which purity was assigned to 99.989 % by the impurity analysis, was diluted by 6 steps with pure N₂ gas. Then, in the final step, O₂ and Ar were added in 10 L aluminium cylinders (Luxfer, UK), of which inner surfaces were electrochemically polished. Impurity analyses of pure N₂, O₂, Ar as dilution gases were very important factor for accurate preparation, considering trace level of aimed SF₆ mole fraction. Even 0.01 ppt of SF₆ impurity in artificial air matrix has a power to exhibit a positive bias resulting in ~0.15% increase in a final mixture. We measured SF₆ impurity in pure gases of N₂, O₂ and Ar by the aid of cryogenic pre-concentrator. It was shown that the SF₆ impurity in the matrix was not detected where a LOD of our precon-GC-ECD system is 0.002 ppt (Figure 2). According to the uncertainty evaluation of the gravimetric preparation, which includes the repeatability and reproducibility of our automatic weighing machine, gravimetric uncertainties of ~ 0.13 % (relative, $k = 2$) were given to every bottles. And a least square fit of quadratic response of SF₆ returned great goodness of fit, $R^2 \sim 0.9999946$ (Figure 3).

Specification	Condition
Detector	GC- μ ECD with cryogenic system
Detector temp.	250 °C
Oven temp.	60 °C
Column	AA-F1 80/100 24ft* 1/8 inch SUS
Carrier gas	P-5, 90 psi
Sample flow	200 mL/min
Cryogenic time	10 min
Trap heating	5 min

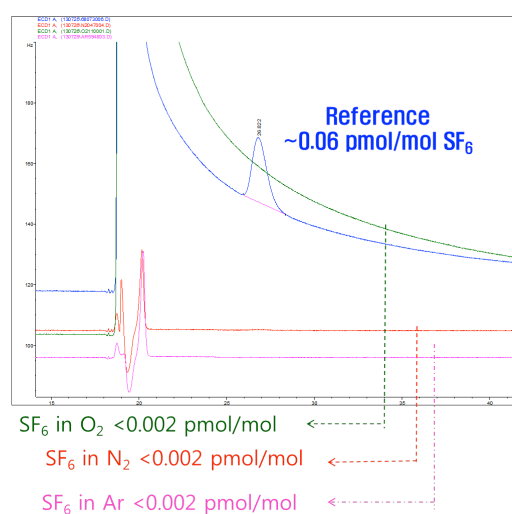
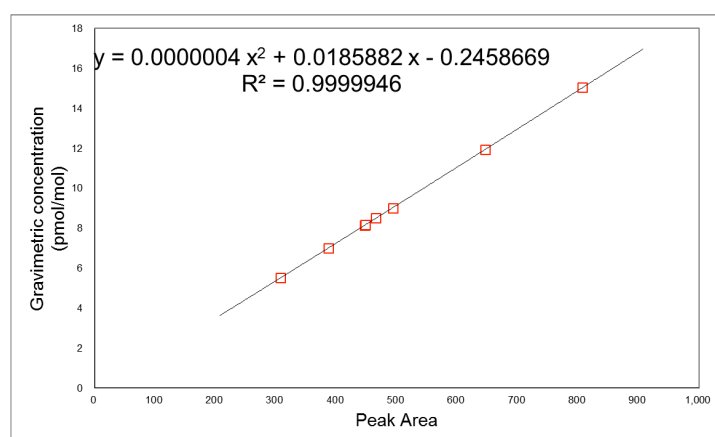


Figure 2 – Analytical condition and chromatograms for trace SF₆ analyses of O₂ (green), N₂ (red) and Ar (magenta). The reference (~0.06 ppt, blue) for showing a degree of response was diluted from the mother cylinder in ppt level. Detection limit determined by 3*SNR (signal to noise ratio)



Mole fraction of SF₆ 5 ppt ~ 15 ppt

Figure 3 – ECD response curve of SF₆/air in the range of 5 ~ 15ppt. The response curve was approximated by a least square fit of a second-order polynomial with an agreement of $R^2 = 0.9999946$

References

- Jeong Sik Lim, Dong Min Moon, Jin Suk Kim, Won-tea Yoon, Jeongsoon Lee, *High precision analysis of SF₆ at ambient level*, Atmos. Meas. Tech. 6, 2336-2342 2013
- ISO 6142, 2001, *Gas analysis -- Preparation of calibration gas mixtures -- Gravimetric method*
- ISO 6143, 2001, *Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures*
- Blake, D., *Methane, Nonmethane Hydrocarbons, Alkyl Nitrates, and Chlorinated Carbon Compounds including 3 Chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) in Whole-air Samples*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge Tenn., U.S.A, 2010.
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BACKGROUND VARIATIONS OF ATMOSPHERIC CO₂ AND CARBON STABLE ISOTOPES AT WALIGUAN (WLG) AND SHANGDIANZI (SDZ) STATIONS IN CHINA

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1. Introduction

In this paper, we systematically analyze the time series of atmospheric CO₂ mole fraction and its $\delta^{13}\text{C}$ composition at WLG and SDZ during the 2007 to 2010 period. We suggest for the first time suggest source-sink processes based on our interpretation of the variations. We also describe a method of data selection of CO₂ and $\delta^{13}\text{C}$ values from discrete air samples that we have been developed to improve the data quality of the time series. The results can help to a better understand the carbon cycle in typical regions of China.

2. Sites

WLG station is the only global background station of WMO/GAW in the Central Eurasia Continent and is located at the edge of the north-eastern part of the Tibetan Plateau (36°17' N, 100°54' E, 3816 m asl)(see Figure 1). The area surrounding the station is predominately desert with arid/semi-arid grassland and sparse vegetation. The population density is less than eight people per km² in an area that is relatively isolated from industries and other populated areas.

SDZ station (40°39' N, 117°07' E, 293 m asl) is one of the regional background stations of WMO/GAW, located in a mountain area about 100 km northeast of urban Beijing. Except for several villages, no larger industrial zone exists within a distance of 30 km. The immediate surrounding area primarily consists of shrubs, orchards, and several farmlands.

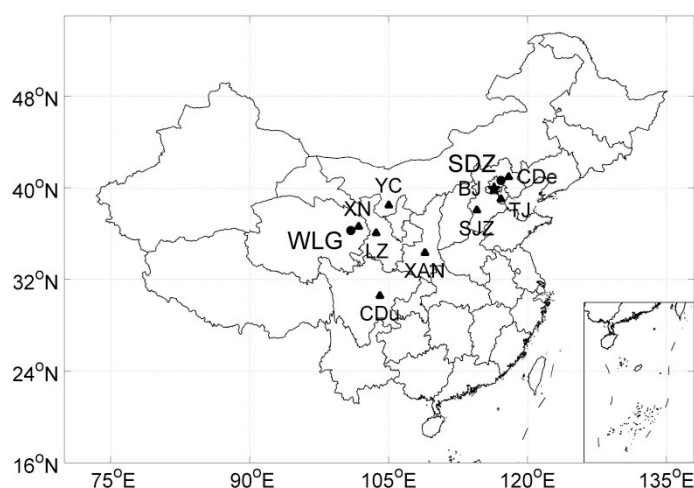


Figure 1 - Maps showing the geographical locations of WLG and SDZ stations and location of main cities

3. Instrument and methods

The sampling equipment consists of a portable pumping unit, the MAKS (HPD, Sherpa 60) and 2 L Pyrex glass flasks with two stopcocks made by NOAA (Lang et al., 1994). In the laboratory, the flasks are connected to the wavelength scan cavity ring down the spectroscopy system (G1301, Picarro, USA) to analyze the CO₂ mole fraction. Prior to 2010, analysis is conducted with a non-dispersive infrared spectroscopy observation system (LI-7000, LI-COR, USA). Then, the flasks are connected with the off-line glass extraction system to extract pure CO₂ gas through the double cold traps. Finally, the glass tube filled with pure CO₂ is connected to a gas stable isotopic ratio mass spectrometer (FinniganTMMAT253, Thermo, USA) through the glass tube cracker and $\delta^{13}\text{C}$ is measured using the dual-inlet system.

The standard gases for the CO₂ mole fraction are decanted from primary whole-air standards calibrated by the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado, USA and are directly traceable to the WMO X2007 standard scale (CMDL, 2001; Zhao, 1997). The standard gases for the isotopes, which are relative to the standard isotopic ratio Vienna Pee Dee belemnite CO₂ are decanted by the Institute of Arctic and Alpine Research (INSTAAR) in the University of Colorado (Coplen, 1995).

4. Results

The atmospheric CO₂ and its $\delta^{13}\text{C}$ at WLG and SDZ possess long-term trend seasonal cycles, which are highly correlated with each other. At WLG station, between 2007 and 2010, the atmospheric CO₂ falls to a minimum in August and rises to the maximum in April and May with average annual seasonal amplitude of 10.8 ± 1.2 ppm. The $\delta^{13}\text{C}$ falls to the lowest in April and rises to the highest during July and August with the average annual seasonal amplitude of 0.54 ± 0.01 ‰ (see Figure 2). These values are indicative of active terrestrial ecosystem source-sink seasonal features in the mid- to high-latitude areas of the Northern Hemisphere. CO₂ annual means vary from 384.0 ppm to 390.2 ppm with a mean growth rate of 2.1 ± 0.1 ppm whereas its $\delta^{13}\text{C}$ varies from -8.30 ‰ to -8.35 ‰ and decreases almost linearly with a mean rate of -0.02 ‰ \pm 0.00 ‰ (see Figure 3). The atmospheric CO₂ mole fraction at WLG shows a long-term linear increase trend whereas the annual growth rate of CO₂ continues to increase gradually.

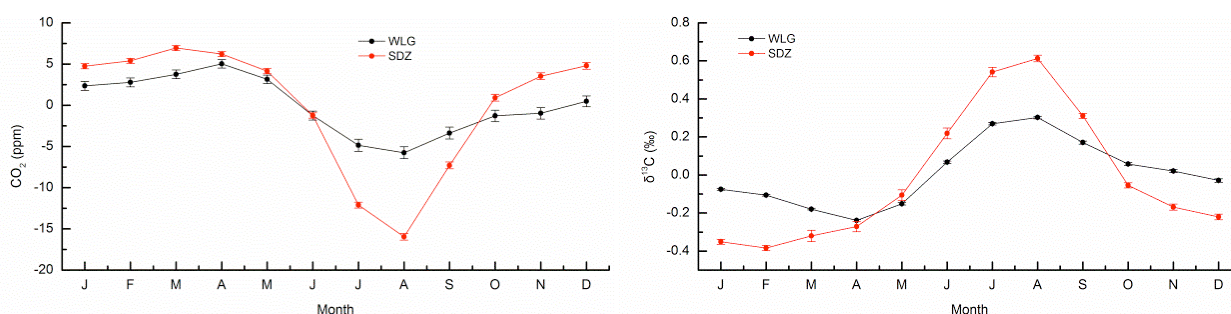


Figure 2 - Monthly mean atmospheric CO₂ and $\delta^{13}\text{C}$ at WLG and SDZ stations

Under the common conditions of human activities and an active natural ecosystem at SDZ station, the atmospheric CO₂ varies dramatically in summer and varies gently in winter. The average annual season amplitude is 22.9 ± 0.7 ppm (see Figure 2). CO₂ annual means vary from 385.1 ppm to 390.6 ppm and increase in an approximately linear manner with a mean growth rate of 1.8 ppm at SDZ station. This is significantly higher than the mean growth rate at WLG. The $\delta^{13}\text{C}$ variation trend is opposite to that of CO₂. The average annual season amplitude is 1.00 ‰ \pm 0.03 ‰.

The $\delta^{13}\text{C}$ annual means vary from -8.27‰ to -8.36‰ between 2010 and 2011, which is slightly steeper than the lapse rate at WLG during the corresponding period (see Figure 3).

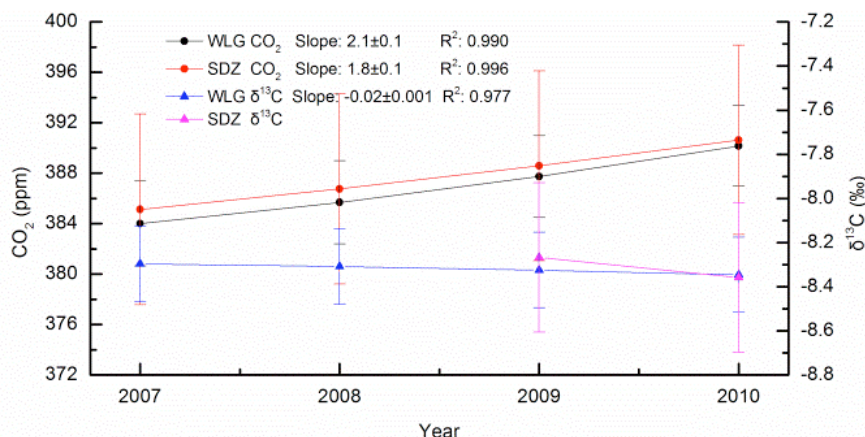


Figure 3 - Atmospheric CO₂, $\delta^{13}\text{C}$ annual means, and growth rates at WLG and SDZ stations

The atmospheric CO₂ and its $\delta^{13}\text{C}$ at WLG and SDZ show an obvious negative correlation. Mean δ_s values of $-23.33\text{‰} \pm 0.75\text{‰}$ and $-20.98\text{‰} \pm 0.87\text{‰}$ for the respective sources are derived by the Miller-Tans model. To examine the seasonality of the δ_s , relevant data sets are partitioned and calculated by season. The estimated δ_s are more negative in winter and spring than in summer and autumn at both stations. At WLG, the variation difference δ_s in the four seasons are extremely slight because of the comprehensive function of the natural and anthropogenic contributions of the climate and geographic features. However, the estimated δ_s values at SDZ are more negative in winter than in summer and range from -25.66‰ to -19.81‰ (see Figure 4). These values are larger than those of WLG because the anthropogenic contributions have more significant impact on CO₂ emissions in winter and the terrestrial biosphere's strong photosynthesis of CO₂ has greater impact on the CO₂ sinks in summer. To better understand and address a specific source or sink and its exchanging processes in the two regions, more intensive observation (e.g. longer time-series, more sites, more observation elements including CO, $d^{14}\text{CO}_2$, O₂:N₂ and the correlation analysis with CO₂) and modelling studies (e.g. the Hybrid Single-Particle Lagrangian Integrated Trajectory model, Potential Source Contribution Function and the Carbon Tracker numerical model, et al) are needed.

References

- CMDL (2001): *Climate Monitoring and Diagnostic Laboratory, 1998-1999 Summary Report*, No.25. NOAA/CMDL, USA.
- Coplen T B. (1995): *Reporting of stable carbon, hydrogen, and oxygen isotopic abundances, in Reference and intercomparison materials for stable isotopes of light elements*, pp.31-34, International Atomic Energy Agency, Vienna.
- Lang P. M., Dlugokencky E. J., Masarie K. A., et al. (1994): *Atmospheric methane data for 1989-1992 from the NOAA/CMDL global cooperative air sampling network*, NOAA Tech. Memo. ERL CMDL-7, NOAA Environ. Res. Lab., Boulder, Colo.
- Zhao C et al. (1997): *A manometric system for absolute calibrations of CO₂ in dry air*. J. Geophys. Res., 102: 5885-5894.

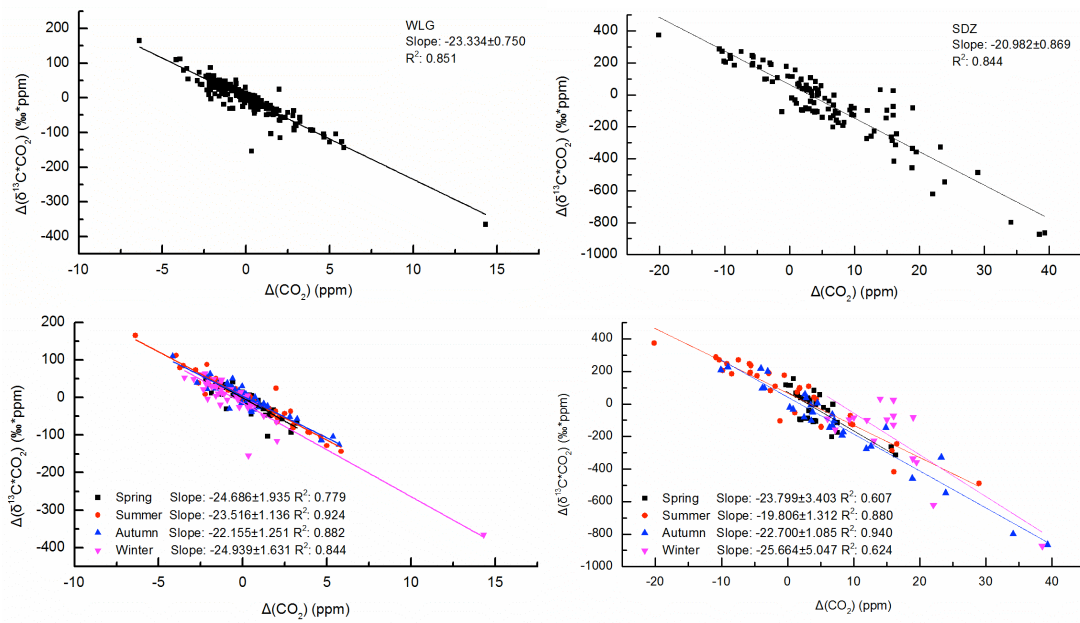


Figure 4 - Atmospheric CO₂ and δ¹³C linear regression results at WLG and SDZ stations

CONTINUOUS MONITORING OF GREENHOUSE GASES IN THE SOUTH ATLANTIC AND SOUTHERN OCEAN: CONTRIBUTIONS FROM THE EQUIANOS NETWORK

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1. The Equianos Network

The Equianos network is bringing together groups making new laser-based measurements of greenhouse gases following a latitudinal transect of the Atlantic from the Arctic to Antarctica and in peripheral regions that influence, or are influenced by, the meteorology and emissions of this region. This includes new sites (e.g. East Falkland Islands, Barra, Jersey, Kjolnes), upgrades to flask sampling sites (e.g. Ascension Island), and equipment upgrades (e.g. Cape Point, Halley). In addition the network includes instrumentation of ships that make latitudinal transects of the Atlantic (RRS James Clark Ross). Flask and bag samples are collected regularly (daily to weekly) at most of the network sites for the analysis of $\delta^{13}\text{C}$ of CH_4 . The aim is to provide information on the sites, basic data in the form of graphs and comparisons of monthly averages to be freely available and for the groups involved to work together on the understanding of inter-site variations, particularly in Tropical and South Atlantic, as these are key areas for understanding short-term changes in the CH_4 growth rate (e.g. Dlugokencky et al., 2011).

1.1 New Measurement Sites in the South Atlantic and Southern Ocean Region

Here we focus on developments from the ITCZ southward. In June 2010 a CRDS instrument was installed at the Meteorological Office site on Ascension Island at 8°S. This site has very high humidity but the instrument is in an air conditioned environment. A second instrument was installed in a hut on Sapper Hill, near Port Stanley, East Falkland at 50°S. This hilltop site has no temperature control and external temperatures can drop close to 0°C in winter months.

A suite of 6 cylinders of air are connected to an auto-inlet at these remote sites and shipboard; 3 calibration gases, 1 working standard, 1 target and 1 long-term target. All are in the range 380-420 ppm CO_2 and 1840-2100 ppb CH_4 . The calibration gases are measured weekly to provide the calibration and slope to correct the raw data. The target gas is measured every 2 days. Repeatability (1σ) of the target gas over 30 months from June 2010 to December 2012 was ± 0.22 ppb for CH_4 and ± 0.039 ppm for CO_2 for the Ascension instrument. Over 26 months from November 2010 at East Falkland the repeatability of the target gas was worse, ± 0.71 ppb for CH_4 and ± 0.052 ppm for CO_2 . As the scatter was generally greater when the gas was being measured overnight it is thought that the variability is due to analysis over a wider range of temperatures. Long-term drift of the target gases after calibration is less than 0.5 ppb CH_4 over 30 months.

Soon after these instruments were installed the South African Weather Service replaced older instrumentation with a CRDS at Cape Point and data for the 3 sites have been compared. Early in 2013 the British Antarctic Survey also upgraded their measurement capabilities by adding

a CRDS at the Halley Bay station and this site will be added to the comparison once a sufficient time interval of data is available.

1.1.2 Data for 2010 to 2012

The first 2 years of data show typical growth rates of CO₂ around 2 ppm/yr, with the Ascension and Cape Point CO₂ time series being closely comparable. East Falkland shows a similar growth rate but has a less pronounced seasonal cycle (Figure 1). CH₄ on the other hand shows high 2010-11 growth rate of 11 ppb on Ascension Island, slowing to 4 ppb in 2011-12. Falklands and Cape Point grew at around 4 ppb for both 2011 and 2012, with closely comparable CH₄ baselines (Figures 1 and 2).

