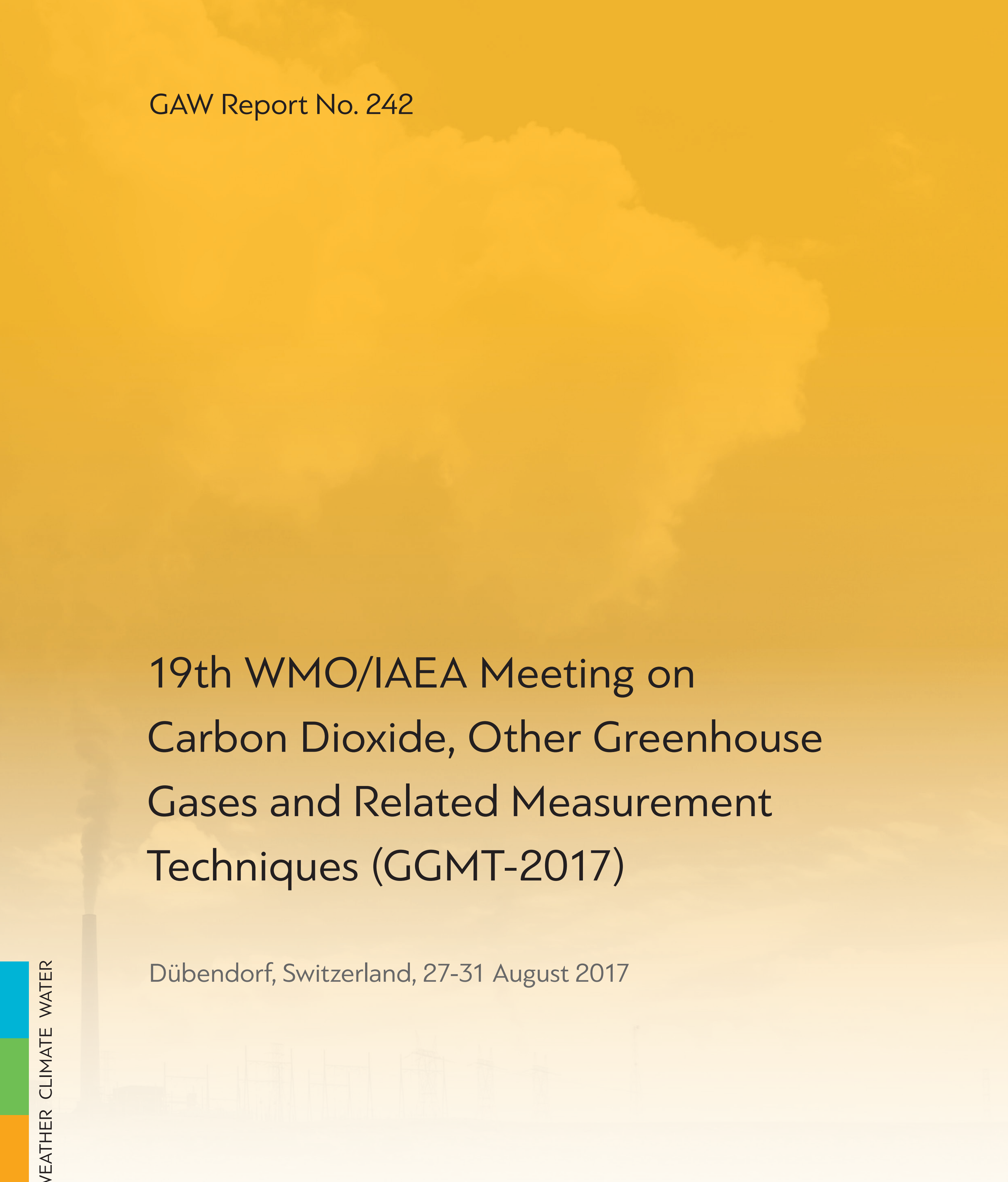

GAW Report No. 242

19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2017)

Dübendorf, Switzerland, 27-31 August 2017

WEATHER CLIMATE WATER

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Edited by Andrew Crotwell and Martin Steinbacher

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THE RECOMMENDATIONS IN THIS REPORT SUPERSEDE THOSE OF
GAW REPORT No. 229

EDITORIAL NOTE

METEOTERM, the WMO terminology database, may be consulted at:
http://www.wmo.int/pages/prog/lsp/meteoterm_wmo_en.html.
Acronyms may also be found at: http://www.wmo.int/pages/themes/acronyms/index_en.html.

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CONTENTS

GROUP PICTURE

Participants attending the 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2017) in Dübendorf, Switzerland, 27-31 August 2017

(http://www.empa.ch/ggmt2017)
(http://www.wmo.int/pages/prog/arep/gaw/ggmt2017.html)

EXECUTIVE SUMMARY

A well-established integrated global greenhouse gas (GHG) observing system is essential for understanding the global carbon cycle and the role greenhouse gases play in climate change. It is also critical for allowing society to take scientifically founded actions on emissions controls and verify the outcomes of these actions. The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) provides a framework for the development and implementation of integrated greenhouse gas observations. Surface measurements of greenhouse gases are performed at fixed stations and on ships by analysing discrete air samples collected in flasks and by making continuous in situ observations. Measurements made by instruments deployed on aircraft and balloon-borne packages, satellite retrievals, and ground-based remote sensing observations provide vertical profile and column averaged signals. All types of measurements can be integrated into global fields via modelling to determine fluxes provided they are of sufficient quality. As part of this GHG programme, WMO with the International Atomic Energy Agency (IAEA) organizes biennially a meeting to review the scientific understanding of greenhouse gas sources and sinks, to evaluate the network development, to review the best practices for quality assurance and quality control, and to examine data quality objectives and measurement techniques.

The 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2017) took place from 27 to 31 August 2017 at the Swiss Federal Laboratories for Materials Science and Technology (Empa) in Dübendorf, Switzerland. This meeting series was initiated in 1975 by Charles Keeling. Over the years, GGMT meetings have become cornerstone events of the international greenhouse gas monitoring programmes, which is reflected in the large attendance of the recent gatherings. In 2017, 168 participants from 26 countries and 6 continents attended GGMT-2017. WMO has provided the framework for all meetings in this series since 1975. IAEA joined WMO as a co-organizer in 1997 due to the increased use of carbon isotopes in studying the carbon cycle. GGMT-2017 was organized back-to-back with the 10th International Carbon Dioxide Conference which took place in Interlaken, Switzerland.

The meeting reviewed current WMO data quality objectives, reference scales and observation strategies, including calibration, quality control, data management and archiving. Target species were carbon dioxide and other greenhouse gases, stable isotopes, and radiocarbon in greenhouse gas measurements. The workshop discussed in detail the harmonization and quality control of isotope measurements, the extension of the measurement network towards more polluted and urban areas, the use of low-cost sensors, and the collaboration of the scientific greenhouse gas and carbon cycle community with the metrology institutes. Many of the discussions were driven by recent technological developments in instrumentations. Analytical advancements have now made possible continuous high precision measurements of many previously difficult to measure compounds. In addition, we discussed the need to calculate and report uncertainties for all measurements.

The group updated the recommendations on WMO data quality objectives, calibration, and data management, as well as on the development of the GAW Programme in general. These recommendations are summarized in this meeting report.

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. The requirement has become more urgent after the 21st Conference of the Parties, Paris, France (COP21) agreement signed in December 2015. The Paris Agreement in Article 7 calls for "strengthening scientific knowledge on climate, including research, systematic observation of the climate system and early warning systems, in a manner that informs climate services and supports decision-making". Since then, much has happened in the global diplomatic arena. Most noteworthy are:

- The launch of the establishment of an Integrated Global Greenhouse Gas Information System (IG^3IS) whose concept paper was approved by the WMO Executive Council in June 2016.
- The addition of anthropogenic greenhouse gas fluxes as an Essential Climate Variable (ECV) and the recognition that "atmospheric composition measurements (ground-based and satellite) are starting to be able to support existing emission estimates made for the UNFCCC" in the Global Climate Observing System (GCOS) Implementation Plan from October 2016 (WMO, 2016a).
- The release of the new GAW Implementation Plan (WMO, 2017), highlighting the growing importance of atmospheric composition observations and the derived products and services in 2017.
- The recognition of the Subsidiary Body for Scientific and Technological Advice (SBSTA) of the UNFCCC of "the increasing capability to systematically monitor greenhouse gas concentrations and emissions, through in situ as well as satellite observations, and its relevance in support of the Paris Agreement" in November 2017.
- The signed cooperation agreement between WMO and UNFCCC to – among others – improve climate products and services and to support climate policy-making in November 2017.

Three main objectives justify atmospheric observations:

1. To monitor atmospheric greenhouse gas burdens and determine their contribution to radiative forcing of the climate system.
2. To quantify natural and anthropogenic emissions and removals of greenhouse gases, including attribution by region and by process, and to understand the controlling processes.
3. To provide science-based tools for improved evaluation of emission mitigation strategies utilizing atmospheric observations and models.

Moreover, it is worth emphasizing that the Earth's radiative budget, and consequently the temperature at the Earth surface, is not directly driven by the rate of emissions into the atmosphere but instead is ultimately determined by the atmospheric burden of the radiative forcers which is the accumulation of past emissions and removals. 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 measurements at both background sites and at locations with regional and local representativeness, as well as the continued development of remote sensing from ground and satellite platforms.

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 using these in situ measurements provide local, regional and global assessments of atmospheric emissions and removals by season, source type and location. These studies are further strengthened by remote sensing estimates of the total column abundances by ground- and satellite-based spectrometers that measure the absorption of solar radiation by specific gases. However, these complementing remote sensing GHG data also rely on high-quality, traceable and calibrated in situ measurements for validation because a direct calibration of those measurements is not possible. This is because one cannot control the sample in the optical path, nor potential interferences. Thus, total column measurements such as within TCCON (Total Carbon Column Observing Network; see Chapter 13) should be regularly validated with calibrated in situ measurements on aircraft of the partial column and with balloon launched AirCore flights (Karion et al., 2010), which collect a vertically resolved in situ sample, which is measured on calibrated instruments, through ~99% of the total column. Several laboratories worldwide are currently working on improvements of AirCore design, sampling and analysis, e.g. leading to a better vertical resolution of atmospheric profiles (Membrive et al., 2017). TCCON and high accuracy in situ measurements play a crucial role in the validation of satellite-based remote sensing studies. Satellite-based measurements offer the prospect of dense global coverage but do not cover with sufficient accuracy the full suite of GHG and associated tracers defined by WMO/GAW and are subject to a number of biases. In the future, these measurements may be complemented by emerging techniques like horizontal open path GHG measurements and dense networks of low-cost and lower-quality sensors.

It is important to understand that atmospheric observations alone have limited information about diverse processes driving sources and sinks of the greenhouse gases. Much better collaboration has to be established with the biosphere and the ocean communities to better quantify the exchange processes. An initial discussion with the ocean community took place at a previous GGMT meeting (GGMT-2015) and further efforts were made during GGMT-2017 to agree on the approaches applied to ocean pCO_2 observations.

A major limiting factor of all studies that infer sources/sinks from observed mole fractions of greenhouse gases is the atmospheric transport models. They not only need to describe the winds correctly, but there are also often serious shortcomings of mixing processes between the boundary layer and the free troposphere, of convective events, of mixing between the hemispheres, of flow over complex terrain, to name a few. Improvements need to come from outside our community but we have to state it as an urgent need. This does not negate our requirements for making the best possible greenhouse gas measurements in today's world. We do not get another chance to do so, whereas models can be retroactively improved.

The scientific priorities for GHG study in WMO/GAW are thus to sustain and enhance the global in situ measurement network, and simultaneously use the network to improve and ground-truth developing satellite products/retrievals (in collaboration with TCCON and other current and future networks) by allowing ongoing 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 CO_2) 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 CO_2 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 accuracy, 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 one part in 4000 in ambient atmospheric CO_2. This is more demanding than current trace gas measurements from space perform, but these are improving. 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. Models have their own biases, and a comprehensive set of calibrated measurements will also be needed to diagnose and minimize such biases. On the global scale, the systematic observations of GHG's in the atmosphere and oceans and linked process-oriented carbon cycle observations will improve our understanding of the workings of the carbon cycle and how it responds to climate change, possibly as a positive feedback to climate forcing. On regional and urban scales, the results provide an additional constraint in assessing GHG emissions and trends to inform the public and policymakers as recognized by several international entities (see above). Sub-national entities like cities and industries will play an even more important role in the future due to their expected contributions to the global stocktake exercise.

Two major regional programmes are acting to improve atmospheric trace gas observations in GAW in North America (North American Carbon Programme, NACP; http://www.nacarbon.org/nacp/) and Europe (Integrated Carbon Observation System, ICOS; https://www.icos-ri.eu/). The Comprehensive Observation Network for Trace gases by Airliner (CONTRAIL; http://www.cger.nies.go.jp/contrail/index.html) and the In-Service Aircraft for a Global Observing System (IAGOS; https://www.iagos.org/) provide global observations of atmospheric composition on-board commercial aircrafts. Several laboratories in Japan operate a large programme of measurements on aircraft and ships, and at surface sites. It is important that these and similar regional programmes remain tightly linked to the international WMO/GAW effort and produce regional datasets 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 through training courses, and stimulating partnerships between laboratories.

Solid and trusted facts are indispensable to successful international treaties, national policies, and regional strategies for emission reductions, efficiency improvements, and emissions offsets. Transparent and 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 (GAW) Programme. However, providing coherent, regional-scale information requires not only enhanced observations, but also improved modelling and meteorological 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 TRACERS

The scientists present at the 19th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (abbreviated as GGMT-2017), 27-31 August 2017, in Dübendorf, Switzerland, recommend the following procedures and actions to achieve the goals for network compatibility among GAW laboratories summarised in Table 1.

While WMO/GAW strives to use terminology based on standardized definitions as released by ISO Guides (International Organization for Standardization; www.iso.org) (see the 3rd edition of the International Vocabulary of Metrology (VIM), http://www.bipm.org/en/publications/guides/vim.html; and the WMO/GAW Glossary of QA/QC-Related Terminology, http://www.empa.ch/gaw/glossary), some of the terms related to measurements as well as to Quality Assurance & Quality Control (QA/QC) in atmospheric science are used differently than in the VIM. For example, two measurements of the same quantity are considered metrologically compatible if the difference between the two measurements is smaller than the combined total uncertainty at some confidence level (see full definition in VIM 3, (2008)). Within the WMO/GAW community, network compatibility (often referred to as simply compatibility in the WMO/GAW community) is a measure of the persistent bias between measurement records. The WMO/GAW network compatibility goals (Table 1) are the scientifically-determined maximum bias among monitoring programmes that can be included without significantly influencing fluxes inferred from observations with models. Even though a bias might be less than the combined total uncertainty of the measurements, if based on a sufficient number of comparisons of measurements, it can still be significant.

Table 1, column 2, lists the network compatibility goals for measurements of well-mixed background air. Some network compatibility goals are difficult to achieve given current measurement and scale transfer uncertainties. However, these network compatibility goals are targeted for application areas that require the smallest potential bias among different datasets or data providers, such as for the detection of trends and gradients used to infer fluxes or atmospheric dynamic processes. An extended network compatibility goal is provided (Table 1, column 3) as a guideline for other studies in which the smallest bias is not required, for example a regionally focused study with large local fluxes, or services related to urban air quality.

Some data quality objectives (e.g. repeatability, measurement uncertainty, etc.) are relatively straightforward to quantify by individual laboratories. Network compatibility, as used within GAW, is not. Network compatibility can only be assessed by comparing measurements of ambient air at a common site (e.g. in situ sampling versus grab samples, co-located comparisons of measurements at a single site by two different laboratories, and by "same-air" comparisons, where two laboratories measure the same discrete air sample). Comparison of gas mixtures in cylinders (e.g. WMO Round Robin Experiments) provide information on scale transfer, but they do not guarantee network compatibility of the measured quantity of interest since these comparisons do not usually involve the entire sampling system (inlets, pumps, drying, etc.). System and performance audits made by the World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide (WCC-Empa) usually include both comparisons of gas mixtures and side-by-side comparisons with a traveling audit instrument (Zellweger et al., 2016). By using an independent inlet system for the audit instrument, the complete sampling system can be tested. However, this quality check is mainly performed at global GAW stations and at intervals of several years. In interpreting comparison data to assess network compatibility, the mean and standard deviations of the differences as well as any trends in the differences should be evaluated. The evaluation of co-located observations and their differences may be affected by atmospheric variability, in particular when using instrumentation with different sampling frequencies and coverages. For the detection of potential trends in the bias, multiple and recurrent assessments are needed. In the end, comparisons of measurements must be assessed within the context of a given study to determine which datasets are sufficiently compatible to include.

Table 1. Recommended network compatibility of measurements within the scope of WMO/GAW

Component	*Network compatibility goal*[1]	*Extended network compatibility goal*[2]	*Range in unpolluted troposphere (approx. range for 2017)*	*Range covered by the WMO scale*
CO_2	0.1 ppm (NH) 0.05 ppm (SH)	0.2 ppm	380 - 450 ppm	250 – 520 ppm
CH_4	2 ppb	5 ppb	1750 – 2100 ppb	300 – 5900 ppb
CO	2 ppb	5 ppb	30 – 300 ppb	30 - 500 ppb
N_2O	0.1 ppb	0.3 ppb	325 – 335 ppb	260 – 370 ppb
SF_6	0.02 ppt	0.05 ppt	8 – 10 ppt	2.0 – 20 ppt
H_2	2 ppb	5 ppb	400 – 600 ppb	140 - 1200 ppb
$\delta^{13}C\text{-}CO_2$	0.01 ‰	0.1 ‰	-9.5 to -7.5 ‰ (VPDB)	
$\delta\ ^{18}O\text{-}CO_2$	0.05 ‰	0.1 ‰	-2 to +2 ‰ (VPDB-CO_2)	
$\Delta^{14}C\text{-}CO_2$	0.5 ‰	3 ‰	-50 to 50 ‰	
$\Delta\ ^{14}C\text{-}CH_4$	0.5 ‰		50-350 ‰	
$\Delta\ ^{14}C\text{-}CO$	2 molecules cm^{-3}		0-25 molecules cm^{-3}	
$\delta\ ^{13}C\text{-}CH_4$	0.02 ‰	0.2 ‰	-51 to -46 ‰ (VPDB)	
$\delta\ ^{2}H\text{-}CH_4$	1 ‰	5 ‰	-120 to -63 ‰ (VSMOW)	
O_2/N_2	2 per meg	10 per meg	-900 to -400 per meg (vs. SIO scale)	

[1] Scientifically desirable level of network compatibility for measurements of well-mixed background air. These represent the maximum bias that can generally be tolerated in measurements of well-mixed background air used in global models to infer regional fluxes. Some network compatibility goals may not be currently achievable within current measurement and/or scale transfer uncertainties. However, these network compatibility goals are targeted for application areas which require the smallest possible bias among different datasets or data providers, such as for the detection of small trends and gradients. Network compatibility goals are not direct metrics for instrument performance, however, instruments with significantly higher short-term imprecision make assessing network compatibility difficult.

[2] Extended network compatibility goals are provided as a guideline for many other studies in which the smallest bias is not required, for example, a regionally focused study with large local fluxes, or services related to urban air quality.

This document defines the common reference scales in the GAW network for trace gases-in-dry-air as the reference for mole fraction measurements of individual gases. They are embodied in unique sets of primary measurement standards with values assigned and linked to SI by primary reference measurement procedures. The scales are propagated over defined mole fraction ranges to secondary measurement standards. The conventional reference scales are maintained over many years through primary reference measurement procedures at regular intervals, with a focus on long-term consistency, and may involve value reassignment (e.g. if primary measurement standards are found to be changing with time).

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 = μmol mol^{-1} = 10^{-6} mole of trace substance per mole of dry air
ppb = nmol mol^{-1} = 10^{-9} mole of trace substance per mole of dry air
ppt = pmol mol^{-1} = 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, nmol mol^{-1} or ppb, 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 acceptable to continue using the term "concentration" or "abundance" instead of "mole fraction" because the latter is an unknown term for most people.

Isotopic ratio measurement results are expressed as deviations from an agreed-upon international reference measurement standard (which defines corresponding isotope scales) using the delta notation:

$\delta = (R_{sample}/R_{reference} - 1)$, with R = [rare isotope]/[abundant isotope].
δ - values are expressed in multiples of 0.001 (‰; per mil 'units'),
e.g. $\delta = (R_{sample}/R_{reference} - 1) \times 1000$ ‰

The international scale for $\delta^{13}C$ is VPDB (Vienna Pee Dee Belemnite). IAEA-603 and NBS19 (now exhausted) calcites are the primary international reference materials used for the realization of the VPDB scale. LSVEC lithium carbonate ($\delta^{13}C = -46.6$ ‰ on the VPDB scale) was introduced as a second $\delta^{13}C$ reference material and was intended to be used for 2-point data normalization (Coplen et al., 2006). However, due to its ability to absorb CO_2 from air, which changes its isotopic composition, use of LSVEC as a $\delta^{13}C$ reference material is no longer recommended (IUPAC, 2018). All reported $\delta^{13}C$ data, including air-CO_2 isotopic values, are still to be 2-point normalized, by using IAEA-603 (or NBS19 if still locally available) and other suitable international reference materials (see Section 4.1.1 and 4.1.2).

For $\delta^{18}O$, multiple scales are in use (VPDB, Vienna Standard Mean Ocean Water (VSMOW), air-O_2). For the $\delta^{18}O$ of CO_2 in air samples, the common scale is the VPDB-CO_2 scale (Brand et al., 2010), which is realized through IAEA-603 or NBS19 by carbonate-H_3PO_4 digestion under controlled conditions. Thus, standardization of the carbonate-H_3PO_4 digestion reaction is of highest importance (Wendeberg et al., 2011). Although the VPDB-CO_2 scale is linked to the VSMOW scale, the 2-point VSMOW-SLAP data normalization cannot be applied to air-CO_2 $\delta^{18}O$ data for practical reasons.

The JRAS-06 realization of the VPDB and VPDB-CO_2 scales is recommended for the WMO/GAW community to improve network compatibility.

For all hydrogen isotope measurement results (e.g. on air methane), the common scale is the VSMOW scale, which includes the 2-point VSMOW2-SLAP2 data normalization.

Abundance variations of O_2/N_2 (and Ar/N_2) ratios in air are also expressed as delta notation:

$\delta\ (O_2/N_2) = (R_{sample}/R_{standard} - 1)$ with $R = O_2/N_2$ (see Chapter 6)

$\delta\ (O_2/N_2)$ values are expressed in multiples of 10^{-6} or per meg ‘units’.

For the O_2/N_2 ratio, the respective international air standard is not yet established. 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 measurement standard. There is also no assigned WMO/GAW Central Calibration Laboratory for O_2/N_2 measurements. Current international comparisons of O_2/N_2 indicate that the network compatibility between any two laboratories is not better than ±5 per meg.

For $\Delta^{14}CO_2$ analyses there is little experience with the long-term network compatibility between laboratories, but for global as well as regional applications the desired reproducibility of individual measurements should be better than ±3 ‰.

1. CALIBRATION OF GAW MEASUREMENTS

1.1 Background

The WMO/GAW Programme conforms to a comprehensive quality management framework (WMO, 2007; WMO, 2011; WMO, 2017) which relates to the overarching WMO guidance for implementation of a quality management system for national meteorological and hydrological services (WMO, 2013), applied to atmospheric composition measurements. As part of the WMO/GAW quality system, several Central Facilities are in place to ensure best possible network compatibility and homogeneity of the global observational network run by a large number of different laboratories. Fundamental roles are assigned to the WMO/GAW Central Calibration Laboratories (CCL) and the World Calibration Centres (WCC). In brief, CCLs are mainly responsible for preparation, maintenance, and dissemination of primary network standards and scales (see Section 1.2). WCCs help to ensure the traceability of network observations to the respective references (see Section 1.3).

In the context of greenhouse gases, relevant WMO/GAW CCLs currently exist for: carbon dioxide (CO_2, at the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (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). Respective WCCs are available for CO_2 (at NOAA/ESRL and the Swiss Federal Laboratories for Materials Science and Technology (Empa)), CH_4 (at the Japan Meteorological Agency (JMA) and Empa), N_2O (at the Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Atmospheric Environmental Research (KIT/IMK-IFU), SF_6 (at the Korea Meteorological Administration (KMA)), and CO (at Empa).

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 network 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 network compatibility goals (Table 1) were set to ensure that biases among monitoring networks do not significantly affect scientific interpretations of combined datasets. The most efficient way to meet the network compatibility goals is for all laboratories to use as their starting point the same WMO scales, propagated by the CCL's. However, WMO/GAW recognizes the importance of independent scales to provide robustness to scientific findings. Long-term comparisons with well-established independent scales maintained by contributing networks and/or standards made by national metrology institutes are essential for making sure that the WMO scales stay as close as possible to true quantity values (Section 2.11 in VIM 3). When independent scales are used, scale differences should be continuously assessed through on-going comparison activities to establish scale conversions. This requires a significant effort but is required to meet the goal of being able to combine and interpret data from different programmes after systematic differences between scales have been eliminated. Established independent scales used for long-term atmospheric monitoring are maintained by: Scripps Institution of Oceanography, USA (CO_2, N_2O, SF_6, and other trace species), Tohoku University, Japan (CO_2, CH_4, CO, N_2O, and SF_6), National Institute for Environmental Studies, Japan (CO_2, CH_4, CO, N_2O, and SF_6), University of Heidelberg, Germany (SF_6).

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) The WMO Mole Fraction Scale for each species is embodied in an adequate set of gas mixtures-in-dry-air in high-pressure cylinders (called "WMO Primary Standards") spanning the range of interest to the WMO community. The CCLs maintain the link of each scale to fundamental quantities (SI) by carrying out regular determinations of each cylinder using primary reference measurement procedures or through other suitable techniques, such as regular comparisons with new sets of gravimetric mixtures or with dilutions from stable mixtures with a high mole fraction of the species of interest. Isotopic ratios should be reported on the existing accepted scales, such as VPDB and VSMOW. In this case, the CCL maintains a common scale realization of the accepted scales to achieve more stringent network compatibility among laboratories than can be achieved through independent realizations.

b) The CCL carries out comparisons with independent primary scales, established either through gravimetric, manometric, or other means.

c) The WMO scale for each trace gas is defined and maintained by a 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 and as such is a primary responsibility of the CCL's.

d) CCLs should strive to transfer the scale with sufficient consistency to allow WMO/GAW stations and contributing programmes to meet the network compatibility goals.

e) To the extent possible, CCLs should develop and maintain a Quality Management System (QMS) for their calibration and measurement capabilities that meets the requirements of ISO/IEC 17025 (2017), and possibly ISO Guide 34 (2009). NOAA can share expertise with the other CCLs on the steps required to establish a QMS.

f) CCLs that have signed a letter of agreement with WMO to act as designated institutes for WMO as a signatory to the CIPM Mutual Recognition Agreement should participate in Key Comparisons of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM).

g) This Expert Group and the GAW Scientific Advisory Group (SAG) on GHG undertake the responsibility for the evaluation of the effectiveness of CCL procedures and for recommending modifications to existing protocols.

h) 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 CO_2 X2007, and the appropriate version number should be included in each standard calibration report. The CCL will notify users of the scale revision with the GGMT list server and internal contact lists. The CCL archives all earlier versions of the WMO scale.

i) The current scales are (as of July 2018):

WMO CO_2 X2007
WMO CH_4 X2004A
WMO CO X2014A
WMO N_2O X2006A
WMO SF_6 X2014
WMO H_2 X2009

The "X" stands for mole fraction.

JRAS-06 is the recommended VPDB-CO_2 scale realization for stable isotopes of CO_2

j) 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.

k) The CCL provides calibrated reference gas mixtures (gas mixtures-in-dried-natural air) at the lowest possible cost and maintains or develops the ability to address changing demand in calibration mixtures, including those characterized in CO_2 stable isotope composition.

l) In view of different specific sensitivities of various instrumentation to the isotopic composition of the analytes, the isotopic composition of the analyte (CO_2, CH_4, N_2O, others) in 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, or provides measured isotopic ratio values for the main isotopologues of the standard ("information values") if the potential impact of anomalous values requires it.

m) The CCL provides for a backup to the embodiment of the primary scale (e.g. a suite of calibrated Primary or Secondary cylinders) in case a catastrophic event occurs.

n) The CCL, or a designated WMO/GAW World Calibration Centre (a complete list of current central facilities is available in the GAW Implementation Plan for the period 2016-2023 (WMO, 2017)), 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 realization 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.

o) 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 rigorous with the status of tank circulation and data submission being posted online on a web page maintained by the laboratory organizing the round-robin. Analysis of CO_2 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.

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-n). More general terms of reference for WCC can be found in the GAW Implementation Plan for the period 2016-2023 (WMO, 2017) available on the WMO/GAW web page.

b) All comparison campaigns should be widely advertised, ensuring that other communities are aware of all comparison activities by WCCs and CCLs.

c) Each WCC must have in-house standards re-calibrated by the CCL every two to four years. Recalibration intervals may be compound-specific depending on the long-term stability of the compounds' mole fractions in the standards. See the individual chapters for recommendations of recalibration intervals. 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.

d) Reference gas standards and travelling standards should be in dried natural air, and when trace gases, in particular CO_2, 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, or measured isotopic ratio information should be provided (see 1.2-l).

e) GAW WCCs 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 network compatibility goals. The comparisons include the round-robins and various comparisons of flask samples and continuous analyser systems. The CCL should be included in comparisons organized by WCCs.

f) The WCC for CO_2, CH_4, and CO (Empa) has demonstrated the benefits of using a travelling instrument for GAW station audits (Zellweger et al., 2016). 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" 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., 2013).

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 conventional reference scale, the WMO Mole Fraction Scale for gas mole fractions in dry air, including its version number, or relative to the appropriate stable isotopic ratio scales through the WMO recommended scale realization where appropriate. 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 another traceable pathway (e.g. by a World or Regional 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 highest level in-house standards to working standards (i.e. standards attached to the operational equipment for regular calibration), and from working standards to atmospheric measurements. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retroactive changes) in the assigned values of higher-level standards all the way to measured values for atmospheric air. The uncertainty propagation at GAW measurement laboratories should include the uncertainties provided for calibration mixtures by CCL, and include all retrospective corrections, if propagated later on.

c) It is recommended that each WMO/GAW measurement laboratory participate in the WMO round-robin comparisons held every two years. Each lab is expected to report their measured values and respective uncertainties. For the latter, they should not report the repeatability of the few measurements made on the round-robin cylinders, but the more relevant measure of long-term reproducibility, which could be based on calibrations of surveillance tanks made over many years, or another equivalent method.

d) 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 ongoing comparison activities to verify that the recommended WMO network compatibility targets (Table 1) are being reached.

e) Laboratories should, when they find inconsistencies between calibration gas mixtures received from the CCL, bring those results to the attention of the CCL.

f) A rule of thumb for internal reproducibility goals is one half the network 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.

g) Calibration and working standards should be contained in high-pressure aluminium cylinders. Steel cylinders are not recommended except for H_2 in which case stainless steel is recommended. Cylinder head valves should be packless, brass valves with PCTFE or metal seats; for H_2 valves made from steel or brass are appropriate.

h) When prepared, calibration and working standards should be dried to a dew point of at most -70°C (at atmospheric pressure), corresponding to 2.6 ppm or less water vapour content.

i) In the case of CO_2 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.

j) Cylinder regulators are a critical component of all analysis systems and a poor choice of the 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 CO_2 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.

k) 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. Regulator flushing is especially important to consider with newer analytical methods that require infrequent calibrations leading to long stagnation periods for the regulators. 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.

l) We recommend the use of natural air for laboratory and working standards. In some cases, commercial gas suppliers can be useful for providing working standards, provided they are then calibrated via the laboratories highest level standards to maintain the link to the WMO scales. However, the matrix must match natural air and potential interferences for the analytical methods used should be known and quantified. If trace gas mole fractions are adjusted in reference air mixtures, for CO_2 in particular, the isotopic composition of the cylinder trace gas should remain unchanged to minimize the influence of isotopic composition on calibrations, or the composition of the leading isotopologues of CO_2 standards should be analysed and provided with the mole fraction of CO_2.

m) 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' standard may be required to periodically adjust the offset of the baseline response.

n) Calibration standards should bracket the range of observed mole fractions at the field station and anticipate long-term trends in background atmospheric mole fraction.

o) The 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 the 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 the 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 network 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.

p) Any calibration analysis made at daily or lower frequency should be run at varying times of day to detect potential diurnal aliasing.

q) 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).

r) 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. The 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.

s) Care should be taken to maintain a single line of traceability of the calibration (see 1.4-b above). The 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 operation and quality assurance and quality control of atmospheric trace gas measurements

To achieve the required levels of network 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 foolproof 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 measurements, the reader is referred to Measurement Guidelines for CH_4 and N_2O (WMO, 2009a) and for CO (WMO, 2010).

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. See Chapter 2 for guidance. In addition, investigators are encouraged to include with their data an estimate of inter-laboratory measurement compatibility based on results from an ongoing 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 (JCGM, 2008) shall be used for uncertainty estimates.

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 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. Potential fractionation in the cylinders is of particular relevance for O_2/N_2 observations (see Chapter 6).

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 network 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 ($Mg(ClO_4)_2$) 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, pressure and humidity.

e) Using water vapour measurements to correct measured CO_2 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 (see e.g. Zellweger et al., 2016). 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 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. This is of particular importance when no sample drying is applied and thus, humidity in the sample can change considerably when switching from dry reference gas from a high-pressure cylinder to moist ambient air. 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 the 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 round-robin comparisons, investigators are required to participate in more frequent and ongoing 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 ongoing 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 ongoing 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 programmes (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 ongoing comparison experiments are encouraged to report at GGMT meetings what they have learned, how the comparison has affected measurement quality and network 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 ongoing quality control, help determine measurement uncertainty and allow the joint use of datasets from different laboratories. New developments in flask sampler design and control facilitate variable sampling strategies, e.g. variable sampling length, sampling time, and triggering by external signals from co-located continuous measurement systems. These may be used to maximize the benefit of the flask sampling programme and to ensure a reliable quality control of the continuous record.

n) Clear protocols and reports of experience gained in comparison projects should be provided. Results should be published and be made readily accessible via the 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 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 Chapter 16 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. The in situ measurement of additional parameters is recommended, as it is beneficial for data interpretation and quality control.

2. RECOMMENDATIONS FOR THE DETERMINATION OF UNCERTAINTY

Measurement uncertainty should be reported along with each measured value, and the methods for estimating uncertainty should be thoroughly described. Practical guidelines for reporting uncertainty can be found in the "Guide to the expression of uncertainty in measurement" (GUM) (JCGM, 2008) and https://physics.nist.gov/cuu/Uncertainty/index.html. Here we give a brief review of key points to consider from the GUM and important considerations for uncertainty estimates particular to atmospheric monitoring applications. A detailed formulation is beyond the scope of this document but see references listed for examples of uncertainty estimation schemes applied to atmospheric monitoring programmes.

Key points from the GUM are:

- Realistic uncertainty estimates are preferable to "safe" but overly conservative estimates of uncertainty.
- The terms "error" and "uncertainty" represent completely different concepts; they should not be confused with one another or misused.
  - Errors result from imperfections in the measurement. Errors arising from random effects can be reduced by increasing the number of observations. Corrections or correction factors should be applied to compensate for known quantifiable systematic effects (biases) such that after correction the expected value for the error arising from the systematic effect is zero.
  - Measurement uncertainty reflects the lack of exact knowledge of the value of the measurand (i.e. the quantity intended to be measured). The result of a measurement after correction for recognized systematic effects is still only an estimate of the value of the measurand because of the uncertainty arising from random effects and from imperfect correction of the result for systematic effects.
  - Uncertainty components have sometimes been categorized as "random" and "systematic" and are associated with errors arising from random effects and known systematic effects, respectively. Such classification can be ambiguous and is discouraged. The term "systematic uncertainty" should be avoided.
- A distinction is made between type A and type B uncertainties, where type A uncertainties are evaluated using statistical methods, and type B uncertainties are evaluated by other means. Examples of Type B uncertainties include previous measurement data, manufacturer's specifications, and data provided in calibration and other certificates.
- Type A uncertainties are characterized by estimated variances, degrees of freedom and covariances where appropriate. The distribution can typically be determined from the observations (e.g. Gaussian).
- Type B uncertainties should be characterized by quantities that may be considered as approximations to the corresponding variances. The distributions are often unknown and must be assumed based on available information (e.g. uniform).
- Any detailed report of the uncertainty should consist of a complete list of the components, specifying for each the method used to obtain its numerical value.
- The uncertainty of a measurement result is usually evaluated using a mathematical model of the measurement and the law of propagation of uncertainties. The model generally includes various influence quantities (input variables) that are inexactly

known. This lack of knowledge contributes to the uncertainty of the measurement result, as do the variations of the repeated observations and any uncertainty associated with the mathematical model itself. The mathematical model should always be revised when the observed data, including the result of independent determinations of the same measurand, demonstrate that the model is incomplete.

- The combined uncertainty should be obtained by applying the usual method for the combination of variances (i.e. as the positive square root of the sum of squared variances and sensitivity coefficients). For a measurand, y, defined as a function, *f,* of uncorrelated input variables, x_i, each with standard uncertainty $u(x_i)$, the combined standard uncertainty is given by:
-

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i)$$

If input variables are known to be correlated, the combined uncertainty should take correlations into account to the extent possible (see eq. 13 in Section 5.2 of the GUM (JCGM, 2008)).

- The combined standard uncertainty is calculated by combining standard uncertainties (e.g. standard deviations). If, for particular applications, it is necessary to multiply the combined standard uncertainty by a factor to obtain an expanded uncertainty (e.g. a confidence interval), the multiplying factor used must always be stated. Confidence intervals depend on explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and the combined standard uncertainty. The level of confidence can be known only to the extent to which such assumptions may be justified.
- It is important not to “double-count” uncertainty components. If a component of uncertainty arising from a particular effect is obtained from a Type B evaluation, it should be included as an independent component of uncertainty in the calculation of the combined standard uncertainty of the measurement result only to the extent that the effect does not contribute to the observed variability of the observations.
- Combining uncertainties using the GUM framework becomes more difficult with a complicated measurement model (as forming partial derivatives can be difficult), or where asymmetric uncertainties are included. A Monte Carlo method is a valid alternative.
- **Repeatability** is a measure of the closeness of the agreement between the results of successive measurements carried out under the same conditions of the measurements (i.e. over a short period of time). **Reproducibility** is a measure of the closeness of agreement of measurements carried out under changed conditions of the measurement. Changed conditions may include new sensors, new measurement principle, new reference standard(s), new location, and/or time.

Propagation of WMO scales: Measured values should be reported on the WMO scale, and investigators should anticipate occasional updates to the scale. Ideally data will be reprocessed whenever the scale changes using updated values for any cylinders calibrated by the Central Calibration Laboratory (CCL). If reprocessing is not possible or is impractical, then an empirical correction should be made to account for scale differences, and uncertainty in the correction should be included in the measurement uncertainty. If a laboratory uses CCL-calibrated cylinders to transfer the WMO scale to in-house standards, then uncertainties for the values of the in-house standards should be obtained by propagating the uncertainties of the assigned values of the CCL-calibrated standards. Reproducibility reported by the CCL is the relevant measure of uncertainty for these purposes rather than the expanded uncertainty associated with the scale itself. The expanded uncertainty associated with the scale includes all known contributions to uncertainty, and is larger than the scale propagation uncertainty. Reproducibility, estimated by the CCL, is based on repeated measurements of many well-behaved cylinders over several years, and is typically reported at 95% C.L., or approximately coverage factor $k=2$.

Typical least-squares propagation of uncertainty requires at least one degree of freedom (e.g. at least three standards if using a linear regression). However, Monte Carlo analysis that accounts for the uncertainty of the assigned values of the cylinders may be used for cases with zero degrees of freedom. Cylinders should be recalibrated periodically according to the guidance of the WMO Central Calibration laboratory. Corrections should be made to account for any drift in a cylinder’s assigned value, and any uncertainty in the drift correction should be included in the measurement uncertainty.

Corrections for systematic errors: Sometimes corrections may be needed to account for known biases in the method. Examples include corrections for differing amounts of water in samples versus standards, nonlinearity in the sensor response, inadequate flushing of the analyser gas cell or upstream components, or matrix effects due to differences in composition between standards and samples (e.g. spectral interference or pressure broadening, due to different isotopic composition or differences in the O_2:N_2 ratio between samples and standards, or the absence of constituents such as N_2O or Ar). In cases where a bias correction is applied, the uncertainty of the correction should be estimated and included in the combined measurement uncertainty.

Aggregated data: When data are aggregated to produce time-averaged data products then random variability corresponding to the aggregation interval should be taken into account. In general, random variability decreases according to the square-root of N, where N is the number of independent measurements. However, it is necessary to characterize the Allan variance in order to estimate the variability corresponding to different averaging intervals. In many cases, there may be little noise reduction for averaging intervals greater than a few hours. Note also that autocovariance related to instrument response time should be considered when computing the number of independent measurements. Uncertainty reporting should be sufficiently detailed so that users can compute realistic uncertainties for time-averaged data.

Unbiased estimation of the standard deviation of small sample sizes: The typical method for computing standard deviations results in values that are too small for cases with small sample sizes (N < 10). The magnitude of the bias depends on the underlying distribution of the data. For normally distributed data, a “rule of thumb” correction exists such that:

$$\hat{\sigma} \approx \sqrt{\frac{1}{N-1.5}\sum_{i=1}^{N}(x_i - \overline{x})^2}$$

where $\hat{\sigma}$ denotes the estimated unbiased standard deviation (Brugger, 1969).

Sensor precision and atmospheric variability: For time-averaged data from continuous or quasi-continuous analysers, standard deviations (SD) should be reported along with the number of independent values included in the average (N). Standard deviations are distinct from measurement uncertainty and should be reported in addition to rather than in lieu of measurement uncertainty. Standard deviations provide a measure of atmospheric variability (AV) plus instrument noise. AV has scientific value separate from the average measured value; for example, AV provides a quantitative indicator of the influence of nearby sources and can be used for data selection and weighting in applications such as inverse modelling. It is, therefore, useful to separately report an estimate of the sensor repeatability u_r corresponding to the averaging interval so that AV can be calculated for cases where SD > u_r. It is possible to estimate u_r from repeatability during calibration periods when the sensor is measuring air with a constant value from a cylinder, and the impact of any drift corrections on timescales corresponding to the averaging interval should also be considered. For discrete measurements such as whole air flask samples, atmospheric variability may affect agreement among replicate samples, but it is generally not practical to directly estimate atmospheric variability from flask samples alone.

Comparisons with independent data: Comparisons among simultaneous observations should agree within combined uncertainties. These comparisons can detect systematic errors that would otherwise remain unknown but should not be used as the sole estimate of measurement uncertainties. Care should be taken to quantify any biases that might be common among the observations being compared (e.g. spectral interferences may be similar among measurements using a similar method of detection, a leak may similarly affect measurements using a shared inlet).

Special considerations for discrete air samples: Measurement uncertainty should account for uncertainty in the analytical system as well as any uncertainty associated with the sample collection. Collection uncertainty can be assessed using test flasks filled simultaneously, but experiments should also be performed to understand any biases that may be associated with real air samples that may result from variations in humidity, pressure, or temperature. If the measured value is the average of *N* multiple aliquots from a single sample, then the appropriate measure of the random uncertainty of the analysis is the standard error of the mean, which equals the standard deviation divided by the square root of *N* (where standard deviations should be corrected for bias due to small sample sizes as described above.)

Compatibility within GAW: Network compatibility goals (see Table 1) as understood here and within the WMO/GAW community are the scientifically-determined maximum bias among monitoring programmes that can be included without significantly influencing fluxes inferred from observations with models and is not the same as uncertainty or sensor precision.

Published examples of uncertainty estimations: Andrews et al. (2014) and Verhulst et al. (2017) describe uncertainty estimation schemes for continuous greenhouse gas measurements. Rella et al. (2013) describe bias correction for measurements in humid air and an assessment of uncertainty in the correction. Yver Kwok et al. (2015) describe monitoring of CRDS instrument uncertainties by distinguishing between continuous measurement repeatability (CMR) and short- and long-term repeatability (STR, LTR respectively). Hazan et al. (2016) describe the ICOS automatic processing including an uncertainty estimation scheme. Work on propagating the standard gas assignment uncertainty is ongoing. Jordan and Rzesanke (2018) describe uncertainty estimates for measurements made by the ICOS Flask and Calibration Laboratory.

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3. SPECIFIC REQUIREMENTS FOR CO_2 CALIBRATION

3.1 Background

The general goals for network compatibility of measurements of CO_2 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 caused by 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 network compatibility goal of Table 1 may be appropriate.

NOAA/ESRL serves as CCL for CO_2 for the GAW Programme. The current (July 2018) version of the WMO mole fraction scale for carbon dioxide is WMO CO_2 X2007. The X2007 scale is embodied in a set of 15 CO_2-in-dried-air mixtures in large high-pressure cylinders (primary standards) covering the range 250 to 520 ppm. Primary standard values are assigned by repeated (approximately every 2 years) manometric determinations.

The CCL transitioned CO_2 calibrations from an NDIR based analysis system to an analysis system based on multiple laser spectroscopic techniques in 2016. The laser spectroscopic system measures the three major isotopologues of CO_2 individually to properly account for isotopic composition differences among the primary standards and between the primary standards and subsequent levels in the calibration hierarchy (Tans et al., 2017). A scale revision is planned for 2018. This scale revision will be identified by a new name and will be propagated back in time to all measurements made since the beginning of the NOAA calibration record. The revision expands the CO_2 scale to 600 ppm by adding two additional primary standards to the current set and fixes two errors in the manometric calculations used to assign values to the primary standards. The effect of fixing the errors introduces a mole fraction dependent difference ranging from approximately 0.05 ppm at 250 ppm to 0.3 ppm at 520 ppm.

The CCL has additional cylinders that have been measured several times manometrically ranging from 70 ppm (covering atmospheric values in ice cores) to 3000 ppm (covering CO_2 partial pressures in the oceans). These provide both a backup and a much larger range.

3.2 Recommendations for CO_2 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 CO_2 isotopic composition of distributed reference standards should anticipate the evolution of CO_2 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 CO_2 calibrations well below WMO network compatibility goals. These information values are thus not isotopic calibration values.

c) The laser spectroscopic calibration system is not sensitive to isotopic composition differences between standards and unknown sample cylinders. It is recommended that labs using standards that are significantly depleted in ^{13}C or ^{18}O (for example cylinders prepared from a fossil fuel sourced CO_2 by a commercial gas company) have them recalibrated on the new system since the NDIR measurements may be biased when measuring cylinders with depleted isotopic compositions against secondary standards with near-ambient isotopic composition.

d) The CCL is encouraged to make available on its website calibration results of all GAW laboratory standards based on the current scale.

e) To help WMO/GAW Programme participants meet the targeted network compatibility goals outlined in Table 1, the CCL shall aim to transfer the CO_2 scale to calibrated CO_2-in-dry-air standards with a scale transfer uncertainty of < ±0.03 ppm (95% confidence level, coverage factor k=2).

f) Each WMO/GAW measurement laboratory should actively maintain its link to the WMO Scale by having a subset of its in-house highest level standards for CO_2 (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.

4. SPECIFIC REQUIREMENTS FOR STABLE ISOTOPE CALIBRATION

4.1 Background

The value of stable isotope data for tracking fluxes in greenhouse gases and changes in sources and sinks has long been recognized. To make the best use of these measurements, datasets from different laboratories must be compatible. The network compatibility goals of stable isotope measurements of CO_2 and CH_4 in air are presented in Table 1. These goals are required to achieve reasonable signal to noise ratios when addressing small, yet globally significant gradients over large spatial and/or temporal scales for background stations. Given that ecological or biogeochemical studies of predominantly local or regional significance generally deal with larger signal gradients in time and space, the network compatibility goals in these cases can be relaxed, and it is possible that larger interlaboratory uncertainties can be tolerated (Table 1). The total combined uncertainty tolerated for local studies is intended to scale with the magnitude of the gradients studied.

However, results from a flask-air comparison for $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO_2 samples, presented at the GGMT-2015 by Ernst (2015), demonstrate that laboratories continue to show persistent offsets that are much larger than those stipulated by network compatibility goals presented in Table 1. The offsets are partly caused by differences in the realization of the VPDB scale in local use. Calibration, measurement, and sampling effects (sample collection, drying, storage etc.) introduce additional sources of error.

Exchanges of high-pressure cylinders in WMO Round Robin experiments (RRs) are designed to exclude sample collection effects from interlaboratory comparisons; however, RRs organized by NOAA also show large variability in measurements of $\delta^{13}C$ and $\delta^{18}O$ of air-CO_2. For RR6[1], using the Institute of Arctic and Alpine Research (INSTAAR) as the reference laboratory, only one laboratory was within the $\delta^{13}C$ network compatibility goal of 0.01 ‰ while the other 13 laboratories showed discrepancies of up to ±0.09 ‰. For $\delta^{18}O$ in air-CO_2, two laboratories were within the network compatibility goal of 0.05 ‰ whereas the other 12 laboratories showed discrepancies of up to ±0.4 ‰. (Note, using a different laboratory as the reference would produce different agreement results but would still show large discrepancies amongst the broad group). Long-term network compatibility for CO_2 isotopes at the WMO level has never been demonstrated.

Similarly, a recent review of comparison results for methane isotopes (Umezawa et al., 2018) demonstrates lab-to-lab discrepancies up to 0.5 ‰ for $\delta^{13}C$ and 13 ‰ for $\delta^{2}H$ for ambient air samples which are 25 and 13 times their respective network compatibility goals (see Table 1).

These discrepancies call for a careful assessment and review of current calibration approaches, and the development of strategies to improve inter-laboratory comparability. In particular, the use of artefact-based isotope scales and artefact-based primary reference materials requires metrological approaches that are different from those used in the area where primary methods (which directly measure the amount of a substance) have been established.

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[1] https://www.esrl.noaa.gov/gmd/ccgg/wmorr/wmorr_results.php

Here we address the issues and outline calibration approaches for stable isotopes of the major greenhouse gas CO_2, primarily with mass spectrometric methods but also with optical techniques. We then make recommendations for implementing more robust calibration strategies for stable isotope measurements of other important atmospheric trace gases CH_4, N_2O, and CO. We also note that sampling effects (sample collection, drying, storage, etc.) may also cause biases and have to be addressed separately.

4.1.1 Stable isotope scales and primary reference materials in use

Mole fraction scales for CO_2 and CH_4 are realized by sets of primary reference mixtures prepared by Central Calibration Laboratories (CCLs) using a primary method. Thus, these primary mixtures are SI-traceable. In contrast, stable isotope scales are artefact-based, that is they are dependent on established reference materials (RMs) with assigned values for both the definition and the scale realization; these primary RMs are not SI-traceable.

Stable isotope data of air-CO_2 ($\delta^{13}C$ and $\delta^{18}O$), air-CO ($\delta^{13}C$), and air-CH_4 ($\delta^{13}C$) are expressed on the VPDB-CO_2 scale[2], and δ^2H of air-CH_4 and $\delta^{18}O$ of air-CO are expressed on the VSMOW scale. All measurement results and all uncertainty propagations should be done relative to the scale in use, as based on the primary RMs used for the scale realization.

The primary RM NBS19 (marble calcite, defined values[3] $\delta^{13}C \equiv +1.95$ ‰ and $\delta^{18}O \equiv -2.20$ ‰), formerly recognized by IUPAC for the definition and realization of the VPDB $\delta^{13}C$ and $\delta^{18}O$ scale (Brand et al., 2014), is now exhausted. A new marble calcite, IAEA-603 ($\delta^{13}C = +2.46 \pm 0.01$ ‰ and $\delta^{18}O = -2.37 \pm 0.04$ ‰, see below and footnote 5), has replaced NBS19; IAEA-603 is currently recommended to be used as the primary RM to realize the VPDB scale (IAEA, 2016). Similarly, VSMOW2 is the international primary RM (replacing VSMOW) intended for the realization of the VSMOW hydrogen and oxygen isotope scales (Brand et al., 2014), its values and uncertainty are $\delta^2H = 0 \pm 0.3$ ‰ and $\delta^{18}O = 0 \pm 0.02$ ‰.

For scale realization, IUPAC recommends one primary RM to define the delta-scale origin (zero-point) and a second scale-anchor RM to define a scale span (Wieser, 2006; Coplen et al., 2006). Until 2017, the second scale-anchor RM for all $\delta^{13}C$ data normalization has been LSVEC ($\delta^{13}C = -46.6$ ‰, assigned with zero uncertainty; Coplen et al., 2006). At its September 2017 meeting, the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) decided to discontinue the use of LSVEC for carbon isotope ratio analysis. However, CIAAW stressed that "carbon isotope delta measurements must still be normalized to the VPDB scale using at least two suitable international reference materials selected by the users as appropriate"[4] (IUPAC, 2018). SLAP2 remains the second primary RM for δ^2H data for all materials ($\delta^2H_{SLAP2} = -427.5 \pm 0.3$ ‰) and $\delta^{18}O$ data for waters and solids ($\delta^{18}O_{SLAP2} = -55.50 \pm 0.02$ ‰). For $\delta^{18}O$ in carbonates and CO_2, the VPDB-CO_2 scale is used without the second RM aimed to define the scale span (Brand et al., 2014).

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[2] For consistency we refer to the VPDB-CO_2 scale which is used both for $\delta^{13}C$ and $\delta^{18}O$ data reporting. Note, $\delta^{18}O$ values for air-CO_2 should be solely expressed on the VPDB-CO_2 scale (Brand et al., 2010). When oxygen isotopes are not included ($\delta^{13}C$ of air-methane and value of LSVEC), reporting $\delta^{13}C$ data on the VPDB scale is allowed as $\delta^{13}C$ values are the same for the VPDB and VPDB-CO_2 scales.

[3] Values for NBS19 were introduced without uncertainty characterization (Hut, 1987).

[4] Other RMs for $\delta^{13}C$ include NIST RMs 8562-8564, see 4.1.2.

$\delta^{13}C$ values are calculated from the raw data obtained by mass spectrometry on CO_2 gas using the ^{17}O-correction algorithm that is specific to the VPDB scale (including the related VPDB-CO_2 scale). Although several algorithms were considered in the past, the revised ^{17}O-correction after Assonov and Brenninkmeijer (2003a, b) is currently recommended, and its simplified approximation (linearized form) is considered in Brand et al. (2010). Inconsistent use of ^{17}O-correction is known to produce $\delta^{13}C$-bias up to ~0.05 ‰ (Assonov and Brenninkmeijer, 2003a, b).

4.1.2 Primary reference materials and the role of international organizations and NMIs

The IAEA is recognized as custodian of the stable isotope scales and primary RMs for H, C, N, O and S (δ^2H, $\delta^{13}C$, $\delta^{18}O$, $\delta^{15}N$ and $\delta^{34}S$) (IAEA, 2016). The IAEA is responsible for making such materials available and for providing replacements when necessary. The uncertainty levels of these RMs must meet or exceed objectives for the most critical applications, including the WMO network compatibility goals (Table 1).

The realization of the VPDB scale is currently under revision. At GGMT-2017 S. Assonov (IAEA) reported on the new RM, IAEA-603, developed to replace the exhausted NBS19 which defines the zero point of the VPDB scale (and the VPDB-CO_2 scale) for $\delta^{13}C$ and $\delta^{18}O$. (Note: NBS19 remains a valid scale-defining RM so laboratories may continue to use remaining amounts of NBS19). The IAEA-603 calcite has been prepared in 5 batches, with the first batch of ~5000 ampoules released in December 2016. The IAEA-603 material is accompanied with a reported value and uncertainty[5] characterizing how a single aliquot if taken from any ampoule (out of the first batch of ~5000 units produced) represents the assigned value; by averaging data obtained on several aliquots one may reduce the uncertainty related to its in-homogeneity. With the release of IAEA-603, the realization of the VPDB-CO_2 scale zero point is expected to continue for decades.

LSVEC, initially developed at NIST as a lithium isotopic standard, was introduced as a $\delta^{13}C$ RM (Coplen at al., 2006) to provide a second anchor, aimed at establishing a 2-point calibration, for the VPDB scale. A consensus $\delta^{13}C$ value was assigned to LSVEC by Coplen et al. (2006) based on measurements of a few LSVEC units by Ghosh et al. (2005) and previous value assignment by NIST (Verkouteren and Klinedinst, 2004). Recent measurements performed at the IAEA and USGS have shown that the isotopic composition measured for LSVEC is drifting due to adsorption of air-CO_2 (Assonov et al., 2016; Qi et al., 2016). In addition to the stability, the IAEA study assessed the variability of LSVEC in unused vials and in bulk containers: a spread of 0.35 ‰ was observed.

As requested at the GGMT-2015, the IAEA has prepared and presented at GGMT-2017 a plan for introducing and characterizing replacement material(s) for LSVEC; additional details can be found in the IAEA meeting report (IAEA, 2016). Given the discontinuance of LSVEC we note that several international RMs were characterized for $\delta^{13}C$ values in accordance with the initial

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[5] Uncertainty components are listed in IAEA-603 Reference Sheet (Table 2), available at https://nucleus.iaea.org/rpst/referenceproducts/ReferenceMaterials/Stable_Isotopes/13C18and7Li/IAEA-603/RM603_Reference_Sheet_2016-08-16.pdf. These include Type A and Type B uncertainties (related to material homogeneity and its characterization against NBS19); contribution of Type A uncertainty can be reduced when several aliquots of IAEA-603 are analysed.

LSVEC value (see Coplen et al., 2006). Limited amounts of NIST RMs 8562-8564, which are pure CO_2 gases characterized for $\delta^{13}C$ and $\delta^{18}O$, are still available; however, the sale is suspended pending a revision of the reference sheet (R. Vocke, personal communication to S. Assonov, December 2017).

The GGMT participants welcome the steps aimed at the revision of the VPDB scale realization. This should lead to a closer cooperation between the IAEA, WMO, the Central Calibration Laboratory for CO_2 isotopes (CCL-isoCO2), BIPM and NMIs for improving metrological traceability and uncertainty evaluation for different kinds of reference materials used for atmospheric measurements. In particular, creating CO_2–in-air mixtures and exploring how to improve the determination of the absolute stable isotope ratio ($^{13}C/^{12}C$)[6] of the VPDB-CO_2 scale origin will be a part of the new EMPIR project SIRS (project led by NPL; project website: http://www.vtt.fi/sites/SIRS/).

Given that no international RMs in the form of N_2O are available, particularly crucial for $\delta^{15}N^a$ and $\delta^{15}N^b$, efforts to release RMs in the form of pure-N_2O gas (in ampoules) or N_2O in air (in cylinders or flasks) are encouraged. GGMT recommends the IAEA be requested to assess their capability to produce appropriate N_2O RMs.

4.1.3 The role of the Central Calibration Laboratory for CO_2 isotopes (CCL-isoCO2)

The CCL-isoCO2 helps to ensure long-term network compatibility of all stable isotope measurements in atmospheric CO_2 by providing appropriately calibrated CO_2-in-air mixtures (e.g. characterized natural air) with values fully traceable to the respective international isotope scales (VPDB-CO_2 in this case). The critical step for the CCL-isoCO2 is to correctly link CO_2-in-air mixtures to the artefact-based VPDB-CO_2 scale realized by $CaCO_3$ RM (NBS19/IAEA-603). Use of CO_2-in-air mixtures well-characterized by CCL-isoCO2 will allow laboratories to follow the principle of identical treatment in making air-CO_2 isotope measurements.

The stable isotope laboratory (BGC-IsoLab) at the Max Planck Institute for Biogeochemistry (MPI-BGC), Jena, Germany, has been selected as CCL-isoCO2. The approach adopted by BGC-IsoLab was developed in collaboration with Environment and Climate Change Canada[7] (ECCC) and the National Institute for Environmental Studies (NIES) in Japan (Brand et al., 2009). The resulting realization of the VPDB-CO_2 scale[8], called the Jena Reference Air Set (JRAS-06), involves mixing CO_2 evolved from two calcites, MAR-J1 and OMC-J1, by reaction with H_3PO_4 under well-controlled temperature conditions, with synthetic CO_2-free air (see Ghosh et al., 2005). The mixtures are prepared in small batches (5L glass flasks at low pressure) and values are assigned by calibration measurements made for each flask against the BGC-IsoLab JRAS CO_2-in-air lab standards (JRAS-secondary standards) which are traceable to the primary RMs. Further description of the development of JRAS-06 can be found in the following publications: Werner et al. (2001); Ghosh et al. (2005), Brand et al. (2009), Wendeberg et al. (2011); Wendeberg et al. (2013) and references therein.

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[6] Previous determinations of the absolute stable isotope ratio $^{13}C/^{12}C$ of the VPDB scale done at IRMM, Belgium (Valkiers et al., 2007) and LGC, UK (Malinovsky et al., 2013; Dunn et al., 2015) still do not address the uncertainty required at ±0.01 ‰.

[7] Previous name - Environment Canada.

[8] Link to VPDB-CO_2 is critical here, as mixtures are characterized in $\delta^{18}O$ values.

Following the 15th WMO/IAEA Meeting (GGMT-2009), it is recommended for laboratories to implement JRAS-06 as their scale realization for stable isotope measurements of CO_2 in air. The scale transfer is realized by one of two methods: (a) JRAS sets: 5-L glass flasks of air with CO_2 derived from lab standard marbles MAR-J1 ($\delta^{13}C \approx +1.96$ ‰, $\delta^{18}O \approx -2.02$ ‰) and OMC-J1 ($\delta^{13}C \approx -4.24$ ‰ and $\delta^{18}O \approx -8.71$ ‰) (details in Ghosh et al., 2005; Wendeberg et al., 2011; Wendeberg et al., 2013); (b) high-pressure air cylinders provided by participating laboratories characterized by the CCL-isoCO2 for the stable isotopic composition of CO_2 via the JRAS-06 scale realization.

One of the roles of the CCL is the assignment of uncertainty following sound metrological principles (WMO, 2016b). As recommended by GGMT-2015, uncertainty propagation for JRAS-06 should be based on the traceability chain to the VPDB-CO_2 scale. The publications relevant to the development of the JRAS scale above describe the analytical procedures and elements of the uncertainty budget. Full uncertainty budgets are provided by BGC-IsoLab to laboratories that use the JRAS-06 realization of the VPDB-CO_2 scale. However, there are concerns within the NMI community that the absolute stability of the JRAS-06 scale realization has not been adequately determined against primary RM's and that the full uncertainty budgets have not been adequately described. This is an area of on-going discussion that will be further addressed at the next GGMT meeting.

4.1.4 Uncertainty and compatibility in the absence of a primary method

The use of artefact-based stable isotope scales and artefact-based primary reference materials requires metrological approaches that are different from those used in the area where primary methods have been established (e.g. preparation of gravimetric gas mixtures) and where the absence of drifts can be validated by newly prepared primary mixtures.

Implementation of metrological concepts for stable isotope measurements is still under development. According to the 3rd Edition of the International Vocabulary of Metrology (VIM 3, 2008), measurement results are *comparable* when they are metrologically traceable to the same stated reference and thus reported on the same scale, e.g. VPDB-CO_2. The VPDB-CO_2 scale is established by utilisation of the primary RMs as described above under standard carbonate-H_3PO_4 reaction conditions.

When one needs to achieve *data compatibility* to a very demanding limit (e.g. 0.01 ‰, for $\delta^{13}C$ of air-CO_2, Table 1), then the compatibility goals dictate the uncertainty objective for each laboratory in its tie to the practical scale-realization (e.g. JRAS-06). It should be noted that this compatibility goal is close to the performance limit of the best dual inlet isotope ratio mass spectrometers (DI-IRMS) and beyond the reach of contemporarily continuous-flow IRMS and optical techniques. In addition, the transfer of the JRAS-06 realization itself brings a non-negligible uncertainty which is comparable to the WMO network compatibility goals, i.e. each JRAS-flask bears an individual value and uncertainty. As JRAS-06 flasks and air-cylinders calibrated by CCL-isoCO2 are used for calibration transfer (fulfilling the function of RMs), it is the role of the CCL-isoCO2 to assign these values and uncertainties (ISO 17034, 2016; WMO, 2017).

To achieve data compatibility over many years, the long-term reproducibility of the scale-realization is crucial. In the absence of primary method(s), this can only be demonstrated by regular verification vs. a high-level scale anchor which is proven to be stable in time[9] and to have a low uncertainty.