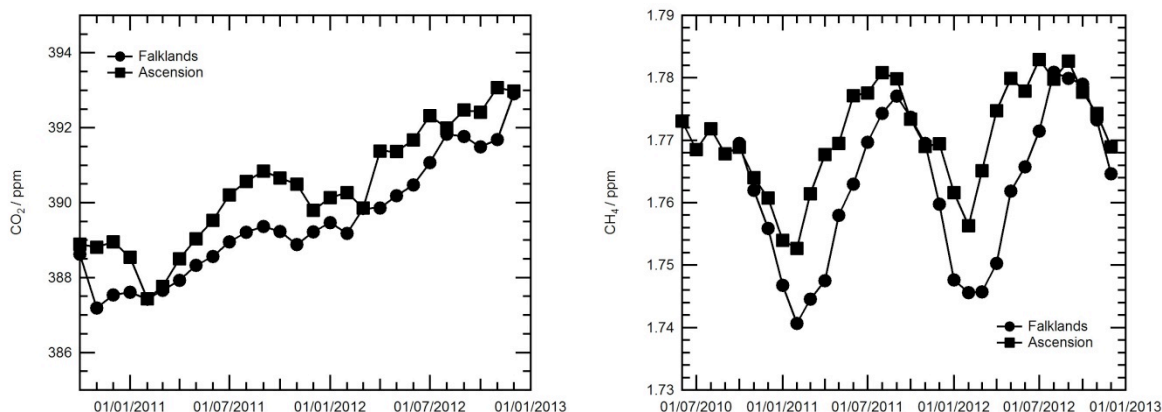


Figure 1 – Monthly averaged CO₂ (left) and CH₄ (right) recorded by the Ascension Island and East Falkland Picarro G1301 instruments between set-up in 2010 and the end of 2012

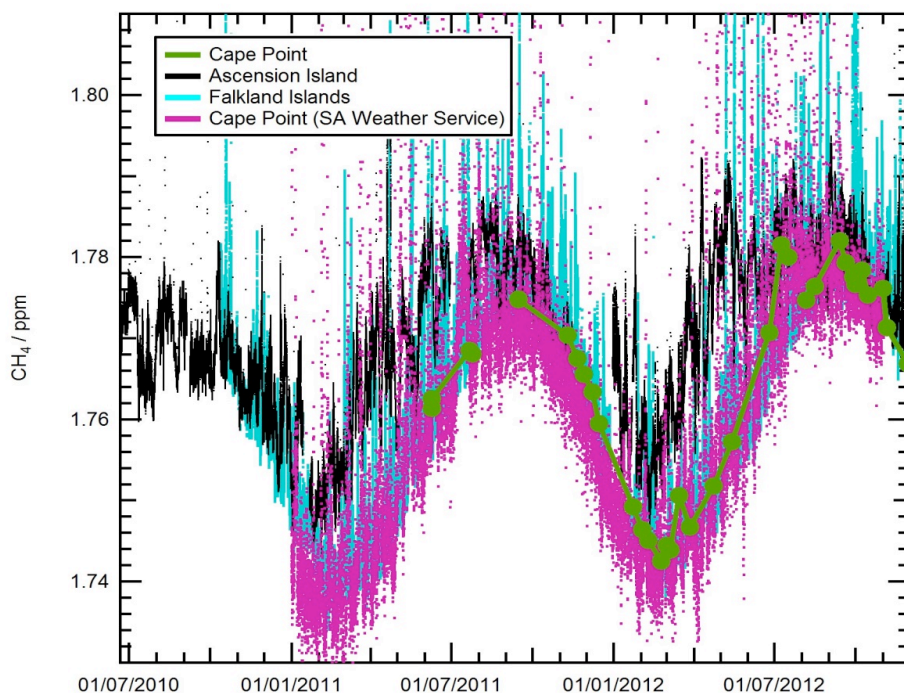


Figure 2 – Comparison of new continuous methane records from the South Atlantic region. The green circles are measurements made on glass flask samples collected by SAWS for measurement of carbon isotopes of CH₄ and CO₂ at RHUL

Compared to Antarctic stations the CO₂ signals in the Atlantic are noisier, showing the impact of the biological cycle and also transient events such as fires. On East Falkland this is seen as much greater diurnal variability during late spring and summer, particularly when the wind is from the west and the air is crossing over more than 100km of pampas grassland before reaching the measurement site. The strong CH₄ baseline seen for air from Antarctica and the Southern Ocean is disrupted by short-lived emission peaks from South America when the air flow is from the NW.

1.2 Atlantic Transect Data from the RRS James Clark Ross

The instrument destined for East Falkland was set up for measurement on route south in October 2010 to gain Atlantic transects from 50°N to 50°S for CO₂ and CH₄. By the same trip south in October 2012 a Picarro 2301 instrument was installed on the ship for a southern tropical methane project lasting until 2016. The ship transect in 2012 gave a very different CH₄ record for the northern hemisphere compared to 2010 (Figure 3). The ship sails close to western Europe and NW Africa, but trajectories are dominantly NW trades, those in 2012 mostly from further north in eastern Canada. Also highlighted is the changing magnitude and position of the 50-80 ppb methane waterfall across the ITCZ. South of this the methane mixing ratios are dominantly in the range 1770 to 1780 ppb, but a methane bulge from 5-30°S was seen in 2010 compared to 2012. This is correlated with a 2008-2011 southern tropical methane anomaly observed in the NOAA flask record. Short peaks of methane emission start to occur only after the ship is south of the influence of the SE Trade winds and emissions from South America are caught up in the air movement. Isotopic analysis suggests that these are dominantly biogenic.

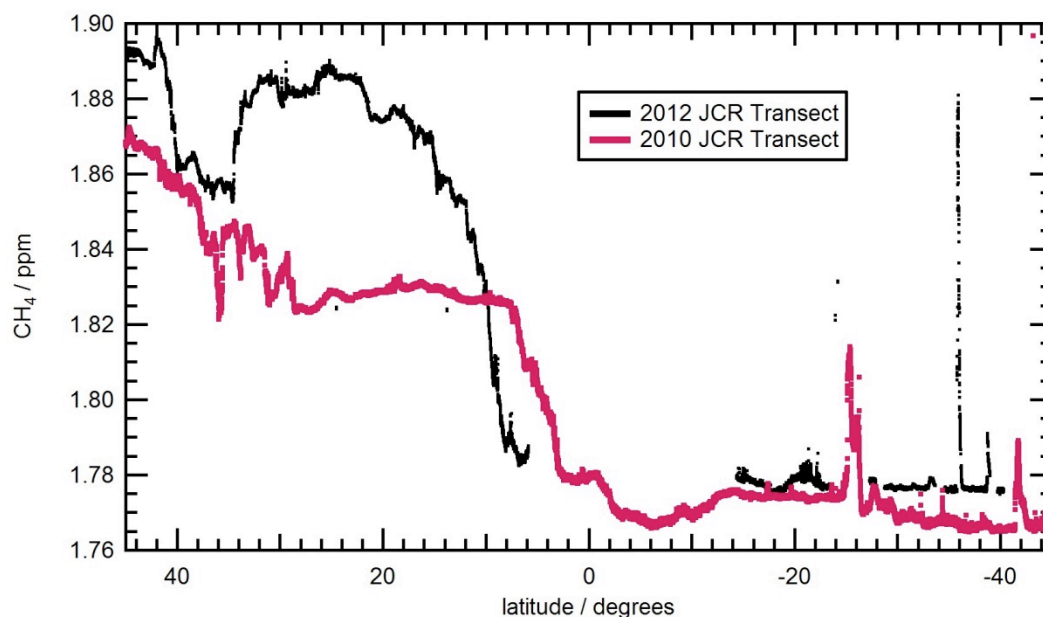


Figure 3 – Comparison of October 2010 and October 2012 shipboard methane transects from 45°N to 45°S. Of note are the Southern Tropical methane anomaly between 6 and 32°S observed in 2010, and the different position of the methane ‘waterfall’ at the ITCZ between 2010 and 2012. The gap in 2012 data around the equator is due to water build-up in the instrument during very hot and humid conditions

1.2 Anomalous Events in the Ascension Island Continuous Record

The 2010-12 RHUL continuous record closely matches the NOAA flask sample record for Ascension Island, with the exception of anomalous peaks during April 2011. These correlate with a decadal latitudinal low in the ITCZ, bringing with it a 30-year high in rainfall as a storm super cell passed over on the night of April 22-23. More than the normal annual rainfall fell on the drier parts of the island in the space of a few hours, bringing well-mixed high-altitude air (possibly with a Northern Hemisphere component) to the ground for a 12-hour period, before the inversion above the SE Trades re-established itself. The CH₄ rose by 35 ppb in 3 minutes and stayed close to 1800 ppb for more than 10 hours (Figure 4). This was accompanied by a rise in CO₂ of close to 4 ppm.

At the start of the event the surface wind changed from the usual SE around to NW and then swung through to ENE as the event progressed, despite trajectory analysis suggesting that near surface winds remained from the SE throughout the event. Such events highlight the importance of continuous records in detecting peaks associated with unusual meteorology or short-lived emissions.

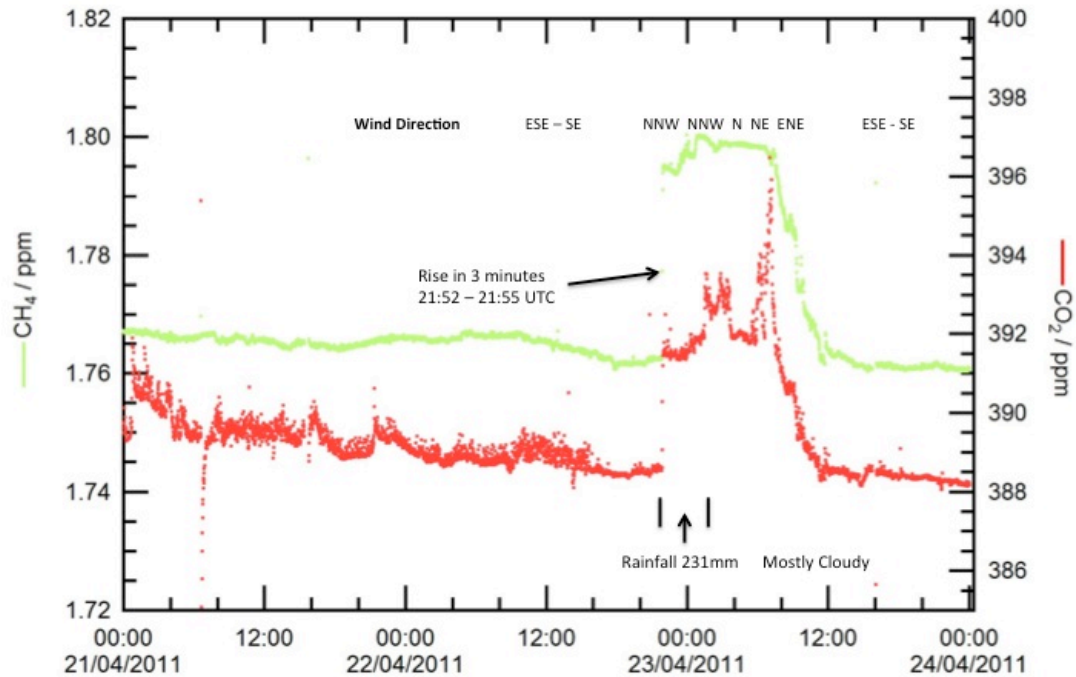


Figure 4 – An incursion of high level, possibly Northern Hemisphere air, to ground level on Ascension Island when the ITCZ had tracked to 8°S in April 2011. A thunderstorm overnight on April 22-23 caused torrential rainfall, flooding, road damage and the formation of clouds to 14000m mixing the SE Trades with the air above

Reference

Dlugokencky, E.J., Nisbet, E.G., Fisher, R., and Lowry, D., 2011, *Global atmospheric methane: budget, changes and dangers*. Phil. Trans, R. Soc. Lond. A. 369, 2058–2072.

ANALYSIS OF THE INFLUENCE OF CO₂ CONCENTRATION AND OTHERS EXTERNAL FACTORS ON THE N₂O QUANTIFICATION

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1. Introduction

Nitrous oxide (N₂O) is the third greenhouse gas with higher global warming potential and its lifetime is about 120 years (IPCC, 2007).

N₂O can be emitted into the atmosphere from natural and anthropogenic sources, including the oceans, soil, combustion of fuels, biomass burning, use of fertilizer and various industrial processes (WMO, 2013). On the other hand, the major sink of this gas is the stratosphere, since it is involved in the destruction of stratospheric ozone (Houghton, 1996). Thus, the N₂O anthropogenic sources should be controlled in order avoid increasing the concentration of this gas into the troposphere and consequently to prevent the reduction of stratospheric ozone.

All the N₂O studies are reliant upon the accurate quantification of atmospheric N₂O concentration, which is very limited in precision and accuracy. The kind of technology applied, the type of carrier gas as well as external factors as CO₂ concentration in the laboratory room, for example, can affect the stability and sensitivity in the N₂O concentration measurements.

The focus of this study is to show how the CO₂ concentration in the laboratory room can influence the N₂O measurements.

2. Methodology

The N₂O measurement was made by gas chromatography (GC) using the Electron Capture Detector (ECD), which is considered as an extremely sensitive technique when compared to the Flame Ionization Detector (FID). The carrier gas used in the system is Ar-CH₄ (5%) and 74 mL.min⁻¹ flow rate. This carrier gas can provide higher ECD sensitivity than N₂ or Ar gases (Wang et al., 2010). The pre-column and column are HaysepQ 100/120 mesh, 183cm length, 3/16" ED. Loop with 15mL volume and oven with constant temperature of 70°C were used. The N₂O measurement system is showed in the Figure 1.



Figure 1 - GEE Analytical System of LQA / IPEN. 1: Chromatograph HP 6890 plus / ECD (Electron Capture Detector) 2: Gas flow controller; 3: Sample and system select valve; 4: Vacuum measurer and samples receiver; 5: Chromatograph's interface

To evaluate how the CO₂ concentration in the laboratory room can influence the N₂O measurements, firstly four people stayed in the laboratory during half an hour and left the laboratory after that time. Once the system has stabilized, 150 grams of dry ice was placed in laboratory room to evaluate the interference of CO₂ higher concentrations.

All the CO₂ concentrations were monitored using the Q-Trak™ Plus IAQ monitor. The N₂O concentrations were determined simultaneously by GC-ECD for the data correlation.

3. Results and Discussion

The influence of CO₂ concentration was correlated with the N₂O quantification. Results demonstrated that ECD signals of N₂O were significantly altered by increasing the CO₂ concentration. Results are showed in the Figure 2.

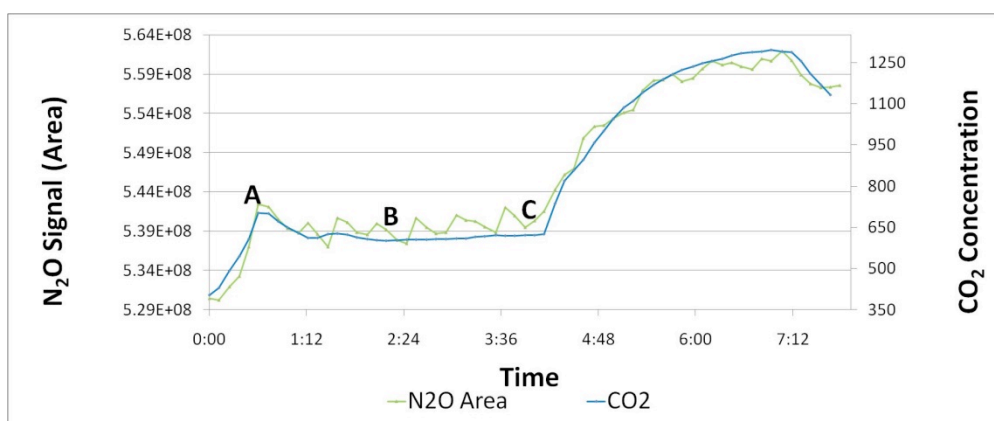


Figure 2 - GC-ECD - N₂O signals peak area in response to the CO₂ concentration. A: influence of four people in the laboratory room; B: stable level; C: influence of 150 g of dry ice in the laboratory room

The linear data for the correlation between N₂O signal peak area and CO₂ concentration is showed in the Fig. 3. The correlation coefficient (R) for the data is 0.991 indicating that N₂O signals (peak area) are very sensitive when CO₂ concentration is changed.

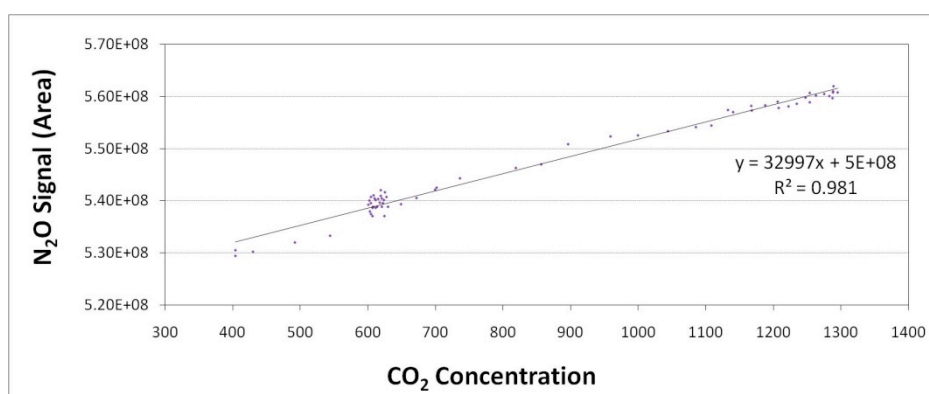


Figure 3 - Nitrous oxide (N₂O) signals peak area in response to the CO₂ concentration

To improve the precision in N₂O analysis LQA/IPEN started to made triplicate analysis for all measurements since 2012. The standard deviations results for the 1223 samples in triplicate are showed in the Figure 4. According to Figure 4, the standard deviations of 95.96% of all samples were below 1.50.

The time series for the tank calibration of the tank CA04533 is showed in the Figure 5. According to Figure 5, our system demonstrated the long-term repeatability.

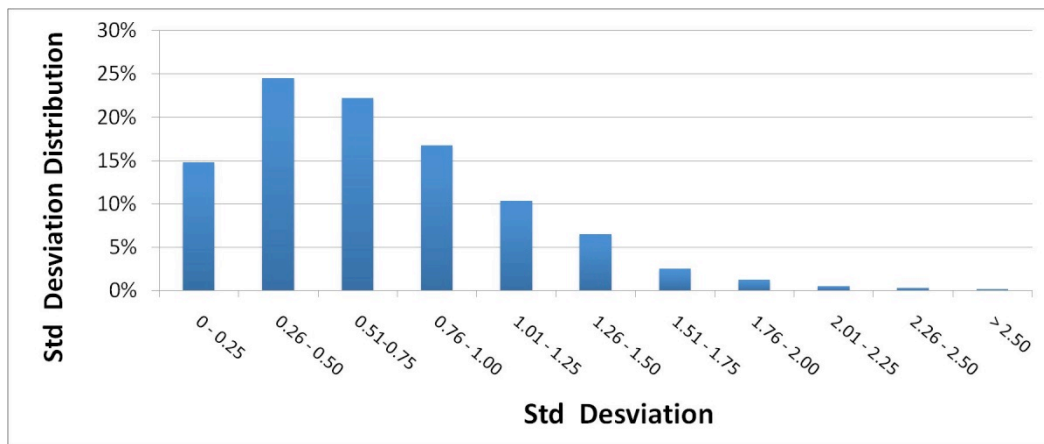


Figure 4 - Standard deviation distribution for the N₂O triplicates analysis

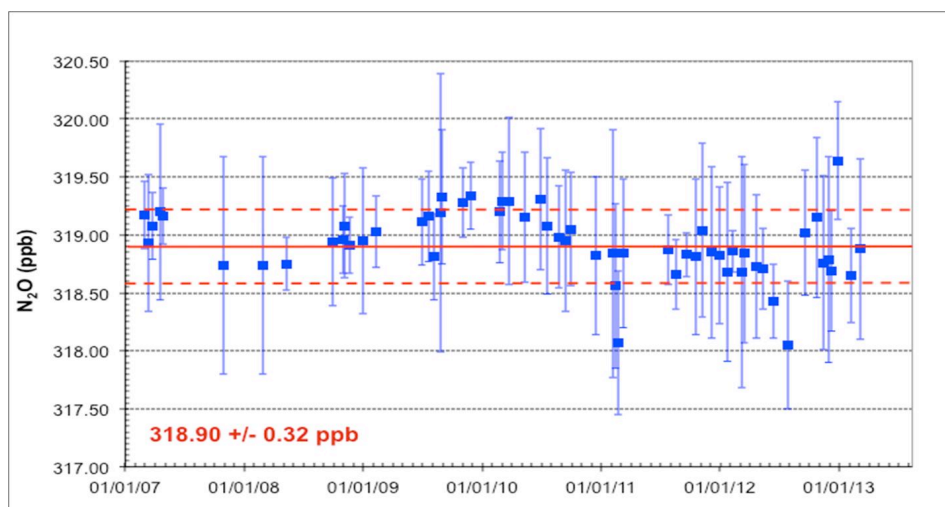


Figure 5 - Time series for the tank CA04533. Each point represents the mean of 20 aliquots by tank calibration; the error bars represent the standard deviation of the 20 analyses. The repeatability is the standard deviation of the results of all tank calibrations (2007–2013). The stability of tank, specially demonstrates the long-term repeatability of our system

4. Conclusions

Results demonstrated that ECD signals of N₂O were significantly altered by increasing the CO₂ concentration in the laboratory room. The influence of CO₂ concentration was correlated with the N₂O quantification and presented a correlation coefficient (R) of 0.991 for the data.

External factors how CO concentration and air relative humidity were correlated with N₂O ECD signals and both of them do not present an influence in the measurements. Since de CO₂ concentration can influence the N₂O determination, the chromatograph of LQA/IPEN laboratory will be isolated with a glove box in order to improve the measurements.

The N₂O concentrations should be as accurate as possible, since its gas concentration data are used for modelling climate change.

References

- Houghton, J. T., et al., *Climate Change 1995*, Cambridge Univ. Press, New York, 1996.
- IPCC - Intergovernmental Panel on Climate Change. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of Intergovernmental Panel on Climate Change*. eds. Solomon, S.; Qin, D.; Manning, M.; Marquis, M.; Averyt, K.; Tignor, M.M.B.; Miller Jr, H.L.; Chen, Z. Cambridge University Press. Cambridge University Press, Cambridge, 2007.
- Wang, Y., Wang, Y., Ling, H., *A new carrier gas type for accurate measurement of N₂O by GC-ECD*. *Advances in Atmospheric Sciences*, Vol. 27, No. 6, 2010, 1322-1330.
- WMO - World Meteorological Organization - *Global Atmosphere Watch - World Data Centre for Greenhouse Gases*. WMO WDCGG Data Summary, n. 37 v. 4. Japan Meteorological Agency em cooperação com World Meteorological Organization, 2013.
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STANDARDIZED AND AUTOMATED DATA QUALITY ASSURANCE AT GAW STATIONS - CONCEPT, METHODS AND TOOLS

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Abstract

Global Atmosphere Watch (GAW) concentrates on standardized measurement and its calibration, on standardized training and data collection. However, operational data processing and quality assurance is neither centrally supported nor standardized. Despite the fact, that a considerable number of institutions worldwide deliver excellent results, it is questionable whether all GAW measurement stations perform the procedures for data processing, data analysis and quality assurance in an effectively comparable manner. How to gain a standardized processing and same standard of expertise at all stations? GAW hitherto requires a worldwide comparability of measured data at the whole number of stations. Therefore a standardization of all procedures applied on measurement data is required to meet data quality objectives.

Procedures and actions taken on measurement data at GAW stations within the global network are of elementary relevance for the resulting data quality and for the comparability of data. This topic deserves particular attention because of the fact that actions taken on data for data preparation and validation often may have a strong effect on the information in the treated measurement data. Decisions for example which correction has to be taken on which case, are not trivial. And for example even the decision when and in what case a mean value or a median has to be used also is not a trivial one. Data quality assurance in connection with data handling and data processing is a highly differentiated task which needs and deserves standardization throughout the global GAW network. Nevertheless GAW has a well-developed scientific infrastructure for quality assurance there is a substantial difference between the given recommendations which itself is the prescription for standardization and several hundred implementations at GAW stations worldwide.

It is proposed, that a systematically applied workflow-software approach can help to overcome this problem.

1. Workflow- Software Approach – Concept and Methodology

The systematic use of software for GAW stations for standardized and automated data acquisition, instrument control and quality assurance will enhance the comparability of measurement data. The whole workflow in order to reach data quality objectives (DQOs) has to be accompanied consistently by software in order to automate, standardize and facilitate the stepwise process of preparing and processing data and controlling data quality in order to gain data quality objectives. The central argument is founded mainly in information theory, but also in statistics and in system analytics: The quality chain has to be kept during the whole process from raw data to final results. The correctness of each single step of the underlying working procedure has to be granted. Software which covers each step of the whole working procedure, contributes to assuring the fulfillment of the quality objectives.

Main advantages are:

- Complexity is encapsulated in the software.
- Application is easier in terms of user requirements. Thus delegation of work items to a larger group of less trained or specialized staff becomes possible.

- In place expertise at the station is reachable -- the right and standardized automated procedure does the right thing at the right moment!
- The number of the degrees of freedom becomes reduced. The identical or very similar treatment of data throughout the whole process from measurement, data acquisition, data preparation, to validation is supported. This can be essential for the removal of artificial differences in the data and supports the requirement for standardization and comparability of measurement results.

According to the GAW framework standardization has to be done. The consequent use of the workflow-software approach gives the basis for the standardization of many practical aspects of data handling and quality assurance in GAW stations. Practical examples from astro-physics and nuclear physics show that a „one software solution” is essential for the comparability of data. As a clear outcome the chance for a comparability of the data is far higher than with several hundred individual implementations on GAW measurement stations worldwide.

2. Practical Solutions

As a result of the ongoing project GAWSTAT of QA/SAC Germany, supported by the Federal Environment Agency, a set of software solutions is free available for measurement stations and institutions which work for the UNO/WMO GAW program. The offer consists of following solutions:

1. Client server system – Daqas for automated data acquisition, instrument control and calibration
2. User client for control of the continuous measurements, input of meta-information via logbook.
3. User client – Isave for the processing of calibrations, for interactive control and flagging of measured time series data and for standardized processing of calibrations.
4. Data acquisition files integration tool – Dafit, for data preparation, flagging and validation of time series data which have been measured automatically with instruments with own data acquisition.¹

3. Client Server System -- Daqas

A project of the Federal Environment Agency gave chance for the development of a software system under the enhanced use of automated procedures for personal efficient data acquisition and data processing and control of: measurement, calibration and data quality. From the very beginning on, the client server database system was developed with an English user interface and documentation in order to give usability to the international GAW community. The software is under continuous maintenance. Following activities are performed automatically:

- Data acquisition: analog, and digital via RS232 and TCP/IP (internet).
- Instrument control: analogue and digital via RS232 (Web Client).
- Instrument-specific and individually structured calibration cycles at arbitrary times. It is possible to define and use several sets of calibrations, individually structured.

¹ Such instruments, producing a large amount of high time resolution data, often times with own software intelligence, which cannot be integrated in the standard data acquisition system of a station, exist at nearly every GAW station.

- Real-time control and warning functions of level of measurement values and instrument parameters.
- Post analysis with individually configured retrievals of arbitrary instrument parameters and measurement data.
- Shewart control cards for means and standard deviations of calibration data such as standard and zeroes.
- Transparent NRT or RT data transfer daily, hourly or shorter by FTP or Email.
- Data acquisition and instrument control, with automated backup.
- Reliable raw data acquisition, also when database is inactive.
- Business-grade free SQL database.
- Generic drivers for direct instrument read-out or from instrument-specific raw data files.
- Task management: Each task runs as an independent thread
- Heavy duty, low maintenance, database, at no cost basis. Database stores raw data, Meta data from digital station log book and intermediate and flagged data as result of data validation as input for the processing of calibrations. Daily backup to a server.
- Operating System: Windows 7

3.1 Practicability

It is well known that usability of software does not only depend on the sum of its features but much more on how well features are organized in order to fulfill the real workflow. Since 2003 the software is continuously in use and is supported by an ongoing project for at least the next 7 years. The sources of Dafit are available for scientific purposes of institutions taking part in the GAW program.

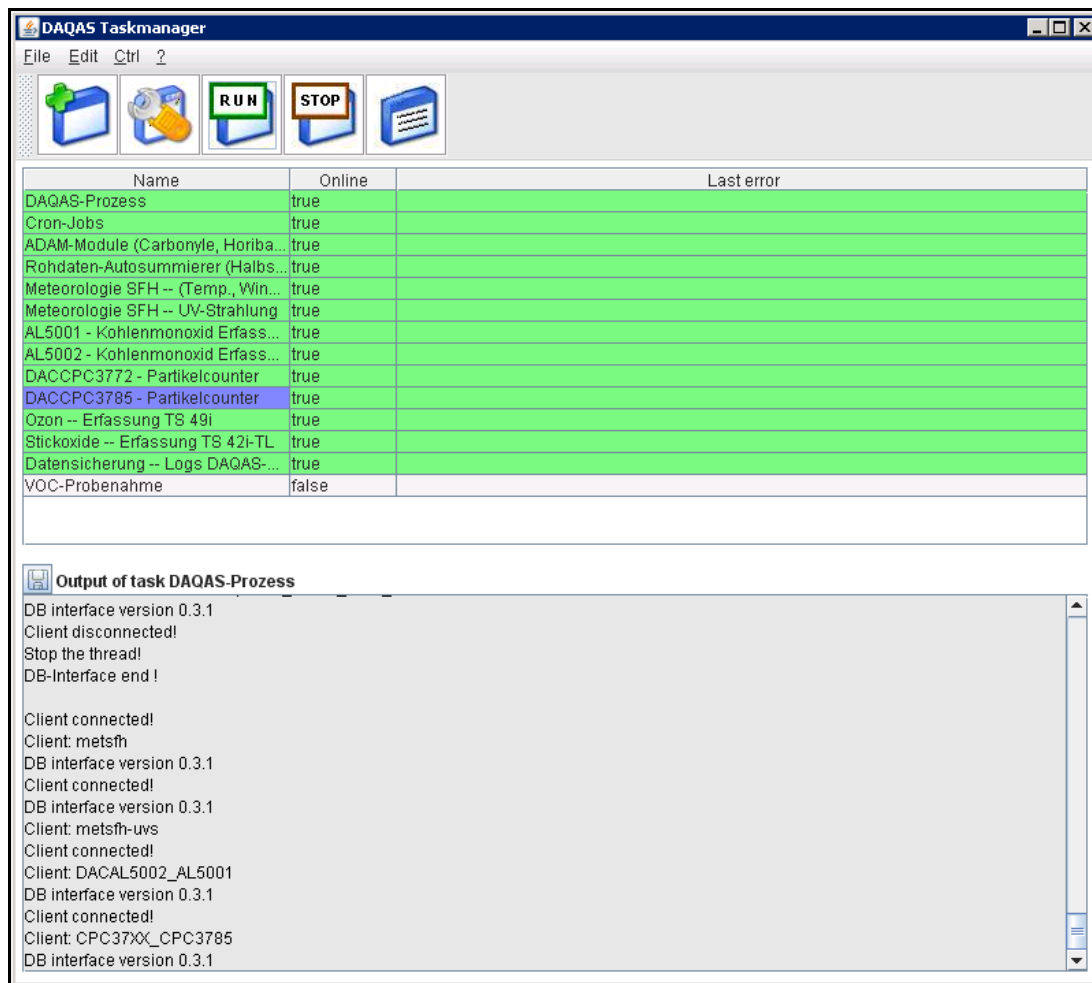


Figure 1 - Task manager of the client server system Daqas – each task runs as an independent client

1. *User Client for measurement and instrument control*

- Define parameter-specific calibrations, Shewhart control cards, (mean, sdev for zeros and span).
- Station log book for the integrated storage and retrieval of meta-data with utf-8 unicode support.
- Automatic check whether measurement values and instrument parameters stay within an individually predefined range.
- System configuration: Definition of instruments in the acquisition system and external instruments, measurement variables, staff, laboratory activities for specific retrieval in the station log book.
- Export of measurement data
- View of historical data with several different time series in one xy-plot.
- Time efficient view of arbitrary predefined sets of xy-plots.
- Analog control (relay) or retrieve (V or mA), measurement of laboratory temperature via Adam 5000 system process computers.
- Manual or automatic switch of valves.
- Multi user client in Java, allows parallel operation from different computers in the measurement station.

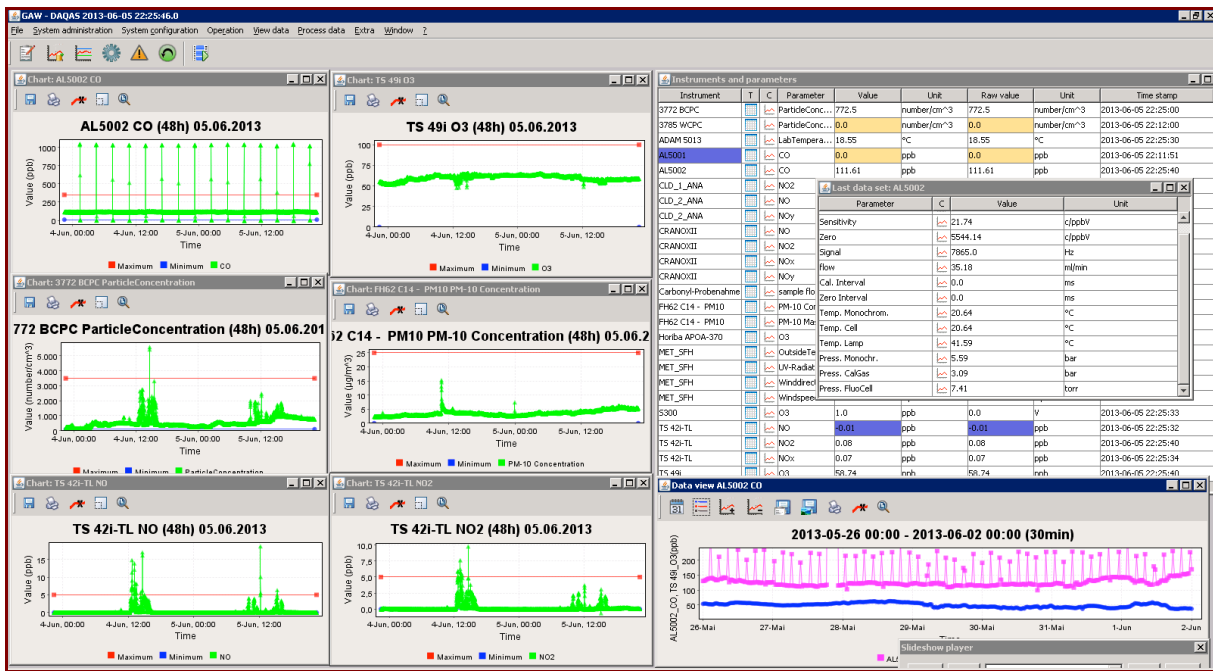


Figure 2 - User client

The system stores raw data, validated data and meta-data from station logbook, multi user access

2. Client for processing of calibrated data - Isave

- Interactive control and flagging of outliers or artefacts for validation.
- Up to three measured time series can be displayed simultaneously.
- 4-step standardized procedure for data flagging and processing of calibrated data.
- Automated integration of time and measurement related meta information from logbook in the xy-plot.
- Automated filtering and flagging of non-relevant calibration data and data of undefined gasmixtures (short after switching valves) from measurement time series.
- Included script language for efficient additional processing of measurement data.
- Import function for the processing of external measurement data.
- This client offers a predefined workflow for validation and the processing and production of calibrated data.

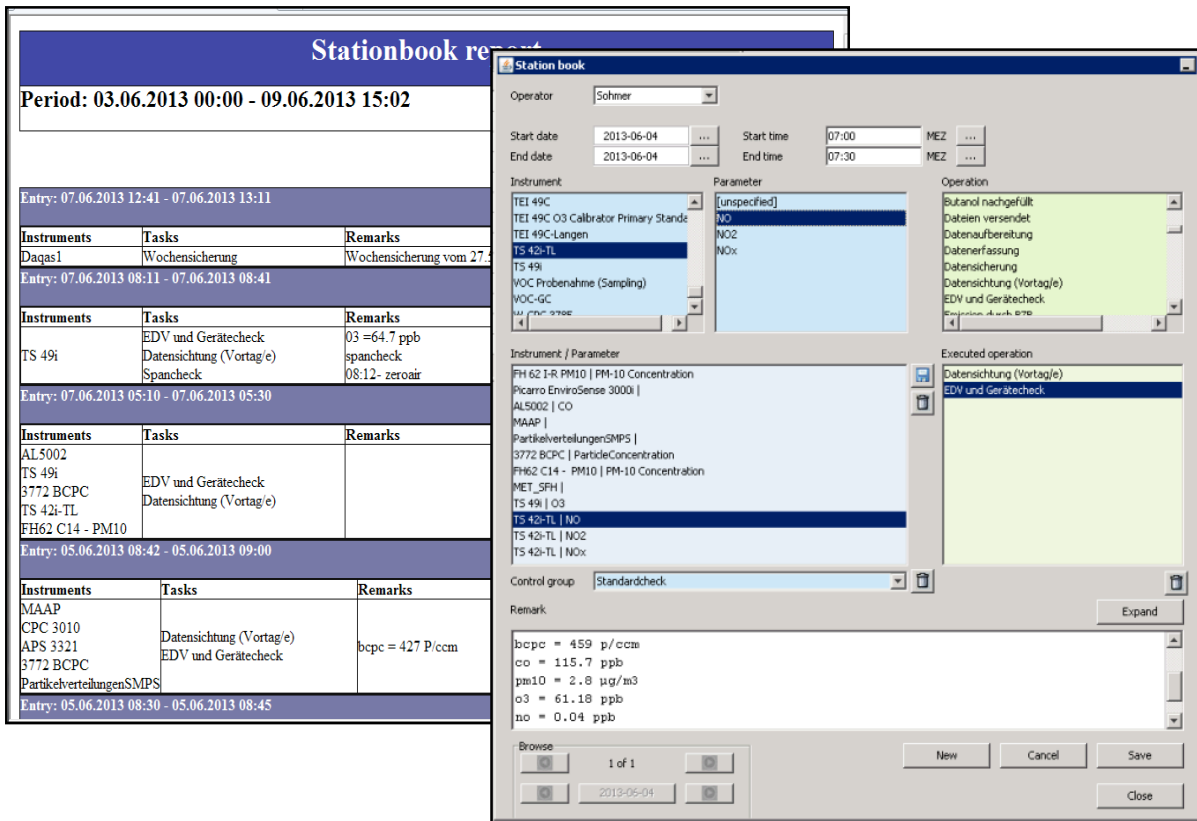


Figure 3 - Logbook report (left) with meta information and input mask for station logbook (right)

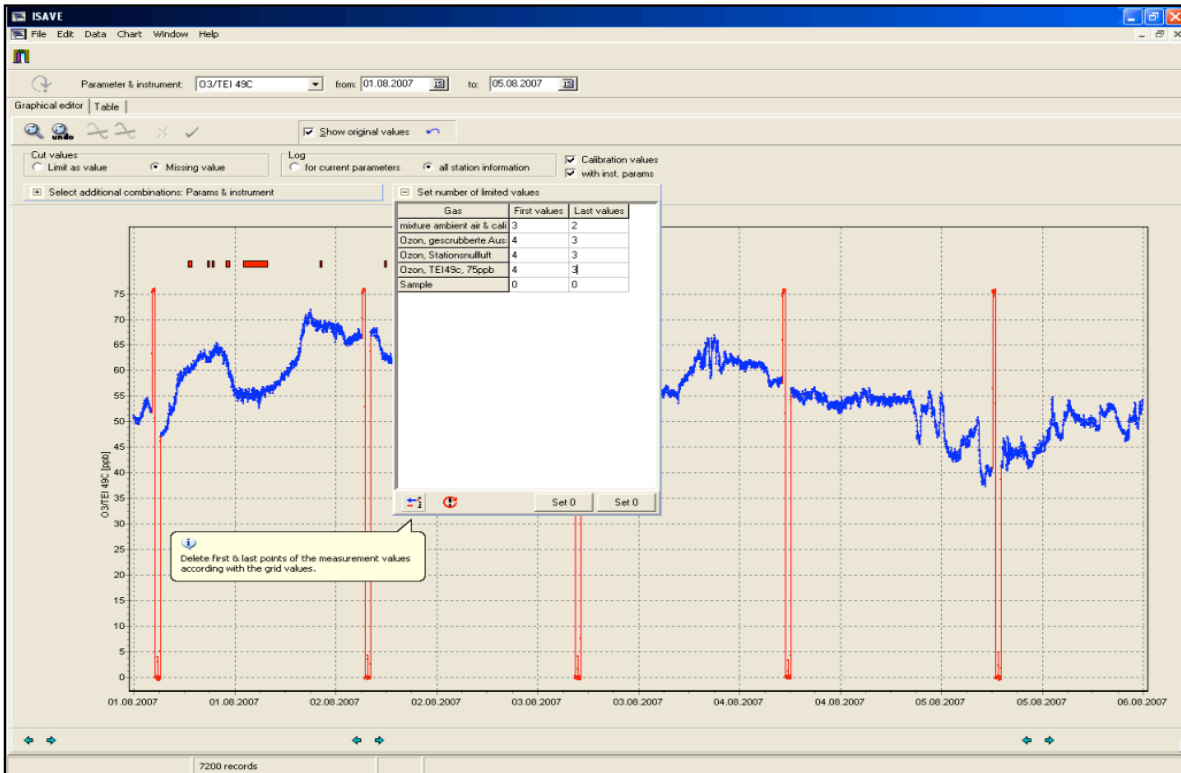


Figure 4 - Interactive control and flagging for validation of measured data

Because the proposed methodology separates methods and its parameters, it can be a good substitution to many situations in data preparation whereas up to now normally for each little change the program source would have to be changed and compiled. This gives an essential facilitation to the whole process of data preparation of time series data in the daily monitoring. The set of methods works with ASCII data files, in case each line has a time stamp with own date and time. The program works on files with arbitrary minute data or higher aggregated time data and provides precision up to the second. Dafit runs on Windows XP-Win 8. Resulting data files are in csv format, can be opened with spreadsheet programs and a show a well-defined contents in order to import to a DBMS system.

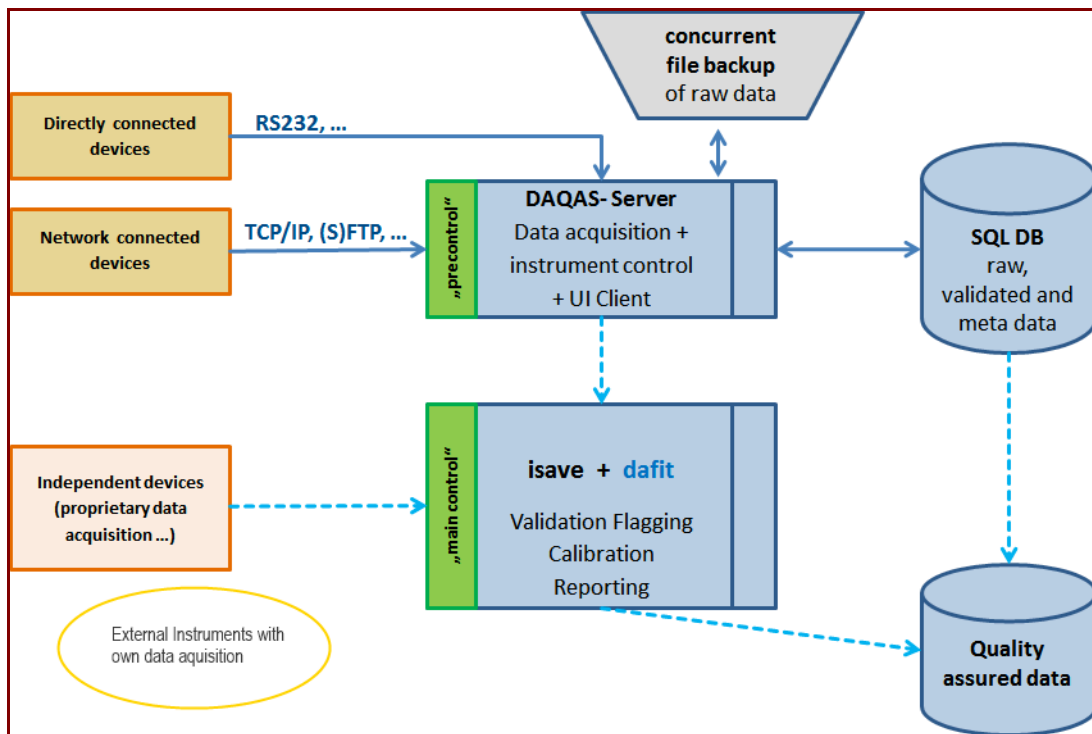


Figure 6 - Scheme of data processing 1. CS system Daqas, 2. UI client, 3. calibration client Isave and 4. Dafit. Continuous lines show processes running 24/7 . Dashed lines show processes running upon request

3.1 General

In this section a work flow oriented methodology for efficient data preparation, validation and data flagging of monitoring time series data is described, following a more general approach.

This software is relatively fast to install and to learn and applicable for all cases, when up to now elementary data preparation was required.

It helps in such situations, when practically the same program for data preparation and validation had to be altered only for a little change and then to be recompiled again and again.

It separates methods and parameters from each other and saves the parameters in an own project file. Because the program uses a format interpreter it can process a larger variety of ASCII files which are produced as an output of different data acquisition programs for different instruments or from larger data acquisition systems which are used at GAW Stations.

Concept

- Separate methods, parameters and processed data.
- Store parameters and data of a problem in an own project.
- Save each step of processed data, from the beginning to the final result in a hierarchical history (Workflow), which allows back traceability.
- You receive an ordered set of methods and parameters, stored in the project (Solution).

3.2 *How to work with (Workflow)*

The program is directory oriented. At first a directory has to be created for data with a certain time interval, for example, one month. The maximum interval of data which can be processed at once is one year. Then a new project name for this data file is created and stored. In the next step the data structure of the file will be opened with an editor and has to be investigated by the user. At next the user will have to find what preparatory steps with the data file will have to be done in which order to receive a usable file for data validation. Usable file means: Each line contains a datum of one time interval. Each line (time interval) is readable. Missing gaps (sometimes e.g. during a power down, data acquisition does not work.) in the time series data time structure are substituted in the file with a missing data flag. The time stamps are in ascending order.

Finally a plan for the stepwise processing of the data will have to be made.