By visualizing the traceability chain one can see how each step introduces uncertainty components which affect the ability to achieve long-term compatibility among measurement programmes using the scale realization. The steps (top-down) are as follows:

a) *Primary reference materials:* To achieve long-term reproducibility of the JRAS-06 (or any other) scale realization, the primary RMs must be stable in time and homogeneous. The heterogeneity of primary RMs (vial-to-vial, aliquot-to-aliquot) and its stability over time are major contributors to their uncertainty. This uncertainty has to be assessed and provided to the RM user by the IAEA.
b) *JRAS-06 long-term reproducibility:* The long-term reproducibility of JRAS-06 can be demonstrated by regular measurements of JRAS-secondary standards vs. the primary RMs. For this purpose, CO_2 has to be freshly released from aliquots of primary carbonate RMs using the standard carbonate/phosphoric acid preparation. This step, repeated over many years, must be included as it introduces an associated uncertainty component that may vary over time.
c) *Scale transfer to user labs:* Isotopic values assigned to JRAS-06 mixtures and/or calibration by the CCL-isoCO2 of high-pressure cylinders belonging to user-labs are based on measurements relative to JRAS-secondary standards. The related steps (CO_2 extraction and measurements) also contribute to the uncertainty.
d) *Within lab scale transfer:* Calibration transfer within each laboratory from JRAS-06 mixtures or cylinders calibrated by the CCL-isoCO2 to lab-standards involves CO_2 cryogenic extraction and measurements; these steps also contribute to the uncertainty budget.

Each step in the calibration hierarchy is critical for long-term compatibility, and each has an uncertainty associated with it. Additional uncertainty components come from preparation steps (such as chemical carbonate-acid reaction, carbonate homogeneity, CO_2 gas mixing, surface exchange effects, CO_2 cryogenic extraction, etc.). All uncertainties have to be propagated in the form of

$$\sqrt{\sum_{i=1}^{n} \sigma_i^2}$$

where σ_i corresponds to each measurement step and various corrections (as based on measurements).

To demonstrate and achieve long-term data compatibility across laboratories contributing to the WMO/GAW programme, the calibration hierarchy and traceability to the VPDB scale at each laboratory should be established (preferably through the current CCL-isoCO2 realization), and different components of uncertainty within the traceability chain at each laboratory should be evaluated. The uncertainty budget is crucial to identify the steps where there is room for

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[9] Only international RMs in the form of marble carbonates are proven to be stable over a long time (NBS19, IAEA-603 and NBS18). Note, as the VPDB-CO_2 scale is based on CO_2 freshly prepared from primary RMs by using carbonate-phosphoric acid reaction, the traceability to the VPDB scale-level including regular recalibrations against primary RMs is critical here.

improvement. This requires close cooperation between analytical laboratories, the CCL-isoCO2, the (potential) WCC-isoCO2 and the international bodies working on the primary RMs (IAEA with the potential involvement of BIPM and NMIs).

4.1.5 The role of a World Calibration Centre

Currently, there is no WCC designated for stable isotopes. To improve network compatibility, the designation of a laboratory (or collaboration of laboratories) to fulfil the WCC functions (see Section 1.3) is urgently needed.

Although laboratory offsets may reduce in value as more laboratories switch to the JRAS-06 scale realization, a WCC would add value, not the least in verifying the scale-realization. Further round-robins and comparisons will be invaluable in verifying calibration scales over time, and would help identify instrumental effects (as did the CLASSIC experiment by circulating whole-air cylinders; see Allison and Francey, 2007). Round Robin 7, organized by NOAA, is scheduled to begin in 2018 and traceability and uncertainty will be major foci of the reporting.

4.2 Current analytical challenges for stable isotopes of CO_2

For achieving harmonized stable isotope ratio measurement results for CO_2 in air, a number of challenges must be addressed. The major issues are outlined below.

a) *Primary reference materials*: marble RM IAEA-603 (replacement for NBS19), with well-characterized uncertainty, was released in 2016. The IAEA is planning to establish a second RM to replace LSVEC. In addition, there is a need to establish several international secondary RMs in the form of pure CO_2 gases with very low calibration uncertainties that cover the $\delta^{13}C$ range of interest.

b) *Scale contraction (η-effect[10])*: During dual inlet mass spectrometric measurements, cross contamination (ion source "memory") shrinks the apparent difference between sample and reference CO_2 gas. Scale contraction can affect dual-inlet measurements in all laboratories, whether they are measuring primary reference materials, propagating the scale of CO_2-in-air, or measuring samples. All measurement operators need to be aware of this effect and minimize it as much as possible. The magnitude of any residual scale contraction should be measured and corrected for (see recommendations).

c) *Storage effects*: Marble carbonates are useful reference materials because they are most stable over time. However, all air sample measurements are performed vs. CO_2 extracted from air mixtures, usually in cylinders. Maintaining laboratory standard gases and mixtures requires careful handling. Regular recalibration and correction for drift, if found, are essential laboratory practice.

d) *Water:* Oxygen isotope exchange between CO_2 and H_2O during sample storage is a known problem for $\delta^{18}O$ and can be addressed by air sample drying and careful flask pre-treatment.

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[10] Following the notation given in (Verkouteren et al., 2003a, b).

e) *Corrections*: Inconsistencies between laboratories can arise from different algorithms and/or parameterizations of the necessary corrections for ^{17}O and N_2O. These algorithms should be standardized.

f) *Estimation and reporting of combined uncertainty*: Uncertainty should be an essential component of sample data reporting, based on metrological traceability chain to the VPDB-CO_2 scale level.

g) *Quality control*: Standard QA/QC procedures for stable isotope measurement communities are not yet well developed and improvements are urgently needed. Compliance with ISO17025 is recommended as a guide to establish in-house Quality Assurance in each laboratory as it has useful recommendations for general management, record keeping, personnel, data management, tests of lab performance, quantification of uncertainty components, and maintenance of an uncertainty-propagation scheme (ISO/IEC 17025 (2017)).

4.3 Recommendations for improvement of CO_2 stable isotope measurements

4.3.1 International organizations

The replacement of LSVEC is a pressing need and requires a metrologically correct solution (IAEA, 2016). GGMT-2017 requests the IAEA, as the scale custodian and principal RM producer and distributor, to address the LSVEC problem and to revise the VPDB scale, following metrological principles of traceability, uncertainty propagation, and quality (as per ISO Guides for reference material production and characterization, ISO Guide 35 (2009) and ISO 17034 (2016). The IAEA is requested to select, test, fully characterize and release a material to replace LSVEC; this must be stable, homogenous, sufficiently abundant, and cover the $\delta^{13}C$ range of interests. As discussed elsewhere, potentially a range of materials may be introduced to help identify drift (IAEA, 2016).

GGMT-2017 requests that IAEA continues to develop the capability to evolve CO_2 from carbonates by H_3PO_4 acid reaction. By using H_3PO_4-carbonate reaction to release CO_2 from primary RMs and creating CO_2-in-air mixtures for at testing purposes, the IAEA can validate the JRAS-06 scale realization. Regular comparisons of pure CO_2 and CO_2-in-air mixtures with the CCL-isoCO2 will be good practice. We recommend that relevant documents and descriptions of critical steps, e.g. standard operating procedures (SOPs), be available from the IAEA.

The IAEA can contribute to the WCC-isoCO2 by providing expert advice on SOPs, metrological traceability and uncertainty propagation. It is essential that the IAEA collaborates with other members of the stable isotope community, including NMIs, in this role.

4.3.2 CCL-isoCO2

In order to have a sustainable calibration scheme, several critical aspects of the operation of a CCL-isoCO2 have been identified and are listed below. These are in addition to those for all analytical laboratories given below. Thus, CCL-isoCO2 has to address both general requirements for CCLs (Section 1.2 of this document, and WMO, 2017) including QA/QC system, requirements for analytical laboratories and specific aspects summarised below:

a) *Traceability chain:* GGMT-2017 recommends that the CCL-isoCO2 continues to provide descriptions of the full measurement traceability chain on the VPDB-CO_2 scale for all calibration measurements. The traceability chain should include the lab standards (lab carbonate and JRAS-secondary standards), all measurement steps, all preparation steps and major instrumental and other corrections. These descriptions should be given on the CCL-isoCO2 website and made available upon request. This process may potentially involve IAEA, NMIs and other experts.

b) *Scale-realization/scale-transfer*: GGMT-2017 requested that the CCL-isoCO2 provide all relevant data pertaining to the transfer of the primary reference materials to CO_2-in-air standards, and an estimate of the uncertainty introduced by the calibration transfer procedure to each individual standard, propagated to the scale level.

c) *Long-term reproducibility of the JRAS-06 scale realization and recalibrations:* The only reliable way to assure long-term reproducibility is to perform regular recalibration of JRAS-secondary standards to the primary RMs and demonstrate integrity (absence of drift) of the scale realization. The JRAS-06 scale was calibrated against NBS19 measurements performed in 2004/2005 (Ghosh et al., 2005; Brand et al., 2009). Given that the VPDB scale is artefact-based and the very strict requirements for long-term network compatibility in the WMO/GAW community, GGMT-2017 suggests that JRAS-secondary standards and lab carbonate standards be regularly verified against primary RMs. In addition, we request that the CCL-isoCO2 maintain close contact with the IAEA regarding the release of an LSVEC-replacement, and prioritize verification of the scale span. Long-term scale consistency tests need to be transparent and the data need to be made available.

d) *Combined uncertainty and uncertainty budget*: The traceability chain is also needed for the identification of all uncertainty components, and evaluation thereof. The uncertainty propagation should include major uncertainty components such as calibration materials, measurements, preparation steps (e.g. acid reaction, gas mixing), and data corrections (e.g. N_2O corrections, ^{17}O corrections, drift). The combined uncertainty should be provided both for the JRAS-secondary standards (including drift corrections) and for each JRAS-mixture produced.

e) *N_2O-correction:* The N_2O correction has been the subject of several publications describing different correction methods. With the provision of reference air (which contains N_2O), biases in the N_2O correction of different laboratories are thought to be extremely small and is not expected to affect the compatibility of networks or scale realization. However, when mixtures contain synthetic N_2O (produced by NH_4NO_3 decomposition) in which $\delta^{15}N$ and $\delta^{18}O$ deviate from the values of air-N_2O, an unpredictable bias of ~0.01 ‰ may arise (Assonov and Brenninkmeijer, 2006). The isotopic composition of the N_2O in the synthetic air used by the CCL-isoCO2 to make CO_2 in air mixtures from carbonates is not known. In light of this potential small bias, we request the CCL-isoCO2 to evaluate the isotopic composition of the N_2O in the synthetic air.

f) *Documentation*: Published literature by the CCL-isoCO2 describes the essential methods, procedures and implemented changes that are involved in producing and maintaining the JRAS-06 scale (Werner et al., 2001; Ghosh and Brand, 2004; Ghosh et al., 2005; Brand et al., 2009; Wendeberg et al., 2011, 2013). To safeguard the future of the scale realization, the CCL-isoCO2 is requested to carefully document all updates, developments, all technical details and detailed

SOPs involved in the realization and maintenance of JRAS-06, and to make these available on the MPI-BGC web page and upon request. Production of this documentation should be a goal for GGMT-2019.

g) *Quality Management System and Data Quality*: We recommend that the CCL-isoCO2 develops a quality management system that uses ISO-17025 as a guideline. In particular, overall measurement performance and reproducibility should be documented. Surveillance cylinders measured at different intervals (daily, quarterly, yearly) and regular recalibrations to the primary RMs can be used to evaluate overall measurement performance and reproducibility.

h) *Comparisons*: The CCL-isoCO2 should participate in comparisons and round-robins, and cooperate with the IAEA and other labs in the community for scale verification and establishment of best practices.

i) *Further developments*: To follow the principle of identical treatment, it is recommended that the CCL-isoCO2 considers developing JRAS mixtures with δ^{13}C at ~-8.5 ‰ and δ^{18}O at ~0 ‰ and thus mimic values of air-CO_2. Alternatively, glass flasks and end-user tanks may be filled with purified natural air and calibrated by CCL-isoCO2.

4.3.3 Analytical laboratories

Since long-term network compatibility is the primary objective, we encourage laboratories to use the JRAS-06 realization. However, an independent lab scale-realization is valuable, because it acts as an independent, external control of JRAS-06. If laboratories are not on JRAS-06, they should be explicit about which realization of the VPDB scale is in local use and provide details regarding its traceability to primary reference materials to the RR coordinator and/or WCC. Specific attention should be paid to the following:

a) *Instrument-specific scale contraction:* Investigations of instrument-specific influences on scale contraction (η or eta effect, see footnote-10) are documented in the literature (Francey and Allison, 1994; Meijer et al., 2000; Assonov and Brenninkmeijer, 2003b; Verkouteren et al., 2003a, b; Ghosh et al., 2005; Allison and Francey, 2007). Laboratories are encouraged to minimize the η effect as much as reasonably possible by adopting the recommended ion source tunings (e.g. minimising emission current) and optimising flushing times (change-over idle time) between the sample and reference CO_2 gas. The magnitude of η can be determined for dual inlet systems by varying the idle time (Francey and Allison, 1994; Verkouteren et al., 2003a, b; Allison and Francey, 2007). The data can then be corrected for the remaining η-effect. Note that the eta-factor for carbon is typically different from that of oxygen in CO_2. Tests aimed at quantifying the magnitude of this memory or cross-contamination should be used to quantify and monitor its magnitude over time, and to correct for it. These should be monitored as a critical component of data quality control.

b) *Selection of laboratory working gases:* During isotope ratio mass spectrometer (IRMS) measurements, the magnitude of scale contraction and memory effects (η effect) critically depend on the reference gases in use. Users should consider the distance of the sample to the working reference gases, especially when measuring reference materials (such as JRAS flasks). To minimize scale contraction effects in day-to-day measurements, the isotopic composition of the working reference gases should be as close as possible to that of CO_2 in ambient air.

c) *^{17}O-correction:* To account for the $^{12}C^{16}O^{17}O$ contribution to the mass 45 measurements, the method described in Assonov and Brenninkmeijer (2003a, b) is recommended as the standard procedure. It can be applied by numerical solution of all equations (Assonov and Brenninkmeijer, 2003a, b) or as a simplified linear approximation (Brand, et al., 2010). Manufacturers of mass spectrometers are asked to update their corresponding software accordingly. Further, to ensure that the effect of the ^{17}O-correction is kept at a minimum, the use of air reference mixtures mimicking samples in $\delta^{18}O$ of CO_2 is recommended and the use of reference materials with a large deviation in $\delta^{18}O$ (e.g. NBS 18) should be avoided.

d) *N_2O-correction*: The N_2O correction has been the subject of several publications, which through different experimental approaches lead to a common correction algorithm which depends on a correct assessment of the relative ionisation efficiency of N_2O and CO_2. Laboratories should make appropriate corrections for N_2O as per Mook and Jongsma (1987), Ghosh and Brand (2004), or Assonov and Brenninkmeijer (2006); all practical details related to this correction should be documented.

e) *Data management and data submission*: All raw mass spectrometry data should be managed in a way to facilitate data re-processing, in case such a need will arise from reference gas recalibration, revision of corrections (for N_2O, ^{17}O and for η-effect), revision of LSVEC-value or other relevant changes. Final processed data should be submitted to WMO/GAW World Data Centre for Greenhouse Gases and include the uncertainty estimation. Furthermore, laboratories are encouraged to include with their data an estimate of inter-laboratory measurement compatibility based on results from an ongoing comparison of actual atmospheric measurements.

f) *Quality Assurance:* Appropriate QA/QC procedures should be established in each laboratory. ISO17025 (ISO/IEC 17025, 2017) is recommended as a guide to establish in-house Quality Assurance in each laboratory. For example, laboratories should develop detailed SOPs for data management, data treatment, and demonstration of lab performance based on QC mixtures. Surveillance cylinders with a range of isotopic values should be used in quality control: those measured at daily intervals allow users to catch problems quickly, and those measured less frequently (quarterly) allow users to catch low-level drift over a longer time period. The highest-level calibration cylinders should be recalibrated by the CCL-isoCO2 every 2 years[11] or replaced by a newly characterized high-level calibration cylinder with appropriate cross measurement of calibration cylinders.

g) *Uncertainty*: It is recommended that all reported measurement results be accompanied with the combined uncertainties (e.g. evaluated as the typical combined uncertainty of quality-control mixtures). This should include scale realization to primary RM (to be based on the uncertainty given by CCL-isoCO2 to each JRAS-06 flask or air cylinder), CO_2 extraction, and data corrections. The total combined uncertainty should be reported on the VPDB-scale. The IAEA has been asked to collaborate in developing a template to aid in this process; collaboration with BIPM and NMIs may be needed. Note: There may be two levels of uncertainty reported by a laboratory: an internal uncertainty, where components of the uncertainty budget common across the laboratory have been removed, that may be useful for comparing measurements made by a single laboratory, e.g. at 2 different

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[11] Following the practice of GHGs concentration measurements, the 2-year period is suggested.

sampling sites, as well as a total uncertainty for comparing measurements from two laboratories.

h) *Inter-Laboratory Comparisons:* All laboratories are encouraged to participate in comparison activities between laboratories, particularly the Round Robins organized by NOAA, as well as co-located or same-air comparisons of atmospheric flask samples. Comparison activities are expected to lead to appropriate follow-up when discrepancies are outside of WMO network compatibility goals. The task should be coordinated by the WCC once the WCC roles are assigned. If causes of discrepancies cannot be found, uncertainties should be re-evaluated using the RR data as a guide. Comparison activities should also include diverse forms of samples, i.e. flasks, low- and high-pressure cylinders, or pure CO_2 ampoules (such as NARCIS sets, which are still available from NIES). Reported values must be accompanied by estimates of total uncertainty as described above. Laboratories that have long histories of participating in comparisons are encouraged to re-assess their comparison data in light of present recommendations regarding corrections and calibration scales.

4.4 Isotopic measurements of CO_2 using optical techniques

In recent years, optical analysers that report mole fractions of individual isotopically substituted molecules, or "isotopocules", have become available and are now in routine use. Many of these instruments can provide isotopic ratios with a precision of around 0.1 ‰ or better for $\delta^{13}C$ of atmospheric CO_2 and are valuable for continuous measurements.

Raw, or uncalibrated, delta-values from such instruments are normally calculated from the ratios of individual mole fractions that have been derived from measured spectra using tabulated absorption line strengths and reference isotopic abundances from the spectral parameter database (typically HITRAN, http://hitran.org/). The reference isotopic abundances incorporate assumptions about the relative abundances of isotopic species and do not provide a link to a common scale realization such as VPDB-CO_2 or JRAS-06. [Note: the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ values in HITRAN[12] may also not be in agreement with the IUPAC accepted value (Brand et al., 2010).] Some corrections that are applicable to mass spectrometric methods, such as those for ^{17}O and N_2O are not required, but other corrections specific to the applied spectroscopic technique may be needed. For example, calculated "apparent" isotopic ratios (given as delta values) may be subject to spectral interference from other atmospheric components, as well as shifting baseline or instrument fluctuations and other effects. Calibration and drift-correction for optical instruments are typically done using CO_2-in-air reference mixtures characterized by the traditional IRMS methods.

An approach for calibrating optical instruments was presented at the GGMT-2017 by D. Griffith and E. Flores (it was earlier used and reported by Wehr et al. (2013)). The advantage of this method is that a range of isotopic ratios in calibration mixtures is not required since the calibration is based on mole fractions of major isotopocules. A similar approach was independently presented by Tans et al. (2017), and additional background is provided in Griffith et al. (2012) and Flores et al. (2017) and Griffith (2018).

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[12] Isotope ratios for CO_2 (HITRAN, http://hitran.org/lbl/, accessed on 24-03-2018) correspond to $^{13}C/^{12}C$=0.011234, $^{18}O/^{16}C$=0.0020052 and $^{17}O/^{16}O$=0.00037288.

This approach is to calibrate the instrument response for isotopocules of interest independently (e.g. for CO_2: $^{12}C^{16}O^{16}O$, $^{13}C^{16}O^{16}O$, $^{12}C^{18}O^{16}O$) based on air mixtures with well-characterized CO_2 mole fractions (WMO CO_2 scale) and isotopic composition assigned on the VPDB-CO_2 scale using IRMS. Mixtures may be of the same or similar isotopic composition, but different mole fractions, since the calibration is based on separate responses for each isotopocule. The mole fractions and isotopic delta values can be easily interconverted with amount fractions of each isotopocule (e.g. of $^{12}C^{16}O^{16}O$) in total CO_2 of the sample. If the total CO_2 mole fraction in calibration-mixtures span three times a range of ambient air samples, the amount fractions of $^{13}C^{16}O^{16}O$, $^{12}C^{18}O^{16}O$ etc. in the mixtures also spans a range of three, which spans the expected range of delta values.

In this way, the detector response, especially if non-linear, can be accurately established over the range of observed signals to confirm that there will be no (or less) dependence on non-linearity. Scale contraction due to memory and absorption in each instrument has to be addressed separately.

This approach demonstrated for FTIR spectroscopy, and applicable to optical methods in general, avoids the complexities of a calibration scheme based solely on isotope ratio differences (delta-values) which may have a total mole fraction dependence that would also need to be characterized. The advantage is in a more direct and transparent way to measure isotope ratios (finally expressed as delta values) than the currently established calibration scheme based on isotope ratio (delta-values) differences[13].

Further studies are suggested to compare the requirements, applicability and performance of both calibration approaches for different isotopocules and different analysers. The same approach may also be tested for N_2O and CH_4 measurements. Practical details how to implement the novel approach for CO_2 can be found in Wehr et al. (2013), Flores et al. (2017), Tans et al. (2017), Griffith (2018) and references therein.

4.4.1 Recommendations for analytical laboratories using optical methods

a) To enable calibration of any analyser and to determine calibrated amounts (mole fraction) of individual isotopocules in a sample, for calibration gases both the total mole fraction of CO_2 and its isotopic composition should be provided by the CCLs (for mixtures produced by NOAA – the mole fractions to be provided by NOAA, the isotope composition on the VPDB-CO_2 scale may be provided by CCL-isoCO2 or INSTAAR). As no calibrated measurement of $\delta^{17}O$, is available at this time, it can be determined with sufficient accuracy for most purposes from $\delta^{18}O$ by assuming a mass dependent relationship.

b) Measured isotopic delta values must be referenced to standards of known isotopic composition and reported on the accepted VPDB-CO_2 scale.

c) Developers and providers of isotopic optical analysers should follow an open philosophy and make available and distribute to the user communities all relevant algorithms used in the calculation of calibrated delta values and the relevant primary measurements used to derive them. The aim is to ensure comparability across instrument types, manufacturers and measurement laboratories, and to

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[13] Presently, calibration based on isotope ratios (δ values) is the most common approach used by manufacturers of optical isotopic analysers.

enable verification of procedures and corrections by individual operators. Measurement information 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, such as those caused by water vapour and other interfering gases, pressure and temperature fluctuations, and variations in isotopic amount fraction of each isotopically substituted molecule.

d) There should be a particular emphasis on matrix effects, which are specific for the particular line set selected by the producer. Such matrix effects should be made public in detail. Related changes and improvements are important information to be disseminated and documented in detail.

4.5 CH_4 isotope calibration and comparison activities

4.5.1 The current situation and analytical challenges to be addressed

The stable isotopic composition of atmospheric methane has been measured by at least 16 laboratories in 8 countries (Umezawa et al., 2018), with a primary focus on $\delta^{13}C$ and to a lesser extent on δ^2H. All $\delta^{13}C$ data are reported on the VPDB scale and δ^2H on the VSMOW scale. The long-term monitoring of $\delta^{13}C$ of atmospheric methane is challenged by its very small signal variability and small long-term trend. $\delta^{13}C$-CH_4 increased by ~0.4 ‰ from the mid-1980s to the mid-2000s, and has decreased by 0.2 ‰ since the late 2000s (Schwietzke et al., 2016, Schaefer et al., 2016, Nisbet et al., 2016). The small variability requires a careful design of the calibration strategy for methane isotopes, which is complicated because RMs in the form of CH_4-gas or gas mixtures are not available. Laboratories have developed calibration strategies and practical solutions that enabled them to pursue their atmospheric monitoring programmes and performed comparisons that enabled the determination of analytical offsets between laboratories.

For $\delta^{13}C$, the calibration strategies have relied on different RMs (including NBS19, NBS18, CO-9 and LSVEC). Such various calibration strategies and use of different RMs have likely contributed to offsets among datasets from different laboratories, although internal precision and reproducibility within labs is relatively good. The review of comparison results for atmospheric methane (Umezawa et al., 2018) demonstrates lab-to-lab discrepancies up to 0.5 ‰ in $\delta^{13}C$ and about 13 ‰ in δ^2H (25 and 13 times the corresponding WMO network compatibility goals). This review implies several inconsistencies in the calibration approaches, in accounting for instrumental effects and the data treatment (see also reviews and open discussion for Umezawa et al., 2018). Causes for lab-to-lab discrepancies observed between laboratories include:

a) *Inconsistent use of available RMs and lack of suitable RMs in the form of methane*: Since no CH_4 specific RMs were available when these measurements commenced several decades ago[14], individual laboratories have developed procedures to relate

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[14] Carbonate RMs were considered more stable than reactive gases and easier to store and distribute. The Ba-carbonate RM CO-9 was developed by C. Brenninkmeijer with the intent to fix $\delta^{13}C$ calibrations for air-methane (personal communication by C. Brenninkmeijer to S. Assonov). One of the purposes of introducing LSVEC in 2006 was also to fix $\delta^{13}C$ calibrations for air-methane (personal communication by W. Brand to S. Assonov); LSVEC was selected as larger amounts were available compared to CO-9.

their measurements to the international VPDB and VSMOW isotope scales. Historically, the laboratories used available primary RMs for δ^2H (waters VSMOW2 – SLAP2 and respective precursors). However, several RMs have been used for the $\delta^{13}C$ scale realization, often materials with very different chemical properties (overview in Sperlich et al., 2016 and Umezawa et al., 2018). The isotope values of some RMs have been revised over time. The $\delta^{13}C\text{-}CH_4$ calibrations need to be updated accordingly to prevent laboratory-specific biases.

b) *Transfer of calibrations from one lab to another:* In some instances, calibrations were transferred from one lab to another by transferring gas mixtures to another lab or by performing characterization measurements in another lab. Thus, the calibration traceability to the scale level includes multiple laboratories (see Umezawa et al., 2018) making retrospective corrections more difficult to apply. In addition, this may preclude the uncertainty propagation to the scale in a consistent way. This calibration transfer practice should be discouraged.

c) *Inconsistent use of ^{17}O correction (for $\delta^{13}C\text{-}CH_4$):* Although there are now optical instruments for these measurements, $\delta^{13}C\text{-}CH_4$ in air has predominantly been measured using isotope ratio mass spectrometers with oxidation of CH_4 to CO_2 prior to IRMS analysis. IRMS measurements of $\delta^{13}C$ in CH_4-derived CO_2 include the ^{17}O-correction algorithm, which has been revised in the past. Laboratories currently measuring $\delta^{13}C\text{-}CH_4$ use different ^{17}O-correction algorithms (Umezawa et al., 2018), which may cause a significant bias between laboratories. In particular, inconsistent use of the ^{17}O-correction due to calibration transfer from one lab to another (see above) appears to be another reason for data biases.

d) *Instability of LSVEC:* The calibration strategies for $\delta^{13}C\text{-}CH_4$ rely on ties to different RMs (including NBS19, LSVEC and CO-9). LSVEC has been used as a second anchor to the VPDB isotope scale to correct for scale-contraction effects and also synchronizes calibration span at negative $\delta^{13}C$ (Coplen et al., 2006). However, instabilities of the LSVEC $\delta^{13}C$ value have recently been reported, introducing a large uncertainty when using LSVEC for a two-point calibration (Assonov et al., 2016; Qi et al., 2016). Due to its depleted $\delta^{13}C$ value of –46.6 ‰, the instability in LSVEC is most critical for measurements of $\delta^{13}C$ in air-CH_4. For robust reliable calibrations of $\delta^{13}C\text{-}CH_4$, introducing a stable and homogenous LSVEC-replacement material (see above) is crucial.

4.5.2 Summary of the situation and recommendations

The need for a consistent isotopic calibration of methane in air ($\delta^{13}C$ and δ^2H) has been recognized by previous GGMT meetings. A practical approach for preparing isotopically characterized methane in air mixtures linked to the accepted international isotope scales (VSMOW, VPDB) was presented at GGMT-2015, and has since been published by Sperlich et al. (2016). Several pure CH_4 gases were selected and then analysed under identical analytical conditions, so that known effects (e.g. interference by Kr, consistent use of ^{17}O-correction, potentially incomplete CH_4 conversion, RM conversion, etc.) were minimized. These CH_4 gases will need to be re-characterized once a successor for LSVEC is determined. The suite of selected CH_4 gases may be used for preparing and distributing CH_4-in-air mixtures in a way similar to JRAS mixtures (5 L glass flasks at low pressure or calibration of high-pressure cylinders).

The intention is to develop a concept for CH_4 isotope calibration in a metrologically correct way and then, potentially, designate a CCL for CH_4 isotopes in 2019. This is expected to improve the δ^2H and $\delta^{13}C$ data compatibility between institutes.

The review of available laboratory practices and several inconsistencies (highlighted above) calls for the need to reconsider and revise developed practices and concepts.

To address the current need to improve δ^2H and $\delta^{13}C$ of methane measurements, as well as understand and quantify instrumental effects and related corrections, NOAA/INSTAAR, in cooperation with the National Institute of Water and Atmospheric Research (NIWA), will prepare a suite of four high pressure cylinders of methane in air for a round-robin to begin in 2018. The δ^2H and $\delta^{13}C$ values of methane will be characterized at MPI-BGC and NIWA. As a temporarily solution until an LSVEC replacement is introduced, one may consider using NIST RM 8563 CO_2, $\delta^{13}C=-41.59\pm0.03$ ‰ (at 1σ) which was characterized against LSVEC in 2006[15].

The need for laboratories to compare techniques remains an important aspect to advance the network compatibility of CH_4 isotope ratio measurements, and laboratories are strongly encouraged to undertake comparisons as part of their observation programmes.

Given the absence of a reliable second anchor on the VPDB scale in the form of a carbonate or CH_4 gas, all laboratories making measurements of $\delta^{13}C$ in atmospheric CH_4 are advised to maintain their calibration strategies as already established and be ready to apply corrections retrospectively when a replacement for LSVEC is released. In light of an upcoming revision of the VPDB-scale for $\delta^{13}C$ and related RMs, it is recommended to archive a sufficient number of historic and current laboratory standard gases for revisions in the future.

4.6 N_2O isotope calibration and comparison activities

The need for N_2O isotope standard reference materials has been recognized by previous GGMT meetings. New technology is increasing the ability to measure N_2O isotopocules and clumped isotopes. GGMT-2017 welcomes the effort to develop new international reference materials for $\delta^{15}N^a$, $\delta^{15}N^b$, $\delta^{15}N$ and $\delta^{18}O$ in N_2O with target uncertainties of 1.0 ‰ ($\delta^{15}N^a$ and $\delta^{15}N^b$) and 0.5 ‰ ($\delta^{15}N$, $\delta^{18}O$) within the European Metrology Program for Innovation and Research (EMPIR) 16ENV06 project "Metrology for Stable Isotope Reference Standards" (2017–2020) coordinated by NPL, UK (project website: http://www.vtt.fi/sites/SIRS/). The N_2O work is planned to be a collaboration between Empa, MPI-BGC, NPL, and the University of Eastern Finland Biogeochemistry Research. Given that no international RMs in the form of N_2O are available, particularly crucial for $\delta^{15}N^a$ and $\delta^{15}N^b$, efforts to release RMs in the form of pure-N_2O gas (in ampoules) or N_2O in air (in cylinders or flasks) are encouraged. GGMT recommends that IAEA be requested to assess their capability to do this. We also note that the scientifically required network compatibility for isotopic measurement of atmospheric N_2O will likely be very demanding due to the long atmospheric lifetime of N_2O. This should be discussed at future GGMT meetings.

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[15] See report in Coplen at al. (2006). A limited amount of NIST RM 8563 is available, although sales are on hold pending an update of reference sheets (personal communication by R. Vocke to S. Assonov in December 2017).

4.7 CO isotope calibration and comparison activities

Isotopic measurements of CO are used to partition different emission sources and to quantify photochemical destruction. As with other species, stable isotope measurements across laboratories require a unified scale realization. Carbon monoxide differs from CO_2 and CH_4 in one very important aspect: its atmospheric chemical lifetime is much shorter. Seasonal cycles are also relatively large for CO, so the required relative precision for stable isotopes is somewhat relaxed. $\delta^{13}C$ and $\delta^{18}O$ of CO are reported on the VPDB and VSMOW scales, with typical analytical uncertainty of about 0.2 ‰ and 0.5 ‰ respectively, though some laboratories are improving on this. Many aspects of CO isotope calibrations should follow the approaches developed for the CO_2 isotope calibrations (the VPDB scale, 2 point data normalization etc.), particularly when the CO is converted to CO_2 for measurement. Note, there is additional uncertainty in $\delta^{13}C$ determinations on atmospheric CO by mass spectrometry when converted to CO_2 gas for measurement (Röckmann and Brenninkmeijer, 1998) due to large and variable deviations in ^{17}O in CO from the generic ^{17}O-^{18}O relationship which is a basic assumption for the ^{17}O correction; this may result in $\delta^{13}C$-biases up to -0.25 ‰.