Besides this the following elementary requirements have to be regarded. The data file has to be in ASCII. Each line of the data file has to contain a date time header with fields of fixed width YYYY or YY, MM, DD, hh, mm (and ss optional for the second). The order of time and date is arbitrary, as the time date fields are interpreted. Each line must contain a minimum of one column of data values and a maximum of 30 columns. At one time only one column can be processed. It is recommended to use list directed data format which means: numbers are separated by a comma or a semicolon, or a blank or tab. The columns after the time data header may consist of numbers and strings in arbitrary order.

3.2.1 *Prepare and repair data structure*

After the first preparatory steps which have been explained above, it has to be tested, whether methods from a first group of elementary methods to correct deficiencies in the data structure have to be applied. The application of these methods is optional. Following methods presently are given:

concatenate files (e.g. daily files to a monthly or annual file or concatenation over an arbitrary interval)

inverse time order (the data have to be in ascending order)

remove multiple empty lines and multiple separation marks (for the list directed format each column has to be separated by one separating character).

substitute separation marks (e.g. TAB by semicolon, or comma or blank)

filter corrupted lines (sometimes data acquisition produces corrupted lines. This filter removes such lines and produces a log file of removed information.)

After this, the application of methods from the next group of higher developed methods has to be prepared and planned.

3.2.2 Apply higher methods for time structure correction, validation, flagging and final aggregation

The following sequence of methods has shown practical usability for high quality atmospheric gas or aerosol measurements for global atmosphere watch data.

- **test and repair for a correct and consistent time structure.** This tests check for an equidistant time grid. Each single time step between start time and end time must be contained in the resulting output. In case there is a gap in the data file then it will be substituted with the appropriate time date fields and a missing data code for the missing data value.
- **aggregate to a time series with time resolution in the minute scale** e.g. aggregate from very high time resolution of 3 sec, 31sec to 1 minute means. It also is possible to aggregate from e.g. 70 or 90 sec data to pseudo 1 minute means. In case already 1 min data would exist, then this step has to be omitted.
- **first validation step: check interactively plausibility of 1 minute time series and flag with graphical editor.** There can be flagged: spikes, calibrations, outliers etc. In one minute data files with higher time resolution, typically short time artifacts like spikes, outliers, because of technical issues can be found.
- **aggregate to a time series with lower time resolution, preferably in the hour scale.** E.g. from 1 min values to 30 min or 1hr mean values.
- **second validation step: interactive check with graphical editor of 30min data:** Flag non representative episodes, local pollutions etc. In such lower time resolution time series, process related information can be seen better and can be analyzed and validated. For example causes for short time sharp shifts in the level of measured values can be verified with a trajectory model like Hysplit or pollution events can be flagged. This step has development potential for inclusion of automated statistical and chemical or physical models for data validation. In case a final delivery of 1hr data is requested, this is no problem. The recalculation to 1 hr data only costs small effort and time.

3.2.3 Methods of the second group for aggregation and validation

Time structure

This test is contained in the methods 2.3.2 and 2.3.3. It is performed each time when an aggregation of data is calculated.

Means of even intervals (method for whole 1 minute data)

This method works with a programmed chain of conditions. It works only for whole minute data. Data intervals with uneven seconds may not be treated. It is slower than method 2.3.3. (Both methods 2.3.2 and 2.3.3 calculate the arithmetic mean, standard deviation, and the percentage of available underlying data. A threshold value for this percentage can be selected. An actual existing percentage over or equal this boundary then allows calculation of a mean value.)

Means of broken intervals (single second precision: method for data in the seconds scale or minute data which end with seconds)

This method works with a large array which contains every second of one whole year. According to the start and end time of each mean value for input it's value is stored correctly. In a second step, new mean values will be calculated according to a selected equidistant time grid with arbitrary grid length in the minute range. With this method a 1min data file can be calculated on the same 1min data file. In that case input equals output, but the time structure has been tested for gaps and gaps have been filled in the output with missing data code.

Graphical editor

The graphical editor has various methods for navigation through large data files. It allows interactive graphical flagging with line editors. This means everything above (or under) an interactively drawn line will be flagged. Additional functions are given for scaling, zoom in and out, selecting a single point and its flags and coordinates, for determination of n, mean and median from selected points in a predefined graphical rectangle. Flagging results and comments can be retrieved and analyzed at any time after the processing of the data. On a modern laptop with an I5 processor one whole year with about 500 thousand data is read in about 25 seconds. It allows simultaneously two hand operation: One hand works with predefined keys and the other operates the computer mouse. Against becoming tired, the function of both hands can be exchanged.

3.3 Program user interface

Start window and graphical editor

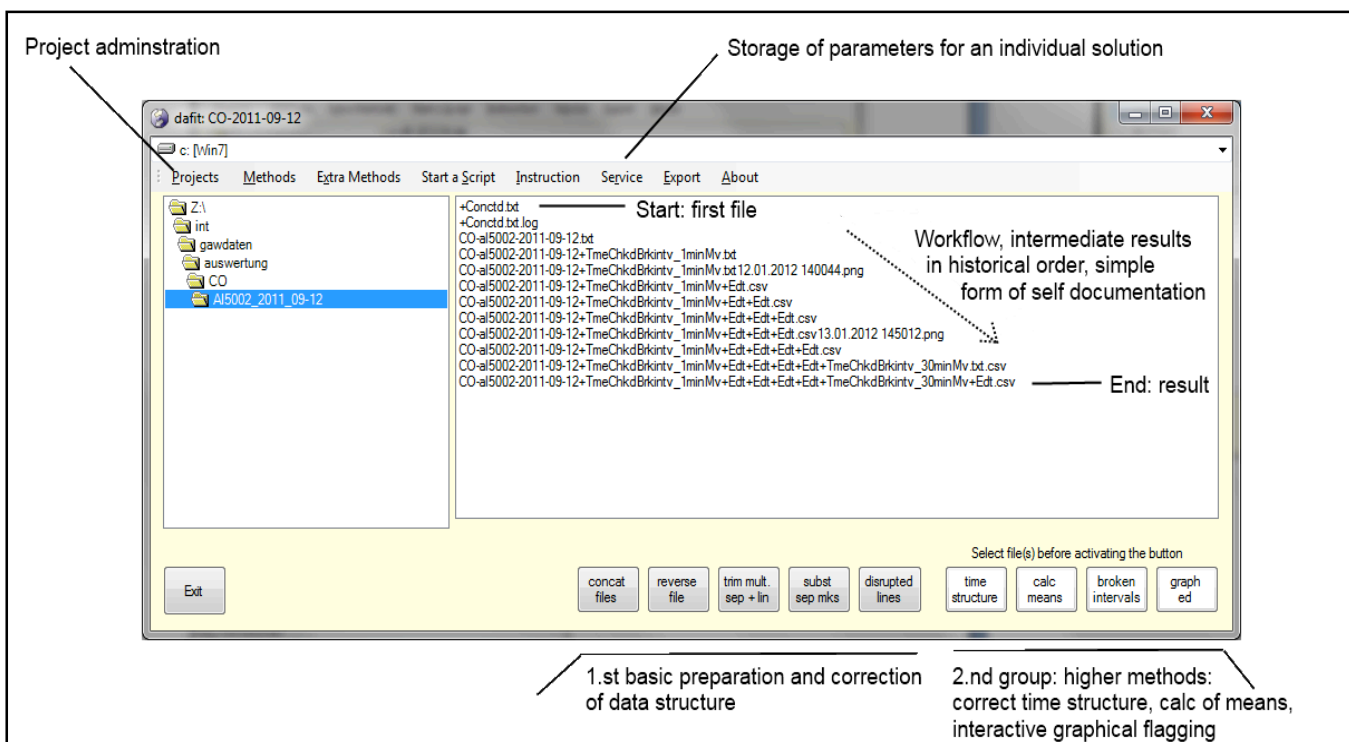


Figure 7- Start window of the program and its essential properties. 1. Create directory and copy data into it. 2. Create project and save. 3. Apply methods for basic preparation and correction 4. Apply higher developed methods for time structure correction, flagging and validation and final aggregation of data

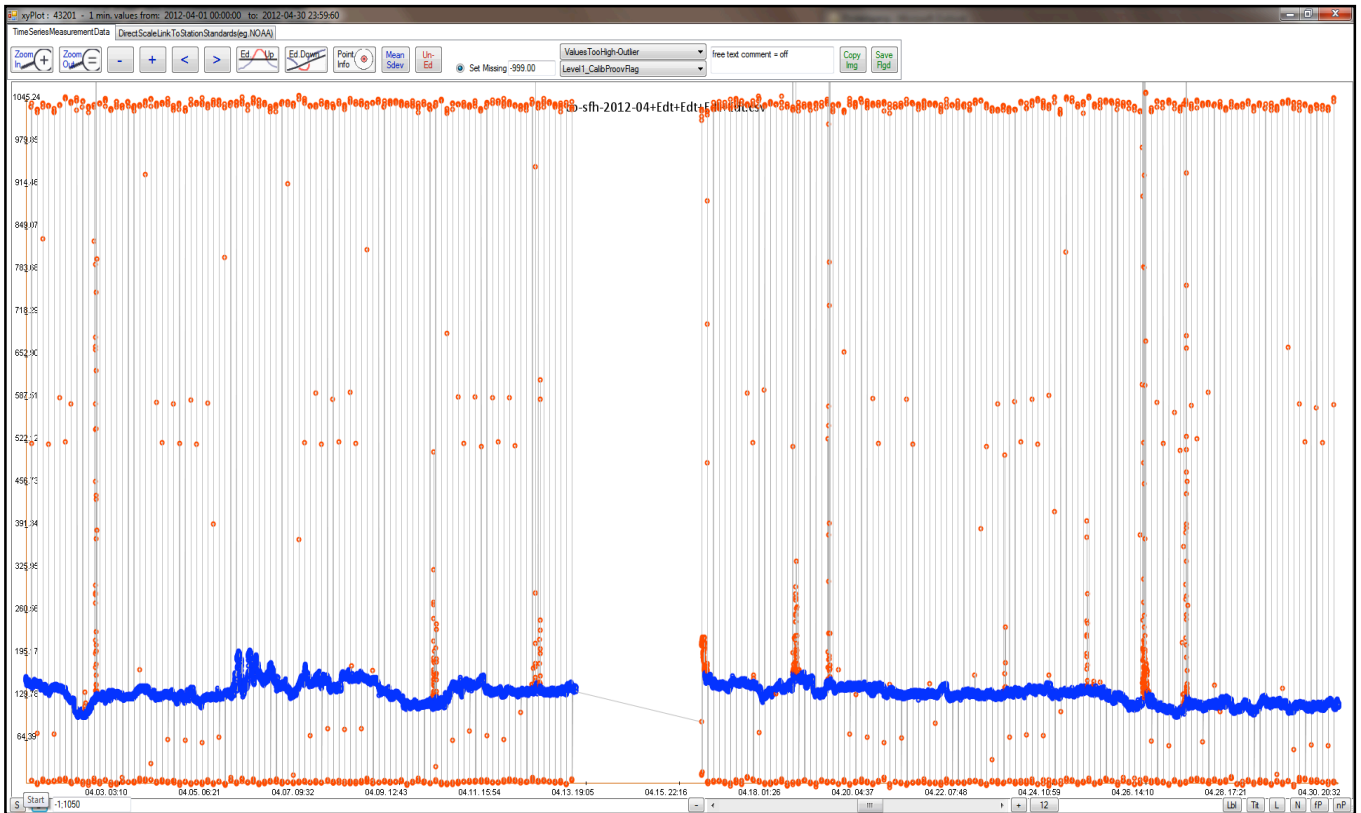


Figure 8 - Graphical editor for interactive control, flagging and plausibility check, with several functions for navigating in the data enables for a productive screening, validation and flagging of the processed time series data

Proposed methodology and software can facilitate essentially the process of data preparation of monitoring time series data. Dafit runs on Windows and is free for station personnel and institutions which work for the UN/WMO Global Atmosphere Watch Programme.

3.4 Interoperability

Format for Dataexport

Format of files with final result is csv. This allows uncomplicated post processing with external programs or scripts from Python or R. The data are well structured in order to be incorporated into data base management systems.

Scripts in R or Python

From within the user interface self- written programs in R or Python can be started. The menu can be configured by the user according to actual requirements.

Conclusion

According to the GAW framework standardization has to be done. The consequent use of the workflow-software approach gives the basis for the standardization of many practical aspects of data handling and quality assurance in GAW stations. Practical examples from astro-physics and nuclear physics show that a „one software solution” is essential for the comparability of data. As a clear outcome the chance for a comparability of the data will be fairly higher than with several hundred individual implementations on GAW measurement stations worldwide.

References

- L. Ries, *How to Keep the Quality Chain - Work Flow-Oriented Data Processing for Global Atmosphere Watch Measurement Stations*. pp. 109-112 In: *Environmental Informatics and Systems Research* . Vol. 2 Workshop and application papers. Eds. Olgierd Hryniewicz, Jan Studzinski, Anna Szediw. Shaker Verlag, 2007, Aachen, 292p.
- L. Ries, *Dafit - a new workflow oriented approach for time efficient data preparation, validation and flagging of time series data from environmental monitoring*. pp. 651-656. In: *Proceedings of the 27th conference on Environmental informatics – Informatics for Environmental Protection, Sustainable Development and Risk Management, Part II* , Shaker Verlag, 2013, Aachen, 938.p, ISBN 979.3-8440-1676-5.

Software Development

Isave – client for processing of calibrations and calibrated data: S. Uhlig, Quo-Data, Dresden,
Daqas – client server system with SQL DB for automated data acquisition, instrument control, calibration, documentation: F. Fell, Informus, Berlin and H. Fell and C. Kernbach, Fell & Kernbach, Berlin
Dafit – Data acquisition files integration tool. L. Ries, Munich

FURTHERANCE OF THE CO₂ MEASUREMENT ERROR CHARACTERISATION FOR THE PROTOTYPE IN SITU FTIR TRACE GAS ANALYSER OPERATED AT LAUDER, NEW ZEALAND

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1. Introduction

A prototype in situ Fourier transform infra-red spectrometer (FTIR) trace gas analyser (Griffith, 2012) has been operating at Lauder, New Zealand (45.04S, 169.68E, 370m amsl) over the period August 2006 to April 2013. Continuous 10 minute measurements of CO₂, CH₄, CO and N₂O are made from air drawn from a 10 metre mast. Daily measurements of a single working tank (prepared by NIWA-Gaslab, Greta point, Wellington, New Zealand) allow calibration of the atmospheric sample to the WMO trace gas scales.

In April 2013 the prototype analyser had a major software and hardware upgrade to bring it into line with the current commercial version of the instrument. Whilst the upgrade has addressed many hardware issues limiting the prototype performance, characterisation of the prototype analyser is still required to analyse and interpret the six year dataset already collected.

We have found that the CO₂ dry mole fraction (*abbr.* CO₂) is sensitive to the temperature error. Such errors arise due to sensor digitisation, sensor response time ('disequilibrium error' Hammer, 2013) or poor representativity of the true gas temperature within the cell volume.

We evaluate the use of a proxy quantity 'CO₂_M' defined as the average of the retrieved scaled mole fraction isotopologues ¹³CO₂ and ¹²CO₂ (in the retrieval, the isotopologue line strengths are scaled by the natural abundance, Griffith, 2012). Through a linear combination of these two isotopologue retrievals overall temperature error sensitivity is minimised. Using CO₂_M, biases between measurements made in sample and calibration modes (arising from cell temperature disequilibrium and representativity errors) are reduced to an acceptable level to allow calibration of the six year 'baseline' data set. Additionally CO₂_M also has the benefit of smaller residual pressure sensitivity than that of CO₂.

We then compare the six-year FTIR CO₂_M atmospheric dataset to CO₂ measurements from a co-located LI-7000 NDIR analyser and coincident CO₂ flask samples.

2. Sensitivity of CO₂ mole fraction to temperature and pressure errors

Mid-infrared transmission spectra recorded by the FTIR trace gas instrument are analysed to retrieve the gas concentrations, C (mol/cm³) of CO₂. The dry air mole fraction X_Y is then calculated by dividing the retrieved gas concentration C_Y by the concentration of air (C_{air}=P/RT) and correcting for the H₂O in the sample: X_Y=C_Y/C_{air}(1-Q), with Q=C_{H₂O}/C_{air}. The sensitivity of the dry air mole fraction to errors in the measurement of sample temperature and pressure can be readily evaluated by forward model calculations, and yield a temperature sensitivity of 2μmol mol⁻¹/°C for the standard CO₂ retrieval (Table 1). This is a significant error source because the temperature sensor used in the prototype analyser can be in error by as much as a few tenths of a degree.

Since the retrieval code 'MALT' (Griffith, 1996) uses prescribed (not fitted) pressure and temperature (measurements from sensors inside the cell) any sensor error or non-representative value will propagate through to the derived CO₂. Such sensitivity to temperature and pressure error is significant in the Lauder prototype analyser as the temperature sensor (a platinum resistance thermometer: PT100) has been shown to have an error of up to 0.1°C in the disequilibrium transition period (Hammer, 2013). This is partially due to the relatively slow response time of the sensor and that calibration measurements were conducted whilst the cell was had not reached thermal equilibrium. These two aforementioned factors contribute to a bias in the measurement of the calibration gas of ~0.2 μmol mol⁻¹ (0.1°C x 2μmol mol⁻¹/°C). Such bias will propagate through to the scaled air sample and cannot be retrospectively corrected for.

Serendipitously, the temperature sensitivities of the CO₂ isotopologues ¹³CO₂ and ¹²CO₂ (retrieved in a different spectral region to CO₂) have opposite sign and of similar magnitude (Table 1). Taking the average of these two ('CO₂_M'), the retrieval sensitivity to temperature error is an order of magnitude less (~0.13 μmol mol⁻¹/°C), but -like CO₂- it is still susceptible to pressure error. Any pressure error is deemed congruent to both sample and working tank measurements thus are minimized in the calibration of sample measurement data set.

Table 1 - Forward model calculations of the retrieval code MALT (Griffith, 1996) show that the CO₂ retrieval has a temperature sensitivity of ~2μmol mol⁻¹/°C. The CO₂_M temperature sensitivity is significantly less

Temperature	CO ₂	¹² CO ₂	¹³ CO ₂	CO ₂ _M
dX/dT [μmol mol ⁻¹ °C ⁻¹]	2.10	-4.10	3.81	-0.13
Pressure				
dX/dP [μmol mol ⁻¹ °C ⁻¹]	-0.66	-0.63	-0.76	-0.7

3. CO₂_M residual sensitivities

Due to the imperfect parameterizations in the HITRAN 2004 spectroscopic database, probable systematic errors in the retrieval code and the folding in of any temperature and pressure measurement errors into forward spectroscopic model calculations there will be a systematic first order residual sensitivity² of the calculated raw mole fractions to the absolute magnitude of prescribed quantities used in the retrieval such as temperature, pressure and water vapour. I.e. Hammer (2013) has derived a linear pressure residual sensitivity for CO₂ (dCO₂/dP) of 0.0085 μmol mol⁻¹/mB. Such residual sensitivities need to be experimentally derived and corrected for in the calibration of the sample dataset. This is also true for CO₂_M.

3.1 Residual pressure sensitivity

The Residual pressure sensitivity (RPS) is a significant contribution to systematic bias as the FTIR had a large operational cell pressure range (815mB –950mB), with differences between sample and calibration cell pressure of up to 50mB. With Cell pressures ranging 100mB CO₂ RPS's of ~0.85 μmol mol⁻¹ are not uncommon thus is it imperative to apply RPS corrections to the Lauder measurements to derive a consistent dataset.

² Residual sensitivity is also referred to as 'cross sensitivity' as in Griffith, 2012

Both CO₂ and CO_{2_M} RTS's were experimentally derived at Lauder. The RPS of CO₂ is linear (0.0075 μmol mol⁻¹/mB) and similar to that measured by Hammer (2013) whilst the RPS of CO_{2_M} is non-linear (Figure 1). Over the operational pressure range CO_{2_M} and CO₂ RPS have opposite signs and CO_{2_M} has a reduced RPS span, about half that of CO₂. Unlike the linear CO₂ RPS, the magnitude of the nonlinear CO_{2_M} RPS term is dependent on the cell pressure thus must be explicitly calculated for each variation in cell pressure.

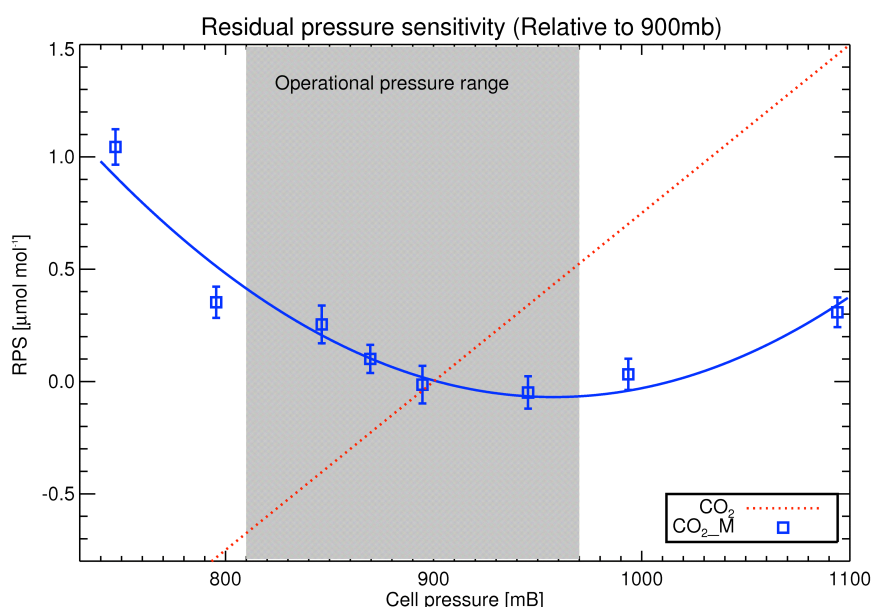


Figure 1 - Residual pressure sensitivity (RPS) of CO₂ and CO_{2_M}. Both RPS's are normalised to 0.0 at 900mB. The pressure range over which sample measurements were made is shaded in grey. The CO_{2_M} RPS is non-linear. Over the operational pressure range CO_{2_M} has an opposite slope to that of CO₂ and half the span

3.2 Residual temperature sensitivity (RTS)

Residual temperature sensitivity (RTS) is assumed to be negligible as the FTIR temperature is maintained within a few tenths of a degree. RTS is experimentally hard to measure and has not been quantified for the Lauder prototype FTIR.