Most CO isotope analyses are based on the pioneering work by Stevens et al. (1972), with improvements introduced by Brenninkmeijer (1993), including continuous-flow technique (e.g. Mak and Yang, 1998; Tsunogai et al., 2002). In brief, CO is either extracted from air by CO-oxidation on I_2O_5 to CO_2, followed by cryogenic collection of the produced CO_2, or CO is separated on several gas chromatographic columns and analysed directly.

Analytical challenges include: (i) complete stripping of air-CO_2 from the sample before CO oxidation; (ii) quantitative oxidation of CO followed by quantitative recovery of the resulting CO_2 for stable isotope analyses; (iii) calibrating oxygen coming from the I_2O_5-oxidation reactor (iv) calibration or elimination of CO produced within the extraction system (i.e. "blank").

Carbon monoxide is chemically reactive and is known to be produced in cylinders, making calibration-transfer mixtures at CO background mole fractions (50-100 ppb) difficult. Cylinders should be chosen carefully; cylinder preparation or passivation may also be considered. Furthermore, differences in extraction techniques between laboratories create different needs for calibration mixtures, using high-concentration calibration mixtures diluted by zero-air at the time of analysis in user-laboratories is an option to be tested.

Round-robins between a few labs have happened in the past and are encouraged moving forward. We recommend that development of best practices in the measurements of stable isotopes of CO_2 be eventually transferred to stable isotopes of CO.

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

5.1 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 primary standard reference materials. Other reference materials of various origins, all traceable to the primary standards, are available and distributed by IAEA and other agencies.

Atmospheric $^{14}CO_2$ measurements are usually reported in $\Delta^{14}C$ notation, the deviation from the absolute radiocarbon reference standard (Stuiver and Polach, 1977, the formula used by the atmospheric community is denoted simply Δ in this reference):

$$\Delta\,^{14}\mathrm{C} = \left\{ \left[\frac{\mathrm{R_{sam}}}{\mathrm{R_{ref}}}\right] \left[\frac{0.975}{\left(1+\frac{\delta^{13}\mathrm{C}}{1000}\right)}\right]^2 \exp\left(\lambda\,(1950-\mathrm{t})\right) \right\} - 1$$

with R=$^{14}C/C$, the corrections are for fractionation and radioactive decay (λ) of the standard and reported in per mil (‰). The date used for the decay correction (typically the date of collection) should be reported with the result. $\delta^{13}C$ should also be reported if it was measured on the original sample (e.g. atmospheric CO_2), along with the $\delta^{13}C$ measurement method. Note that $\delta^{13}C$ measured by Accelerator Mass Spectrometry (AMS) will provide the most reliable fractionation correction for the $\Delta^{14}C$ measurement and failure to measure $\delta^{13}C$ by AMS is likely to result in poorer long-term reproducibility. However, the AMS $\delta^{13}C$ may be fractionated from the original sample material and we strongly recommend that this value, although used to calculate $\Delta^{14}C$, should not be reported as the $\delta^{13}C$ value of the original sample.

When $\Delta^{14}C$ 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 $\delta^{14}C$ (Stuiver and Polach, 1977) if the original sample $\delta^{13}C$ is known, but as some sampling strategies preclude measurement of ambient $\delta^{13}C$, we recommend $\Delta^{14}C$ be reported to provide consistency amongst laboratories. The accepted $\delta^{13}C$ normalization procedure (Stuiver and Polach, 1977) assumes that the relation of ^{13}C and ^{14}C fractionation is in quadrature, whereas mounting evidence shows that in fact, an exponent of 1.9 (vs 2) is more correct (Fahrni et al., 2017). However, this is a small correction well within the current measurement uncertainties and therefore it is recommended that laboratories continue to use the quadrature formulation to be consistent with accepted radiocarbon reporting guidelines.

For atmospheric measurements of $\Delta^{14}C$ 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 AMS. The current level of measurement uncertainty for $\Delta^{14}C$ in CO_2 is 1-5 ‰. As atmospheric gradients in background air are currently very small, a target of 0.5 ‰ for network compatibility is recommended (Table 1). We emphasize again that network 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 $^{14}CH_4$ measurements are also reported in $\Delta^{14}C$ notation. However, 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.

5.2 Current $^{14}CO_2$ calibration and comparison activities

The first comparison activity for $\Delta^{14}C$ in CO_2 was initiated at the 13th WMO/IAEA Meeting of CO_2 Experts in Boulder, Colorado, and is ongoing every few years (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. A similar comparison between laboratories within China began in 2015. A comparison of conventional and AMS ^{14}C analysis was begun in 2014. CO_2 from whole air was measured by gas counting at the University of Heidelberg and subsequently aliquots of the same pure CO_2 were distributed to AMS labs for measurement; this pure CO_2 comparison will be ongoing on an ad hoc basis (Hammer et al., 2017). Plans for future atmospheric ^{14}C comparison exercises are laid out in the report of the atmospheric $^{14}CO_2$ workshop at the 21st International Radiocarbon Conference (Turnbull et al., 2013; Lehman et al., 2013). The comparison exercises indicate that compatibility between labs is currently 2-4 ‰, short of the 0.5 ‰ goal but generally consistent with the single sample uncertainties currently reported by each laboratory. We note that some ad-hoc comparisons have met the WMO network compatibility goal.

5.3 Recommendations for $^{14}CO_2$ 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 working standard.

b) Measurement uncertainties must be reported with results. Reported uncertainties must reflect long-term reproducibility of target materials as well as traditional counting statistical uncertainties. A sufficiently detailed description of how the uncertainty was determined should be reported with results.

c) We recommend co-located sampling at observation stations to compare the full measurement process between different techniques and laboratories, where possible, before GGMT-2019.

d) We recommend the continuation of the whole-air and pure-CO_2 comparison exercises at a frequency of once per year to increase the statistical robustness of the results. The number of participating laboratories and analytical techniques should be expanded.

e) It is also recommended that laboratories participate in comparison exercises conducted by the wider radiocarbon community (Scott et al., 2010).

f) We recommend ongoing workshops to discuss comparability and standardization for $\Delta^{14}C$ in CO_2 measurements and to harmonise the data from different laboratories.

g) We recommend efforts to reduce measurement uncertainty, to generally improve the usefulness of $\Delta^{14}CO_2$ results, and because trends in atmospheric composition are gradually reducing the sensitivity of $\Delta^{14}CO_2$ to local fossil fuel CO_2 additions.

h) We recommend that the community monitor development of new measurement methods (e.g. optical ^{14}C measurement techniques) which could potentially make in situ atmospheric ^{14}C measurement realistic but are currently far from the needed levels of precision.

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

No calibration materials or comparisons for other trace gases ($^{14}CH_4$, ^{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.

6. SPECIFIC REQUIREMENTS FOR O_2/N_2 CALIBRATION

6.1 Background

Measurements of the changes in the 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 the O_2/N_2 ratio are very small but can now be observed by at least six established analytical techniques plus the emerging technique of laser spectroscopy. 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, laser spectroscopy). A convention has emerged to convert the raw measurement signals, regardless of technique, into equivalent changes in the 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/N_2 ratio. By convention, O_2/N_2 ratios are expressed as relative deviations compared to a reference

$$\delta\,(O_2/N_2)=(O_2/N_2)_{\text{sample}}\,/(O_2/N_2)_{\text{reference}}-1$$

in which $\delta\,(O_2/N_2)$ is multiplied by 10^6 and expressed in per meg 'units.' Per meg is a dimensionless unit equivalent to 1 per meg = 0.001 per mil (Coplen, 2011). The O_2/N_2 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 O_2/N_2. Several laboratories report results on the Scripps Institution of Oceanography (SIO) O_2 scale. Though there have not historically been named scale versions, this is planned.

There is considerable scientific value to be gained from different laboratories reporting O_2/N_2 measurements on a common scale. The O_2/N_2 measurement community recognizes the Scripps O_2 scale as the best candidate for a common reference. With a goal of establishing this as the common scale for reporting and comparing O_2/N_2 measurements, we recommend that all O_2/N_2 measuring laboratories participate in the Global Oxygen Laboratories Link Ultra-precise Measurements (GOLLUM) comparison exercise, and we recommend that laboratories take steps to link their internal laboratory scales directly to the SIO O_2 scale. In support of this, we recommend that the Scripps O_2 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 O_2/N_2 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, and taking care to dry cylinders to 1 ppm of H_2O or better. Nevertheless, improved understanding of the source of variability of measured O_2/N_2 ratios delivered from high-pressure cylinders is an important need of the community. An independent need is the development of absolute standards for O_2/N_2 calibration scales to the level of 5 per meg or better.

The relationship between changes in O_2/N_2 ratio and equivalent changes in O_2 mole fraction has been discussed in the peer-reviewed literature (Keeling et al., 1998). However, confusion does still exist. Adding 1 µmol of O_2 per mole of dry air increases the O_2/N_2 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 O_2 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 of the trace gas per mole of dry air increases the mole fraction by almost exactly 1 ppm. The factor 4.77 per meg per ppm relates the change in O_2/N_2 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 O_2/N_2 ratios in an air parcel corresponding to a photosynthetic or respiratory flux of CO_2, or calculating changes in O_2/N_2 ratios resulting from O_2 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).

6.2 Current O_2/N_2 calibration and comparison activities

At the 12th WMO/IAEA Meeting in Toronto (GGMT-2003, WMO, 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. The GOLLUM round-robin cylinder programme ran from 2004-2014, and compared 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 (2005) and at a dedicated website: 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.

The repeated round-robin cylinder analyses at SIO showed drift in the cylinders through 2014 that was within ±5 per meg, allowing a robust assessment of inter-laboratory differences. All results are available to participants 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.

6.3 Recommendations for O_2/N_2 calibration and comparison activities

a) Restart the GOLLUM round-robin cylinder comparison programme and maintain it 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 the influence of thermal fractionation.
- An additional suite of circulating cylinders that incorporates those field stations making in situ measurements of atmospheric O_2 and which are not presently included in any O_2 comparison programme.

c) Sustain the website for logistical support and for rapid dissemination of results of the GOLLUM 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 and turnaround time.

f) Encourage additional comparison efforts, such as co-located flask sampling, to compare O_2/N_2 scales and methods between programmes.

g) Encourage the sharing of information on well-tested O_2/N_2 techniques, with the particular goal of identifying and correcting any weaknesses in 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 O_2 measurements such as developing intake and 'tee' designs that do not fractionate O_2 relative to N_2, and to investigate the influence of dip-tubes installed in high pressure cylinders.

i) Continue efforts to produce gravimetric standards for O_2/N_2 to solidify the long-term calibration of O_2/N_2 measurements.

j) Encourage efforts by the relevant laboratories to assess the influence on their O_2/N_2 measurements (using different analytical techniques) of variations in CO, H_2, CH_4, N_2O, H_2O, and any other species that are commonly present in air samples with the potential to interfere at the per meg level.

k) Continue evaluation of the SIO O_2 scale for future implementation as the common scale for reporting and comparing O_2/N_2 measurements, and establish named versions of this scale for tracking updates.

l) Propagate the planned revised SIO O_2 scale to historic measurements and GOLLUM results.

7. SPECIFIC REQUIREMENTS FOR CH_4 CALIBRATION

7.1 Background

NOAA/ESRL serves as the WMO/GAW Central Calibration Laboratory (CCL) for methane. In 2015 the scale was expanded and a new calibration scheme was implemented. All historical calibrations have been updated. For details see http://www.esrl.noaa.gov/gmd/ccl/ch4_scale.html. The current (July 2018) version of the WMO mole fraction scale for methane is WMO CH_4 X2004A. The calibration scale consists of 22 gravimetrically prepared primary standards which cover the nominal range of 300 to 5900 ppb, so it is suitable to calibrate standards for measurements of air extracted from ice cores and contemporary measurements from GAW sites. The range of secondary standards is nominally 390 to 5000 ppb. In August 2017, the CCL switched the CH_4 calibration system from a GC-FID to a CRDS instrument. The same suites of primary and secondary standards are used on the new analytical system. Agreement between the two analysis systems was shown to be excellent over a 9-month period when they were run in parallel (average CRDS – GC-FID = 0.0±0.3 ppb, based on 267 cylinders with CH_4 values between 300 and 3000 ppb).

7.2 Recommendations for CH_4 calibration and comparison activities

a) The CCL will transfer the CH_4 scale to calibrated CH_4-in-dry-air standards with a scale transfer uncertainty of <2 ppb (95% confidence level, coverage factor k=2).

b) The CCL should routinely assess its ability to transfer the scale using the new multipoint calibration strategy and new analytical system.

c) All laboratories that participate in the GAW Programme must calibrate measurements relative to the WMO CH_4-in-dry-air mole fraction scale and report them to the WMO/GAW World Data Centre for Greenhouse Gases in Japan.

d) 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 CH_4 re-calibrated by the CCL every six years. Each laboratory should also participate in WMO round-robin comparisons of working standards and in regional comparisons.

8. SPECIFIC REQUIREMENTS FOR N_2O CALIBRATION

8.1 Background

Measurements of nitrous oxide made by GAW partners are used to better understand the sources and sinks of this greenhouse gas. While network compatibility is improving, systematic differences among N_2O mole fractions reported by different laboratories are still large compared to atmospheric gradients. The mean inter-hemispheric difference in N_2O 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 N_2O in the troposphere. This necessitates not only high measurement precision, but also high consistency among assigned values for standards. Network compatibility of measurements from different laboratories of 0.1 ppb is needed.

NOAA/ESRL serves as the CCL for nitrous oxide. The current (July 2018) version of the WMO mole fraction scale for nitrous oxide is WMO N2O X2006A. The scale consists of 13 gravimetrically-prepared N_2O-in-dry-air Primary Standards covering the range of 260–370 ppb (Hall et al., 2007). Calibrations at the CCL are performed using gas chromatography with electron capture detection (GC-ECD) (current method described in Hall et al., 2011). The reproducibility of NOAA N_2O calibrations is estimated to be 0.2 ppb at the 95% confidence level.

8.2 Recommendations for N_2O 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 N_2O 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 N_2O. The CCL should strengthen collaborations with Empa and KMA, since N_2O can sometimes be incorporated in CO_2 audits performed by Empa and SF_6 audits performed by KMA.

c) The use of a travelling N_2O instrument during audits by the WCC-N_2O is encouraged. Parallel measurements should be made using an independent sampling system whenever feasible.

d) The CCL should continue development of new primary standards to address minor mole fraction dependent bias observed in X2006A. New standards should have a suitable composition and matrix for use with spectroscopic methods.

e) The expert community should explore the use of alternative analytical methods, compare them to current GC-ECD techniques and share the findings with GGMT community.

f) The CCL should investigate observed divergence from the Advanced Global Atmospheric Gases Experiment (AGAGE) N_2O scale.

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9. SPECIFIC REQUIREMENTS FOR SF_6 CALIBRATION

9.1 Background

Sulphur hexafluoride (SF_6) is a very long-lived trace gas with strong infrared absorbance. SF_6 is ~22500 times more effective as a climate forcing agent than CO_2 on a per-mass basis over a 100-year time scale. The tropospheric mole fraction of SF_6 has increased steadily, with a growth rate of 0.2-0.3 ppt/year. The steady growth rate, long lifetime (~850 years with an uncertainty range of 580–1400 years) (Ray et al., 2017), and low solubility in water make it a useful tracer of atmospheric transport, including stratospheric "age-of-air determination".

SF_6 is typically measured using gas chromatography with electron capture detection (GC-ECD), similar to N_2O. NOAA/ESRL serves as the WMO/GAW Central Calibration Laboratory (CCL) for atmospheric SF_6. The current (July 2018) version of the WMO mole fraction scale for sulphur hexafluoride is WMO SF_6 X2014. The scale is defined by 17 primary standards over the range 2-20 ppt and calibrations are performed using GC-ECD (Hall et al., 2011).

The Korea Meteorological Administration (KMA), assisted by Korea Research Institute of Standards and Science (KRISS), serves as a World Calibration Centre for SF_6. A SF_6 comparison was initiated by KMA, WCC-SF_6, in 2016 and the first comparison report is now available on the WMO website (http://www.wmo.int/pages/prog/arep/gaw/documents/FinalreportofSICE_2016.pdf).

9.2 Recommendations for SF_6 calibration and comparison activities

a) The expert community is encouraged to explore new analytical techniques to improve measurement precision.

b) KMA is encouraged to organize round-robin comparisons of SF_6 working standards among WMO participants.

c) 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 SF_6 re-calibrated by the CCL every four years.

10. SPECIFIC REQUIREMENTS FOR CO CALIBRATION

10.1 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. Differences among reference scales and drift of CO standards have been a serious problem for in situ CO measurements and validation of remote sensing measurements in the past. The present recommendations, however, pertain to the calibration of in situ observations only; the validation of remote sensing data is a separate issue not addressed here.

10.2 Current CO calibration and comparison activities

NOAA/ESRL is the WMO/GAW CCL for carbon monoxide. The current (July 2018) version of the WMO mole fraction scale for CO is WMO CO X2014A. Due to the lack of stability of CO in high-pressure cylinders, the CO scale has historically been defined by repeated sets of gravimetric standards. Secondary standards calibrated versus multiple sets of gravimetric standards have been used to ensure consistency across the gravimetric sets. Gravimetric standards that define the scale were made in 1996/1997, 1999/2000, 2006, 2011, and 2015. The CCL has made revisions of the CO scale each time new gravimetric standard sets indicated a significant drift in the scale. Scale revisions are indicated by name (WMO CO X2000, WMO CO X2004, WMO CO X2014, and WMO CO X2014A). Current analytical methods used to propagate the scale include both off-axis integrated cavity output spectroscopy (OA-ICOS) and vacuum ultraviolet resonance fluorescence spectroscopy (VURF).

The latest scale revision (WMO CO X2014A, introduced in December 2015) reflects a decision by the CCL to change the method used to define the scale with the goal of simplifying the definition of the scale and improving the ability to track drift of the standards that define the scale. The 2011 gravimetric standards have been designated as the Primary Standards and all measurements are related to their values in a strict hierarchal calibration scheme. There are 14 primary standards covering the nominal range 30–1000 ppb. Growth of CO in the primary standards is occurring. The drift rates in the primary standards are measured by regular comparisons of the primary standards to a suite of static dilutions (termed dilution standards) of three very high mole fraction gravimetric mixtures of CO (~0.1 to 0.9%) and CH_4 (~ 3%) in air. Potential rates of CO growth in these percent level mixtures (termed parent tanks) is assumed to be insignificant relative to their mole fractions giving a known and stable CO to CH_4 ratio. CH_4 is measured in each dilution standard and used with the known CO:CH_4 ratio of the parent to assign a CO value to the dilution standard. Over time, drift in the primary standards is determined from repeated comparisons to new sets of dilution standards made from the stable parent tanks. (See CCL website for more detailed information http://www.esrl.noaa.gov/gmd/ccl/co_scale.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 assignments and drift corrections of individual working standards used at stations.

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

a) The CCL shall aim to propagate the CO scale with a scale transfer uncertainty of ±1 ppb or 0.5% (whichever is greater, 95% confidence level, k=2). All GAW participants should use standards traceable to the WMO CO X2014A or a subsequently revised version of the WMO scale.

b) The CCL should maintain one set of standards that defines the WMO scale (see Section 1.2-a).

c) The CCL should maintain a strict hierarchy of standards. All intermediate levels of reference standards (secondary and tertiary standards) that are part of this hierarchical calibration chain should be reassigned relative to the scale at appropriate intervals to ensure 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. This documentation should involve disclosure of the development of mole fractions in the individual primary standards that define the scale and procedure for their measurement.

e) The replacement of the gas chromatographic technique with HgO reduction and photometric detection at the CCL with spectroscopic techniques 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 spectroscopic techniques (May 2006) are recalibrated.

f) Growth of CO in high pressure cylinders is a known issue. The CCL is actively tracking and accounting for the growth of CO in primary and secondary standards to provide a stable scale. However, to maintain a tight linkage to the WMO scale users must account for growth of CO in individual tertiary standards by returning them to the CCL for recalibrations. Based on recent assessments of standard drifts a recalibration interval of three years is recommended.

g) Laboratories are encouraged to develop techniques to monitor cylinders for drift. Options include a comparison to well-characterized target tanks, on-going comparison with other laboratories, and static and dynamic dilution techniques using an internal tracer.

h) If drift is suspected in the laboratories highest level standards, then they should be returned to the CCL for recalibration to maintain traceability.

i) Drift corrections applied to the primary standards for the X2014A scale are thought to be too high leading to a time-dependent bias in the scale. The CCL is investigating further with the goal of another scale revision in 2019 which corrects this bias.

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11. SPECIFIC REQUIREMENTS FOR H_2 CALIBRATION

11.1 Background

Molecular hydrogen plays a significant role in global atmospheric chemistry due to its role in CH_4 – CO - OH cycling. 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, 2011).

11.2 Current H_2 calibration and comparison activities

MPI-BGC serves as the WMO/GAW CCL for atmospheric molecular hydrogen. The current (July 2018) scale is WMO H_2 X2009. It has been embodied in a set of 13 primary standards of hydrogen in air ranging from 140 to 1200 ppb (Jordan and Steinberg, 2011). This set consisted of five different high-pressure cylinder types that all had been tested for their properties of maintaining a stable hydrogen mole fraction. However, in 2013, H_2 growth in two of the primary standards (at 415 ppb and 850 ppb, respectively) was detected. These standards were stored in one specific steel cylinder type that was also used for the primary standard with the highest hydrogen mole fraction. In consequence, all three standards stored in this type of cylinder were disregarded and replaced by alternative standards (similar mole fractions) that had been prepared as part of a secondary (scale back-up) set in canisters with proven superior properties (internally electro-polished stainless steel). These replacement standards have been analysed since 2010 and 2011, respectively. Thus, the calibration record can be revised back to 2010. Recently increases in hydrogen at rates of 0.3 ppb/year have been detected in two additional primary standards. These drifting primaries have also been replaced by back-up standards from 2011 with corresponding mole fractions. Experimental results suggest a mole fraction related bias in the scale of about 2 ppb in the atmospheric range. A revision of the WMO scale will be made after concluding experiments and a final evaluation of all standard stabilities.

11.3 Recommendations for H_2 calibration and comparison activities

a) It is recommended that the CCL regularly produce additional standards that provide a check for the stability of the WMO scale (every 3-5 years).

b) In addition, time-dependent biases between laboratories that have not always been related to scale changes underline the necessity to continue the comparison of hydrogen data. These exercises will be a valuable tool to monitor the network compatibility of the measurements and shall be continued at regular intervals.

c) 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 develop 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 electro-polished stainless steel. Recalibration by the CCL after two years is highly recommended for aluminium cylinders or cylinder types with unknown stability characteristics. For cylinders expected to show better stability, such as electro-polished stainless steel, a 5-year recalibration interval is recommended.

d) 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 (Novelli et al., 2009) and should be considered for new installations.

e) Due to the strong non-linearity of the HgO reduction detectors, it is particularly important for H_2 measurements that the mole fraction of the working standard gas is close to the mean annual H_2 level observed at the site. In contrast, the target standard gases used for quality control purposes are recommended to have H_2 mole fractions that are at the high end of the observed values to provide good diagnostic information.

12. RECOMMENDATIONS FOR GREENHOUSE GAS NETWORKS IN AREAS OF HIGH DENSITY EMISSIONS

12.1 Background

Recent studies have strived to improve the understanding of the spatial and temporal scale in greenhouse emissions beyond what is possible from a global background network, leading to greenhouse gas measurements in areas of high-density emissions. Quantification of regional emissions using atmospheric observations is the subject of ongoing research, and recommendations will likely evolve as methods mature. However, some differences from the requirements of global background measurements are already clear. Instrument calibration and operation strategies should account for the typically elevated and often highly variable signals in such areas. Characterizing the spatial variability of the emissions in these areas will often require multiple measurement sites in a regional network configuration. Site selection in regional networks should include consideration of the footprint of each sampling location such that the combined footprints of the regional network sites reasonably represent the region. Network compatibility between sites within a regional network is necessary over the often large measurement ranges. Of central importance is the ability to quantify the local excess relative to the regional background GHG mole fractions of the study area. Relevant background levels may be derived from adequately filtered subsets of regional or global baseline observations. Moreover, accurate measurements of the enhancements caused by the emissions within the investigated area are required. Suitable approaches to define the regional backgrounds may strongly depend on the meteorological conditions (wind speed, direction, planetary boundary layer height) and cannot be expected to be universal for all GHGs due to the different spatial distribution of emissions and the impacts of biogenic fluxes for different species.

The required uncertainty of measurements and tolerable maximum bias within the network in high-density emissions areas is a function of the magnitude of the enhancement, with stricter requirements where the local GHG excess is small. Requirements for measurements in areas with small GHG excess values should be comparable to the WMO requirements for measurement of background air. For elevated measurements, we recommend network compatibility of 5% (or better) of the excess dry mole fraction over the appropriate regional background. At this level, measurement uncertainties and biases will be small relative to other sources of uncertainty in calculated fluxes based on imperfect knowledge of atmospheric transport. However, we recommend that high-density emissions area measurements still adhere to WMO guidelines for near background level observations including traceability to WMO scales (see Section 1.2-i), but we recognize that compatibility requirements for elevated measurements are far less stringent.

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

12.2 Recommendations

a) We recommend the IG^{3}IS working group for urban greenhouse gas emissions to interact with the WMO/GAW Urban Research Meteorology and Environment (GURME) Project.

b) Adequate approaches to determine suitable regional background levels of GHGs are an essential element for the quantification of emissions and thus, need to be considered when setting up a network in areas of high-density emissions.

c) Networks in areas of high-density emissions should have an uncertainty of 5% or better for the excess greenhouse gas dry air mole fraction over the regional background, with the exception of $\Delta^{14}C$ for which reproducibility of 30-50% over the local boundary condition may be sufficient.

d) It is recommended that the CCL CO_2 dry mole fraction scale be increased to 600 ppm with the highest mixing ratios having the least accuracy whilst establishing more accuracy closer to the background levels of the region being sampled. Care should be taken to avoid any systematic biases.

e) If dense networks of lower-cost sensors are deployed the individual measurements have to remain traceable to WMO scales and significant biases due to instrument drift or cross-sensitivity to ambient conditions have to be avoided. A currently tested approach is to complement networks of lower-cost sensors by a small number of mature instruments to allow for ongoing quality control of the network. We recommend following and supporting the development of lower-cost GHG sensors. Results of current community efforts are summarized in a special WMO report (WMO, 2018) following a lost-cost sensor experts meeting in February 2018.

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13. RECOMMENDATIONS FOR GROUND-BASED REMOTE SENSING TECHNIQUES

13.1 Background

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 $O_{2.}$ 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://tccon-wiki.caltech.edu/). Adherence to these controls is a necessary condition to contribute to the TCCON data archive (http://tccondata.org).

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. See Chapter 15 on emerging techniques for more information on AirCore observations and the limitations of TCCON – AirCore comparisons.

Low-resolution spectrometers which are capable of solar remote sensing measurements at lower cost and greater portability than TCCON instruments have recently become available. This has the potential to expand the coverage of this type of atmospheric measurement (Frey et al., 2015; Hase et al., 2015; Frey et al., 2018). The precision, accuracy, drift, susceptibility to interference and general performance of these sensors must be assessed and quantified through co-located and coincident measurements at TCCON sites before these measurements can be related to validated TCCON measurements.

In recent years remote sensing systems that allow horizontal open path GHG mole fraction observations have become available (Waxman et al., 2017; Griffith et al., 2018 and references therein). Pathlengths of several hundred meters up to several kilometres are possible. Given the variability of mixing ratios over these distances and the need to correct for variable water vapour across the measurement path, a validation relative to WMO dry-air mole fraction scales is difficult.

13.2 Recommendations

a) Ground-based remote sensing measurements of CO_2, CH_4, N_2O and CO must follow the formal TCCON data protocols and be accepted in the TCCON network and to be acceptable to GAW.

b) TCCON sites play a key role in the validation of satellite-based GHG observations and therefore an extension of this network to cover tropical regions is recommended.

c) Future networks of inexpensive and portable FTIR spectrometers (such as the Collaborative Carbon Column Observing Network (COCCON) (Frey et al., 2018)) should use standardized spectrometers which should undergo an initial performance check and calibration at the network's primary calibration site before acceptance. As with TCCON, standardized spectrum analysis protocols should be followed to minimise the risk of bias in derived total columns and mole fractions. Once in operation, each spectrometer contributing to the network or measurement campaigns must undergo regular re-verification of its characteristics (side-by-side validation at a TCCON site).

d) The community should work towards a scheme to validate horizontal remote sensing instruments (e.g. by using dense in situ observations, GHG sensors on-board unmanned aerial vehicles, or deploying them in regions with very small spatial variability of greenhouse gas mole fractions in parallel with well calibrated in situ instruments.

14. RECOMMENDATIONS FOR AIR MEASUREMENTS OF CO_2 ON SHIPS

14.1 Background

Measurement of the partial pressure of CO_2 (pCO_2) throughout the global oceans is an important constraint on the role that oceans play in absorbing anthropogenic CO_2 that has been released into the atmosphere. These measurements are being made on a combination of research ships and ships of opportunity that, in most cases, can also make measurements of atmospheric CO_2. Provided that these air measurements meet the basic requirements of the GGMT community, the more than 250 transects of ships that contribute to the global ocean pCO_2 database (Surface Ocean CO_2 ATlas – SOCAT, https://www.socat.info) can provide a valuable addition to the currently available atmospheric CO_2 datasets.

On Tuesday, 29 August 2017, a break out session was convened as part of the GGMT-2017 meeting to discuss the benefit, measurement requirements and path forward for making shipboard measurements of atmospheric CO_2 that could become part of the global cooperative network of greenhouse gas measurements. As part of this discussion, the role of the GGMT in helping to verify the reproducibility of the surface ocean pCO_2 measurement was also discussed.

14.2 Recommendations

1) Benefits

The atmospheric CO_2 community will benefit from high accuracy atmospheric measurements of CO_2 mole fractions over oceans because ocean measurements will provide a valuable addition to the currently available atmospheric CO_2 datasets. Owing to the complexity of CO_2 land-based emissions additional measurements over ocean regions could provide the boundary conditions for inversion models focused on constraining continental-scale fluxes.

The ocean community will benefit in several ways as well. For example, ocean flux estimates are based on the measurements of the air-sea CO_2 gradient, where the typically used GlobalView Marine Boundary Layer (MBL) Reference product estimates of atmospheric CO_2 can lead to significant biases, particularly in coastal regions. As shown from an analysis of the difference between NOAA’s CarbonTracker and NOAA’s GlobalView MBL product, these differences can also lead to biases of the ocean basin scale estimates because of the lack of east-west gradients in NOAA’s GlobalView MBL product. More reliable fluxes would be obtained if, instead of using the interpolated NOAA MBL product, atmospheric CO_2 measurements from the ships themselves were used, provided that these measurements are sufficiently accurate. Additionally, an improvement in the quality control of atmospheric measurements on ships will improve the traceability of oceanic measurements of pCO_2 to the WMO scale.

2) Measurement requirements

Other than stack gas contamination, high humidity conditions and potential inlet contamination issues related to sea salt build up, the approach to making measurements traceable to the WMO CO_2 scale is similar to other land-based in situ CO_2 measurements discussed in this document. These include a set of standards that are clearly traceable to the latest WMO CO_2 scale; span the expected range of atmospheric values; are numerous enough in concentration-space and spacing between measurements to account for non-linearities and drift of the CO_2 analysis system, respectively. A well-defined plan will also be needed to filter out contamination from the ship's exhaust system so that local ship emissions do not bias the measurements. It also will be necessary to test ways to independently verify that inlet lines and procedures for deriving the dry mole fraction of CO_2 are not biasing the final data product. These approaches will vary depending on which CO_2 analyser is used and on the methods used to correct for humidity in the sample stream. In addition, it is recommended that a thorough uncertainty assessment of the data is carried out, and that measurements are reported with corresponding uncertainties that account for all the major sources of error (for guidelines refer to Chapter 2. Recommendations for the determination of uncertainty).

3) Next steps for implementation

a) Establish a working group consisting of interested members from both the ocean and atmospheric communities.
b) Establish a Standard Operating Procedure (SOP) document to guide the ocean community in making high precision, traceable measurements of atmospheric CO_2 dry mole fraction from ships, and work towards meeting the WMO network compatibility goals for CO_2 as outlined in Table 1 of this document. This SOP should be concise and simple, and will primarily focus on improving or validating traceability/accuracy, along with the goal of achieving high precision measurements. The SOP will be distributed via the SOCAT website.
c) Maintain an ocean community presence at the next GGMT for further input and report on progress made.
d) Define requirements for network compatibility, traceability and precision of atmospheric measurements from research ships and ships of opportunity.
e) Quantify potential impact of ocean-based atmospheric measurements using Observing System Experiments (OSO) and Observing System Simulation Experiment (OSSE).
f) Design an independent calibrated analyser system that can be deployed for single transect comparisons to verify quality of measurements on ships and quantify biases. Such a system should:
    i. Be compact and easily installed.
    ii. Be relatively stable (low drift and sensitivity to environmental conditions like temperature and pressure) and easy to operate.
    iii. Include a separate inlet system.
    iv. Have its own standards traceable to the latest WMO CO_2 scale.
g) In addition to the system described in (f), encourage flask sampling on ships for additional, more widespread comparisons, and establish protocols for flask sampling to verify air measurements from underway pCO_2 systems.

h) Use comparisons from ships that currently have atmospheric CO_2 measurement systems from both the ocean and atmospheric communities to assess the feasibility of including existing ocean community measurement systems into the atmospheric CO_2 network, and for determining the key technical challenges to achieving the WMO CO_2 network compatibility goals in Table 1.

15. NEW AND EMERGING TECHNIQUES

New techniques and applications for quantitative atmospheric trace gas composition and isotope measurements will continue to emerge from research laboratories. To be acceptable for use in the GAW community, new and emerging techniques must be extensively compared and validated against existing techniques, and their uncertainties must be well understood and quantified. This section firstly sets out general principles to be followed in validating a new technique for GAW applications. Secondly, particular issues for individual currently emerging techniques are listed and should be reviewed with each renewal of the GAW GGMT reports.

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

The following topics should be addressed before recommendations for best practice can be defined or revised. We strongly encourage the community to investigate these topics and report their findings at future WMO/IAEA GGMT meetings.

a) The development of new or improved techniques that would lead to improvements in precision and reproducibility is encouraged. This 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 against existing, accepted techniques (e.g. Tuzson et al., 2011; Hammer et al., 2013; Morgan et al., 2015; Lebegue et al., 2016). New techniques should allow measurements with adequate reproducibility to achieve the WMO network compatibility goals given in Table 1. Specific areas that need to be investigated are applicability for long-term continuous operation, calibration frequency, ability to correct for water vapour dilution or interference, interference from other trace substances, and other artefacts besides sample drying. Manufacturers are encouraged to offer detailed technical training, perhaps through the GAW Training and Education Centre (GAWTEC, http://www.gawtec.de) if requested by the community. 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 instrument characterization 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 characterized using dry air of known composition 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 or isotopic composition 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 the method by which standards are introduced to the instrument. The response of the instrument should also be characterized in response to step function changes in at least a) humidity, b) inlet pressure, c) flow rate and d) ambient temperature.

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.

- Water vapour
- Carbon dioxide
- Methane
- Composition of main air components N_2, O_2, and Ar
- Nitrous oxide
- Isotopic composition of the target gas or potential interfering species
- Other trace species

d) *In situ application validation:* The instrument should be located at a measurement site or at an appropriate proxy site for long term monitoring. Drift of the instrument response function should be thoroughly quantified over a long period, preferably six months or more, using known reference standard mixtures. A high frequency of individual standard measurements should be chosen initially; this may be relaxed once sufficient experience is gained to identify an optimum time between the standard measurements. The instrument should be evaluated at least hourly (or another time interval suitable to the application) against 1) another well validated in situ monitoring technology AND, if appropriate, 2) co-sampled flasks that are analysed 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.

Specific comments on currently emerging techniques

Isotopic analysis with optical spectroscopic analysers

This topic is covered in Section 4.4 of Chapter 4 on specific requirements for stable isotope calibration.

Low-cost sensors for CO_2, CH_4 and other trace gases

Driven in particular by the need to monitor urban emissions at high spatial resolution, low-cost CO_2 sensors have increasingly been developed and evaluated. It is important to point out a few specific requirements for such sensors:

1) The measurements should be reported as dry mole fractions of CO_2, which requires either correction for ambient water vapour or drying of ambient air.
2) Accurate measurements are required to derive unbiased surface fluxes from the urban areas.
3) The cost of the sensor is only a small part of the full budget to obtain and quality-control the observations. Time and money costs of related maintenance and verifications should also be considered.
4) Careful work is needed to characterize the performance of the low-cost sensors themselves.
5) The low-cost sensor network requires verification with medium or higher cost reference sensors in the field.
6) Special attention should be paid to designing the network in a way avoiding or minimizing the biases and the interferences in the low-cost sensors, especially for long-term field deployed sensors or low-cost sensor networks.

A recent report (WMO, 2018) critically assesses the current performance of commercially available low-cost sensors. It highlights that low-cost sensors are not currently suitable to substitute mature instruments and provides some advice on key considerations for future low-cost sensor monitoring strategies.

Laser-based O_2 measurements

Besides the six traditional analytical techniques (see Chapter 6), laser-based O_2 measurements (QCLS, CRDS) are emerging, although they are currently less precise than the established techniques. The laser-based techniques measure O_2 mole fractions, potentially in humid air with water correction instead of drying the ambient air. To convert O_2 mole fractions to O_2/N_2 ratios, the dilution by CO_2 must be corrected for. Therefore, concurrent CO_2 measurements in the same instrument are highly desired on the laser-based analysers.

Open-path and total column measurements

Open path techniques record the absorption spectrum of air over an extended open path near the ground, from which path-average concentrations or mole fractions of traces gases can be retrieved. Open path techniques include mid infrared, near infrared and UV/visible spectral regions using a range of spectroscopic methods such as mid and near infrared FTIR spectroscopy (Smith et al., 2011; Griffith et al., 2018), frequency comb spectroscopy (Waxman et al., 2017) or DOAS (Platt et al., 2008). Solar remote sensing in the mid or near infrared (such as in TCCON, Chapter 13) is a special case of open path spectroscopy where the light source is the sun and the path average is the whole atmospheric column. Low resolution, portable solar remote sensing systems are emerging but require validation alongside TCCON. A promising approach is the COCCON (Collaborative Carbon Column Observing Network) activity, which uses smaller, portable, lower resolution FTIR spectrometers. These specifications limit the ability to retrieve vertical information and make the instruments more susceptible to internal line shape imperfections. However, the stability of the instrumental calibration of the COCCON spectrometers has been recently demonstrated (Frey et al., 2015; Frey et al., 2018). COCCON spectrometers may also be used for long-term observations in very remote regions for improving the coverage of ground-based trace gas measurements, if the local conditions do not support the operation of a TCCON site. Used as a travelling standard, COCCON spectrometers can be used for verification of the site-to-site consistency of TCCON measurements.

Open path measurements cannot be calibrated in the metrological sense that an unknown sample is replaced with a known standard under controlled conditions to quantify bias or scaling factors with respect to reference mole fraction scales. For solar remote sensing, this issue is covered in Chapter 13 of this document. For ground-based open path spectroscopy techniques, measurements should be compared as well as is feasible with in situ measurements along the open path made by instruments calibrated on WMO-GAW accepted scales. The simplest approach is in situ measurements at one point on the path under well-mixed conditions, such as high winds and turbulence. Comparison with co-incident calibrated measurements made along the path with a portable analyser, or from an AirCore (see below) sampling along the path are preferable, but at this time not well established. Further research is recommended before open path measurements can be linked to established scales and their accuracy assessed. Attention should be paid to recording temperature and pressure variations along the measurement path.

AirCore

AirCore is a newly-available and innovative tool to passively sample the atmosphere in a long, thin tube during descent from high altitude for accurate measurements of greenhouse gases and other tracers (Karion et al., 2010). AirCore samples can effectively resolve the vertical structure of the trace gases in the atmosphere. To obtain accurate mole fraction measurements that meet the WMO network compatibility goals, AirCore samplers should be carefully characterized for potential interferences, e.g. water vapour, surface and dryer effects. Comparison of the same and/or different AirCores should be carried out to characterize the consistency, the vertical resolution, and the profile retrieval algorithm. In addition, the altitude registration of the retrieved AirCore profile should be validated against stratospheric measurements, e.g. from stratospheric sampling or in situ measurements on balloons and high-altitude aircraft.

In an alternative application, AirCore can be used with the addition of a pump to create an “active” AirCore to sample the atmosphere for both vertical and horizontal transects when deployed on unmanned aerial vehicles. The position registration of the active AirCore measurements should be validated against other available measurements.

AirCore is a useful tool to link path-averaged measurements of greenhouse gases and other tracers from remote sensing techniques such as TCCON and open path measurements to the WMO scales. It is worth pointing out that AirCore and TCCON do not measure the exact same atmospheric path and differences due to natural variability are expected on any individual comparison. Routine comparisons over time are required for validation.

16. RECOMMENDATIONS FOR DATA MANAGEMENT, ARCHIVING, AND DISTRIBUTION

16.1 Data management

All GAW measurement laboratories regardless of programme size are required to manage all new and existing atmospheric trace gas and isotope data 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 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 (2003) 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. During the GGMT meeting, John Mund from NOAA ESRL illustrated how these recommendations are implemented at NOAA using a (conventional) relational database management system.

Table 1 lists those in the WMO/GAW community who have offered to share their expertise during GGMT-2015. The area of expertise described in the table is general; interested researchers are encouraged to e-mail the contact person directly for more detail.

Table 1. WMO/GAW members who have offered to share expertise (2015)

Name		*Lab*	*Location*	*Area of Expertise*
WDCGG		JMA	Japan	Data management in WDCGG
Lynn Hazan		LSCE	France	Data management
Paul Krummel		CSIRO	Australia	Quality control, non-CO_2 scale conversions, inter-comparisons
NOAA data team		NOAA	United States	Data management, quality control, scale conversion
Ludwig Ries		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		Empa	Switzerland	Data acquisition and processing with commercially available and custom-built software
Doug Worthy		EC	Canada	Near real-time data processing via GC, NDIR, and CRDS technologies

16.2 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 the GAW Implementation Plan for the period 2016-2023). A co-ordinated annual submission of data before the end of August of the following year, with a clearly identified version number of submitted data and calibration scale, as well as supporting details is strongly recommended for data inclusion in the WMO Annual Greenhouse Gas Bulletin. 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 for other public-access data archive centres.

b) The revised WDCGG Data Submission and Dissemination Guide (WMO, 2009b) 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 the current version 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, Netherlands Institute for Space Research, to provide guidance on ways to improve the usability of data distributed by the WDCGG.

e) This community will continue to develop best practices designed to standardize the reporting of 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.

Reactive gas data from WDCGG has been transferred in 2017 to the newly-established WDCRG at NILU, with the exception of CO, as the majority of GGMT attendees strongly opposed the transfer of CO data to WDCRG because CO observations are made by many of the same laboratories contributing CO_2, CH_4, and other greenhouse gas records to the WDCGG. WDCGG will continue its efforts toward archiving of the long-lived greenhouse gas observational data and will remain the primary archive for Carbon Monoxide (CO) data (a reactive gas by definition, but of key importance in relation to carbon cycle interpretations). It would be extremely valuable to researchers if GAW data were readily available from any of the WDCs. Thus, the GGMT attendees strongly recommend that the GAW Expert Team on World Data Centres (ET-WDCs) explore ways in which GAW data can still be archived at the appropriate WDC but discoverable and accessible from any WDC. ET-WDCs can consider GAW Station Information System (GAWSIS) as a potential hub for ensuring seamless data access to the GAW WDC and archiving centres of the contributing networks.

16.3 Cooperative 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 and OBSPACK enhance the value of any one individual measurement record by including it in a much larger cooperative network of observations.

Historically, NOAA has prepared comprehensive cooperative data products (e.g. GLOBALVIEW) using measurements made by GAW and non-GAW laboratories. It is likely more laboratories will begin to prepare and distribute smaller complementary data products including data from one or a few measurement groups. Products are complementary if their content and structure are fully compatible, data are prepared in a consistent and unambiguous manner; and no two products include the same original data. To ensure complementary products are fully compatible and easily accessible to users, this community recommends establishing a working group tasked with defining compatibility standards and compiling best practices to maximize the likelihood of full compatibility among products made by different laboratories.

16.4 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)). NOAA has already done considerable work in this area, which is described in Masarie et al. (2014). 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.

16.5 WDCGG website update

Seiji Miyauchi from Japan Meteorological Agency presented the new WDCGG website and plans for providing satellite data from the WDCGG. The new website has been considerably delayed due to safety restrictions and is not in production at this moment (July 2018). The new setup will provide a much-enhanced user experience for submission and editing of metadata.

Comments from the community raised concerns about the lack of added value of including satellite data at WDCGG because comprehensive solutions for access to this data already exist.

The efforts of WDCGG on the improvements of the website are much appreciated and are welcomed by the community, however, it was also stressed that user feedback from test users should be timely taken into account, before the roll-out of the website into production. Also, up to date documentation of the new metadata and submission procedures would be much appreciated.

17. RECOMMENDATIONS FOR THE COOPERATIVE WMO/GAW NETWORK

GGMT-2017 was the first meeting in the series under the new GAW Implementation Plan (WMO, 2017) covering the period from 2016 to 2023. This plan builds upon the concept of "science for services" by promoting the idea of the broader use of observations and modelling tools to deliver services relevant to society. Observations of greenhouse gases play a very prominent role in support of climate-relevant services like the understanding of historic GHG trends and the delivery of improved emissions estimates based on observations and inverse modelling techniques as promoted by the Integrated Global Greenhouse Gas Information System (IG^{3}IS). The 17th World Meteorological Congress adopted a resolution on IG^{3}IS in 2015, while consecutive constituent body meetings (Executive Council 68 in 2016 and Executive Council 69 in 2017) adopted the IG^{3}IS concept paper and the annotated outline of the IG^{3}IS Implementation Plan.

The Meeting of the Parties to the United Nations Framework Convention on Climate Change (UNFCCC) held in Paris in December 2015 served as a landmark agreement in the history of climate negotiations. The Paris Agreement builds upon the Convention and – for the first time – brings all nations into a common cause to take ambitious efforts to combat climate change and to adapt to its effects, with enhanced support to assist developing countries in these efforts. As such, it charts a new course in the global climate effort. The Paris Agreement's central aim is to strengthen the global response to the threat of climate change by keeping this century's global temperature rise well below 2 degrees Celsius above pre-industrial levels and to pursue efforts to limit the temperature increase even further to 1.5 degrees Celsius. Additionally, the Paris Agreement aims to increase the ability of countries to deal with the impacts of climate change and provides a framework to ensure enhanced transparency in actions taken.

The WMO Executive Council 69 (EC-69) in May 2017 adopted Decision 7 that articulates the support provided by WMO in the implementation of the Paris Agreement. This decision states:

" *Observing that:*

(1) The forty-fifth session of the Subsidiary Body for Scientific and Technical Advice (SBSTA- 45) held at COP 22 in November 2016 welcomed the submissions from WMO on the Global Climate in 2011–2015 and the WMO Greenhouse Gas Bulletin;

(2) SBSTA-45 invited WMO to provide submissions on the state of the global climate on a regular basis, as appropriate, at subsequent sessions of SBSTA;

(3) The Integrated Global Greenhouse Gas Information System (IG^{3}IS) will provide information that may contribute to actions of nations, sub-national governments including cities, and the private sector to reduce GHG emissions through a measurement and-modelling-based approach;

….

Having considered that:

(1) Enhanced observation of Essential Climate Variables (ECVs) may be important for the global stocktake, since the climate data records based on ECVs are used to close budgets of energy, carbon and water and to study changes in the

growth rate of the atmospheric greenhouse gases (GHGs), or interaction between land and atmosphere, in a more integrated way,

……

Decides:

(1) That appropriate measures should be taken to promote the value and relevance of ***scientific information and data*** *for the global stocktake under the Paris Agreement through WMO submissions and reporting mechanisms to UNFCCC, noting that the inputs of the global stocktake are to be decided by Parties to the Paris Agreement;*

(2) To assist NMHSs to engage at national level, as appropriate, to design and implement GCF proposals, coordinate with National Designated Authorities (NDAs), develop and implement NAPs, and generate relevant climate information and services, particularly ***through implementation of the GFCS and IG^{3}IS pilot projects;***

Invites Members:

(1) To work at national level to fully engage NMHSs as critical actors in the cataloguing of extreme events, adaptation programmes, mitigation, and other areas that fall within the competency of their respective Services, and to contribute to the development of nationally determined contributions (NDCs), ***greenhouse gas monitoring systems and other observing systems;***

…

(4) To work towards the full implementation of the Global Climate Observing System (GCOS)Implementation Plan;

…."

The new Implementation Plan of the Global Climate Observing System (GCOS) (WMO, 2016a) approved by the GCOS Steering Committee at its 24th meeting in Guayaquil, Ecuador, in October 2016 and submitted to the UNFCCC at COP22 in Marrakesh, Morocco, November 2016, contains several action items directly relevant to the greenhouse gas observations within the GAW Programme.

Action A33: Maintain WMO GAW CO_2 and CH_4 monitoring networks	
Action	Maintain and enhance the WMO GAW Global Atmospheric CO_2 and CH_4 monitoring networks as major contributions to the GCOS Comprehensive Networks for CO_2 and CH_4. Advance the measurement of isotopic forms of CO_2 and CH_4 and of appropriate tracers to separate human from natural influences on the CO_2 and CH_4 budgets
Benefit	A well-maintained, ground-based and in situ network provides the basis for understanding trends and distributions of GHGs.
Who	National Environmental Services, NMHSs, research agencies, and space agencies under the guidance of WMO GAW and its Scientific Advisory Group on Greenhouse Gases
Time frame	Ongoing

Action A34: Requirements for in situ column composition measurements	
Action	Define the requirements for providing vertical profiles of CO_2, CH_4 and other GHGs, using recently emerging technology, such as balloon capture technique (e.g. AirCore)

Benefit	Ability to provide widespread, accurate, in situ vertical profiles economically; an excellent tool for validating satellite retrievals and improving transport models
Who	GCOS AOPC and space agencies
Time frame	Requirements to be defined by 2018
Action A36: N_2O, halocarbon and SF_6 networks/measurements	
Action	Maintain networks for N_2O, halocarbon and SF_6 measurements
Benefit	Informs the parties to the Montreal Protocol, provides records of long-lived, non-CO_2 GHGs and offers potential tracers for attribution of CO_2 emissions.
Who	National research agencies, national environmental services, NMHSs, through WMO GAW
Time frame	Ongoing

We, the Expert Group convened at GGMT-2017, recommend the following observational strategies:

1) Sustain, improve and increase the number of stations with continuous in situ measurements of multiple greenhouse gases in the boundary layer and in the troposphere by aircraft and AirCore sampling. The WMO/GAW community should make an effort to establish and sustain observations in under-sampled regions. In addition, efforts should be made to expand aircraft flights over vegetated areas that are currently not sampled or under-sampled, with priority given to tropical South America, Africa, and South East Asia. Station twinning, partnership and collaboration programmes (like CATCOS (Capacity Building and Twinning for Climate Observing Systems) by MeteoSwiss) should be further encouraged.
2) The community should make an effort in assessing the emerging low-cost sensor techniques as a potential approach in the areas of high-density emissions.
3) 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). Recognizing the importance of total column measurements to satellite validation and modelling, total column measurements should be compared to vertical profiles of calibrated in situ and calibrated full-column AirCore measurements on a regular basis.
4) WMO recognizes the importance of independent measurement methods, calibration scales and calibration techniques that are consistent with the data quality objectives, quality control, transparency and traceability defined elsewhere in this document. The goal of this diversity is to assure that the global atmospheric measurement enterprise remains robust and less vulnerable to systematic or method-specific error. A key component of this diversity is the rigorous and frequent comparison of independent methods.
5) Develop high-quality measurements of carbon cycle tracers (i.e. O_2/N_2, $^{14}CO_{2,}$ and stable isotopes in CO_2, CH_4 and CO) that can be used to attribute fluxes to their controlling processes, especially to distinguish and quantify the recent fossil fuel component from CO_2 variations caused by natural sources/sinks. Measurements of additional tracers such as hydrocarbons (e.g. ethane) and halocarbons are useful for attribution of fluxes and due to their own contributions to radiative forcing.
6) Commonalities with other GAW focal areas and other international bodies should be examined and collaborations should be sought. For instance, collaboration with the reactive gases community in GAW should be intensified, interaction with the

Scientific Advisory Group on Applications should be established and collaboration with IAEA should be improved.

7) Following on the initial productive discussion with the ocean community, collaboration with the biosphere and the ocean communities should be further expanded to improve spatial coverage of the measurements and data compatibility between the communities that may lead to improving source/sink estimates. Ship based observations of both atmospheric and ocean dissolved GHG should be encouraged. The same traceability principle is recommended for the atmospheric GHG measurements above the ocean using ship platforms as for the rest of the network. Laboratories measuring GHGs from ships are invited to take part in regular comparison taking place within the GAW network and are recommended to collect flasks to be analysed in the GAW labs to assess compatibility of the ship-based observations with continental sites.

8) Similarly, measurements of atmospheric composition at flux towers (e.g. FluxNet, ICOS, NEON, Ameriflux, AsiaFlux, etc.) should be linked to WMO calibration scales. Investigators at key laboratories in these networks should be encouraged to take part in WMO Round Robin exercises and flask samples of air could be exchanged or comparative measurements could be made at key sites in these networks.

9) To achieve the above goals, thorough quality control procedures are necessary to ensure that WMO/GAW data meets the recommended network compatibility goals and is suitable for a variety of different applications.

10) Atmospheric observations are used with inverse modelling techniques to quantify sources and sinks on various spatial and temporal scales. WMO encourages the development of improved atmospheric transport models and data assimilation techniques. Frequent comparisons of independent models are needed to improve understanding of the uncertainties of inferred fluxes. In addition, community models that are numerically efficient and can run on standard computer platforms with a modest amount of training are encouraged and should be made available to the entire scientific community.

11) Atmospheric measurement methods and high-resolution models should be developed that can provide support for improved emission estimates of CO_2 and other gases for regions with high-density emissions, such as urban areas and oil and gas fields. It is recognized as an essential element that detailed spatially and temporally resolved emissions inventories of fossil fuel CO_2, CH_4, and CO are being developed and pursued. To achieve this, better collaboration with the emission inventory community should be developed.

18. ORGANIZATION OF GGMT-2019

There was general agreement among all that it would be desirable to convene the next meeting, the 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, on Jeju Island in South Korea. The meeting will take place from 2-5 September 2019. Haeyoung Lee from the Korea Meteorological Administration (KMA) / National Institute of Meteorological Sciences (NIMS) has agreed to organize and host this meeting.

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ANNEX I

19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2017)

(Dübendorf, Switzerland, 27-31 August 2017)

LIST OF PARTICIPANTS

First name	***Last name***
Hermanni	Aaltonen
Colin	Allison
Truls	Andersen
Arlyn	Andrews
Nobuyuki	Aoki
Emmanuel	Arzoumanian
Sergey	Assonov
Carl	Bengtsson
Jonathan	Bent
Antoine	Berchet
Tesfaye	Berhanu
Sebastien	Biraud
Reinhard	Bischoff
Viviane Francisca	Borges
Paul	Brewer
Elise	Broekema
Neil	Brough
Dominik	Brunner
Brigitte	Buchmann
George	Burba
James	Butler
Huilin	Chen
Sebastien	Conil
Cedric	Couret
Andrew	Crotwell
Roger	Curcoll Masanes
Phil	DeCola
Marc	Delmotte
Frederic	Despagne
Edward	Dlugokencky
Jeremy	Dobler
Lucas	Domingues
Volker	Ebert
Flores	Edgar

Sarah	Eggleston
Lukas	Emmenegger
Markus	Eritt
Shuangxi	Fang
Andrea	Fischer
Rebecca	Fisher
James	France
Luciana V.	Gatti
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Daisuke	Goto
Heather	Graven
Rebecca	Gregory
David	Griffith
Claudia	Grossi
Myriam	Guillevic
Brad	Hall
Samuel	Hammer
Sang-Ok	Han
László	Haszpra
Juha	Hatakka
Klaus	Hecker
Joram	Hooghiem
Erkan	Ibraim
Tracey	Jacksier
Mohd Firdaus	Jahaya
Armin	Jordan
Kristýna	Kantnerová
Anna	Karion
keiichi	katsumata
Teruo	Kawasaki
Ralph	Keeling
Jooil	Kim
Duane	Kitzis
Joerg	Klausen
Paul	Krummel
Dagmar	Kubistin
Casper	Labuschagne
Olivier	Laurent
Jost	Lavric
Raymond	Lee
Haeyoung	Lee
Emma	Leedham Elvidge
Graham	Leggett
Céline	Lett
Markus	Leuenberger

Pingyang	Li
Miao	Liang
Bing	Lin
Zoe	Loh
Morgan	Lopez
Dave	Lowry
Toshinobu	Machida
Magda	Mandic
Francis	Mani
Andrew	Manning
Lynwill	Martin
Ken	Masarie
Shinji	Masuda
Kathryn	McKain
Sylvia	Michel
Natasha	Miles
Bill	Miller
Blagoj	Mitrevski
Seiji	Miyauchi
Joachim	Mohn
Heiko	Moossen
Eric	Morgan
Josep-Anton	Morguí
Rowena	Moss
Hitoshi	Mukai
Michael	Müller
John	Mund
Hideki	Nara
David	Nelson
Euan	Nisbet
Masahide	Nishihashi
Shohei	Nomura
Vincent	Omarjee
Yumi	Osonoi
Rutger	Oudwater
Penelope	Pickers
Ignacio	Pisso
Katherine	Pugsley
Michel	Ramonet
Stefan	Reimann
Christopher	Rella
Scott	Richardson
Craig	Richmond
Leonard	Rivier
Daniel	Rzesanke
Caio S C	Correia

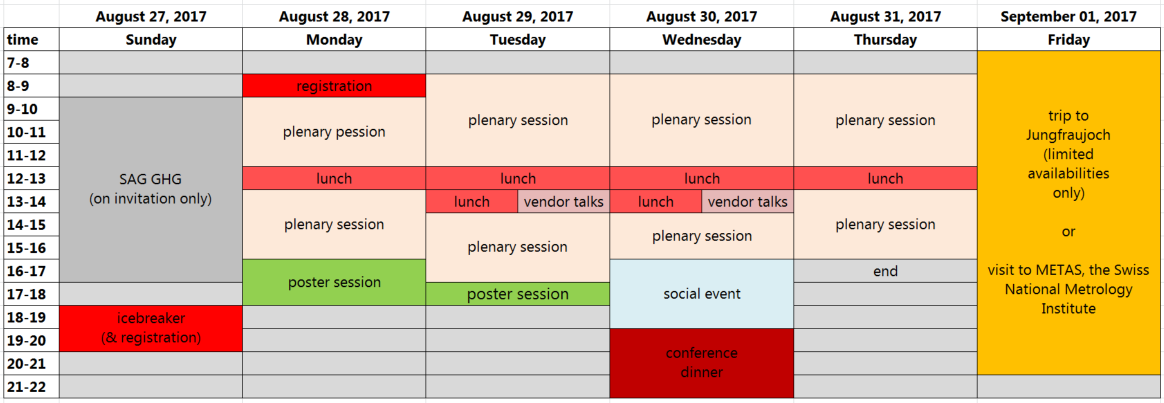
Karri	Saarnio
Ece	Satar
Budi	Satria
Yosuke	Sawa
Bert	Scheeren
Michael	Schibig
Oliver	Schlegel
Martina	Schmidt
Hannah	Sonderfeld
Peter	Sperlich
Kieran	Stanley
Ann	Stavert
Martin	Steinbacher
Andreas Alois	Steininger Ilardi
Britton	Stephens
Colm	Sweeney
Oksana	Tarasova
Yukio	Terao
Yogesh Kumar	Tiwari
Yasunori	Tohjima
Sakae	Toyoda
Jocelyn	Turnbull
Mikio	Ueno
Bruce	Vaughn
Alex	Vermeulen
Felix	Vogel
Martin	Vollmer
Thi Quynh Hoa	Vu
Kuo-Ying	Wang
Rik	Wanninkhof
Ray	Weiss
Robert	Wielgosz
Renato	Winkler
Doug	Worthy
Simon	Wyss
Bo	Yao
Longfei	Yu
Mark	Zahniser
Daniel	Zavala-Araiza
Giulia	Zazzeri
Christoph	Zellweger
Lingxi	Zhou

ANNEX II

19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2017)

(Dübendorf, Switzerland, 27-31 August 2017)

MEETING AGENDA



	August 27, 2017	August 28, 2017	August 29, 2017	August 30, 2017	August 31, 2017	September 01, 2017
time	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
7-8						trip to Jungfraujoch (limited availabilities only) or visit to METAS, the Swiss National Metrology Institute
8-9		registration	plenary session	plenary session	plenary session	
9-10	SAG GHG (on invitation only)	plenary pession				
10-11						
11-12						
12-13		lunch	lunch	lunch	lunch	
13-14		plenary session	lunch vendor talks	lunch vendor talks	plenary session	
14-15			plenary session	plenary session		
15-16						
16-17		poster session		social event	end	
17-18			poster session			
18-19	icebreaker (& registration)					
19-20				conference dinner		
20-21						
21-22						

Sunday, 27 August 2017

18:00	20:00	Ice Breaker

Monday, 28 August 2017

08:00	09:00	**Registration**
09:00	09:10	Welcome and Opening Remarks, *Brigitte Buchmann
09:10	09:30	News from the GAW secretariat, *Oksana Tarasova
		Quality Assurance, GHG Standards & Comparison Activities Chair: Paul Krummel
09:30	09:50	T01- Uncertainties of NOAA GHG measurements from discrete air samples and zonal means, *Ed Dlugokencky
09:50	10:10	T02- Efforts to separately report random and systematic measurement uncertainty for continuous measurements in the NOAA Global Greenhouse Gas Reference Network, *Arlyn Andrews
10:10	10:40	**Photo and Coffee Break**
		Quality Assurance, GHG Standards & Comparison Activities Chair: Martin Steinbacher
10:40	11:00	T03- An update of comparisons of non-CO_2 trace gas measurements between AGAGE and NOAA at common sites, *Paul Krummel
11:00	11:20	T04- Revision of the WMO CO_2 calibration scale, *Brad Hall

11:20	11:40	T05- An update on the WMO CO X2014A scale, *Andrew Crotwell
11:40	12:00	T06- The result of the first SF$_6$ inter-comparison Experiment (SICE) 2016-2017, *Haeyoung Lee
12:00	12:20	T07- A new method to produce SI-traceable, primary calibration standards for halogenated greenhouse gases, *Myriam Guillevic
12:20	13:40	**Lunch Break**
		Quality Assurance, GHG Standards & Comparison Activities **Chair: Paul Krummel**
13:40	14:00	T08- Quality assurance and quality control of the upcoming ICOS-RI atmospheric dataset, *Michel Ramonet
14:00	14:20	T09- QA/QC of IAGOS NRT GHG data, *Christoph Gerbig
14:20	14:40	T10- WCC-Empa – Activities and Achievements, *Christoph Zellweger
14:40	15:10	**Recommendations A: QA/QC, Standards and Comparisons, Chapters 1, 2, 6, 9:** **Calibration of GAW Measurements, CO, CH$_4$ and CO$_2$ Calibration** **Lead: Andrew Crotwell, Rapporteur: Christoph Zellweger**
15:10	15:40	**Coffee Break**
15:40	16:40	Speed talks for Posters "Site and Network Updates"
16:40	18:30	**Poster Session**

Tuesday, 29 August 2017

		Isotope Measurements - Chair: Joachim Mohn
08:30	08:50	T11- Introduction: Data Quality Objectives for stable isotopes in greenhouse gases: current status and future needs, *Sergey Assonov
08:50	09:10	T12- Delta-13C scale realization based on the primary Reference Materials in the form of carbonates, *Sergey Assonov
09:10	09:30	T13- JRAS-06: Keeping up with changing internationally-distributed, light-element stable isotopic reference materials, *Heiko Moossen
09:30	09:50	T14- Maintaining quality with quantity: lessons learned in the corrections and calibrations of INSTAARs large isotopic dataset, *Sylvia E. Michel
09:50	10:10	T15- Measurement and Calibration Uncertainty in the CSIRO atmospheric CO2 Stable Isotope Program, *Colin Allison
10:10	10:40	**Coffee Break**
		Isotope Measurements - Chair: Sergey Assonov
10:40	11:00	T16- On the calibration of isotopologue-specific optical trace gas analysers, *David Griffith
11:00	11:20	T17- Calibration strategies for FTIR and other IRIS instruments for accurate δ^{13}C and δ^{18}O measurements of CO$_2$ in air, *Edgar Flores
11:20	11:40	T18- Gaseous reference materials to underpin measurements of amount fraction and isotopic composition of greenhouse gases, *Paul Brewer