3.3 Residual H₂O sensitivity (RQS)

Residual H₂O sensitivity (RQS) correction is not applied. RQS is experimentally challenging to measure (Hammer, 2013) and also exhibits its own pressure sensitivity. Due to these non-trivial issues and that both sample and calibration H₂O measurements never exceed 10 μmol mol⁻¹-and do not differ by more than 2 μmol mol⁻¹- we choose not to apply a RQS term.

4. Assessment of CO_{2_M}

Before accepting CO_{2_M} as a valid CO₂ proxy, we evaluated its performance. This was done by comparing (to CO₂) its 1) precision, 2) stability across instrument and calibration gas changes, and 3) accuracy/precision from target tank measurements. From these comparisons we conclude CO_{2_M} is more stable and less susceptible to temperature sensor drift and error without compromising measurement precision. Regardless of CO_{2_M}'s performance there are associated caveats of use. At this preliminary stage of CO_{2_M} assessment, it cannot be employed in all measurement situations without further investigation of retrieval sensitivity to varying isotopic composition.

4.1 Precision

Allan variance analysis of CO_{2_M} and CO₂ (result not shown) reveals both have a 10 minute spectra integration precision of 0.02-0.03 $\mu\text{mol mol}^{-1}$. By employing CO_{2_M}, measurement precision is not compromised.

4.2 CO₂ and CO_{2_M} stability across instrument and calibration gas changes.

The daily working tank measurements of CO₂ and CO_{2_M} were divided by the assigned working tank value to obtain a scale factor. This ratio allows comparison (Figure 2, top panel) of the stability and variance of CO₂ and CO_{2_M} across working tank and instrument changes (vertical dashed lines in the plots). The standard deviations of the CO_{2_M} scale factor (over a 7-day running mean period) are twice as small as those inferred from CO₂ (Figure 2, bottom panel) demonstrating the use of CO_{2_M} to minimize the effect of temperature errors. The difference in trends in the two scale factors prior to mid-2010 could be due to drift in the temperature sensor calibration, which impacts CO₂ more than CO_{2_M}. The temperature probe was replaced in Nov 2010, since then both scale factor trends are similar but CO_{2_M} scatter is still smaller indicating that whilst temperature error is still present the new sensor does not suffer significant drift.

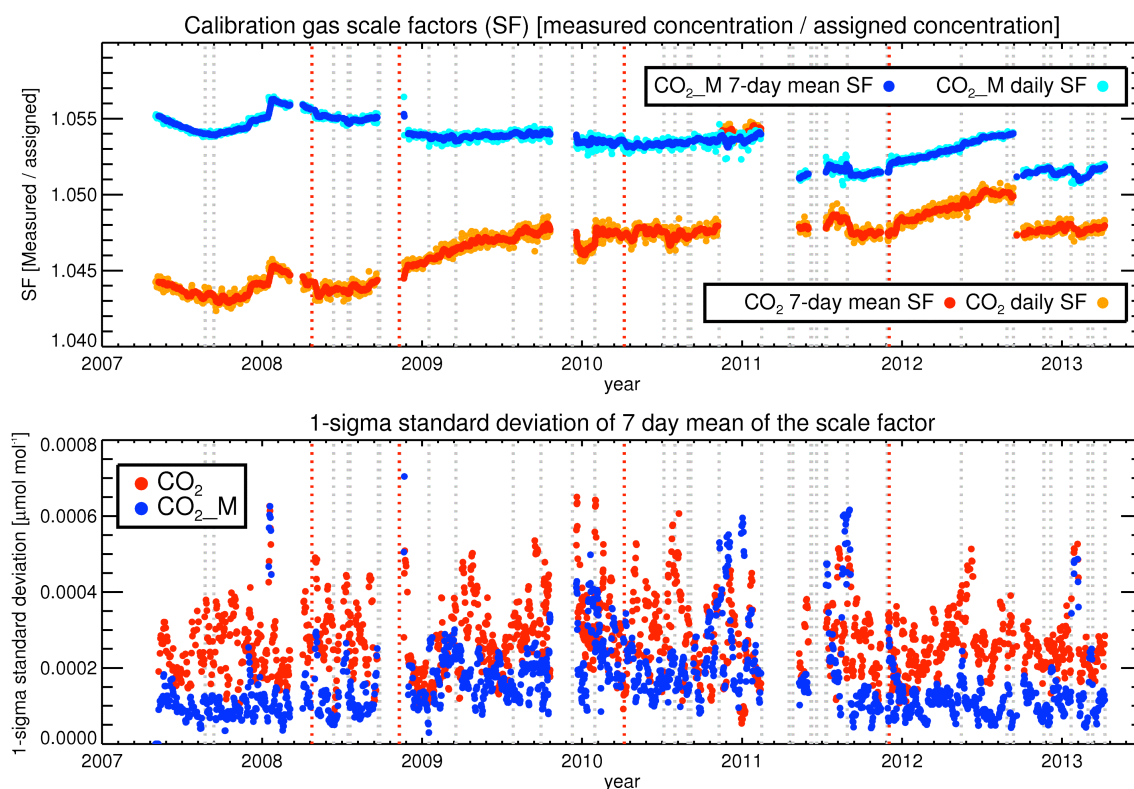


Figure 2- Top panel: RPS corrected CO₂ and CO_{2_M} scale factors of the daily working tank. The scale factor is the measured amount divided by the assigned tank value. Grey and red vertical lines indicate instrument and working tank changes respectively. Bottom panel: 7-day running mean standard deviations of CO₂ and CO_{2_M} scale factors.

4.3 Caveats of use: effect of the variations in isotopic composition

To interpret the Lauder time series we rely on the fact that there is minimal variation in the isotopic composition of sample measurements during 'baseline' (well mixed boundary layer) conditions (confirmed via co-located $\delta^{13}\text{C-CO}_2$ flask sample measurements, but not shown) and that the working tanks (for calibration) that have been employed to date are of similar isotopic composition to baseline air composition. Work is on-going to encompass CO_{2_M} sensitivity to

variations in the isotopic composition of a given sample. Additionally, when we use CO₂_M as the proxy natural isotopologue abundance of CO₂, we cannot derive a meaningful δ¹³C-CO₂ quantity.

4.4 Comparison of FTIR and Li-7000 coincident target tank measurements

In addition to using the daily working tank to quantify the performance of CO₂_M, measurements of a series of target tanks (TT) were also made. CO₂_M and CO₂ concentrations of these tanks were compared against an independent CO₂ analyser operating in parallel with the FTIR.

Since June 2008 a Licor-7000 NDIR CO₂ analyser (Li-7000) has been operating at Lauder, in parallel with the FTIR. The Li-7000 operates continuously, logging 5 minute averages of CO₂ concentrations. The Li-7000 system, analysis procedures and operation are similar to the latest incarnation of the Baring Head CO₂ measurement system (Brailsford 2012). Four working tanks of differing CO₂ concentrations are used to define the instrument response to calibrate sample measurements. These tanks are measured daily along with the same target tanks the FTIR measures.

There were four periods in which the FTIR and Licor-7000 measured the same target tank. Figure 3 displays FTIR CO₂ and CO₂_M against that of the Licor-7000. The composition assignment of the target tank in the last three intervals is unknown, a proxy value has been assigned so only the relative difference of instrument measurements can be assessed.

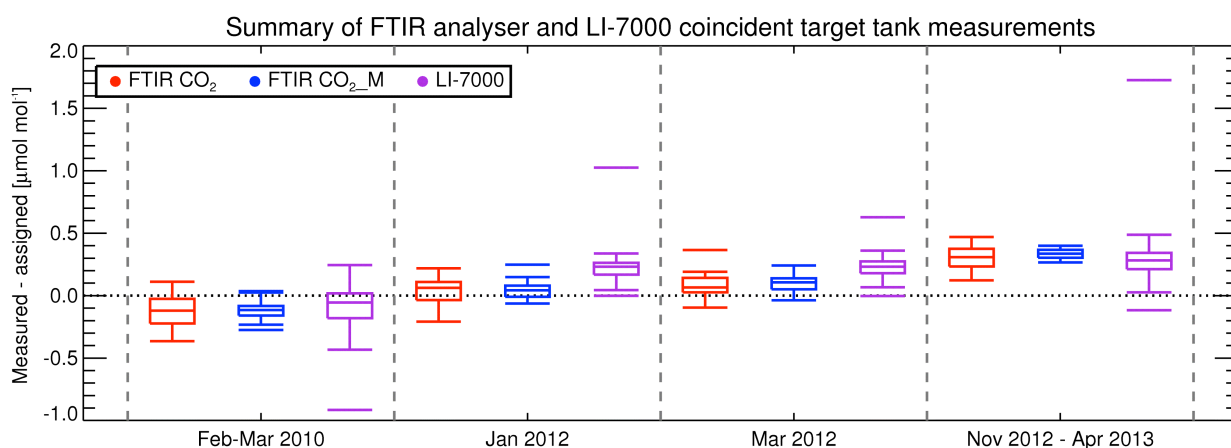


Figure 3 - A display of four coincident intervals in which weekly measurements of a common 'Target' tank were made by both the FTIR and Licor-7000 NDIR analyser. In the last three intervals the same TT is measured and is pending composition assignment so in the interim, a proxy TT value is used. Over the last three intervals only the relative difference can be assessed

In all four intervals CO₂_M has a smaller scatter than the normal FTIR CO₂ retrieval and the Li-7000. The FTIR system has reproducibility that is comparable or better than the NDIR analyser. In August 2012 the procedure for the FTIR target tank and working tank measurements was altered to shift the start of the measurement away from the disequilibrium transition period (the cell was filled slowly ~1L min⁻¹ and left to settle for 4 minutes before spectra acquisition). This alteration has reduced the CO₂_M scatter to <0.2 µmol mol⁻¹ and has brought both FTIR measurements into line with the Li-7000. Thus by careful operation of the FTIR along with employing CO₂_M as the proxy CO₂ measurement the effect of temperature errors propagating through to the retrieved CO₂ concentration can be minimized with an increase in accuracy and reproducibility.

5. Lauder CO₂ time series measurements

Fortnightly flask samples (CO₂, CH₄, N₂O, CO, δ¹³C-CO₂) have been acquired at the Lauder since May 2009, the majority of such samples purposely taken during baseline³ conditions. The flask sampling system is operated in accordance with the methodology described in Brailsford (2012). With a trio of CO₂ measurement systems any anomalies arising in a single instrument are easily identified.

Hourly means of corrected and calibrated CO₂ measurements for the three systems ('CO₂_M' for the FTIR) taken in baseline conditions are displayed in Figure 4. All three datasets capture the continuing ubiquitous upward trend in CO₂. The high temporal resolution of the two continuous analysers reveals an annual seasonal cycle amplitude of ~ 2 μmol mol⁻¹ at Lauder.

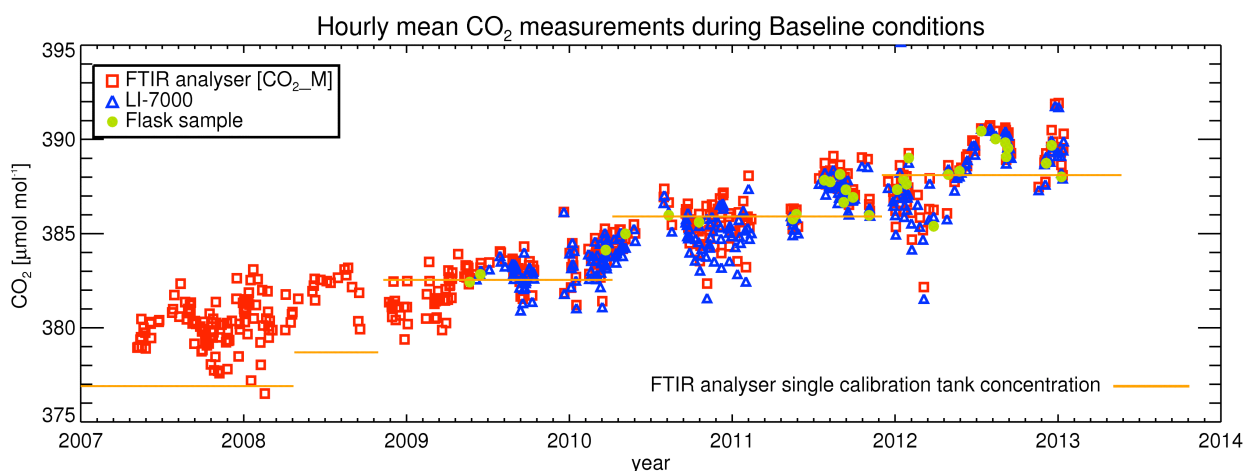


Figure 4 - Hourly mean of CO₂_M and Li-7000 CO₂ measurements taken between 1500-1600 NZST when the wind speed > 5ms⁻¹ (so called 'Baseline' conditions). Overlaid are CO₂ flask samples taken in the same conditions along with the FTIR analyser single working tank assigned value

5.1 Differences in the three time series

Once the Li-7000 target tank difference is taken into account there is a ~0.3 μmol mol⁻¹ high bias in the FTIR CO₂_M and CO₂ measurements (the FTIR CO₂ time series is not shown) relative to the Li-7000 (Figure 5, top panel). This is perplexing as this bias is not present in the most recent coincident target tank measurements (the double difference⁴ is ~0 μmol mol⁻¹). The induced bias from using a single working tank is too small account for the difference (explained in section 5.1.1) and the bias is common to both CO₂ and CO₂_M indicating temperature error is not the main source. A pressure sensor or pressure representivity error of 0.4mB would be needed to account for 0.3 μmol mol⁻¹ bias (table 1). Is there an unknown systematic temperature error between static (calibration) and flow (sample) modes? Such possibilities will be investigated and is a source of concern.

³ Analysis of the monthly diurnal cycle at the Lauder site shows a minimum in CO₂ variability in the mid-afternoon in all months. We consider the hourly mean CO₂ from 15:00-16:00 NZST when the mean wind speed is greater than 5 m/s. We assume these data are representative of CO₂ mixing ratios within a well-mixed planetary boundary layer and/or spatial scales that can be adequately represented in atmospheric models. We label such data as 'Baseline'.

⁴ Double difference = (FTIR-TT) - (Li-7000-TT)

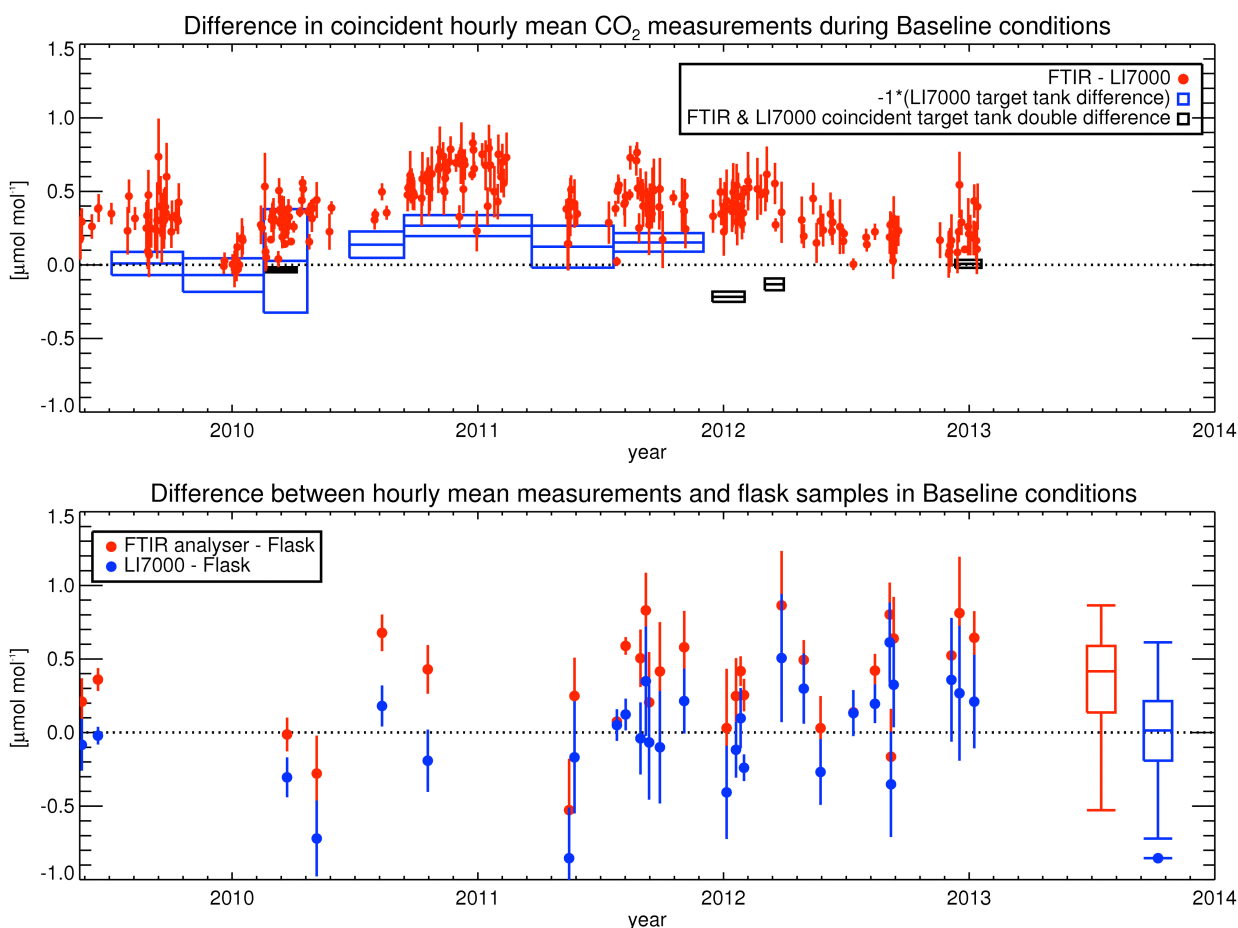


Figure 5 - Top panel: Differences between the FTIR CO₂_M and Li-7000 baseline time series displayed in Figure 4. The negative of the Li-7000 TT difference and the co-incident Li-7000 FTIR target tank double difference are also shown. Bottom panel: The two continuous analyser CO₂ time series relative to coincident flask measurements (in baseline conditions)

Since 2012 both continuous CO₂ analysers show a high offset relative to the coincident flask sample measurements (Figure 5, bottom panel) with the Li-7000 being in better agreement indicating that the FTIR measurements are potentially the main source of instrument inter-comparison bias. The GAW inter comparability criteria (for southern hemisphere) of 0.05 µmol mol⁻¹ is not met in any comparison combination of the three systems highlighting not only differences in the co-located instrumentation, but also intra-lab comparability (flask samples measured at the NIWA-Gaslab).

5.1.1 Linear calibration of the FTIR with a single working tank

The FTIR response is linear with a non-zero y-intercept (Griffith, 2012 & Hammer, 2013). Linear calibration with a single working tank (such as the case in operation of the Lauder FTIR) cannot account for a non-zero y-intercept term. The resultant calibration bias by assuming a zero offset has a dependence on the difference between the working tank assignment and sample abundance. An estimated maximum bias of ~0.05 µmol mol⁻¹ was calculated (using a multi tank suite experiment, results of which are not shown) which is an order of magnitude too small to account for differences between the FTIR analyser and the Li-7000 (Figure 5, top panel).

6. Discussion

The temperature sensor in the Lauder prototype FTIR can have an error of up to 0.1°C which can cause biases in CO₂ of up to 0.2 μmol mol⁻¹. By defining the quantity 'CO₂_M' the impact of the temperature probe error is significantly reduced. Additionally, the RPS of CO₂_M is substantially less than that of CO₂ over the operational pressure range.

CO₂_M can be used at Lauder because baseline δ¹³C-CO₂ variations are small and the working tanks employed to date are of comparable isotopic composition.

Analysis of the target tank measurements and daily measurements of the working tank show that CO₂_M has better temporal stability than CO₂ without compromising precision. The temporal stability (day-to-day repeatability) can be further improved by scheduling measurements to avoid the worst of the disequilibrium transition period. With improvement of the FTIR target tank measurement schedule CO₂_M reproducibility was better than that of CO₂ and the also the Li-7000.

Whilst GAW instrument comparability guidelines are not met, the FTIR captures seasonal cycles and trend (systematic bias is ~10% of seasonal cycle amplitude).

A bias of ~0.3 μmol mol⁻¹ between the FTIR and Li-700 cannot be fully explained. The two most probable sources are a pressure error and/or a static-flow mode bias both of which require further investigation. Such bias is a source of major concern and hence a focus of coming work.

6.1 Outlook

The FTIR was upgraded in April 2013. A fast response thermocouple replaced the PT100 temperature sensor and the cell pressure is now actively controlled (+/- 0.5 mB). The effects of these changes will be analysed in the near future. Daily target tank measurements will be conducted along with employing a multiple working tank suite (of differing concentrations) to quantify the linear calibration offset of the FTIR.

Acknowledgements

We would like to thank Sam Hammer for detailed discussions and advice. We would also like to thank Sylvia Nichol for extracting flask sample data from the NIWA Gaslab database. Nicholas Deutscher, Stephen Parkes, Martin Riegenbach and Graeme Kettlewell for provided invaluable technical advice and support on the operation of the Lauder prototype FTIR analyser. This research is supported by NIWA through funding from New Zealand's Ministry for Business, Innovation and Employment.

References

- Brailsford, G. W., B. B. Stephens, A. J. Gomez, K. Riedel, S. Mikaloff-Fletcher, S. E. Nichol, and M. R. Manning, *Long-term continuous atmospheric CO₂ measurements at Baring Head, New Zealand*, Atmos. Meas. Tech., 5, 3109-3117, 2012
- Griffith, D. W. T.: *Synthetic calibration and quantitative analysis of gas phase infrared spectra*, Appl. Spectrosc., 50(1), 59-70, 1996
- Griffith, D. W. T., N. Deutscher, C. Caldow, G. Kettlewell, M. Riegenbach, S. Hammer, *A Fourier transform infrared trace gas analyser for atmospheric applications*, Atmos. Meas. Tech., 5, 2481–2498, 2012
- Hammer, S., D. W. T. Griffith, G. Konrad, S. Vardag, C. Caldow, I. Levin, *Assessment of a multi-species in-situ FTIR for precise atmospheric greenhouse gas observations*, Atmos. Meas. Tech., 6, 1153–1170, 2013

INTERCOMPARISON EXPERIMENTS FOR GREENHOUSE GASES OBSERVATION (iceGGO) IN JAPAN

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1. Introduction

In harmony with the WMO/BIPM cooperation in the international community, the Japan Meteorological Agency (JMA) and active observation laboratories in Japan have established a national alliance with the National Metrology Institute of Japan (NMIJ), which is part of the National Institute of Advanced Industrial Science and Technology (AIST), to compare standard gas scales each other. In the framework of this alliance, we started intercomparison experiments named iceGGO (InterComparison Experiments for Greenhouse Gases Observation) in 2012, and two intercomparison experiments for CH₄ and CO₂ were conducted in iceGGO from 2012 to 2013.