11:40	12:00	T19- Using Isotopic Fingerprints to Trace Nitrous Oxide in the Atmosphere, *Joachim Mohn
12:00	12:20	T20- Methane isotopes – clues to the budget changes: and the need for independent isotopic measurement programs, *Euan Nisbet
12:20	14:00	**Lunch Break (including vendor presentations for final 60 minutes)**
13:00	13:15	Air Liquide
13:15	13:30	Decentlab
13:30	13:45	Mirico
13:45	14:00	LosGatos
14:00	*17:30*	***Side event: -Metrology for Stable Isotope Reference Standards (SIRS) stakeholder meeting***
		Urban Networks and Megacities - Chair: Jooil Kim
14:00	14:20	T21- Integrated urban Greenhouse Gas Information System (IG^3IS): Advances in the urban GHG monitoring implementation plan and results of previous and current city-scale studies, *Felix Vogel
14:20	14:40	T22- Detection of trends in urban CO_2 emissions: Results from the INFLUX tower network, *Natasha Miles
14:40	15:00	T23- The North-East Corridor: Baltimore-Washington DC Urban Greenhouse Gas Network, *Anna Karion
15:00	15:30	**Coffee Break**
		Site and Network Updates - Chair: Lingxi Zhou
15:30	15:50	T24- Amazon Greenhouse Gas Measurement Program, *Luciana V. Gatti
15:50	16:10	T25- CO_2, CH_4, and CO with CRDS technique at the Izaña Global GAW station: instrumental tests, developments and first measurement results,*Angel J. Gomez-Pelaez
16:10	16:30	T26- Atmospheric CO_2 and other greenhouse gases monitoring in India,*Yogesh K. Tiwari
16:30	17:00	**Recommendations C: Urban Networks, Site and Network Updates** **Chapters 11 & 12 - Lead: Felix Vogel, Rapporteur: Casper Labuschagne**
17:00	18:00	**Poster Session**
18:00	*19:00*	***Side event: -Discussion on Stable Isotopes Recommendations***
18:00	*19:00*	***Side event: -Discussion on Shipboard Atmospheric CO2 Measurement Recommendations***

Wednesday, 30 August 2017

08:10	08:40	**Recommendations B: Isotope Measurements, Chapters 3, 4: Stable isotopes and radiocarbon - Lead: Sergey Assonov, Rapporteur: Bruce Vaughn**
		Measurement Techniques & Calibration - Chair: Zoe Loh
08:40	09:00	T27- Fractionation of O_2/N_2, Ar/N_2, and CO_2 at Aircraft Sampling Inlets,*Britton Stephens
09:00	09:20	T28- Comparison of interferometric and mass spectrometric measurements of O_2/N_2 by the Scripps O_2 program, *Ralph Keeling
09:20	09:40	T29- Preparation of high precision standards (with ±1 ppm) using a gravimetric method for measuring atmospheric oxygen, *Nobuyuki Aoki
09:40	10:00	T30- Towards the Unifying of the Detection Systems for the Measurement of the Major Greenhouse Gases and Related Tracers, *Blagoj Mitrevski
10:00	10:30	**Coffee Break**
		Measurement Techniques & Calibration - Chair: Arlyn Andrews
10:30	10:50	T31- Calibration and Field Testing of Cavity Ring-Down Laser Spectrometers Measuring Methane Mole Fraction and Isotopic Ratio Deployed on Towers in the Marcellus Shale Region, *Natasha Miles
10:50	11:10	T32- Adaptation of a commercial greenhouse gas analyser for airborne measurements with expanded altitude range and application on the ORCAS and ATom campaigns, *Kathryn McKain
11:10	11:30	T33- A new lightweight active stratospheric air sampler, *Joram Hooghiem
11:30	12:00	**Recommendations D: Measurement Techniques & Calibration, Chapters 5, 7, 8, 10: Calibration of O_2/N_2, N_2O, SF_6 and H_2 Measurements** **Lead: Britt Stephens, Rapporteur: Brad Hall**
		Emerging Techniques - Chair: Christoph Gerbig
12:00	12:20	T34- Low-cost sensors for CO_2 monitoring: calibration, characterization and assessment, *Lukas Emmenegger
12:20	14:00	**Lunch Break (including vendor presentations for final 45 minutes)**
13:15	13:30	Picarro
13:30	13:45	Aerodyne
13:45	14:00	Ecotech
14:00	14:20	T35- Measurements of atmospheric oxygen using a newly built CRDS analyzer and comparison with a paramagnetic cell and an IRMS, *Markus Leuenberger
14:20	14:40	T36- Microwave sensing column oxygen amounts for surface air pressure and greenhouse gas mixing ratio estimates, *Bing Lin
14:40	15:00	T37- The AirCore atmospheric profiler: methods, challenges, applications and updates, *Jonathan Bent

15:00	15:20	T38- A UAV-based active AirCore system for accurate measurements of greenhouse gases, *Truls Andersen
15:20	15:50	**Coffee Break**
17:00	19:00	**City tour of historical Zurich**
19:00		**Conference Dinner**

Thursday, 31 August 2017

		Emerging Techniques - Chair: Michel Ramonet
08:30	08:50	T39- Stratospheric measurements of ozone-depleting substances and greenhouse gases using AirCores, *E. Leedham Elvidge
08:50	09:10	T40- APRECON-TOF-MS: A new state-of-the art instrument for the analysis of halogenated greenhouse gases, *Martin K. Vollmer
09:10	09:40	**Recommendations E: Emerging Techniques** **Lead: David Griffith, Rapporteur: Huilin Chen**
		Ocean Measurements, Chapter 13 - Chair: Martin Vollmer
09:40	10:00	T41- Medusa-Aqua System: Development of Analytical Techniques for Novel Halogenated Transient Tracers in the Ocean, *Pingyang Li
10:00	10:20	T42- Fifteen years of surface water CO_2 measurements from cruise ships in the Caribbean Sea, *Rik Wanninkhof
10:20	10:50	**Coffee Break**
10:50	11:10	T43- Towards including atmospheric CO_2 data from the oceanic community into the global high-accuracy atmospheric CO_2 network, *Penelope A. Pickers
11:10	11:30	T44- The PGGM measurements of atmospheric carbon dioxide concentrations over the Asia-Pacific and the Asia-Europe commercial shipping routes: The 2009-2017 results, *Kuo-Ying Wang
11:30	11:50	T45- Atmospheric CO_2, CH_4 and N_2O mixing ratios in the China sea-shelf boundary layer during the spring 2017 campaign, *Lingxi Zhou
11:50	12:20	**Recommendations F: Ocean Measurements** **Lead: Rik Wanninkhof, Rapporteur: Hideki Nara**
12:20	13:20	**Lunch Break**
		Data Products and Policy - Chair: Alex Vermeulen
13:20	13:40	T46- Updated Guidelines for Atmospheric Trace Gas Data Management, *John Mund
13:40	14:00	T47- Introduction of new WDCGG website, *Seiji Miyauchi
14:00	16:00	**Expert group recommendations** **Lead: to be assigned, Rapporteur: to be assigned**
		MEETING CLOSE and Coffee

ANNEX III

19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2017)

(Dübendorf, Switzerland, 27-31 August 2017)

POSTER SESSIONS

Posters Quality Assurance, GHG Standards & Comparison Activities

P01	Mobile Laboratory improving the data quality of ICOS atmospheric station network, *Hermanni Aaltonen
P02	5 years of ICOS compliant in situ GHG measurements at OPE: set up, quality control and calibration system, *Sébastien Conil
P03	Optimal dry cylinder sequencing on Picarro G2301 and G2401 CRDS instruments, *Rebecca Gregory
P04	Quality control of flask sample data using Ar/N_2 measurements, *Armin Jordan
P05	Comparison of Picarro and Los Gatos analysers for CO and N_2O at Hohenpeissenberg, *Dagmar Kubistin
P06	Update of Operation of the Flask and Calibration Laboratory for ICOS (Integrated Carbon Observation System), *Daniel Rzesanke
P07	QA/SAC Switzerland – Activities and Achievements, *Martin Steinbacher

Posters Isotope Measurements

P08	Methane in Hong Kong: isotopic characterisation of local and regional methane sources, *Rebecca Fisher
P09	European atmospheric $^{14}CO_2$ activities within the ICOS-RI network, *Samuel Hammer
P10	Simultaneous field-scale in situ measurements of the four most abundant N_2O isotopocules, *Erkan Ibraim
P11	High precision spectroscopic measurement of N_2O clumped isotopic species, *Kristýna Kantnerová
P12	Development of new N_2O reference materials for $\delta^{15}N$, $\delta^{18}O$ and ^{15}N site preference within the EMPIR project SIRS, *Joachim Mohn
P13	$^{14}CO_2$ measurements from Baring Head, New Zealand, Rowena Moss
P14	Performance of radiocarbon analysis using NIES-CAMS and initial results for air samples obtained in Indonesia, *Yumi Osonoi
P15	Towards SI traceability for CO_2 isotope ratios: Identifying sources of error in optical spectroscopy measurements, *Craig Richmond
P16	Measurement of nitrous oxide isotopomers in air, *Peter Sperlich
P17	Stable isotope and mixing ratio measurement of atmospheric CO_2 over India, *Tania Guha, Yogesh K. Tiwari

P18 Pilot study measuring N_2O mole fraction, $\delta^{15}N^{bulk}$-N_2O, $\delta^{15}N^{\alpha}$-N_2O, and $\delta^{15}N^{\beta}$-N_2O using Picarro G-5101i instrument reveals analytical challenges, *Bruce H. Vaughn

P19 Measurement of N_2O isotopes at the high-altitude station Jungfraujoch, *Longfei Yu

P20 Evaluation of methane sources by isotopic analysis in central London, *Giulia Zazzeri

Posters Measurement Techniques & Calibration

P21 Inter-comparison study of European atmospheric ^{222}Rn and ^{222}Rn progeny monitors, *Claudia Grossi

P22 Evaluation of an OA-ICOS (Off-axis Integrated Cavity Output Spectrometer) for N_2O measurements at Schauinsland station, *Johannes Gry

P23 Estimation of BG CO_2 concentration from CRDS measurements at AMY site in South Korea using Quality Assurance Flagging Codes, *Sang-Ok Han

P24 Synthesis and evaluation of near real air CO_2 reference gas, *Keiichi Katsumata

P25 Replacement of CH_4 calibration system for WCC-JMA, *Teruo Kawasaki

P26 Stability and Material Testing Results of Aluminum Cylinders and Regulator Comparisons, *Duane Kitzis

P27 Causes of Instability in the Relative Abundance of the Major Constituents of Reference Air in High-Pressure Tanks, *Eric J. Morgan

P28 Investigation of adsorption / desorption behavior of high pressure small volume cylinders and its relevance to atmospheric trace gas analysis, *Ece Satar

P29 11-year statistics for in situ CO_2 data obtained in airliner project of CONTRAIL, *Yousuke Sawa

P30 A Nafion-based air sample dryer for atmospheric flask sampling allowing accurate measurements of CO_2 and its stable isotopes in humid air, *Hubertus A. Scheeren

P31 Potential bias in the NOAA manometric measurement system, *Michael F. Schibig

P32 Comparison of in situ N_2O and CO measurements using gas chromatography, reduction gas analysis and off-axis integrated cavity output spectroscopy, *Kieran Stanley

P33 Quantifying Nafion cross-membrane CO_2 and CH_4 gas leakage and it’s dependence on sample mole fraction and water content, *Ann Stavert

P34 Optimisation of the Spectronus FTIR instrument for tall tower greenhouse gas observations, *Alex Vermeulen

Posters Emerging Technique

P35 Developing a lower-cost medium precision urban GHG monitoring system using commercial NDIR sensors, *Emmanuel Arzoumanian

P36 High-resolution Mobile Measurements of Methane Concentrations and Fluxes Using High-Speed Open-Path Technology on Cars, Ships, Airplanes, Helicopters and Drones, *George Burba

P37 The automated air sampler for the ICOS network, *Markus Eritt

P38 Measurement of greenhouse gases from novel ground-based remote sensing instruments; the FRM4GHG campaign at the Sodankylä TCCON site, N. Finland, *Mahesh Kumar Sha, David Griffith

P39 Technical challenges of using high precision atmospheric O_2 measurements as a tracer for determining carbon fluxes in terrestrial ecosystems, *Penelope A. Pickers

Posters Ocean Measurements

P40 Continuous observation of atmospheric oxygen concentration onboard a cargo ship sailing between Japan and North America, *Yu Hoshina

P41 Japan Meteorological Agency’s ship-based observations for carbonate parameters in the surface and interior ocean, *Shinji Masuda

P42 Long-term monitoring of atmospheric greenhouse gases and data validation in NIES-VOS program, *Hideki Nara

Posters Urban Networks and Megacities

P43 CarboSense: a low-cost low-power CO_2 network for the city of Zurich and Switzerland, *Antoine Berchet

P44 Continuous Near-IR and Mid-IR CRDS Measurements of Atmospheric CO_2, CH_4, N_2O, and CO in the Megacities Los Angeles Network: Design Criteria, *Jooil Kim

P45 New monitoring project of GHGs and air pollutants around Jakarta, Indonesia, *Masahide Nishihashi

P46 Start of greenhouse gases and related tracer measurements at Tokyo Megacity, *Yukio Terao

Posters Site and Network Updates

P47 Trace gas mixing ratios, carbon, water, and energy exchanges measurements at ARM facilities, * Sébastien C. Biraud

P48 Greenhouse Gases: Background Concentrations in Brazilian coast, *V.F. Borges

P49 Observations and modelling combine to inform network developments, *Gordon Brailsford, Rowena Moss

P50 “CASLab”: The United Kingdom’s Clean Air Sector Laboratory at Halley Research Station, coastal Antarctica, *Neil Brough

P51 The Franco-Belgian greenhouse gases monitoring program at La Réunion Island, *Jean-Pierre Cammas

P52 Long Term Nitrous Oxide Measurements Over Amazon Basin Using Small Aircraft, *C.S.C. Correia

P53 Continuous observations of CO_2, CH_4 and O_3 in the boundary layer of the central Mediterranean basin, *Paolo Cristofanelli

P54 Carbon Monoxide Measurements as a Biomass Burning Tracer at the Amazon Basin, *L.G. Domingues

P55 Amazon Basin and Brazilian Coast SF_6 Study in a 15 Years Time Series, *R.S. Santos

P56 Atmospheric molecular hydrogen (H_2) at the WMO/GAW stations in China, *Shuangxi Fang

P57 Japanese observation programs of atmospheric greenhouse gases in polar regions, *Daisuke Goto

P58 First results of tall tower surface-atmosphere N_2O flux measurements over a mixed agricultural region in Central Europe, *László Haszpra

P59 Recent updates from the Cape Point long-term data records, *Casper Labuschagne

P60 Atmospheric CO_2/CH_4/CO measurements at the Amazon Tall Tower Observatory (ATTO, Brazil), *Jost V. Lavric

P61 Combined balloon, aircraft, and surface greenhouse gas measurements at Traînou supersite, France, *Céline Lett

P62 Atmospheric nitrous oxide observations at Mount Waliguan station in China, from 1995 to 2014, *Miao Liang

P63 The Australian Greenhouse Gas Observation Network – where we are and where we are heading, *Zoë Loh

P64 Atmospheric CH_4 and N_2O measurements at Suva, Fiji, *Francis S. Mani

P65 MOYA and Equianos: UK methane measurement and GHG monitoring, *Euan G. Nisbet

P66 Atmospheric greenhouse gas concentrations for five years over a tropical forest in Borneo Island, *Shohei Nomura

P67 Monitoring of Greenhouse Gases with in situ FTIR in East Anglia, UK, as part of a regional sampling network, *Hannah Sonderfeld

P68 Implementation of New Greenhouse Gas Measurements in Cholpon Ata, Kyrgyz Republic, *Martin Steinbacher

Posters Data Products and Policy

P69 ICOS ATC near real time greenhouse gases data: from collection to model validation on the importance of proper water correction and primary scale propagation, *Amara Abbaris, Léonard Rivier

P70 Data Services for Carbon Cycle Science at the ICOS Carbon Portal, *Alex Vermeulen

ANNEX IV

LIST OF ABBREVIATIONS

AGAGE	Advanced Global Atmospheric Gases Experiment
AMS	Accelerator Mass Spectrometry
AOPC	Atmospheric Observation Panel for Climate
BGC-IsoLab	Stable isotope laboratory at the Max Planck Institute for Biogeochemistry
BIPM	International Bureau of Weights and Measures
CATCOS	Capacity Building and Twinning for Climate Observing System
CCL	Central Calibration Laboratories
CCQM	Consultative Committee for Amount of Substance – Metrology in Chemistry
CIAAW	Commission on Isotopic Abundances and Atomic Weights
CIPM	International Committee for Weights and Measures
COCCON	Collaborative Carbon Column Observing Network
COP21	21st session of the Conference of Parties, Paris, France, 2015
CRDS	Cavity Ring-Down Spectroscopy
CSIRO	Commonwealth Science and Industrial Research Organization
DBMS	Database Management Strategy
DOAS	Differential Optical Absorption Spectroscopy
DOI	Digital Object Identifier
DQO	Data Quality Objectives
ECCC	Environment and Climate Change Canada (formerly Environment Canada (EC))
ECV	Essential Climate Variable
Empa	Swiss Federal Laboratories for Materials Science and Technology
EMPIR	European Metrology Programme for Innovation and Research
ESRL	(NOAA) Earth System Research Laboratory
ET-WDC	Expert Team on World Data Centres
FTIR	Fourier-transform infrared spectroscopy
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GAWTEC	GAW Training and Education Centre
GCF	Green Climate Fund
GC-ECD	Gas chromatography with electron capture detection
GC-FID	Gas chromatography with flame ionization detection
GCOS	Global Climate Observing System
GFCS	Global Framework for Climate Services
GGMT	Greenhouse Gases and Measurement Techniques
GHG	Greenhouse gas
GOLLUM	Global Oxygen Laboratories Link Ultraprecise Measurements
GUM	Guide to the Expression of Uncertainty in Measurement
GURME	GAW Urban Research Meteorology and Environment
IAEA	International Atomic Energy Agency
IAGOS	In-Service Aircraft for a Global Observing System
ICOS	Integrated Carbon Observation System
ICP	Intercomparison Programmes
IG^3IS	Integrated Global Greenhouse Gas Information System
IRMM	Institute for Reference Materials and Measurements

IRMS	Isotope ratio mass spectroscopy
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JCGM	Joint Committee for Guides in Metrology
JMA	Japan Meteorological Agency
JRAS	Jena Reference Air Set
KIT/IMK-IFU	Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Atmospheric Environmental Research
KMA	Korea Meteorological Administration
KRISS	Korea Research Institute of Standards and Science
LSCE	Laboratory for Sciences of Climate and Environment
LSVEC	the reference material (Li-carbonate) introduced by Coplen et al. (2006) as the second anchor on the VPDB scale, with $\delta^{13}C$=-46.6 ‰, to be used for synchronizing the $\delta^{13}C$ scale-calibration over the range +1.95 ‰ to -46.6 ‰. This synchronization is known as the 2-point data normalization.
MBL	Marine Boundary Layer
MPI-BGC	Max Plank Institute for Biogeochemistry
MRA	Mutual Recognition Arrangement
NACP	North American Carbon Program
NAP	National Adaptation Plans
NARCIS	Pure CO_2 in glass ampoules prepared by H. Mukai (Mukai, 2003)
NBS19	primary reference material (marble Ca-carbonate, with ^{13}C = 1.95 ‰ and $\delta^{18}O$ = -2.20 ‰) used for the realization of the VPDB scale and VPDB-CO_2 scale, by means of NBS19-CO_2 gas produced by reaction with H_3PO_4 under specified standard conditions. In 2016, a replacement for NBS19, IAEA-603 (also marble Ca-carbonate) was released by the IAEA. Some amounts of NBS19 remaining at the IAEA and potentially at some user labs are still valid as RM.
NDA	National Designated Authorities
NDC	Nationally Determined Contribution
NDIR	Non-Dispersive Infrared (spectroscopy)
NIES	National Institute for Environmental Studies
NIST	National Institute of Standards and Technology
NIWA	National Institute of Water and Atmospheric Research
NMHS	National Hydrometeorological Service
NMI	National Metrology Institutes
NOAA	National Oceanic and Atmospheric Administration
NPL	National Physical Laboratory
OA-ICOS	Off-axis Integrated Cavity Output Spectroscopy
PCTFE	Polychlorotrifluoroethylene
QA/QC	Quality Assurance & Quality Control
QCLS	Quantum Cascade Laser Spectroscopy
QMS	Quality Management System
RM	Reference Material
RR	Round Robin
SAG	Scientific Advisory Group
SBSTA	Subsidiary Body for Scientific Technological Advice
SI units	Système international (d'unités)
SIO	Scripps Institution of Oceanography

SLAP/SLAP2	Standard Light Antarctic Precipitation - RM water to be used for 2-point data normalization at negative δ^2H and δ^{18}O.
SOP	Standard operating procedure
SRM	Standard Reference Material
TCCON	Total Carbon Column Observing Network
TT	Target Tank
UBA	German Environment Agency
UEA	University of East Anglia
UNFCCC	United Nations Framework Convention on Climate Change
USGS	United States Geological Survey
VIM	International Vocabulary of Metrology
VPDB	Vienna Pee Dee Belemnite - the international conventional scale used to express δ^{13}C and δ^{18}O measurement results relative to the (non-existing) artefact VPDB. The VPDB δ^{13}C and δ^{18}O scale is realized through the metrological reference material NBS19 (now replaced by IAEA-603), see above. The VPDB-CO_2 scale is used to express δ^{18}O of CO_2 gases.
VSMOW	Vienna Standard Mean Ocean Water - the international conventional scale used to express δ^2H and δ^{18}O measurement results (excluding δ^{18}O of carbonates and CO_2 gases).
VURF	Vacuum Ultraviolet Resonance Fluorescence Spectroscopy
WCC	World Calibration Centre
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization

ANNEX V

WORKSHOP PROCEEDINGS

QUALITY ASSURANCE IN STABLE ISOTOPE MEASUREMENTS: THE CURRENT SITUATION AND FUTURE NEEDS

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Introduction

It is well recognized that systematic observations of the atmospheric greenhouse gases (GHGs) CO_2 and methane are needed in order to understand regional and global GHG budgets and their changes. In addition, stable isotope signals of CO_2 and methane provide signals which are widely used as "source" signatures for data interpretation. Interpretation of observed GHG signals, gradients and trends is based on global atmospheric models which include data from different laboratories, different stations and different years. The datasets have to be fit-for-purpose, namely to be comparable (be on the same scale) and compatible (be of the same data quality). Thereafter, data compatibility targets have been introduced and agreed upon ([1], also see GGMT-2017 Recommendations); in the GAW Implementation Plan 2016-2023 [2] these are called Data Quality Objectives (DQOs). The problem is that compatibility targets for air-CO_2 and methane stable isotopes are the same as - or very close to - the best analytical uncertainty currently achieved. This makes the task to achieve these targets extremely complex.

Furthermore, the desired compatibility for stable isotopes for air-CO_2 have never been demonstrated, either by comparison on flask air samples or by Round Robins (RRs) on pure gas mixtures in high pressure cylinders ([3] and Session 4.1 in GGMT-2017). Though in 2009 CCL-isoCO2 has introduced the JRAS-06 scale-realization for $\delta^{13}C$ and $\delta^{18}O$ based on CO_2 mixtures (this aims to provide harmonized calibrations on the artefact-based interactional VPDB-CO_2 scale), it was recognized that not all laboratories participating in RR-5 and RR-6 are on this scale-realization (Session 4.1 in GGMT-2017].) This fact may in some degree explain the discrepancies observed in RR-5 an RR-6. At the same time, this underlines the need for QA and World Calibration Centre (WCC) to be established. Similar, the comparison for methane isotope results demonstrated discrepancies up to 0.5 ‰ for $\delta^{13}C$ and 13 ‰ for $\delta^{2}H$ [5] which are 25 and 13 times their respective compatibility targets [1]; neither CCL nor WCC for methane isotopes do not exist.

The above situation has called for a careful analysis of stable isotope calibrations and the need to establish Quality Assurance (QA) for stable isotopes was presented at GGMT-2017 [5]. QA is a necessary part of GAW-WMO observational system for GHGs and it is designed to guarantee the data quality over years [2]. All that triggered discussions after GGMT-2017, and several needs for improvements were articulated in the GGMT-2017 Recommendations (Session 4). The implementation of these recommendations will require joint efforts by analytical laboratories, CCL-isoCO2 and the IAEA, with potential involvement of the metrology community (BIPM and NMIs).

The manuscript below gives the analysis of the situation and describes why the QA approach developed for GHG concentration measurements (i.e. for CO_2) cannot be applied to stable isotope measurements.

NOTE: The terminology used here aims to describe hierarchical levels of gas standards both for CO_2 concentrations and for stable isotopes. It is adapted from GGMT-2017 Recommendations and GAW-WMO Implementation Plan [2]. In particular, the term "tertiary standards" is used for gas-standard mixtures to be distributed to analytical laboratories (see below and Fig. 1). This reflects the fact that secondary gas standards prepared by corresponding CCLs are designed for the scale propagation (from primaries) and drift monitoring purposes, and not for distribution. Thus, the terms "secondary" and "tertiary" simply reflects their hierarchical levels, including the position in uncertainty propagation schemes. We stress: the use of terminology in the area of stable isotope RMs (in the form of solids materials) is different; tertiary level materials often correspond to in house-lab standards.

1. Major differences in calibration approaches for CO_2 concentrations and CO_2 stable isotopes

There is a fundamental difference in scale-definition and scale-realization approaches for GHG concentration measurements and stable isotope measurements. Namely, the WMO CO_2 X2007 volumetric scale (volume-to-volume ratio) is realized based on the primary method which allowed to make a set of 15 CO_2-in-dried-air primary standard mixtures (the highest scale-realization) linked to SI (volume, T & P). The method is the anchor of the scale and it can be used to prepare new mixtures of desired CO_2 concentrations. Besides, gravimetric CO_2 mixtures can be prepared independently, in order to verify the scale realization based on CO_2 volumetric mixtures.

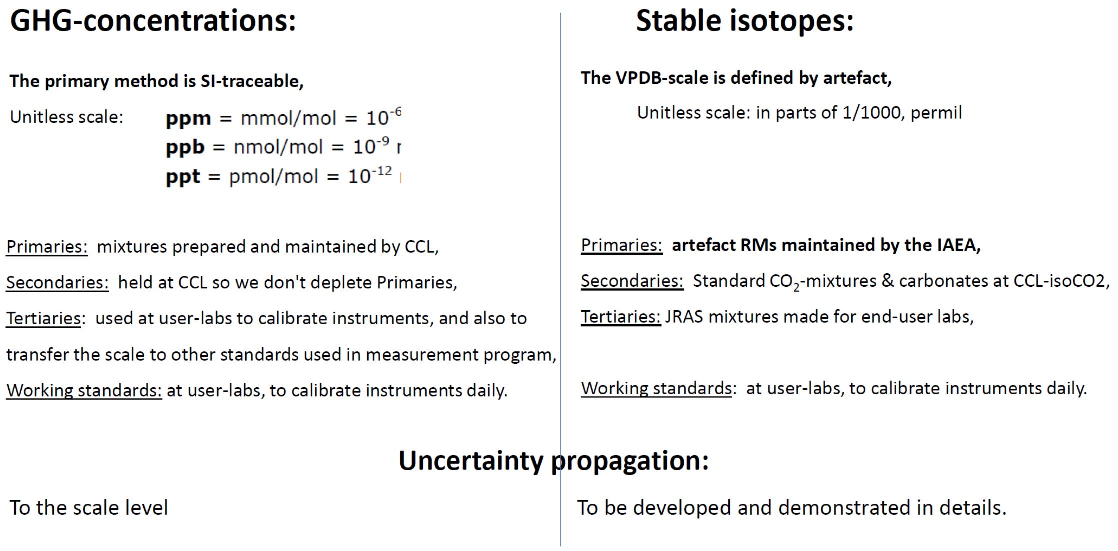
In contrast to the concentration scale, the VPDB-scale for $\delta^{13}C$ and $\delta^{18}O$ (see Chapter 4) is an artefact-based scale which means it is defined based on an historical artefact and realized by using artefact RMs. Notably, there is no primary method and CO_2 preparation with a desired isotope composition is not directly possible. To synchronize the calibration range, the principle of 2-point data normalization was introduced [6], which also belongs to the highest level of the scale realization (see Session 4 in GGMT-2017). The primary RM NBS19 used for the scale-definition and for many years also for the highest scale-realization [7] is exhausted and replaced by IAEA-603 in 2016.

The major aspects of the scale-definition, scale-realization and calibrations for GHG concentrations and stable isotopes are listed in Table 1. In particular, there is no primary method to be used independently to realize or verify $\delta^{13}C$ and $\delta^{18}O$ values of artefact-based scale-realization. Thereafter, verification of any drift is very difficult.

Table 1. Differences in calibration approaches for concentrations and for isotopic ratios.

Relevant parameters	*CO_2 concentration measurements*	*Stable isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ for CO_2*
Scale definition	Volumetric scale (volume-to-volume ratio in dry air) is linked to SI.	VPDB-scale for $\delta^{13}C$ and $\delta^{18}O$ is artefact-based, defined based on historical artefact NBS19.
Highest scale realization	Primary method used to prepare primary 15 CO_2 mixtures (the range of 250 to 520 mmol/mol) and link their volumetric ratio to SI (volume, T & P). Based on the primary method, new primary mixtures of desired CO_2 concentration can be prepared.	Artefact primary RM used for the scale realization is maintained by the IAEA. In 2016, IAEA-603, a replacement for NBS19 (used as primary RM since 1987) was introduced. VPDB-scale is not linked to SI and primary method does not exist. This means - CO_2 of desired $\delta^{13}C$ and $\delta^{18}O$ cannot be prepared independently from artefact RMs.
Units	mmol/mol, volumetric scale.	1/1000 part (permil) relative to $^{13}C/^{12}C$ of VPDB scale-defining artefact.
Verification of the calibration range.	Based on the primary method. 15 CO_2 mixtures covering the range of 250 to 520 mmol/mol) prepared by CCL; new mixtures of desired concentration can be prepared.	Artefact-based. The 2-point data normalization for all $\delta^{13}C$ data [7], to be based on international RM LSVEC which was introduced as the 2nd anchor of the VPDB scale. Given 2nd scale-anchor LSVEC is found to have drifting $\delta^{13}C$, other available RMs are recommended to be used for 2-point data normalization (Session 4 in GGMT-2017 and [8]).
Hierarchy of standards for GHG observations.	Scale-definition - based on SI. Primary mixtures prepared at CCL, to be used for calibration transfer to secondaries and monitoring of drifts. Several secondary mixtures – for calibration transfer and monitoring of drifts. Numerous tertiary mixtures aimed at calibration transfer in user-labs. Working standards for daily operation at user labs.	Scale-definition - linked to historical artefact RM. Primary RM (artefact) maintained by the IAEA. IAEA-603, replacement for NBS19 was introduced in 2016; the 2nd scale anchor is currently not available. Secondary level materials – such as other carbonate reference materials and also standard-carbonates and standard-CO_2 mixtures at CCL-isoCO2 are characterized against primary RMs. Tertiary level mixtures (JRAS mixtures in 5L flasks at 1.7 bars) aimed at calibration transfer in user-labs. Working standards for daily operation at user labs.
Analyte gas	CO_2 mixtures in dry air.	Pure CO_2 extracted either by H_3PO_4 from carbonates or cryogenically extracted from CO_2-mixtures or from air. In some cases, pure CO_2 is used without preparation septs (NIST RMs 8562-8564, NARCISS CO_2)

Purity	Pure gases used for primary CO_2 mixtures.	High purity CO_2 required to avoid isobaric interferences. Low water traces are critical to maintain $\delta^{18}O$ in CO_2.
Means to verify calibration and absence of drifts.	Careful cross-checks of several mixtures prepared (primary and secondary ones), preparation of new primary mixtures at CCL based on the primary method. Preparation of gravimetric mixtures is possible.	Monitoring of drift of primarily RMs is very complex, no way to prepare desired isotope composition independently as based on the primary method (no primary method exists). Absence of drift for secondaries can be verified only by new chemical extraction of CO_2 from other (numerous) aliquots of primary RMs.
Scale transfer	Based on the hierarchy of standards, see above.	
Uncertainty propagation	To be based on the traceability chain. In practice, this shall be based on the uncertainty assigned by CCL to the calibration transfer (tertiary) mixtures distributed to analytical laboratories and include uncertainty of all measurement steps involved.	
Levels of uncertainty propagation.	To the level of the primary method (means – not including its uncertainty) or to the SI level. Given the same primary method is always in use, the first method is sufficient to assess the data compatibility in time.	To the level of the VPDB scale which includes the uncertainty of primary international RMs used for the scale realization (NBS19 or IAEA-603) and also the second RM used for the 2-point data normalization).
Uncertainty propagation scheme.	Well established.	To be demonstrated, shall include all the uncertainty components related to instrumental corrections and all CO_2 extraction steps involved.