The purpose of the first experiment named iceGGO-1 (CH₄) for CH₄ is to compare the standard gas scales used by observation laboratories with the SI (International System of Units) traceable standard gases prepared by NMIJ. This was the first comparison experiment conducted in cooperation with the observation laboratories and the national metrology institute in Japan. On the other hand, the second experiment named iceGGO-2 (CO₂) for CO₂ was carried out to estimate the isotope effect on various NDIR analyzers in CO₂ measurement, as well as to intercompare standard gas scales used by domestic observation laboratories.

2. Overviews of two intercomparison experiments conducted in iceGGO

Table 1 shows the overviews of two intercomparison experiments conducted in iceGGO. In iceGGO-1 (CH₄), seven laboratories participated, and six standard gases with a range of CH₄ mole fractions from about 1665 ppb to about 2240 ppb were circulated from Oct. 2012 to Mar. 2013 in the following sequence: JMA, National Institute of Polar Research (NIPR), AIST, Meteorological Research Institute (MRI), National Institute for Environmental Studies (NIES), Tohoku University (TU) and JMA again. Four of the 6 standard gases were prepared by using purified natural air as a diluent gas and pure CH₄ gas. CH₄ mole fractions in these standard gases ranged from about 1665 ppb to about 1920 ppb. These gases were provided by JMA, and two of these gases were used for CH₄ reference gas intercomparison as the activity in the GAW World Calibration Centre (WCC) in Asia and the South-West Pacific. The other two standard gases were SI traceable, and were prepared by a gravimetric method of NMIJ using synthetic air (mixture of pure N₂, O₂ and Ar) and pure CH₄ gas. CH₄ mole fractions in these cylinders were about 1830 ppb and about 2240 ppb. These gases were prepared additionally at the time of CCQM-K82 intercomparison.

In iceGGO-2 (CO₂), five laboratories participated, and nine standard gases were circulated from May 2012 to Aug. 2012 in the following sequence: AIST, NIES, JMA, NIPR and TU. Six of the 9 standard gases were prepared using purified natural air and pure CO₂. CO₂ mole fractions in these standard gases ranged from about 340 ppm to about 450 ppm. The isotopic compositions of CO₂ ($\delta^{13}\text{C}$) in these standard gases were -30 ‰ (VPDB), and were significantly lighter than that in natural air because the pure CO₂ gas was derived from burned petroleum. The six standard gases were provided by TU. In addition, to estimate the isotope effect on various analyzers, three of the 9 standard gases were provided by NIES. Two of them were prepared using dry natural air and CO₂ mole fractions were about 405 ppm and about 410 ppm. $\delta^{13}\text{C}$ in these standard gases were -8.8 ‰ and -9.0 ‰, respectively. The last one was an enriched ¹³CO₂ gas. CO₂ mole fraction in this cylinder was about 370 ppm, and $\delta^{13}\text{C}$ was +55 ‰ (Tohjima et al., 2009).

Table 1 - Overviews of two intercomparison experiments conducted in iceGGO

	iceGGO-1 (CH ₄)	iceGGO-2 (CO ₂)
Period of Intercomparison	Oct.2012 - Mar.2013	May 2012 - Aug.2012
Participants	JMA, NIPR, AIST, MRI, NIES, TU and NMIJ (7 participants)	AIST, NIES, JMA, NIPR and TU (5 participants)
Detail of standard gases	<p><4 cylinders> Provider: JMA CH₄ mole fraction: about 1665 - 1920 ppb These cylinders were prepared using purified natural air and pure CH₄ gas.</p> <p><2 cylinders> Provider: NMIJ CH₄ mole fraction: about 1830, 2240ppb These cylinders were prepared by a gravimetric method using synthetic air and pure CH₄ gas. CH₄ mole fractions in these cylinders were SI traceable.</p>	<p><6 cylinders> Provider: TU CO₂ mole fraction: about 340 - 450 ppm $\delta^{13}\text{C}$: -30 ‰ These cylinders were prepared using purified natural air and pure CO₂. Pure CO₂ gas was derived from burned petroleum.</p> <p><2 cylinders> Provider: NIES CO₂ mole fraction: about 405, 410 ppm $\delta^{13}\text{C}$: -8.8, -9.0 ‰. Cylinder number: CPB16443, CPB29524 These cylinders were prepared using dry natural air.</p> <p><1 cylinder> Provider: NIES (Tohjima et al., 2009) CO₂ mole fraction: about 370 ppm $\delta^{13}\text{C}$: +55 ‰ Cylinder number: CPB28548 This cylinder was prepared using an enriched ¹³CO₂ gas.</p>

3. Result of iceGGO-1 (CH₄)

Table 2 lists the standard gas scales and analytical methods used in seven laboratories participated in iceGGO-1 (CH₄). Figure 1 shows the differences in measured CH₄ mole fractions from those of JMA at the beginning of circulation, which used the WMO mole fraction scale propagated from the CCL (Central Calibration Laboratory) of NOAA. The analytical precisions for all laboratories were around 1-2 ppb, and the expanded uncertainties of NMIJ gravimetric values were 1.3 ppb ($k=2$). The differences of measured CH₄ mole fractions of JMA between the beginning and

the end of circulation were around -0.4 - +0.8 ppb. The plots in Figure 1 show a consistent dependency between the differences of measured CH₄ mole fractions at each laboratory from JMA and the absolute CH₄ mole fraction levels, although their values have systematic differences.

Table 2 - Standard gas scales and analytical methods used in seven laboratories participated in iceGGO-1 (CH₄)

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

Figure 2 shows differences of measured CH₄ mole fractions from NMIJ gravimetric values. The differences except JMA are distributed within about ± 3 ppb.

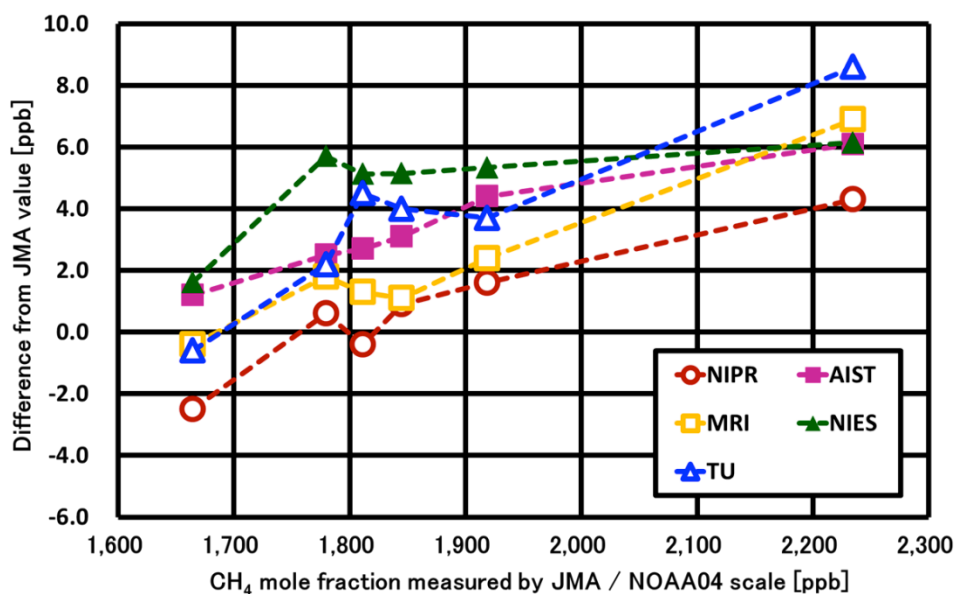


Figure 1 - Differences of measured CH₄ mole fractions from those of JMA

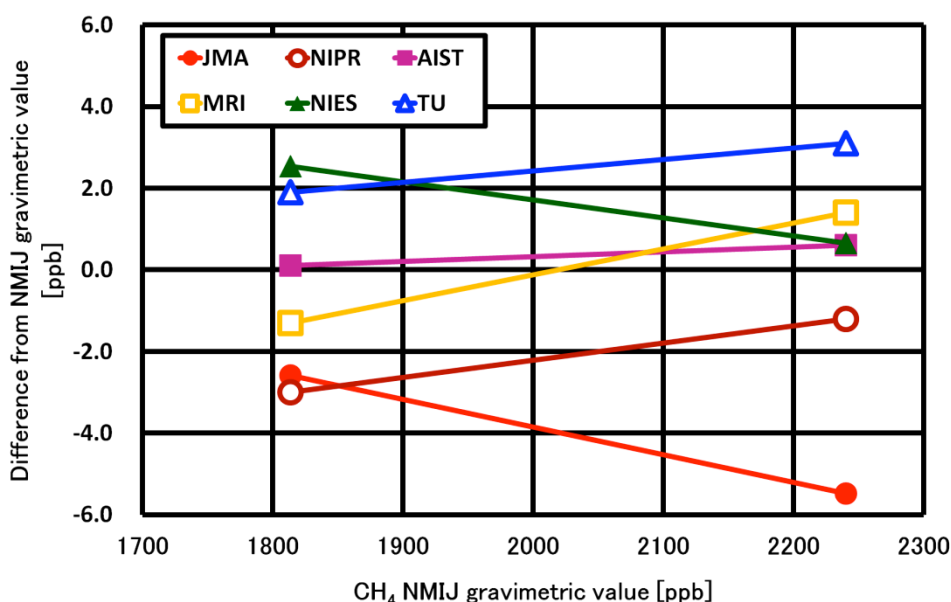


Figure 2 - Differences of measured CH₄ mole fractions from NMIJ gravimetric values

4. Result of iceGGO-2 (CO₂)

Table 3 lists the standard gas scales and instruments used for the five laboratories participated in iceGGO-2 (CO₂). The analytical precisions for all the laboratories were around 0.01 - 0.03 ppm. Figure 3 shows the differences of measured CO₂ mole fractions from those of JMA for the six standard gases with $\delta^{13}\text{C}$ of about -30 ‰. Almost no isotope effects are included in the result of Figure 3, because standard gases used in all participants have similar isotopic compositions of CO₂ with $\delta^{13}\text{C}$ of about -30 ‰ even though they used different NDIR. The CO₂ mole fractions measured by AIST, NIPR and TU are higher than those measured by JMA, while those by NIES are lower than those by JMA. Because the CO₂ standard scales for AIST and NIPR are derived from that for TU, the differences in these scales are small, less than 0.06ppm. In addition, the differences of the CO₂ standard scales for AIST, NIPR, TU, and NIES against that for JMA show similar increasing trends with the CO₂ mole fraction.

Table 3 - Standard gas scales and instruments used in five laboratories participated in iceGGO-2 (CO₂)

	AIST	NIES	JMA	NIPR	TU
Standard gas scale	TU-X10	NIES09	WMO X2007	TU-X10	TU-X10
Instrument1 (NDIR)	LI-COR6252 LI-COR	LI-COR6252 LI-COR	VIA-510R HORIBA	VIA-510R HORIBA	LI-COR6252 LI-COR
Average σ [ppm]	0.017	0.018	0.013	0.017	0.029
Instrument2 (NDIR)	VIA-500R HORIBA				VIA-500R HORIBA
Average σ [ppm]	0.010				0.012

On the other hand, not only the standard gas scale differences but also the isotope effects were included when we measured the other three reference cylinders of CPB28548, CPB16443 and CPB29524, because their isotopic compositions were largely different from those of standard gases used by all participants. Taking the differences in the CO₂ standard scales among the laboratories and the isotope effect of the NDIR used by NIES (Tohjima et al., 2009) into account, we roughly estimated the isotope effects for NDIR analyzers of the other laboratories.

Figure 4 shows the estimated isotope effects largely depends on the analyzers, indicating that corrections of measured values due to the isotope effects should be determined for individual instrument as pointed out by Tohjima et al. (2009).

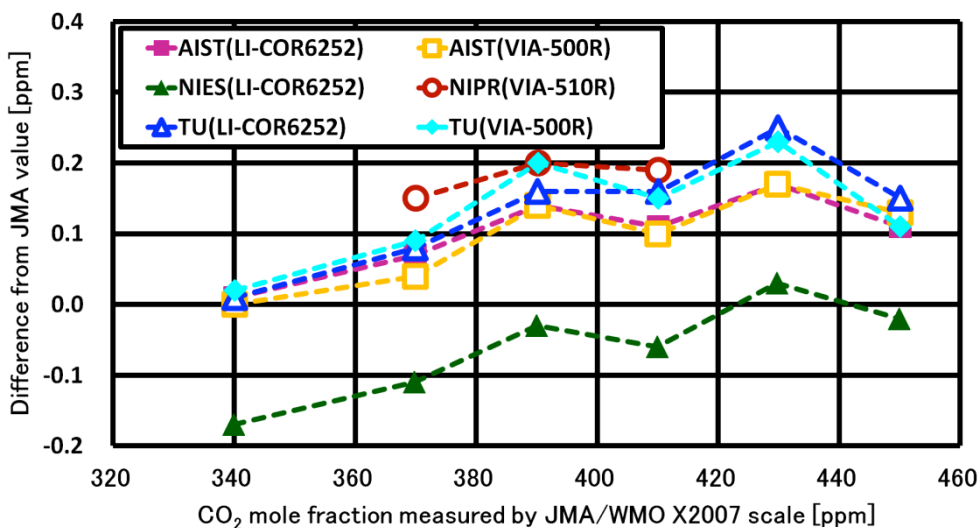


Figure 3 - Differences of measured CO₂ mole fractions from those of JMA

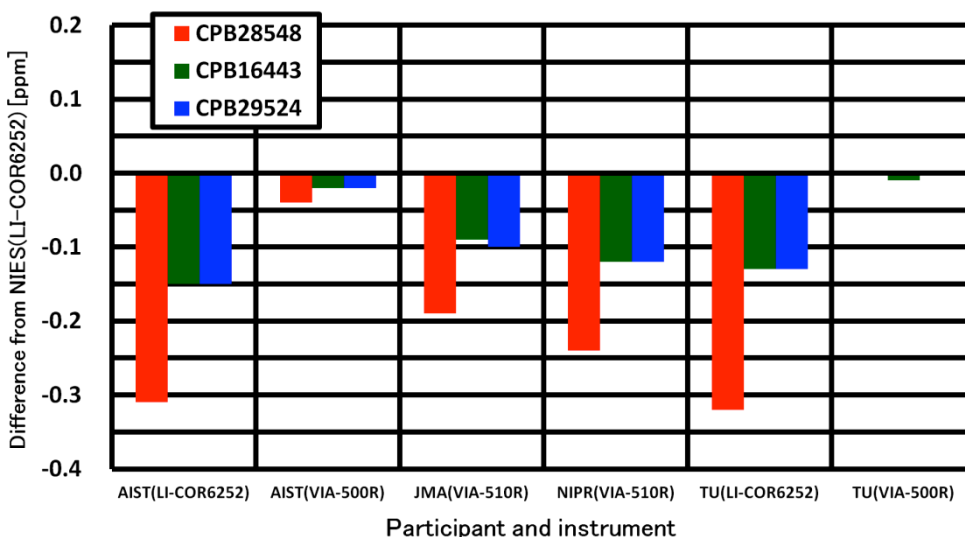


Figure 4 - Isotope effects of the respective NDIR analyzers estimated by adjusting all measured values to the NIES09 scale

5. Summary

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

The first experiment named iceGGO-1 (CH_4) for CH_4 was conducted with SI traceable standard gases provided by NMIJ, in combination with CH_4 reference gas intercomparison operated by JMA. The result of this experiment shows that most of the differences in measured CH_4 mole fractions from those of JMA are positive and the differences increase with absolute CH_4 mole fraction values although these values have systematic differences.

The result of the second experiment named iceGGO-2 (CO_2) for CO_2 shows that the CO_2 mole fractions measured by AIST, NIPR and TU are higher than those measured by NIES, and that the difference of each participant from JMA tends to be more positive with increase of the absolute CO_2 mole fractions. Also, the result of this experiment suggests that the isotopic effect on the measurement value is dependent on the type of the NDIR. The effect needs to be further studied in detail.

The alliance will continue the series of the intercomparison to clarify the relation among their scales and to ensure their stability.

References

Tohjima, Y., K. Katsumata, I. Morino, H. Mukai, T. Machida, I. Akama, T. Amari, and U. Tsunogai (2009), *Theoretical and experimental evaluation of the isotope effect of NDIR analyzer on atmospheric CO_2 measurement*, J. Geophys. Res., 114, D13302, doi:10.1029/2009JD011734.

FLASK SAMPLE AND TOTAL COLUMN GREENHOUSE GAS MEASUREMENTS AT OBNINSK AND ISSYK-KUL STATIONS

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1. Introduction

Greenhouse gases and more widely, minor gas components (MGC) play an important role in various atmospheric processes, determining radiative balance and climate of the Earth. One of methods used for MGC measurements is the method of absorption spectroscopy. This method allows to measure the total gas content in column of an atmosphere, and concentration of gases in the samples of air. This report presents the results of total column content and surface air (flask samples) MGS measurements in Obninsk, which is located in European Russia 105 km southwest of Moscow (55.1° N, 36.9° E, 186 m above sea level). Obninsk has no powerful industrial sources of carbonaceous gases excluding motor transport. Since 1980, as a result of cooperation between Russian and Kyrgyz scientists, the method of absorption spectroscopy has been used at the Issyk Kul high-altitude monitoring station (42.6° N, 77° E, 1650 m above sea level). The station is located in central Eurasia on the northern shore of a high-mountain lake, Issyk Kul, which is presumed to be a pollution-free area. The lake region represents an almost closed canyon with the surrounding ridges of the northern Tien Shan with altitudes from 4.5 to 5.2 km.

2. Methods

The total (integrated) content of gas in a column of an atmosphere is determined by a method of solar absorption spectroscopy. This method consist in measurement of solar radiation absorbed in the atmosphere in various absorption bands in infra-red (CO₂, CO, CH₄, H₂O) and ultra-violet (O₃, NO₂) regions of a spectrum. Concentration of gases in the samples of surface air was measured with a system consisting of Fourier spectrometer with an optical multipass cell with the absorbing layer 30 m (figure 1). At present a new gas analyzer MR-32 for simultaneous measurements of MGC and other gases both in samples of air, and in all thickness of an atmosphere is tested. The gas content is determined by comparison of the experimental spectrum with a spectrum calculated by line-by-line method with absorption lines parameters from Rothman et al., 2005. The random error of individual measurement of the total column gas content does not exceed 2-4 % depending on the meteorological conditions and the number of spectra recorded.

For measurements of MGS in air samples estimated statistical errors are 0.3-1 % for CO₂, CH₄ and 5-10 % for CO, NO₂. The detailed description of the instrumentation and the data processing method is given in earlier papers (Kashin et al. 2000, 2008, Visheratin et al. 2006, Aref'ev et al. 2013).

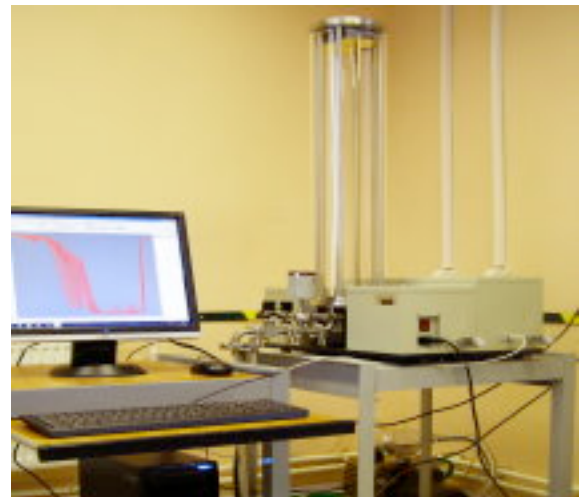


Figure 1 - Experimental setup with FTIR spectrometer and multipass cell (left) and new gas analyser MR-32 (right)

2. Measurements results

2.1 CO₂

Figure 2 shows the monthly mean values (in volume mixing ratios, ppm) of total carbon dioxide column at Issyk Kul station (hereafter "ISK") and CO₂ abundances in surface air at Obninsk station (hereafter "OBN"). Seasonal variations are characterized by spring maximum and autumn minimum. The linear trend for measurements at ISK (period from 1980 to 2012) is (0.13 ± 0.01) ppm per month. The linear trend for measurements at OBN (1998 – 2012) is (0.14 ± 0.02) ppm per month, and the values of the trends for the surface air and total column content coincide within the error limits.

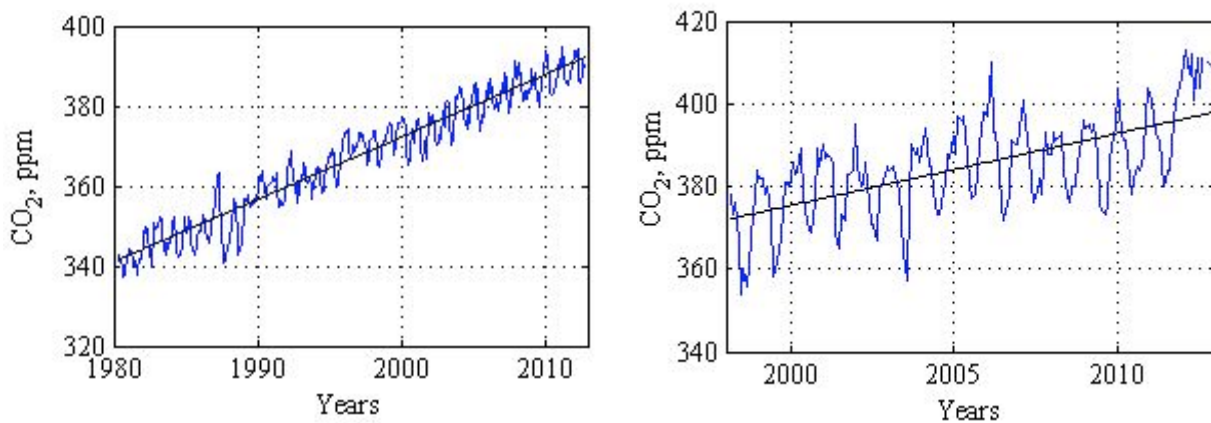


Figure 2 - Variations of the total CO₂ column at ISK (left) and results of CO₂ measurements in surface air samples at OBN (right)

2.2. CH₄

Daily mean methane abundances (in mole fraction, ppb) in surface air during 2010, and monthly mean concentrations of methane for all period of measurements are given in figure 3. The maximal values of average monthly concentration fall to winter months, and minimal - on summer. Basically in December - January high values may be a result of meteorological conditions (accumulation of methane under inverse layers). The abnormal high concentrations in the summer 2010 are caused by forest fires. It is seen from the right panel of the figure that methane concentration gradually diminished during the entire measurement period, and the value of a negative linear trend is significant at one sigma (STDV): $(-0,18 \pm 0,08)$ ppb per month.