GHG-concentrations:

The primary method is SI-traceable,

Unitless scale:
ppm = mmol/mol = 10^{-6}
ppb = nmol/mol = 10^{-9}
ppt = pmol/mol = 10^{-12}

Primaries: mixtures prepared and maintained by CCL,
Secondaries: held at CCL so we don't deplete Primaries,
Tertiaries: used at user-labs to calibrate instruments, and also to transfer the scale to other standards used in measurement program,
Working standards: at user-labs, to calibrate instruments daily.

Stable isotopes:

The VPDB-scale is defined by artefact,

Unitless scale: in parts of 1/1000, permil

Primaries: **artefact RMs maintained by the IAEA,**
Secondaries: Standard CO_2-mixtures & carbonates at CCL-isoCO2,
Tertiaries: JRAS mixtures made for end-user labs,
Working standards: at user-labs, to calibrate instruments daily.

Uncertainty propagation:

To the scale level

To be developed and demonstrated in details.

Figure 1. Major differences in calibration approaches for CO_2 concentration measurements and CO_2 stable isotopes.

2. Relationship between data compatibility targets and the data uncertainty

Generally speaking, discrepancies in any data comparison cannot be evaluated for their significance, if data uncertainty (propagated to the scale level) is not provided. Besides, data compatibility targets shall imply its relationship with the target uncertainty; this target uncertainty is currently not established.

There are several ways to demonstrate data compatibility. Direct lab-to-lab comparison on the same material(s) can help to assess the data compatibility for the year of 20XX. The discrepancies observed in RRs do not include flask sampling and storage effects (notably, RRs that do not guarantee absence of bias in calibrations). (Note-1: when data uncertainty is not fully estimated, results are hardly possible to compare. Note-2: the magnitude of discrepancies depends on the selection of reference laboratory).

When data compatibility has to be demonstrated over many years, one cannot guarantee absence of drifts in RR cylinders and/or also absence of calibration drifts at participating laboratories. The only way to demonstrate data compatibility over years is to stay consistently on the same scale and the same scale-realization, avoiding any drifts. In case of CO_2 concentration mixtures, this can be verified by cross-check among several primary mixtures at CCL including their secondary (surveillance) mixtures. The most important is preparing new primary mixture(s) based on the primary method (see Table 1).

For the stable isotopes the situation is different. Namely, the CCL-isoCO2 cannot prepare primary mixtures of any desired $\delta^{13}C$ and $\delta^{18}O$ (primary method for stable isotopes does not exist) and is therefore limited to reproduce isotopic values of existing reference materials. Other independent methods do not exist (such as gravimetric CO_2 mixites be used to verify volumetric CO_2 scale-realization). The only way to demonstrate absence of drift of CCL-isoCO2 materials (secondaries) is to make regular re-calibration against primary international RMs which stability and homogeneity has to be carefully and independently assessed by the RM producer (by IAEA, NIST, USGS or others).

Notably, both CO_2 extraction from primary RMs by carbonate-H_3PO_4 reaction as well as mixture preparation involves numerous and sophisticated steps. The uncertainty shall be prorogated to the VPDB scale-level and include the uncertainty of primary RMs or other international RMs in use as well as the uncertainty of all corrections and preparation and other steps involved. Besides, independent verification of calibration-transfer mixtures prepared at CCL-isoCO2 by independent body is necessary, in order to demonstrate the absence of any unrecognized drifts/biases in the scale realization at CCL-isoCO2 (see GGMT-2017, Session 4).
Next, data discrepancies shall be considered as significant (or not significant) when discrepancies exceed the uncertainty of the difference. In case of CO_2 concentrations as long as realization of the primary method is not changed (hardware and its tests), the comparability can be linked to the uncertainty propagated to the level of this primary method, not to SI.

3. Quality Assurance

QA is a necessary part of GAW-WMO observations for GHGs and it is designed to guarantee the quality of observational data and data compatibility over years [2]. QA system for GHG concentrations is well established and is linked to the availability and use of the primary method at CCL (Fig. 2).

In contrast to, QA system for CO_2 and methane stable isotopes shall be established, keeping in mind the major differences outlined above. Fig. 3 illustrates the major differences and the gaps, these include:

- Absence of WCC, QA/SAC as well as SOPs harmonized among all GAW laboratories (for daily measurements, calibrations, uncertainty estimations).
- No performance audits.
- No trainings and workshops aimed to knowledge dissemination.

As a part of QA system, general requirements for CCL and WCC [1, 2] have to be addressed.

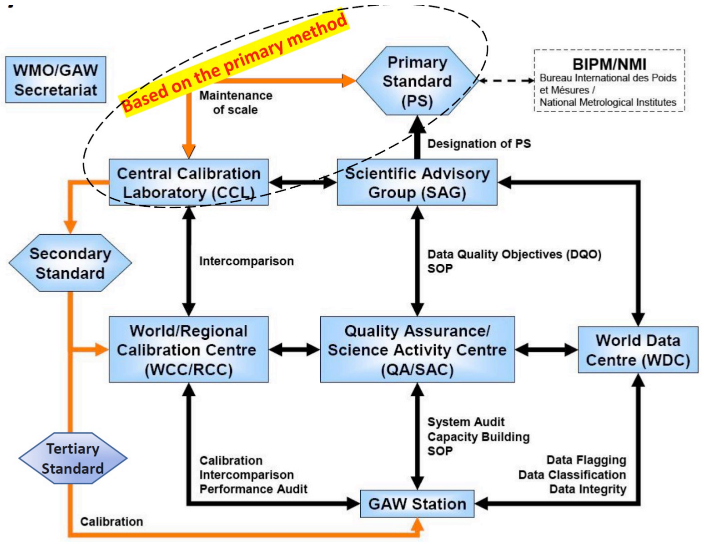


Figure 2. Quality Assurance scheme for GHG concentration measurements (adapted from [2]).

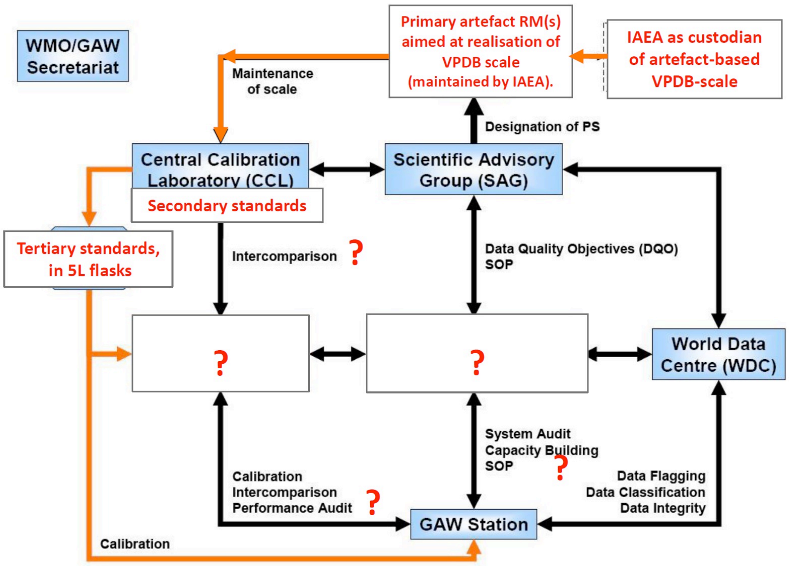


Figure 3. Quality Assurance scheme for CO$_2$ isotopes, to be developed (adapted from [5]). Comparison with Fig. 2 helps to recognize differences (text marked in red) and identify existing gaps (shown by question-marks).

Summary and outlook

- In contrast to GHG concentration scales (e.g. WMO CO_2 scale) which are SI traceable, the scale-definition for stable isotopes and the highest scale-realization (primary RMs) are artefact-based. There is no primary method to prepare CO_2 of desired $\delta^{13}C$ and $\delta^{18}O$ composition independently from these RMs. This situation implies principal differences in the approaches to be used at CCL-isoCO2 for the scale realization and also for QA schemes. In particular for the artefact-based stable isotope scale, it is difficult to verify drifts, if any and to verify the scale-span range. Particularly, validation of zero-drifts of primary RMs and other international RMs in use is the unique role of scale custodian which is fulfilled by the IAEA (and potentially involving other expert laboratories).
- The principles of calibration-transfer for CO_2-concentration scale transfer and the VPDB scale transfer (CO_2 stable isotopes) are very similar and includes a hierarchy of standard gas mixtures.
- The Quality Assurance for stable isotopes shall be developed and shall include: establishing WCC, independent verification of the calibration-transfer mixtures prepared by CCL-isoCO2, establishing QA/QC at all levels, creating SOPs for analytical practices (mainly focused on calibrations, daily measurements and uncertainty propagation). Besides, performance audits have to be developed, and the target uncertainty to be established.
- As a part of QA system, uncertainty propagation scheme(s) shall be established for mandatory use by all laboratories to ensure data comparability. The combined uncertainty provided by analytical laboratories shall be based on the traceability chain and be propagated to the VPDB scale level. The target uncertainty for stable isotope data shall be established, and data discrepancies demonstrated by RRs shall be analysed based on the target uncertainty.

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GREENHOUSE GASES: BACKGROUND CONCENTRATIONS IN BRAZILIAN COAST

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1. Introduction

In Tropical areas, and specifically in the Atlantic Ocean, there are not enough measures on greenhouse gases (GHG), and Amazon Basin represent around 50% of the world's rainforest [1]. Understand the characteristic GHG concentrations in Tropical Global range on Atlantic Ocean is an important task for many studies to determine GHG balances. The motivation of this study was understanding better the typical background for Amazon Basin from the air masses that arrived on North and Northeast Brazilian coast, come from the Atlantic Ocean in the period 2006 to 2016.

2. Materials and methods

We started to collect air samples on the Brazilian coast in Arembepe/BA, Salinopolis/PA, Maxaranguape/RN then the site moved to Natal/RN, Camocim/CE, and it was started a newl place at Itarema/CE, where the inlet was installed in the top of a 100 m tower in the beach (see Figure 1 and Table 1).

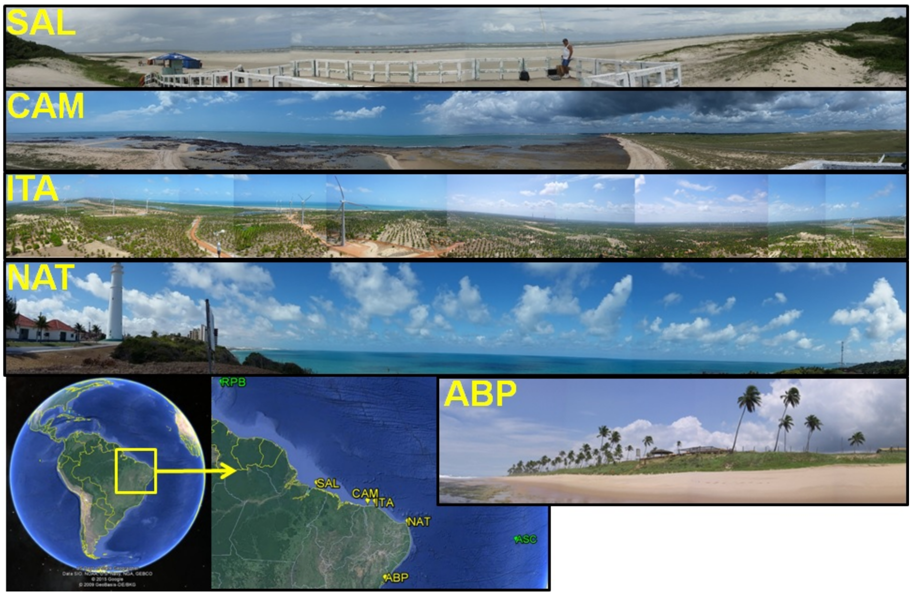

Figure 1. Study sites on the Brazilian coast

Table 1. Study sites on the Brazilian coast

Sites	*Code*	*Latitude*	*Longitude*	*Elevation*	*Opening*	*Closure*	*Status*
Salinópolis/PA	SAL	00º36’15.03”S	47º22’25.02”W	10 masl	01/2010	02/2017	Terminated
Camocim/CE	CAM	02º51’47.00”S	40º51’36.70”W	21.5masl	07/2014	-	Ongoing
Itarema/CE	ITA	02º55’57.11”S	39º50’38.49”W	115 masl	12/2016	-	Ongoing
Maxaranguape/RN	NAT	05º29’22.05”S	35º15’39.64”W	15 masl	05/2010	07/2015	Terminated
Natal/RN	NAT	05º47’42.77”S	35º11’07.10”W	87 masl	11/2015	-	Ongoing
Arembepe/BA	ABP	12º45’46.79”S	38º10’08.39”W	15 masl	10/2006	01/2010	Terminated

In each site, the air samples, with variable height were collected weekly between 12–13h local time by using a pair of glass flasks (2.5L) and a portable sampler. The samples were collected in pairs, like a quality assurance sample control. Initially, flasks were flushed with around 50 L of air (6 L/min) for conditioning the flasks in local conditions. The final sample pressure in flask is around 6-8 psi above ambient pressure. The air samples were analysed on the Greenhouse Gas Laboratory (LaGEE) at IPEN (until April 2015) and later at INPE/CCST. It was quantified the respective gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), sulphur hexafluoride (SF_6) and carbon monoxide (CO).

3. Results and discussion

Results showed that each site presents seasonality when compared to Ascension Island (ASC: 07º96'67.00"S; 14º0'00.00"W, South Atlantic Ocean) and Ragged Point Barbados (RPB: 13º16'50.00"N, 59º43'20.00"W, North Atlantic Ocean) global stations.

SAL and CAM presented higher CO_2, CH_4, SF_6 and CO concentrations between Jan-May because the ITCZ position is below the SAL and CAM latitude. NAT and ABP presented CO_2, CH_4, SF_6 and CO concentrations closer to the ASC global station. All sites presented N_2O concentrations between the ASC and RPB global stations. And all the sites, between Aug-Oct presented higher CO concentrations related to the biomass burning (see Figure 2). During this time, it is happening biomass burning in Africa, and the air masses came from the Atlantic Ocean can arrive in the study sites due atmospheric transport. The average concentration in the study sites on Brazilian coast for 2016 are showed in Table 2.

Table 2. Average concentration in 2016 in the study sites on the Brazilian coast

Average Concentration in 2016						
Sites	*Code*	*CO_2 (ppm)*	*CH_4 (ppb)*	*N_2O (ppb)*	*SF_6 (ppt)*	*CO (ppb)*
Salinópolis/PA	SAL	402.4	1825.4	329.5	9.0	96.1
Camocim/CE	CAM	402.6	1823.1	329.4	8.9	94.3
Natal/RN	NAT	402.1	1812.1	329.0	8.9	86.7

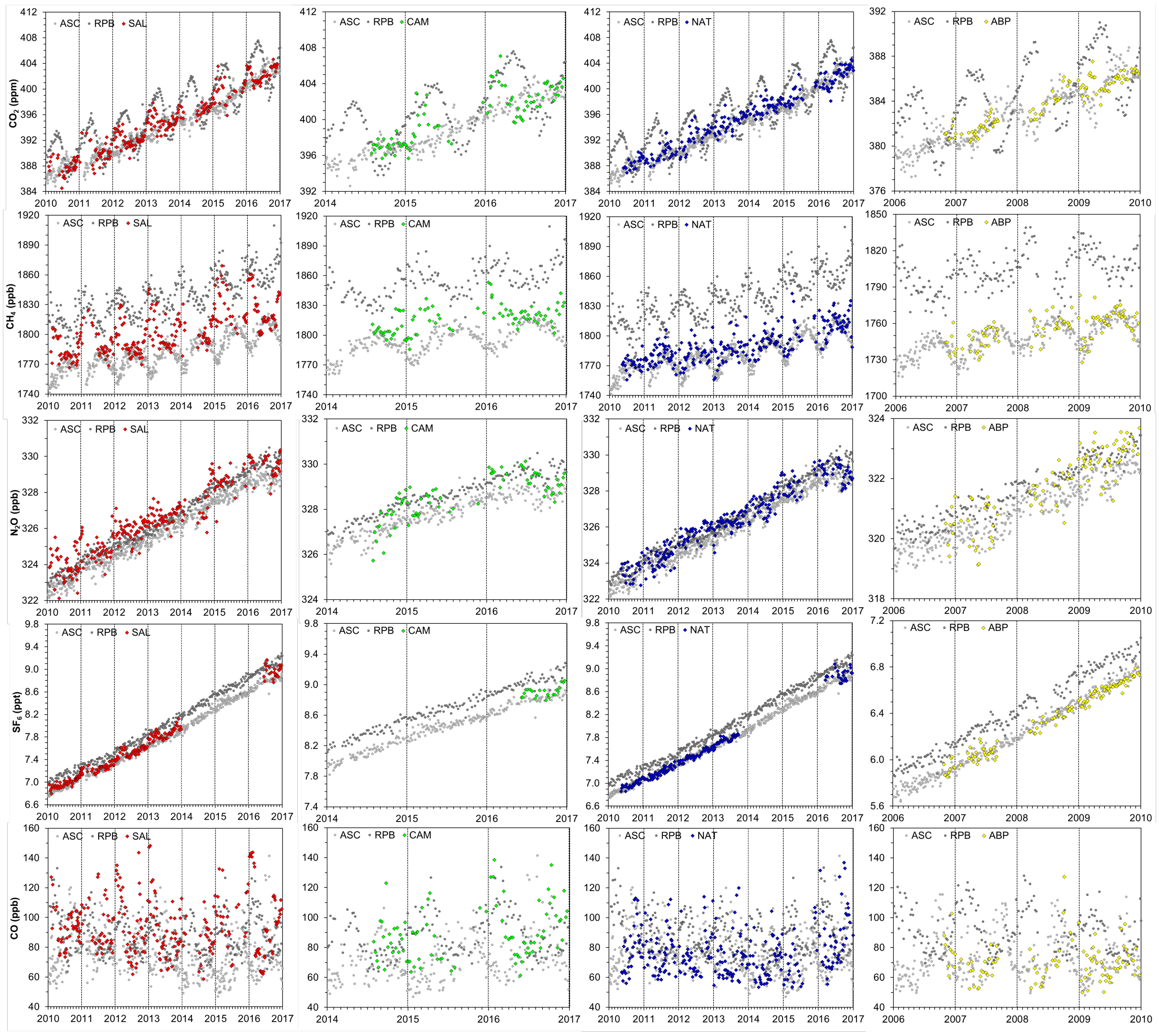

Figure 2. Temporal Series GHG concentrations in Brazilian Sites and global stations.

Simulations of backward trajectories by HYSPLIT model (using 240 hours) [2], allowed observing how each study site is influenced by global circulation and process like Intertropical Convergence Zone [3].

The ITCZ is below SAL latitude between Jan-May and on Jan-Apr is below CAM latitude, influencing the air masses that arrived at sites in this period. At SAL and CAM the air masses came from both North and South Atlantic Ocean depending on time of the year, but between Jun-Dec in SAL and May-Dec in CAM, the air masses came from only South Atlantic ocean. At NAT and ABP the air masses came from only South Atlantic Ocean all the year (see Figure 3).

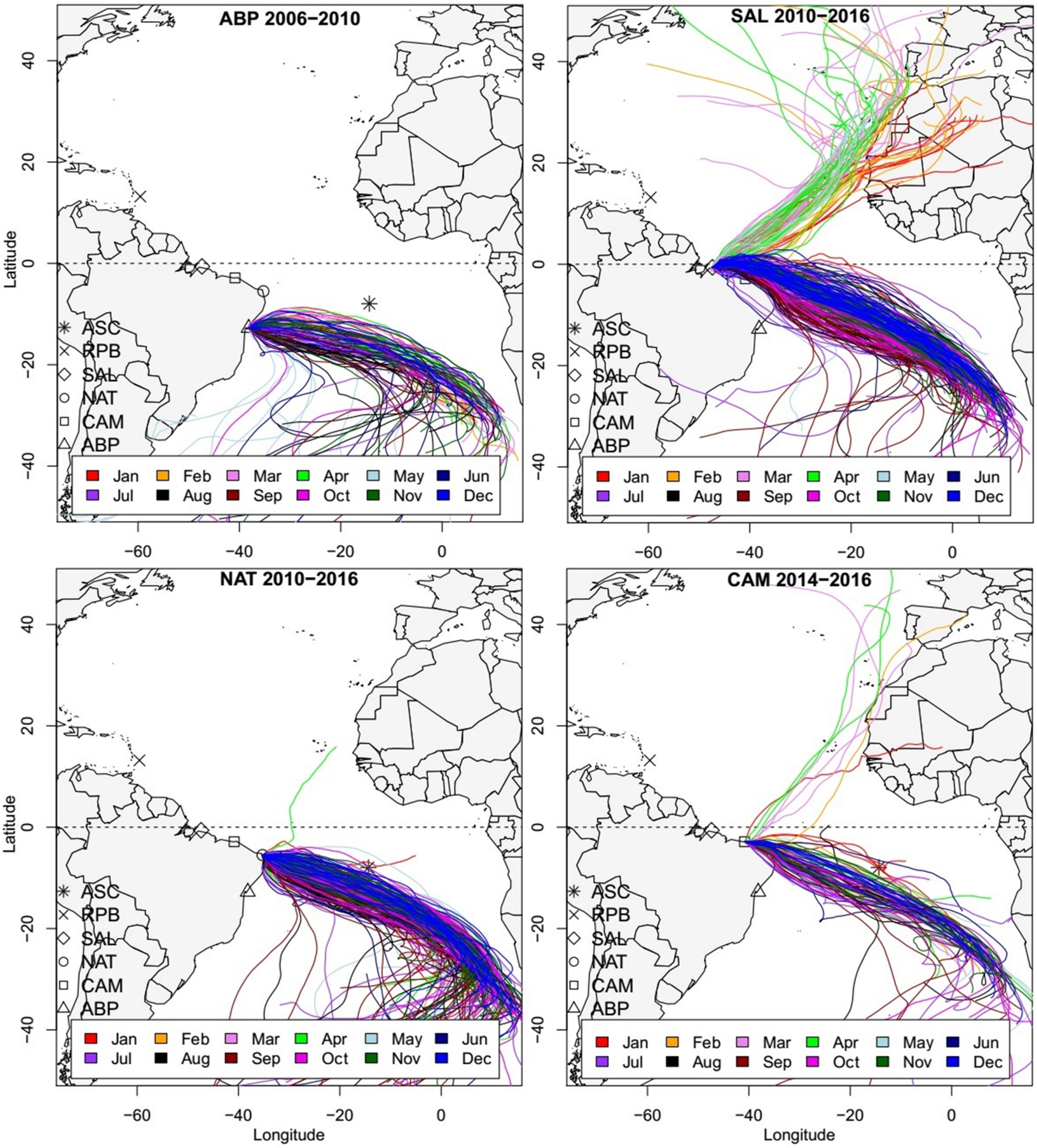

Figure 3. Backward trajectories of air masses in Brazilian sites

4. Conclusions

The latitudinal geographical position determines how the Brazilian sites can be influenced by the Intertropical Convergence Zone position. Simulations of backward trajectories allowed observing how each site was influenced by global circulation and process like ITCZ. At SAL and CAM the air masses came from both North and South Atlantic Ocean, depending on time of the year, and at NAT and ABP the air masses came from only South Atlantic Ocean. Sites below 5ºS showed homogeneous concentrations, indicating that in the South Atlantic Ocean the variability and gradients are lower than observed in the North Atlantic Ocean. Since 2006, the

GHG concentrations showed an increase over the years in the north and northeast Brazilian coast, following the global growth.

5. Acknowledgments

CNPq, NERC, FAPESP, MCTI, NOAA, Marinha do Brasil, Eólicas Itarema, INPE/CRN/LAVAT, INPE/CCST and IPEN.

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LONG TERM NITROUS OXIDE MEASUREMENTS OVER AMAZON BASIN USING SMALL AIRCRAFT

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1. Introduction

The Nitrous Oxide (N_2O) is the third most important natural greenhouse gas (GHG) on Earth, due to its atmospheric mixing ratio and global warming potential of around 300 times higher than the Carbon Dioxide (CO_2) in a hundred years scenario (WMO, 2016). The main sources of N_2O are the nitrification and denitrification processes in soil promoted by microorganisms; it is also emitted in oceans, in biomass burning processes and by industry. Around 40% of these emissions are from anthropogenic activities, two thirds of the soil emissions are originated in tropics and ~20% are from rainforest ecosystems, as the Amazon forest (WMO, 2016; Van Haren et al., 2005; Melillo et al. 2001). The Amazon rainforest has a total area of 8 million square kilometres, which ~5 million km^2 are in Brazilian territory (58,74% of Brazil's total area) and hosts one quarter of global biodiversity (Malhi & Phillips, 2005). It's one of the main rainforests in the world, corresponding to 50% of the total of this biome, however, human extractive activities in Amazon has been destroying the forest by wood cutting activities, forest conversion, agricultural and other resources exploration. The greatest part of GHG emissions in Brazil are from land use change, agricultural activities and biomass burning, these activities influence directly the N_2O emissions since they are its main sources.

2. Methods

In this study, natural air was sampled in glass flasks using small aircraft over four sites in the Brazilian Amazon Basin, as described in Gatti et al*.* 2014, in order to have a great quadrant to better understand the whole area: Alta Floresta (ALF; 8.80ºS, 56.75ºW), Rio Branco (RBA; 9.38ºS, 64.8ºW), Santarém (SAN; 2.86ºS, 54.95ºW) and Tabatinga (TAB; 5.96ºS, 70.06ºW), ALF, RBA and TAB sites started in 2010 and we still perform sampling in these sites, the last one (TAB) changed to Tefé (TEF; 3.39°S, 65.6°W) in 2013 due to technical problems. During a short period (2013-2015) we performed flights over Salinópolis (SAH; 0.76°S, 47.84°W) for comparison with background mixing ratios, which are the ones found in the global stations of Ascencion Island (ASC; 7.9°S, 14.4°W), Barbados (RPB; 13.2°N, 59.4°W) and Cape Point (CPT; 34.3º S, 18.4º E). The reason to use the information obtained in these stations is that the studied region has an atmospheric air circulation pattern where the air entering at the Amazon basin is dominated by trade-wind easterlies coming from the tropical Atlantic Ocean (Miller et al., 2007) in direction to Andes (West). The profiles are performed in a descendant helicoidally pattern in which a flask is sampled in a pre-determined altitude from top to bottom. The inlet was installed in the aircraft such the gases from its engine combustion wouldn't interfere in the sample, it was also installed a temperature and relative humidity sensor and also a GPS in order to register the conditions and positioning of each sample. The sampling system consists in two units, one containing two pumps and rechargeable batteries and another containing the glass flasks. It was chosen to sample between 12:00 and 13:00 local time because at this time of the day the troposphere is more stable, therefore providing a better repeatability of the atmospheric conditions. The analyses were performed by gas chromatography using an Electron Capture Detector (ECD), and a carrier gas containing 5% of methane in Argon, each glass flask is analysed individually, the analysis system uses a reference standard tank with a known concentration of N_2O, each flask result is compared with two shots of reference gas, one before and one after the quantification, so any external factors influences are minimized to improve the precision. The measurements in SAN started in 2000 and the quantification was done by NOAA laboratories until 2003, after this year the analysis started to being performed by our laboratory. This data is very valuable and can be used to calculate regional fluxes and help in the better understanding of the Amazon Basin role in the global N_2O emissions.

3. Results

The N_2O mixing ratios had enhanced along the years in the studied region, these results are presented in the figure bellow (Figure 1). The dots represent the average concentration found in each vertical profile while the lines ate the smooth curves of the concentrations found in the global stations situated in the Atlantic Ocean.

Both the mixing ratios found by our measurements and the ones measured in the global stations are increasing, this shows the relevance of the study of the N_2O emissions to better understand it since it’s an important GHG and directly affected by human activities.

It can be observed in Figure 1 the ranges and values vary along the sites and years, although, the growth rate found wasn’t so discrepant. This can be observed in Table 1.

Table 1. N_2O emissions Growth Rate for each site and the average for the whole Amazon Basin.

Site	*Growth Rate (ppb yr^{-1})*
ALF	0.83
RBA	0.77
SAH	0.87
SAN	0.81
TAB	0.83
TEF	0.73
Average	0.81

In Figure 2, it’s presented as examples, two time series of all flasks of each vertical profile sampled both in ALF and RBA. The ranges are from red (bottom of the profile) to blue (top of the profile). In this figure it’s possible to observe that in general the lower part of the profile (red dots) shows higher mixing ratios which indicates local emissions since the higher in altitude the sample is the farthest it represents. This too shows the relevance of this region in global N_2O emissions.

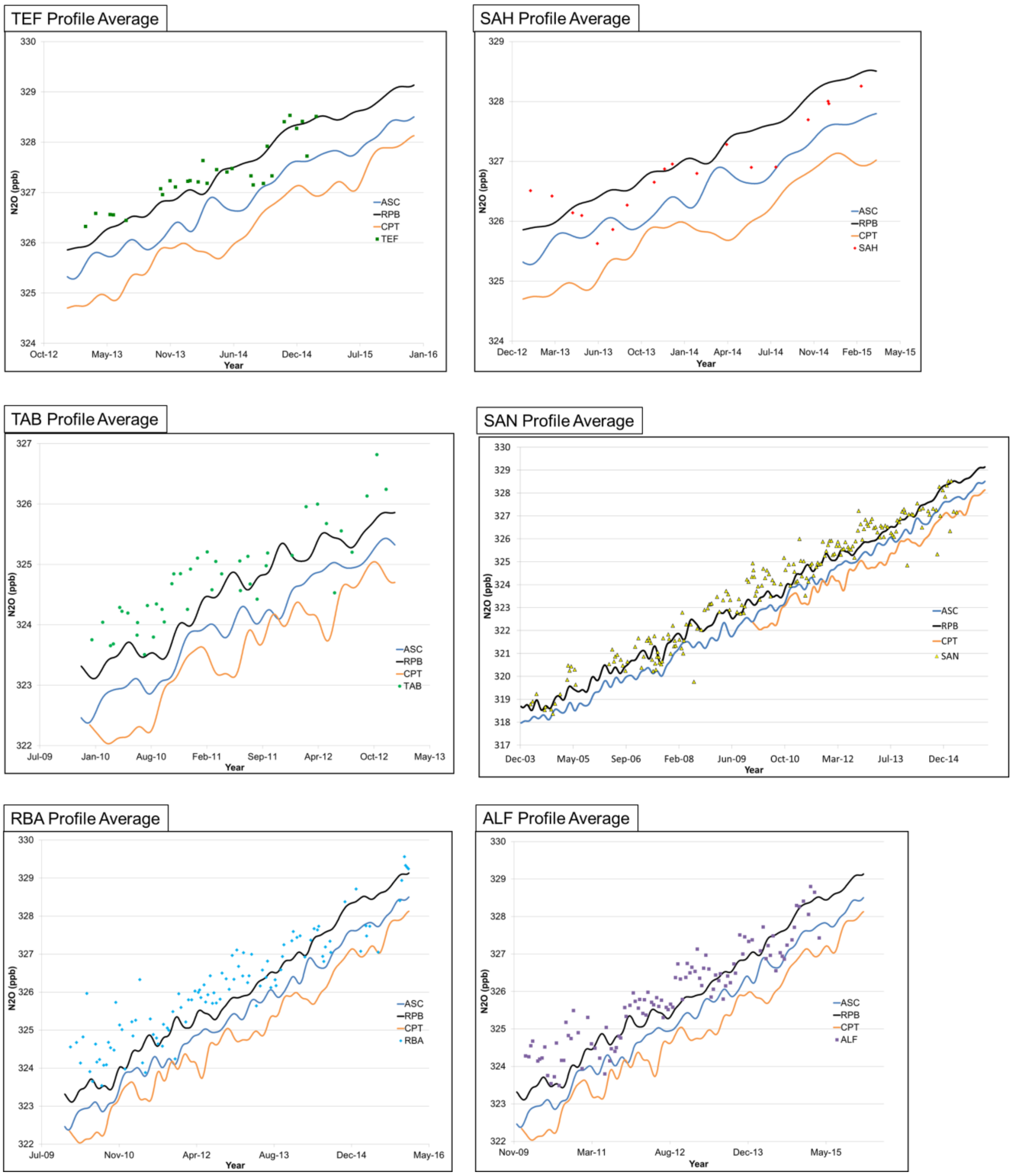

Figure 1. N_2O mixing ratios distributed by site per year. The dots represent the average mixing ratios found in each profile and the lines represent the smoothed mixing ratios of the global stations used for comparison for the whole period of study.