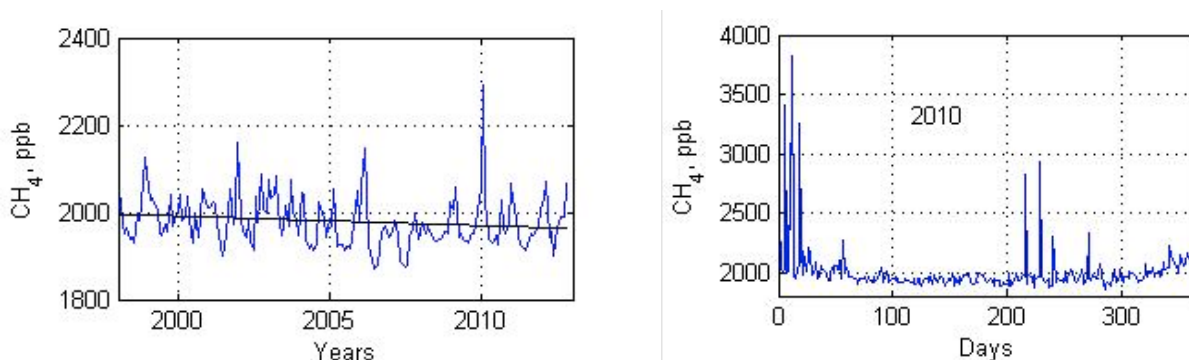


Figure 3 - Results of CH₄ measurements in the surface air samples at OBN. Right figure - daily mean concentrations in 2010 and left figure - monthly means from 1998 to 2012

2.3. H₂O

As is known, the basic greenhouse gas is water vapour. Measurements of the total H₂O column at ISK are continued since 1980. The H₂O and CO₂ abundances are determined on the same record of experimental spectrum of sunlight passed through an atmosphere. Results of H₂O measurements in terms of deposited layer (g/cm²) are plotted in figure 4. The linear trend of the total water vapour column is positive, however insignificant: $(0,0002 \pm 0,0003)$ g/cm² per month. It should be noted, that since 1999, small reduction of the water vapour column both for maximal (summer) and for the minimal (winter) values is observed.

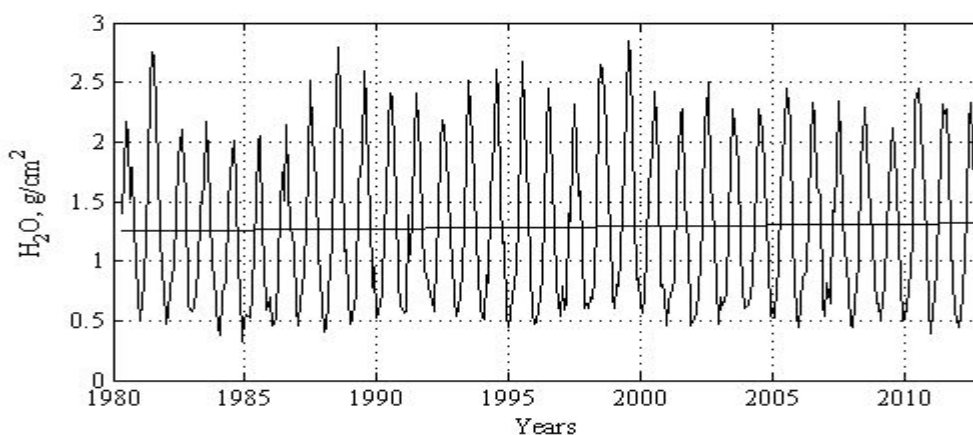


Figure 4 - Variations of the total column H₂O at ISK

3. Spectral analysis

The spectral analysis of time series was carried out with the help classical Fourier and wavelet decompositions.

3.1. CH₄

The analysis of variability of surface air concentrations of methane (OBN) has shown, that the basic oscillation with the period of 12 months has amplitude approximately 45 ppb, and there are also noticeable periodicities with periods 27, 40 and 110 months with amplitudes between 15-20 ppb. Wavelet transform of CH₄ time series is shown in figure 5 (the amplitude of fluctuations is in relative units).

3.2. CO₂

The amplitude of CO₂ annual harmonic for surface air (OBN) amounts 10 ppm, and noticeable oscillations with the periods 40 and 70 months has amplitudes less than 4 ppm. Wavelet transform of CO₂ time series is given in figure 5.

3.3. H₂O

The large amplitude of an annual harmonic (about 0.9 g/cm²) and numerous harmonics with more than 20 months periods and amplitudes less than 0.1 g/cm² are characteristic for spectral structure of total column water vapour variations at ISK. Wavelet transforms of CO₂ and H₂O variations with period more than 20 months are compared in figure 6. It is interesting, that water vapour maxima in region of quasidecadal variations (120-140 months) coincide with maxima of solar activity (approximately 1980-1981, 1990-1991, 2000-2001), but such maxima in CO₂ variations coincide more likely with minima of solar activity. Additionally it is necessary to note, that the amplitude of water vapour quasidecadal variations since 2000 has decreased. It is probable that such diminishing is connected with low activity of the Sun in the current 11-years cycle with maximum in 2012 (see also Visheratin, 2012).

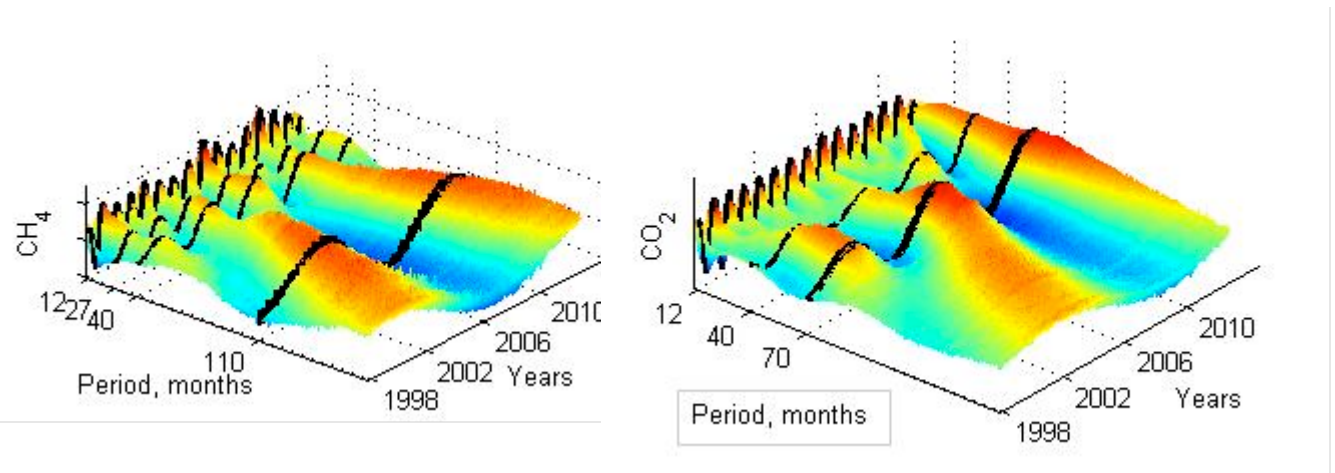


Figure 5 - Spectral structure of CH₄ (left) and CO₂ (right) oscillations (surface air samples measurements at OBN). For clarity thick black lines represent temporal variation of basic oscillations (see text)

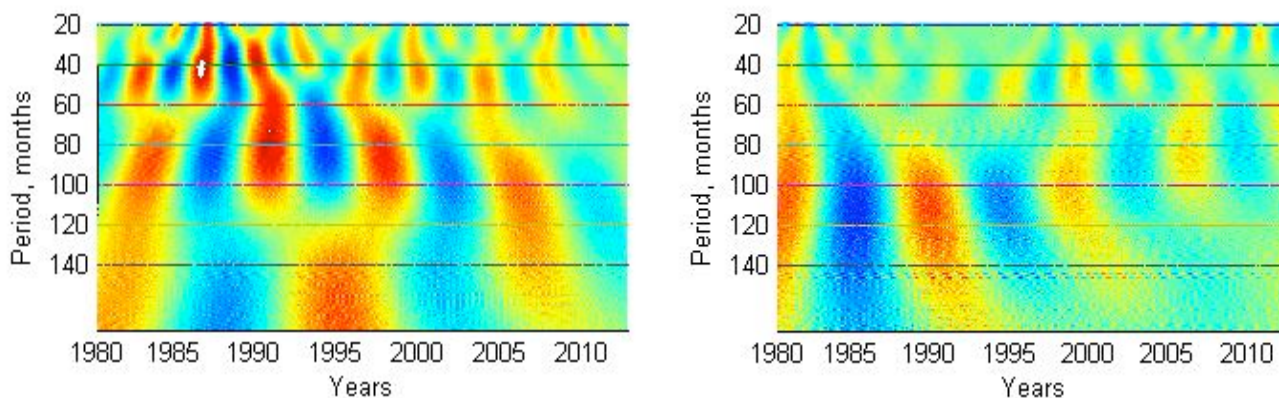


Figure 6 - Spectral structure of total column CO₂ (left) and H₂O (right) variations at ISK. Red and blue colours represent maxima and minima of oscillations

References

- Rothman L.S., D.A. Jacquemart, A. Barbe, et al., *The HITRAN 2004 Molecular Spectroscopic Database*, *J. Quant. Spectrosc. Radiat. Transfer*, **96**, 39–204, 2005.
- Kashin F.V., V.N. Arefev, K.N. Visheratin, et al., *Results of Experimental Studies of Radiatively Active Atmospheric Constituents in Central Eurasia*, *Izv., Atmos. Ocean. Phys.* **36**, 425–453, 2000.
- Visheratin K.N., N.E. Kamenogradskii, F.V. Kashin et al., *Spectral–Temporal Structure of Variations in the Atmospheric Total Ozone in Central Eurasia*, *Izv., Atmos. Ocean. Phys.* **42**, 184–202, 2006.
- Kashin F.V., V.N. Arefev, V.K. Semenov, et al., *Structure of Time Variations in Carbon Dioxide in the Atmospheric Thickness over Central Eurasia (Issyk Kul Monitoring Station)*, *Izv., Atmos. Ocean. Phys.* **44**, 90–99, 2008.
- Arefev V.N., F.V. Kashin, M.D. Orozaliev et al., *Structure of Carbon Monoxide Time Variations in the Atmospheric Thickness over Central Eurasia (Issyk Kul Monitoring Station)*. *Izv., Atmos. Ocean. Phys.*, **49**, 148–153, 2013.
- Visheratin K.N. *Relationship between phases of quasi-decadal oscillations of total ozone and the 11-year solar cycle*. *Geomagnetism and Aeronomy*, **52**, 94–102. 2012.

A PRELIMINARY STUDY ON TRACING FOSSIL FUEL CO₂ IN THE ATMOSPHERE IN XI'AN USING AMS-¹⁴C TECHNIQUE

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To protect the environment and limit temperature rise to 2°C, all countries are in obligations to reduce their carbon emissions. Quantifying the fossil fuel CO₂ in the atmosphere can provide an accurate basic and important data to authorities and policy makers for monitoring if the individual nations reach their obligations for CO₂ emissions reductions. Due to dead carbon (extremely low ¹⁴C) in fossil fuel, measurement of ¹⁴C in the atmosphere can precisely estimate the amount of fossil CO₂ emission in the local area. Accelerator Mass Spectrometry (AMS) is the most sensitive method for measurement of ¹⁴C, and therefore an effective tool for this purpose. In our lab, a time-integrated air sampler has been designed for collection of CO₂ from the atmosphere using so called Displacement of Phosphoric Acid Solution Method. Air samples have been collected from October, 2011 to December, 2012 in Xi'an, China; one-year growth vegetation samples (*Setaria viridis*) were also collected in 2010 in urban areas. The collected atmospheric CO₂ was purified and carbon in the vegetation samples was converted to CO₂, which was then converted to graphite by reduction. ¹⁴C in the graphite was then measured using the 3MV multi-nuclides AMS in Xi'an AMS Center. The results show that the concentration of fossil fuel CO₂ in Xi'an ranges from 17.0 to 66.5 ppm between October, 2011 and December, 2012. Higher values in winter peaked in January were observed, which suggest that fossil fuel CO₂ emission was greatly enhanced by domestic heating in winter, the peak emission in January is attributed to the coldest month of the year; The lower fossil CO₂ concentration between April and August is attributed to the reduced amount of fossil fuel use with the rise of temperature. The results of summer growth vegetation samples show the highest concentration of fossil fuel CO₂ in downtown (33.6 ppm), and the lowest in suburban areas (20.5 ppm), which are distant from industrial and densely populated areas.

References

- Levin, I., Hammer, S., Eichelmann, E., and Vogel, F. R., 2011, *Verification of greenhouse gas emission reductions: the prospect of atmospheric monitoring in polluted areas*, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, v. 369, no. 1943, p. 1906-1924.
- Levin, I., Kromer, B., Schmidt, M., and Sartorius, H., 2003, *A novel approach for independent budgeting of fossil fuel CO₂ over Europe by ¹⁴CO₂ observations*, Geophysical Research Letters, v. 30, no. 23.
- Turnbull, J., Rayner, P., Miller, J., Naegler, T., Ciais, P., and Cozic, A., 2009, *On the use of ¹⁴CO₂ as a tracer for fossil fuel CO₂: Quantifying uncertainties using an atmospheric transport model*, Journal of Geophysical Research, v. 114, no. D22.

ANALYSES FOR CO₂ SOURCE IN THE URBAN AREA: SIMULTANEOUS MEASUREMENT OF STABLE ISOTOPE RATIO OF CO₂ ($\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$), ISOTOPE RATIO OF WATER (δD AND $\delta^{18}\text{O}$), AND CONCENTRATIONS OF CO, NO

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1. Atmospheric chemistry of nitrogen oxides and their relevance for the GAW programme

The increase of CO₂ concentration is most effective in the global climate change, because CO₂ has the largest positive radiation forcing (IPCC 2007). The emission and loss flux of CO₂ are important for predicting the global trend of CO₂ concentration associated with the global climate change. The variations of CO₂ concentration are based on the anthropogenic emission (fossil fuel combustion, biomass burning), biogenic emission from the ecosystem respiration and ocean surface, absorption of the photosynthesis and ocean surface. In the urban area, the variations of CO₂ concentration were depended on the fossil fuel combustion (gasoline and natural gas) and background CO₂ concentration mainly. We identified the CO₂ source of an urban city in the summer and winter, according to the variations of CO₂ concentration and CO₂ stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). $\delta^{13}\text{C}$ of CO₂ emitted gasoline combustion, natural gas combustion, and biogenic respiration were reported as the range from -26‰ to -29‰, from -38‰ to -40‰, and from -14‰ to -29‰ (Bush et al., 2007; Newman et al., 2007; Pataki et al., 2005; McAlexander et al., 2011). $\delta^{18}\text{O}$ of CO₂ emitted fossil fuel combustion and biogenic respiration were reported as -17‰ (Zimnoch et al. 2004) and the range from -8‰ to -17‰ (Ogee, et al., 2004; Bowling et al., 2003).

2. Measurement of CO₂ concentrations, CO₂ stable isotope composition, water vapour concentration, H₂O stable isotope compositions simultaneously

We conducted the continuous measurement of carbon and oxygen isotope of CO₂ ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) using the laser isotope ratio spectrometer based on the infrared laser absorption spectrometry with the wavelength of 4.3 μm . The measurement of CO₂ isotope composition reveals the contribution of the fossil fuel combustion and ecosystem respiration to the carbon cycle in the urban area of Nagoya city. The CO₂ isotope laser spectrometer can continuously measure $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ in high time resolution (10 seconds). The measurement periods were from July 20 to August 10, 2012 and from November 22 to December 11, 2011 at Nagoya University. Simultaneously, we measured the concentrations of nitrogen oxides, CO, water vapor and stable isotope (δD and $\delta^{18}\text{O}$ -H₂O).

Measured CO₂ concentrations and stable isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) show the diurnal variation in the measurement period. CO₂ concentration had the minimum in the daytime, on the other hand, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ had the maximum. CO₂ concentration variation was affected by the local CO₂ emission and long range transported CO₂. The local emission of CO₂ such as fossil fuel combustion, biomass burning, and biogenic respiration were changed in short term period because the local emission associated with the variations of meteorological condition. On the other hand, long range transported CO₂ was changed in longer time scale because air mass was varied in several days. This indicates that the variation of CO₂ concentration was substantially affected by the ecosystem respiration and photosynthesis in the urban area.

Measured H₂O and stable isotope composition (δD and $\delta^{18}\text{OH}_2\text{O}$) show the long term variation. This indicated that the variations of H₂O concentration and stable isotope composition were dominated by the long range transport of air mass rather than the variations of local meteorological condition.

3. CO₂ source identification from the two different analyses

3.1. Keeling plot analysis for CO₂ isotope composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$)

We conducted the Keeling plot analyses to show the contribution of the fossil fuel combustion and ecosystem respiration in the night time. CO₂ peaks in the night time were picked out and analysed to identify stable isotope composition of CO₂ source ($\delta^{13}\text{C}_s$ and $\delta^{18}\text{O}_s$) by Keeling plot. $\delta^{13}\text{C}_s$ was changed from -32.5‰ to -26.3‰ in the winter and changed from -30.0‰ to -22.6‰ in the summer. $\delta^{13}\text{C}_s$ in summer and winter were close to $\delta^{13}\text{C}$ of gasoline combustion. $\delta^{13}\text{C}_s$ in the winter were lower than those in the summer. This indicates that CO₂ from the natural gas combustion had more contribution for CO₂ concentration variation in the winter. The lower $\delta^{13}\text{C}$ in the winter would be due to the increment of the natural gas consumption which used in the heating. $\delta^{18}\text{O}_s$ changed from -23.3‰ to -9.2‰ in the winter and changed from -23.6‰ to -1.4‰ in the summer. $\delta^{18}\text{O}_s$ in summer and winter were varied between $\delta^{18}\text{O}$ of combustion (-17‰ ; Zimnoch et al. 2004) and that of biogenic respiration (-8‰ to -17‰ ; Ogee, et al., 2004; Bowling et al., 2003).

3.2 CO₂ source identification from the relationship between CO and excess CO₂

The comparison of CO and excess CO₂ concentration were also conducted to estimate the relationship between the fossil fuel combustion and CO₂ variation. CO is emitted by the fossil fuel combustion mainly. On the other hand, CO₂ concentration variation was associated with the fossil fuel combustion and biogenic respiration. Therefore, the relationship between CO and excess CO₂ concentration shows CO₂ source. The larger ratios of CO to increment of CO₂ from the background level ($\text{CO}/\Delta\text{CO}_2$) show the contribution of the fossil fuel combustion, on the other hand, the smaller ($\text{CO}/\Delta\text{CO}_2$) shows the contribution of the biogenic respiration.

$\text{CO}/\Delta\text{CO}_2$ were varied between -1.1 and 5.2 in the summer, between 5.1 and 23.9 in the winter. $\text{CO}/\Delta\text{CO}_2$ in the winter were higher than those in the summer. In the winter, air mass was flown from the Asian Continent, CO/CO_2 in the Asian Continent is higher than that in Japan; $\text{CO}/\Delta\text{CO}_2$ in the Asian Continent and Japan were reported as $28-40$ and $14-18$, respectively (Takegawa et al. 2004). Therefore, in the winter, CO and CO₂ concentration would be affected by the transport from the Asian Continent.

We discussed the source of CO₂ from the comparison of the Keeling plot and $\text{CO}/\Delta\text{CO}_2$.

$\delta^{18}\text{O}_s$ decreased with the increase of $\text{CO}/\Delta\text{CO}_2$ in the summer and winter. Especially, $\text{CO}/\Delta\text{CO}_2$ were lower than 1, $\delta^{18}\text{O}_s$ were ranged from -15.5‰ to -1.4‰ which is close to $\delta^{18}\text{O}$ of biogenic respiration CO₂. This result indicates that the biogenic respiration in the boundary layer had the large contribution to the CO₂ concentration variation in the urban area. $\delta^{13}\text{C}_s$ also decreased with the increase of $\text{CO}/\Delta\text{CO}_2$. $\text{CO}/\Delta\text{CO}_2$ in the winter was higher than that in the summer and $\delta^{13}\text{C}_s$ in the winter was lower than that in the summer. According to the Keeling plot analysis, CO₂ from the natural gas combustion had more contribution to CO₂ concentration variation in the winter. The relationship between CO concentration variation and CO₂ concentration variation were consistent with the Keeling plot analysis.

4. Analysis of the variations of H₂O stable isotope composition

Stable isotope composition of H₂O ($\delta^{18}\text{O}\text{-H}_2\text{O}$) changed drastically from August 5 to August 7. The averaged $\delta^{18}\text{O}\text{-H}_2\text{O}$ in August 4 and August 7 were -13.4‰, and -17.0‰, respectively. $\delta^{18}\text{O}\text{-H}_2\text{O}$ had the minimum (-22.5‰) in August 5. $\delta^{18}\text{O}\text{-H}_2\text{O}$ variations were mainly due to the variations of background air mass. Air mass sources were identified by using the backward trajectory analysis (Hysplit-4 model) provided from National Oceanic and Atmospheric Administration (NOAA). Air mass source were changed from west in August 4 to north in August 7. Water vapour in northern area has the lower stable isotope composition of H₂O. The lower $\delta^{18}\text{O}\text{-H}_2\text{O}$ in August 7 was due to the variations of air mass source.

$\delta^{18}\text{O}\text{-H}_2\text{O}$ in August 6 had the minimum. The transport pathway of air mass source in August 6 predicted by the backward trajectory was similar with that in the period from July 29 to August 5. However, low pressure system was near the transport pathway. The total precipitation during the transport was highest in August 6. Stable isotopic fractionation due to the precipitation made $\delta^{18}\text{O}\text{-H}_2\text{O}$ low.

$\delta^{18}\text{O}\text{-H}_2\text{O}$ changed with the air mass source rather than local meteorological condition. Water vapour in north area has lower $\delta^{18}\text{O}\text{-H}_2\text{O}$ than that in south area. Precipitation during transport also affected $\delta^{18}\text{O}\text{-H}_2\text{O}$.

References

- Bush, S.E., D.E. Pataki, and J.R. Ehleringer, *Sources of variation in $\delta^{13}\text{C}$ of fossil fuel emissions in Salt Lake City, USA*, *Applied Geochem.*, 22, 715-723, 2007.
- Bowling, D.R., N.G. McDowell, J.M. Welker, B.J. Bond, B.E. Law, and J.R. Ehleringer, *Oxygen isotope content of CO₂ in nocturnal ecosystem respiration: 2. Short-term dynamics of foliar and soil component fluxes in an old-growth ponderosa pine forest*, *G. Biogeochem. Cycles*, 17, doi:10.1029/2003GB002082, 2003.
- Newman, S., X. Xu, H.P. Affek, E. Stolper, and S. Epstein, *Changes in mixing ratio and isotopic composition of CO₂ in urban air from the Los Angeles basin, California, between 1972 and 2003*, *J. Geophys. Res.*, 113, doi:10.1029/2008JD009999, 2008.
- McAlexander, I., G.H. Rau, J. Lien, T. Owano, R. Fellers, D. Baer, and M. Gupta, *Deployment of a carbon isotope ratiometer for the monitoring of CO₂ sequestration leakage*, *Anal. Chem.*, 83, 6223-6229, 2011.
- Ogee, J., P. Peylin, M. Cuntz, T. Bariac, Y. Brunet, P. Berbigier, P. Richard, and P. Ciais, *Partitioning net ecosystem carbon exchange into net assimilation and respiration with canopy-scale isotopic measurement: An error propagation analysis with $^{13}\text{CO}_2$ and CO^{18}O data*, *G. Biogeochem. Cycle*, 18, doi:10.1029/2003GB002166, 2004.
- Pataki, D.E., B.J. Tyler, R.E. Peterson, A.P. Nair, W.J. Steenburgh, and E.R. Pardyjak, *Can carbon dioxide be used as a tracer of urban atmospheric transport?*, *J. Geophys. Res.*, 110, doi:10.1029/2004JD005723, 2005.
- Takegawa, N., Y. Kondo, M. Koike, G. Chen, T. Machida, T. Watai, D.R. Blake, D.G. Streets, J.-H. Woo, G.R. Camichael, K. Kita, Y. Miyazaki, T. Shirai, J.B. Liley, and T. Ogawa, *Removal of NO_y and NO_x in Asian outflow plumes: Aircraft measurements over the western Pacific in January 2002*, *J. Geophys. Res.*, 109, doi:10.1029/2004JD004866, 2004.
- Zimnoch, M., T. Florkowski, J.M. Necki, and R.E.M. Neubert, *Diurnal variability of $d^{13}\text{C}$ and $d^{18}\text{O}$ of atmospheric CO₂ in the urban atmosphere of Krakow, Poland*, *Isot. Environ. Healt. S.*, 40, 129-143, 2004.

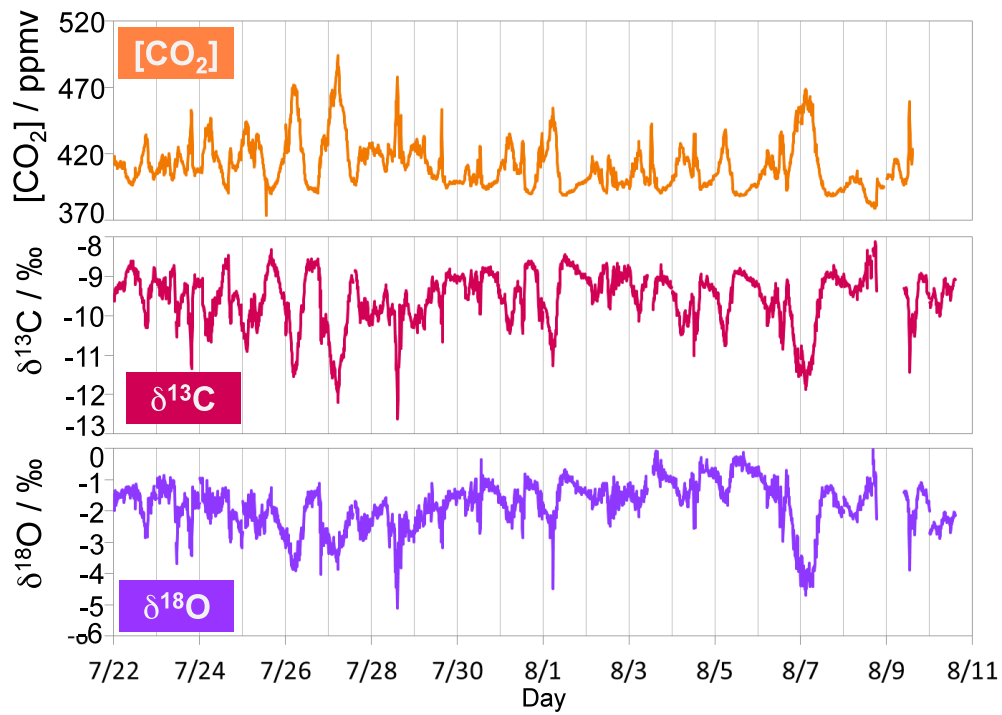


Figure 1 – Temporal variations of CO₂ concentration and CO₂ stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) measured at urban city Nagoya from July 22 to August 11, 2012

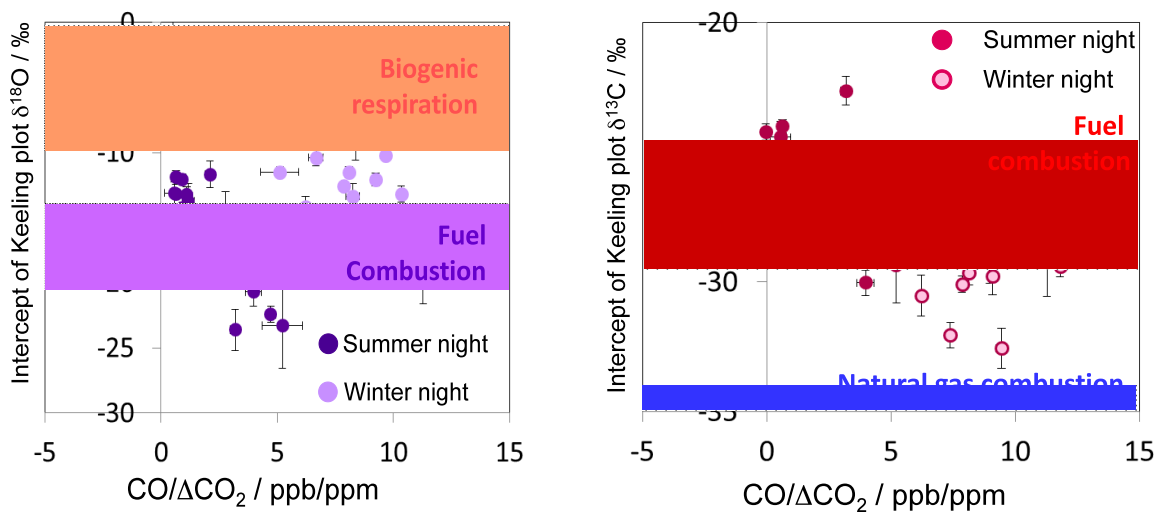


Figure 2 – The relationship between the ratios of CO to excess CO₂ and a) $\delta^{13}\text{C}$ and b) $\delta^{18}\text{O}$ which are calculated from the Keeling plot

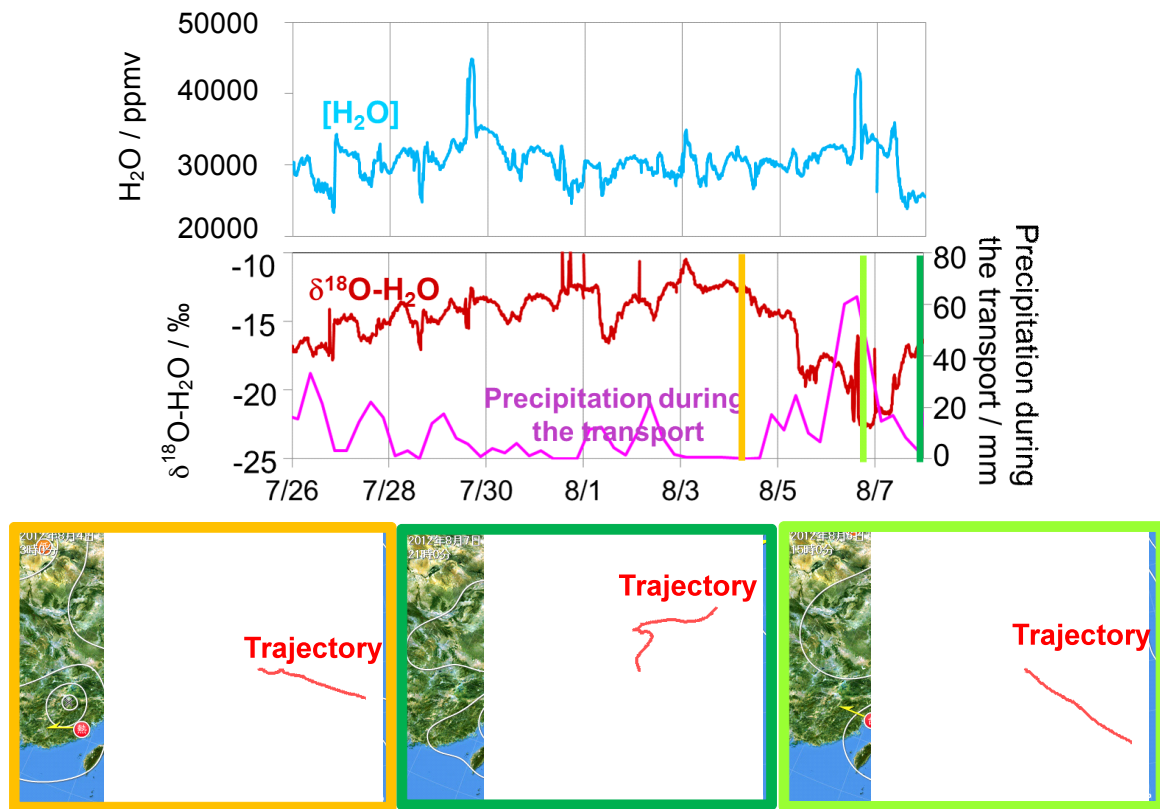


Figure 3 – a) Temporal variations of water vapour concentration, b) temporal variations of $\delta^{18}\text{O}-\text{H}_2\text{O}$ and total precipitation during 120-h transport calculated from the backward trajectory, c) meteorological charts in August 5, 6, 7

ADDED VALUE OF SIDE-BY-SIDE COMPARISONS WITH A TRAVELLING ANALYZER DURING WCC-EMPA AUDITS

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1. New approach for system- and performance audits by WCC-Empa

The World Calibration Centre at Empa (WCC-Empa) has conducted more than 50 system- and performance audits at global GAW stations since 1996. Until 2011, these audits were solely based on travelling standards, i.e. high pressure cylinders containing natural air with mole fractions assigned by WCC-Empa that are tied to the respective WMO scales. In recent years, the value of parallel measurements e.g. by collocated flask sampling (Masarie et al., 2001) or with travelling instruments (Hammer et al., 2013) has been recognised as an important aspect of quality assurance. This was also addressed by the GGMT expert group (WMO, 2011, 2012), which recommended using a travelling instrument for GAW station audits and including the air intake in the testing process.

WCC-Empa addressed this recommendation by changing the audit procedure; a more detailed description of the performance audit procedure without using travelling instruments is given in Buchmann et al. (2009). The new approach comprises parallel measurements using a travelling instrument for carbon dioxide, methane and carbon monoxide. The practical realisation of the on-site comparison is illustrated in Figure 1.

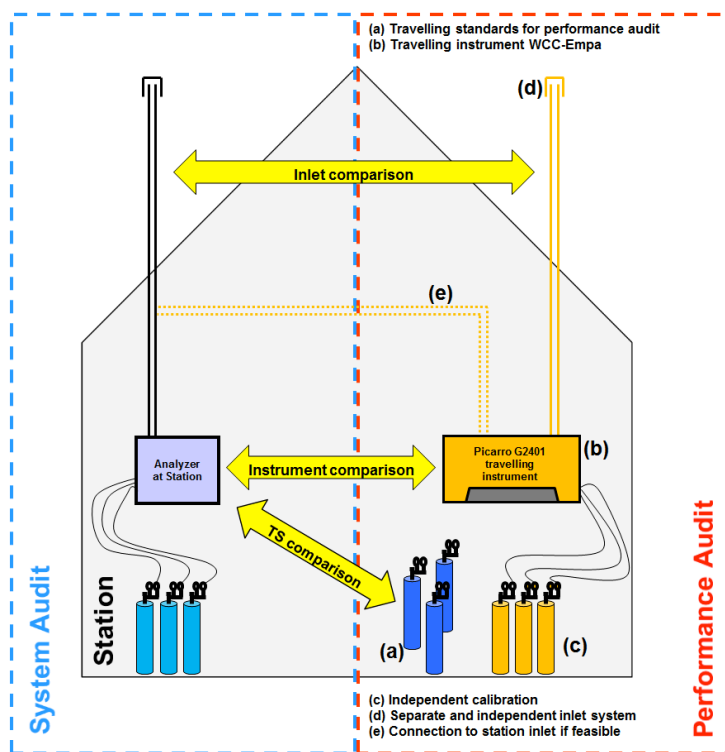


Figure 1 – Realisation of side-by-side comparisons with a travelling instrument during WCC-Empa audits

Whenever possible, the inlet system is included in the parallel measurement. For this purpose, an independent inlet system (d) is set up during the audit. If feasible, the travelling instrument (b) switches between the station and the independent inlet system (e). Furthermore, the travelling instrument is independently calibrated using its own set of standards (c). For further confirmation of the compatibility of the two systems, the travelling standards (a) are measured on both the station analyser and the travelling instrument during the audit.

2. Selected results of on-site comparisons with the WCC-Empa travelling instrument

In the ideal case, the results of the performance audit (comparison of standard gases) are confirmed by the on-site comparison with a travelling instrument. For example, a measurement campaign performed at the Pallas GAW station showed agreement between the WCC-Empa travelling instrument (Picarro G2401, without drying prior to analysis) and the station analyser (also a Picarro G2401, with Nafion dryer) of better than 0.1 ppm CO₂ even on the level of one minute data (Rella et al., 2013). This experiment demonstrated that the Picarro G2401 is suitable as a travelling instrument and that the humidity interference can be corrected. During this campaign, the agreement with a LI-COR LI-7000 analyser was also investigated. Again, very good agreement of ± 0.2 ppm CO₂ was observed for 1-minute averages. The average bias of the two data series was not significant with 0.03 ± 0.06 (1 σ) ppm CO₂, which clearly demonstrates that the two independent data sets are compatible within the WMO compatibility goals of 0.1 ppm CO₂. Furthermore, the measurements also showed no difference between the station inlet system and the independent inlet of WCC-Empa that was temporarily installed during the audit. The added value for the station is a confirmation that the whole measurement set-up including instrumentation, calibration, inlet system and data processing is fully appropriate.

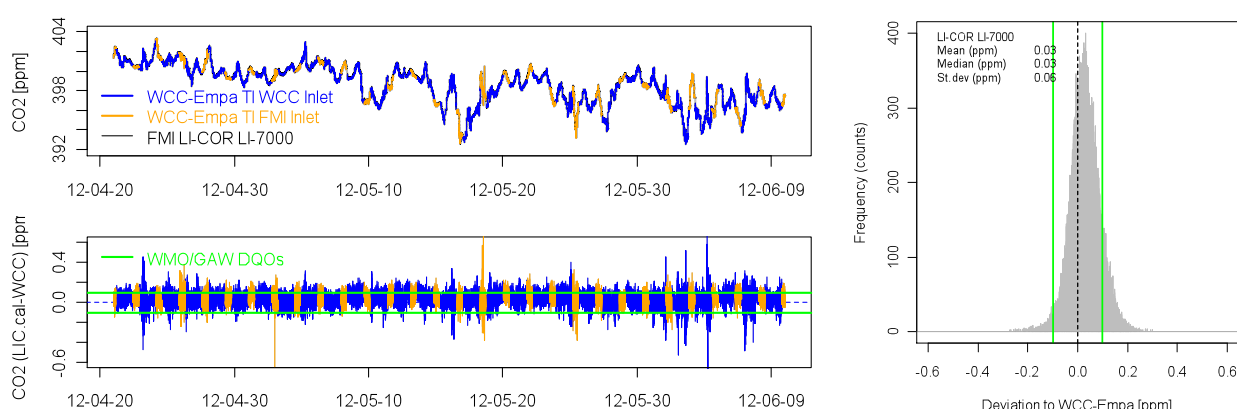


Figure 2 - Left, upper panel: Parallel measurements of CO₂ at the Pallas GAW station between the WCC-Empa travelling instrument and the Pallas LI-COR LI-7000 (1 minute averages). The WCC instrument alternately sampled from the independent WCC inlet and the Pallas inlet. Lower panel: Deviation of the Pallas instrument to WCC-Empa. Right: Frequency distribution of the CO₂ deviation

Another added value of parallel measurements is that potential other issues such as leaks in the inlet system can be detected. For example, the measurements made during the audit at the Zeppelin (ZEP) GAW station showed slightly lower methane reading of the ZEP analyser (Picarro G2401) that was also observed during the measurements of the travelling standards when both instruments sampled from the same inlet line. However, a small positive bias was observed when the WCC-Empa instrument sampled from the independent inlet line. This indicates a small leak in the station inlet system, since the CH₄ content inside the ZEP station is significantly higher compared to ambient air. The elevated mixing ratio of methane is due to exhaust of the carrier gas (CH₄ in Ar) of a GC/ECD system. The results are illustrated in Figure 3.

Further examples of parallel measurement results can be found in recent WCC-Empa audit reports (e.g. Cape Point, Mt. Cimone, Cape Verde, Zeppelin Mt. and Pallas), with are available from the station reports in GAWSIS (GAWSIS, 2013).

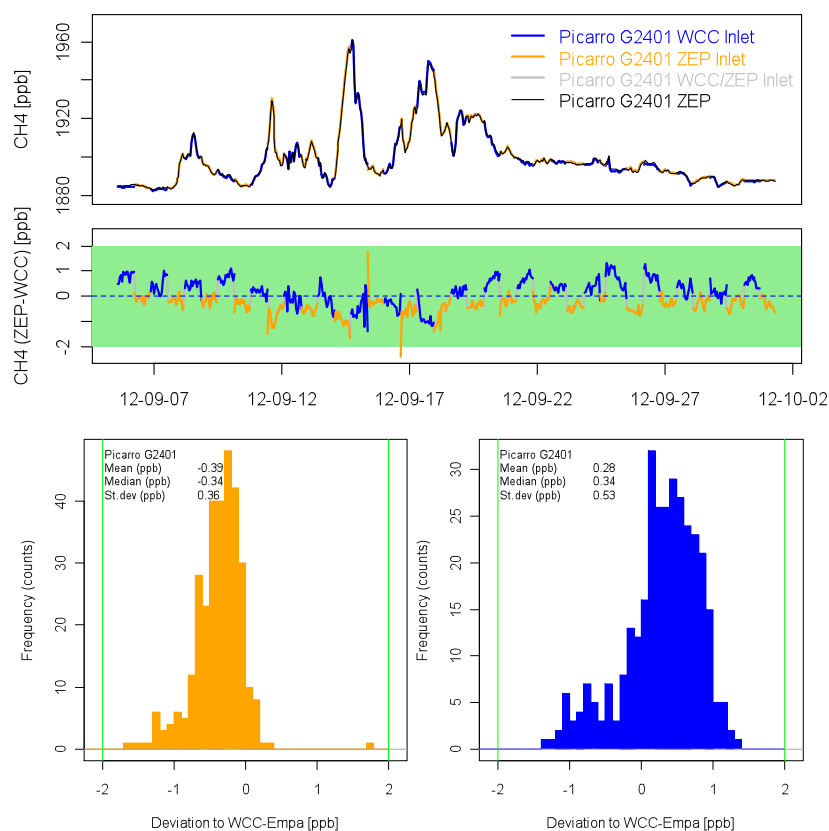


Figure 3 - Upper panel: Parallel measurements of CH₄ at the Zeppelin GAW station between the WCC-Empa travelling instrument and the ZEP Picarro G2401 (1 h averages) and the deviation of the ZEP instrument to WCC-Empa. The WCC instrument alternately sampled from the independent WCC inlet and the ZEP inlet. Lower panel: Right: Frequency distribution of the CH₄ deviation when both instruments sampled from the same inlet line. Left: Same as right panel but for independent inlet lines

3. Conclusions

Parallel measurements during audits are an independent check that includes the whole measurement process, i.e. inlet system, instrumentation, air pre-treatment, instrumentation, calibration and data processing. Such measurements provide additional information which can only be partly achieved by a performance audit using travelling standard or by round robins. In the ideal case, the results of the parallel measurements confirm the findings of the performance audit. If good agreement is observed, the whole system including the inlet system is fully appropriate. The parallel measurements performed until today have clearly shown that problems with a measurement set-up can be identified and that additional information on the uncertainty of a time series is obtained. Due to these added values, WCC-Empa will continue using travelling instruments during on-site audits whenever feasible.

References

- Buchmann, B., Klausen, J., and Zellweger, C.: *Traceability of Long-Term Atmospheric Composition Observations across Global Monitoring Networks*, *Chimia*, 63, 657-660, 10.2533/chimia.2009.657, 2009.
- GAW SIS: *GAW Station Information System*, <http://gaw.empa.ch/gawsis>, access: 10 October, 2013.
- Hammer, S., Konrad, G., Vermeulen, A. T., Laurent, O., Delmotte, M., Jordan, A., Hazan, L., Conil, S., and Levin, I.: *Feasibility study of using a "travelling" CO₂ and CH₄ instrument to validate continuous in situ measurement stations*, *Atmos. Meas. Tech.*, 6, 1201-1216, 10.5194/amt-6-1201-2013, 2013.
- Masarie, K. A., Langenfelds, R. L., Allison, C. E., Conway, T. J., Dlugokencky, E. J., Francey, R. J., Novelli, P. C., Steele, L. P., Tans, P. P., Vaughn, B., and White, J. W. C.: *NOAA/CSIRO Flask Air Intercomparison Experiment: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories*, *Journal of Geophysical Research-Atmospheres*, 106, 20445-20464, 2001.
- Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: *High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air*, *Atmos. Meas. Tech.*, 6, 837-860, 10.5194/amt-6-837-2013, 2013.
- WMO: 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurements Techniques, Jena, Germany, 7-10 September 2009 (WMO TD No. 1553), GAW Report No. 194, 2011.
- WMO: 16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2011), Wellington, New Zealand, 25-28 October 2011, GAW Report No. 206, World Meteorological Organization, Geneva, Switzerland, 2012.
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