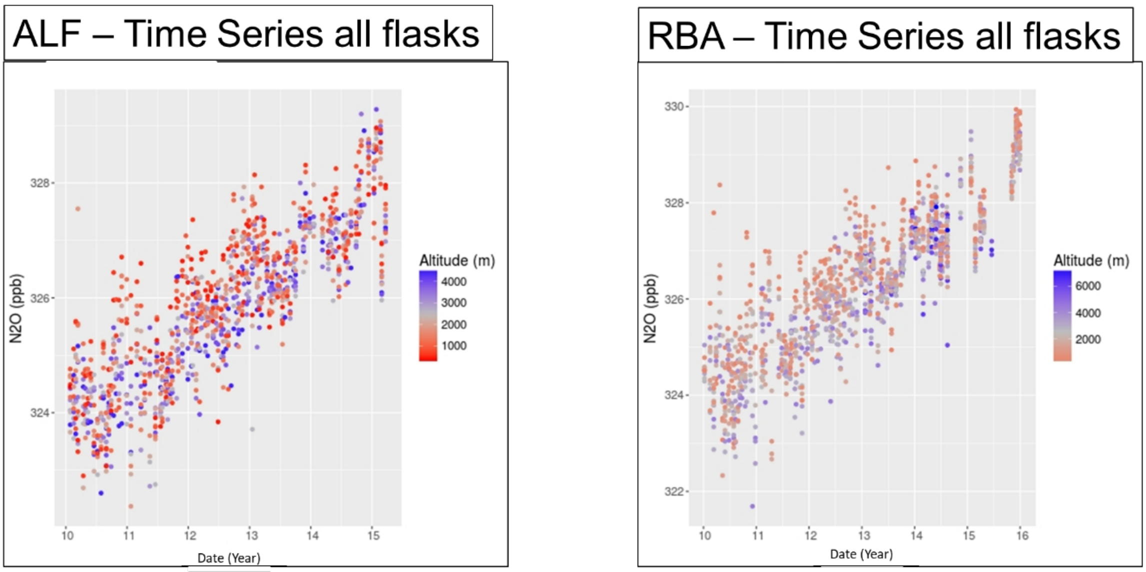

Figure 2. N_2O mixing ratios found for each flask for each profile divided by altitude ranging from red (bottom portion of the profile) to blue (highest portion).

4. Conclusion

The mixing ratios in all the studied stations have presented an increase along the years, varying from ~316 ppb in 2000 (not presented in this work) to ~330 ppb in the present days, *i.e*. a mean growth rate of ~0.81 ppb yr^{-1}, which is consistent with global data available where the growth rate for the past 10 years is around 0.89 ppm yr^{-1} (WMO, 2016).

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CARBON MONOXIDE MEASUREMENTS AS A BIOMASS BURNING TRACER AT THE AMAZON BASIN

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The tropical rainforests have an amount of carbon stored into its plants and soil comparable to half of the amount of atmospheric carbon contained at the atmosphere before the start of industrialization at the 18th century. Among the tropical regions, the Amazon forest covers the largest area and also hosts the largest carbon pool (~200 PgC), corresponding for 50% of its biome globally (1). Considering the capability of rapid release and the amount of storage carbon, there are surprisingly few studies of emission ratios (2) and, in order to elucidate the actual contribution and the carbon emission from biomass burning in the Amazon Basin, measurements of carbon monoxide are an important tool.

Over recent years, the Amazon Basin hydrological cycle has changed considerably which presented severe droughts in 2005, 2010 and 2015/2016, at the Figure 1 we can identify the variability at this cycle from 2010 until 2015. 2015 is likely the largest drought over the past 15 years. Another issue that has to be highlighted is the biomass burning. At 2004/2005 the number of fire hot spots reached its maximum followed by the same years of extreme drought, 2010 and 2015. 2011 had the fewest number of fire hot spots, but since 2013 a positive trend was identified, reaching the largest level in 2015.

Official Brazilian government information on deforestation rates based on remote sensing suggests an important reduction over the period from 2004 to 2012 (71% reduction on total). Deforestation then stabilized at a constant value and started to increase again slightly in 2016. Although according to these estimates deforestation has decreased strongly over the last decade, estimates of fire related carbon fluxes to the atmosphere estimated using regular atmospheric carbon monoxide concentration measurements indicate that there may be a discrepancy (Figure 2).

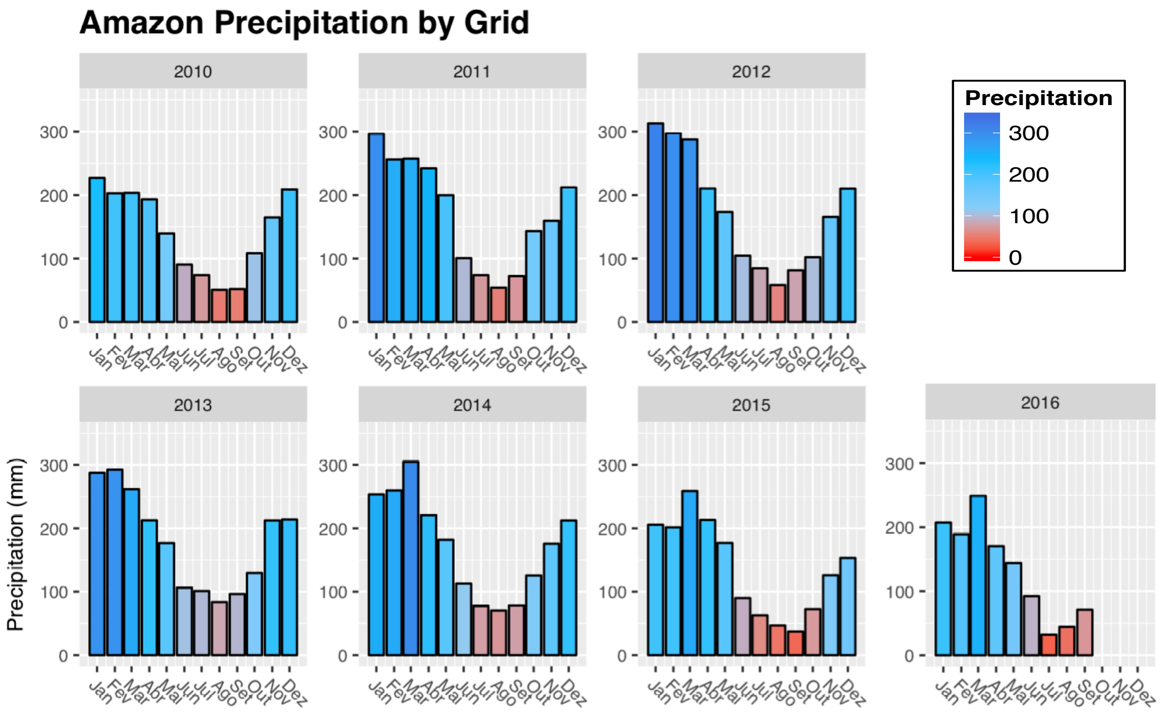

Figure 1. Precipitation results per year over the Legal Amazon area calculated by the automatics and conventional stations maintained by the National Institute of Meteorology (INMET).

These data do suggest a much smaller decrease, which lead us to believe that deforestation, as observed from satellite, is not the only process causing release of carbon by fires. Thus, understanding the relation between carbon emissions from biomass burning and climate, fire hot spots based on remote sensing and deforestation is important as it may reveal biases in remote sensing based estimates of deforestation. In turn, it may help to evaluate the effectiveness of actions to preserve the forests.

For this objective, were performed vertical profiles at 4 sites in the Amazon Basin (SAN - Santarém, TAB -Tabatinga, RBA -Rio Branco and ALF -Alta Floresta) two times per month over the period 2010-2013 and to calculate the CO flux it was applied the Column Integration Method(3). At the 4 locations were identified a correlation between the CO flux, precipitation and counts of fire spots.

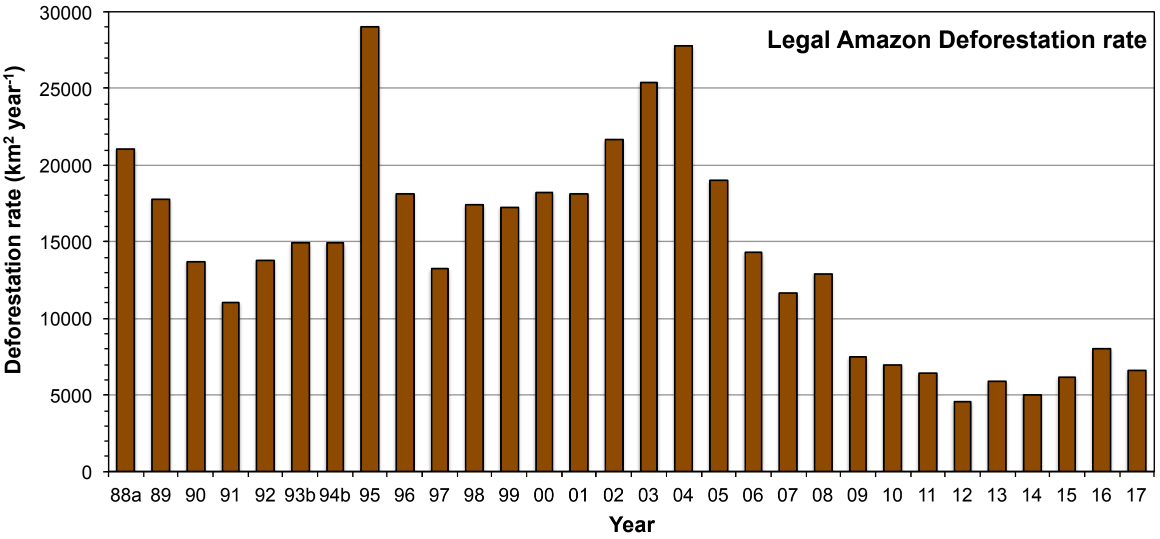

Figure 2. Official Brazilian Deforestation index

Source: PRODES - (http://www.obt.inpe.br/OBT/assuntos/programas/amazonia/prodes)

In the Figure 3 is presented a time series of the CO concentrations in parts per billion (ppb) in a scale color by altitude without any insource of calculation. It is possible to see that usually the highest concentrations occur bellow the boundary layer that is presented generally between 1000 - 1500 meters of altitude. Also, is possible to identify a clear trend of emission at the second half of the year (August to October), which corresponds the dry season. In 2010 was observed a great emission of CO in all sites followed by 2016, which we believe that happened as a reflex of the huge emission occurred in 2015. Unfortunately, 2016 it was not performed aircrafts profile at SAN and TEF and in 2015 the measurements were interrupted at April and returned in November at RBA and February 2016 at ALF.

In ALF, located at Arc of Fire (Arco do Fogo), was observed that the peak of CO emission coincides with the maximum of hot spots and precipitation decreases, thereby making evident the emission from the wet and dry season. This is the site where the highest concentrations of CO were observed and, unlike TAB and SAN, were determined a strong vertical mixing. At the sites, where there is a predominance of forest like TAB and RBA, the observed flux showed the same behaviour than ALF, however in a minor emission.

SAN, located in the Amazon northeast region, receives a great influence of anthropogenic emissions from the northeast Brazil region.

The relation between the concentrations of CO and CO_2 in the profiles was calculated, considering only the profiles with a clear plume to determine the emission ratio, where it was used only the portion of profile above 1.5 km, approximately the PBL (Planetary Boundary Layer). It was found a mean ratio of CO:CO_2, for the Amazon Basin of 57.5 ± 22.7. Each site showed a different result. The West sites of the Basin, with fewer anthropic impacts, had a higher and a similar ratio, in contrast to what was determined in Santarém.

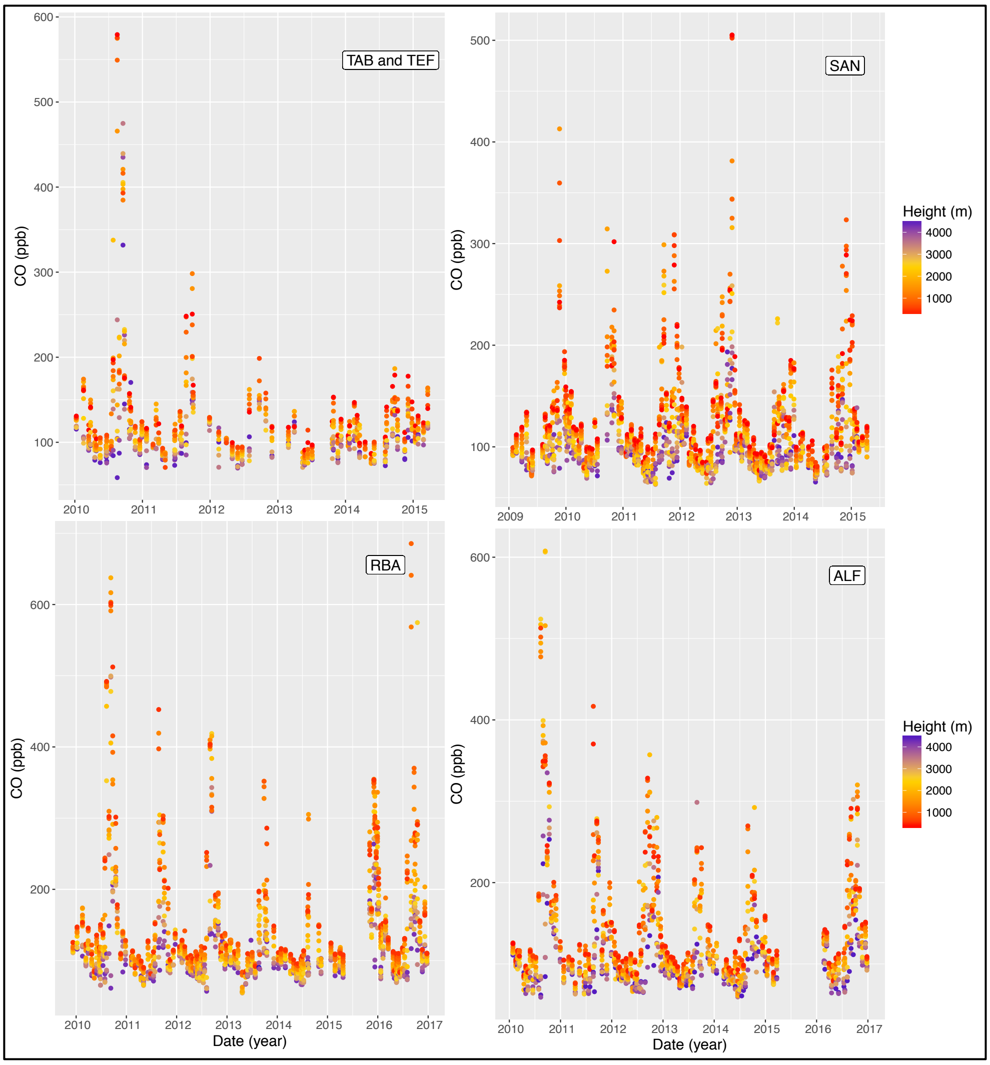

Figure 3. Concentrations of CO in ppb by site in a scale colour by altitude

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AMAZON GREENHOUSE GAS MEASUREMENT PROGRAMME

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1. Introduction

With the objective of understanding the role of the Amazon in the global carbon balance and the effect of the climatic variation in this balance, we developed a scientific strategy of GHG measures involving different scales, since local until regional scales, using measures with small aircraft performing vertical profiles, tower, flasks, satellite and FTIR. The activities started in 2003 by constructing a replica of NOAA/ESRL/GMD GHG Laboratory and installing it in Brazil in 2004. Since this time the places studied and the types of measures taken have grown to reach our goal.

Tropical land is a very poorly constrained component of the carbon cycle, although it is potentially very important because it hosts a very large fast releasable carbon pool in forests and soils potentially amenable to feedbacks with climate. The tropics are a poorly constrained component because until recently there have been very few lower troposphere greenhouse gas measurements that are regionally representative. Amongst the tropical land regions the Amazon is by far the largest and also hosting the largest carbon pools around 200 PgC.

According the Third National Communication of Brazil to UNFCC (2016), related to 2010 from the Ministry of Science, Technology and Innovation, the total anthropogenic emissions in 2010 was 1,554 Tg CO_2 eq, and in 2015 was 1,676 Tg CO_2 eq according the MCTIC (2017). Considering the regrowth of vegetation, in areas considered managed, generates CO2 removals, 2010 was 1,274 Tg CO_2 eq, and in 2015 was 1,368 Tg CO_2 eq.

The greenhouse gas (GHG) monitoring activities conducted firstly by IPEN/LQA from 2004 to 2015 (Atmospheric Chemistry Laboratory) and later by INPE/CCST/LaGEE conduct measurements in the Amazon Basin with light aircrafts and Brazilian surface samples at coasts. Our main objective is contributing to the understanding of the role of the Amazon in the Brazilian and global scenario of the global carbon balance. We report here a complete picture from the GHG vertical profiles measures, long-term programme, distributed in the 4 sites to represent entire Amazon Basin started 2000 at Santarem (SAN) and the other 3 sites RBA, ALF, TAB/TEF started January 2010, and until 2017 we performed around 600 vertical profiles over the Amazon Basin. The sampling Brazil Maps are presented in Figure 2.

This aircraft measurement programme over the Amazon Basin it is a result of international collaboration principally with NOAA and University of Leeds and others partners like University of Colorado, Sao Paulo, Wageningen, Groningen, Leicester, etc. This effort was funded by many research agencies like NASA, NERC, FAPESP, ERC, CNPq.

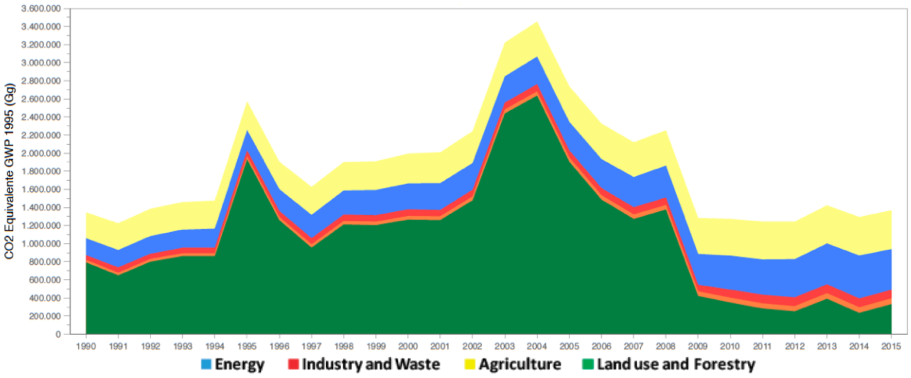

Figure 1. Brazil Greenhouse gas emissions in CO2 equivalent (Gg) by sector since 1990 until 2015 (MCTIC, 2017).

2. Aircraft measurement sites in Brazil

The aircraft measurement programme was started in 2000 with monthly/biweekly vertical profile sampling at SAN (2.86S 54.95W). At 2010, three more aircraft sites: TAB (5.96S 70.06W), RBA (9.38S 67.62W) and ALF (8.80S 56.75W). In 2013, we moved TAB site to TEF (3.39S 65.6W) and add two more aircraft sites with vertical profiles from 300m to 7300 m, at Salinopolis (SAH 0.60S; 47,37W) near the Atlantic coast and RBH at the same place then RBA, in the western Amazon. Until December 2017, LaGEE performed 731 vertical profiles. In all of the profiles CO2, CH4, N2O, CO and SF_6 were measured on between 12 and 17 flask samples, depending on site (Figure 2 aircrafts and coast sites).

In 2016, new measurements using FTIR (total Column Instrument) was initiated, with a partnership of BIRA-IASB / IFRO and INPE. The instrument is installed at IFRO campus at Porto Velho, Rondonia (8.74°S, 63.87°W). In 2013, we added two more sites in our programme with profiles from 300m to 7.3km, at Salinopolis (SAH 0.60S; 47,37W), near the Atlantic coast and RBH at the same place then RBA, in the western Amazon (Figure 2). These profiles are interesting to compare and validate satellite measurements over Amazonia and other important objectives with these high profiles is to answer one important question about what information we are losing above 4.4 km height and what is the concentration distribution between 4.4 and 7.3 km.

The analyses were made in a replica of NOAA GHG analysis system (MAGICC), installed in Brazil, São Paulo, initially at IPEN/CQMA/LQA and later (2015) at LaGEE/CCST/INPE. We follow the recommendations for quality assurance control and performer a weekly comparison programme between NOAA/GMD and INPE at NAT.

Figure 2. 4 aircraft sites TAB, RBA, ALF, SAN (0.3 to 4.4km) until 2010 and more 2 sites until 7.3km RBA and SAL with 3 coast sites SAL, CAM and NAT. TEF is the substitute of TAB site.
Brazilian GHG measurements Programme conducted by LaGEE/INPE laboratory.

3. Measurement methodology

Air sample was collected with portable flask sampling systems consisting of separate compressor and flask (PFP and PCP) units (Tans et al., 1996). GPS, temperature and relative humidity sensors have also been attached to the compressor unit. We used two kinds of flask units: one contains 17 (SAN) flasks and other 12 (RBA, TAB and ALF) with each 700 mL and pressurized to about 40psi. The flights consisted of one descending profile from 4500 m to 300 m. Profiles were usually taken between 12-13h local time, because this is the time when the boundary layer is close to being fully developed and stable. The profiles are made 2 times per month in the four places and in the two coast stations the sample is weekly. The locations for aircraft stations are: SAN (running since 2000), RBA (since Dec 2009), ALF (since Jan 2010), TAB (since Jan 2010 to 2012) and TEF (starting 2013) The actual two coast stations in Brazil: SAL (since Jan 2010) and NAT (since may 2010). Coastal studies are conducting actually at 3 sites: SAL (started 2010), NAT (started 2010) and CAM (started 2014).

4. Results and discussion

Taking advantage of the consistent trade winds that enter Amazonia from the Atlantic coast, a column integration technique is used to calculate fluxes for all gases (Miller et al., 2007; D'Amelio et al., 2009, Gatti et al., 2010 and 2014 and Basso et al., 2016). This technique implicitly accounts for emissions resulting from all biosphere-atmosphere exchange processes between the site and the coast, excepting some "leakage" (via convection) above 4.5 km asl. Usually at the 4 aircraft sites, during the wet season (generally December to June), it is observed uptake by the forest, because the profile mean below PBL (<1.5km) is lower than ASC and RPB mole fractions or near neutral due to mean profile being similar to the background. During the dry season, the profile mean below PBL is higher than ASC and RPB.

This period corresponds to biomass burning season at Amazon, where it is more intense between Augusts to October. The time series are shown in Figure 3.

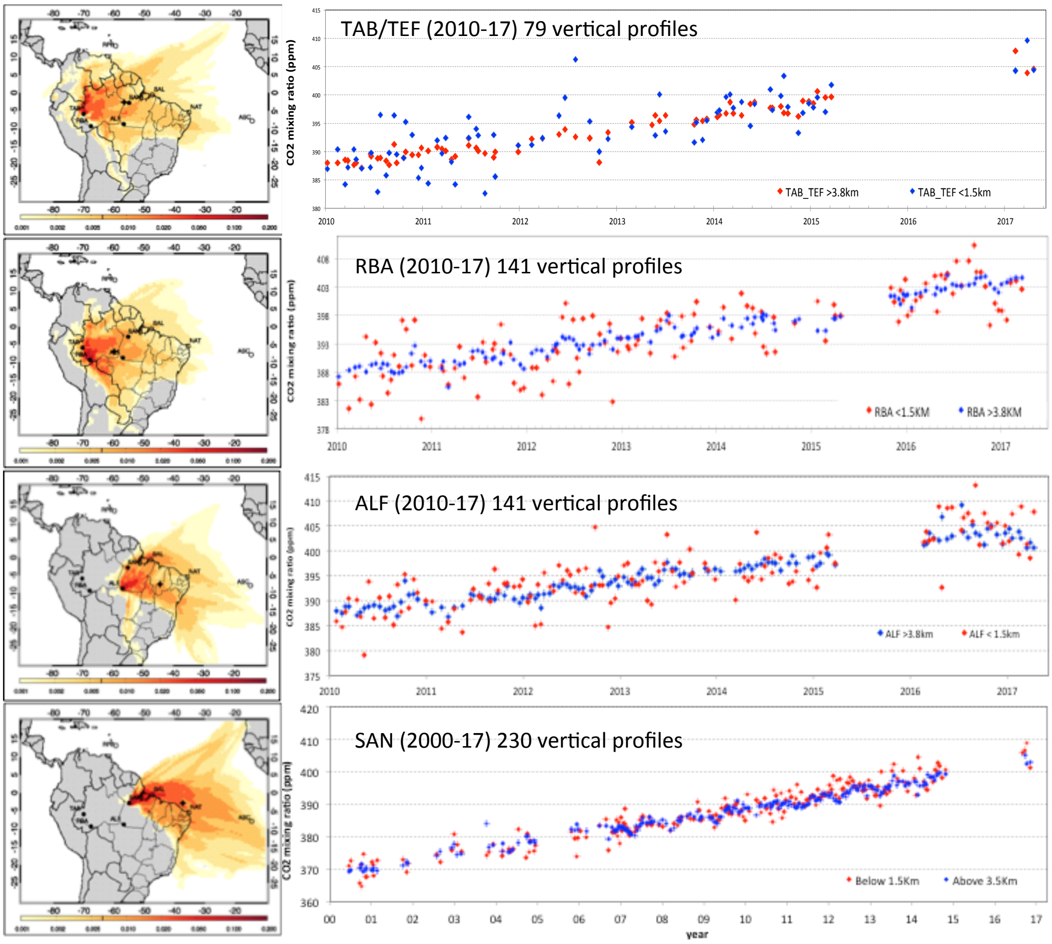

Figure 3. Time series for the sites (TAB/TEF, RBA, SAN and ALF), where red points is the mean concentration below PBL (<1.5km height) in the vertical profiles and blue points is the mean above 3.5km height. In the right side is the footprint area for each site calculated by Flexpart modelling.

5. Conclusions

The efforts to construct a Brazilian network are very important because of the great importance of Amazonia in understanding, and eventually predicting, the global carbon cycle and its feedbacks with climate. Also, it is an important tool to verify the inventories and compare the emissions and the supposed uptake from the forest. We observed very strong climate parameters correlation and impact in the Carbon Balance.

6. Acknowledgments

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AMAZON BASIN AND BRAZILIAN COAST SF_6 STUDY IN A 15 YEARS TIME SERIES

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1. Introduction

The sulphur hexafluoride (SF_6) is known as a potent long lived greenhouse gases and it is a synthetic gas with a millennia lifetime, about 3200 years[1], and has a Global Warm Potential 23500 times higher than the Carbon Dioxide (CO_2), according AR5-IPCC, 2014[2]. Due its very long lifetime, SF_6 emissions are accumulating in the atmosphere. Its global mole fraction increased nearly linearly in recent decades and in 2014 is about twice the level observed in the mid-1990s[3]. Its concentration is measure as parts per trillion (ppt) and increases almost linearly, like shown in Figure 1, implying that emissions are approximately constant. Since 1995 to 2017 the annual global increase is 0.27ppt SF_6/year (NOAA[4]).

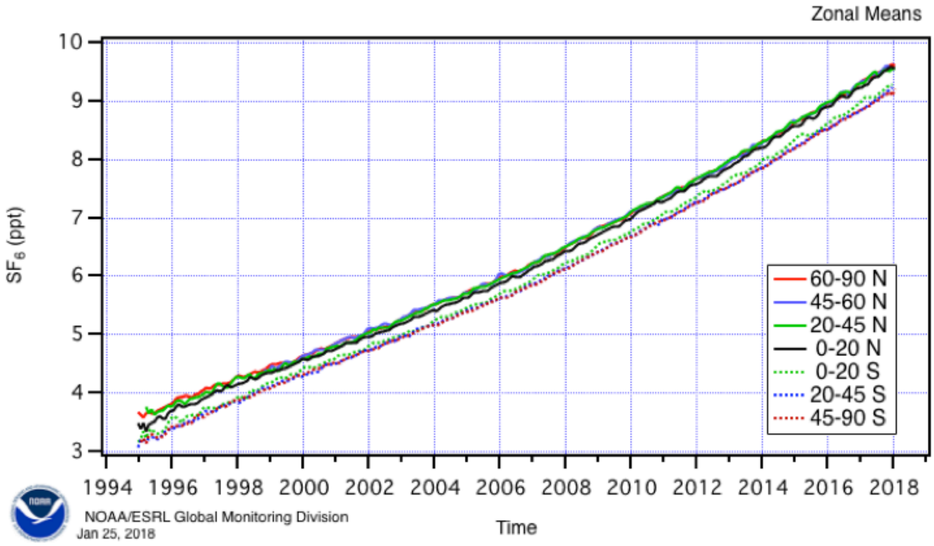

Figure 1. SF_6 global mean per latitude range from 1995 to 2017 (NOAA, 2018)

The total SF_6 Brazilian emission related to 2010 was 8.7 tons, which came from electrical equipment emissions, due to loss in equipment, especially during maintenance or disposal. Between 1990 and 2005, Brazil emissions of SF_6 decreased 63.5%[5]. Between 2005 and 2015[6], SF_6 Brazilian emissions decreased due to substitution using this gas in magnesium production by SO_2. According to the EDGAR database, Brazilian emissions for 2005 were 51.2 tons, which corresponds to 0.8% of the global emission estimate for this year[7]. Our interest in SF_6 mole fractions is to use this gas as a transport tracer to calculate CO_2, CH_4 and N_2O fluxes over the Amazon Basin.

The emissions of SF_6 in the Amazon Basin are considered non-existents and, a time series of 15 years has the potential to show the behaviour of this gas in a large area.

2. Methodology

SF_6 atmospheric measurements were started with vertical profiles using small aircrafts, since 2000 in Santarém (SAN: 02.8°S, 54.9°W), 2009 in Rio Branco (RBA: 9.3°S, 67.6°W), 2010 in Alta Floresta (ALF: 8.8°S, 56.7°W) and Tabatinga (TAB: 5.9°S, 70.1°W) and this site was substituted in 2013 by Tefé (TEF: 3.4°S, 65.6°W). All these sites located in Brazilian Amazon Basin (Figure 2) performed 2 vertical profiles per month with PFP 17 or 12 flasks. Since 2010, we started flasks measurements at two coast sites located at the Brazilian Atlantic coast: in Salinopolis (SAL: 0.6°S, 47.4°W) and in Natal (NAT: 5.5°S, 35.2°W). Figure 2 shows all the sites.

Figure 2. Sample sites located in Brazilian Amazon and Brazilian coast

3. Results and discussion

SAN is the site with the longest time series with more than 230 vertical profiles, RBA and ALF, performed around 150 vertical profiles in each site, TAB/TEF performed around 100 vertical profiles. To define the annual mean increase of each site, since we start SF_6 measurements until 2014, we used the linear regression equation to calculate for all time series. We observed in SAN site a change in the increase around 2007. When we consider all years studied in SAN the annual mean increase is 0.26ppt SF_6/year. When we consider the time series from 2007 until actually, we found an annual mean increase of 0.29ppt SF_6/year. The others aircraft sites ALF, RBA, TAB/TEF also showed the annual mean increase of 0.29ppt SF_6/year. Figure 3 shows all aircraft sites time series and the NOAA sites Ascension (ASC: 7.92se of 0.29ppt SF

Barbados (RPB: 13.17^0N, 59.43^0W) representing the South and North Atlantic Ocean SF_6 concentrations, respectively.

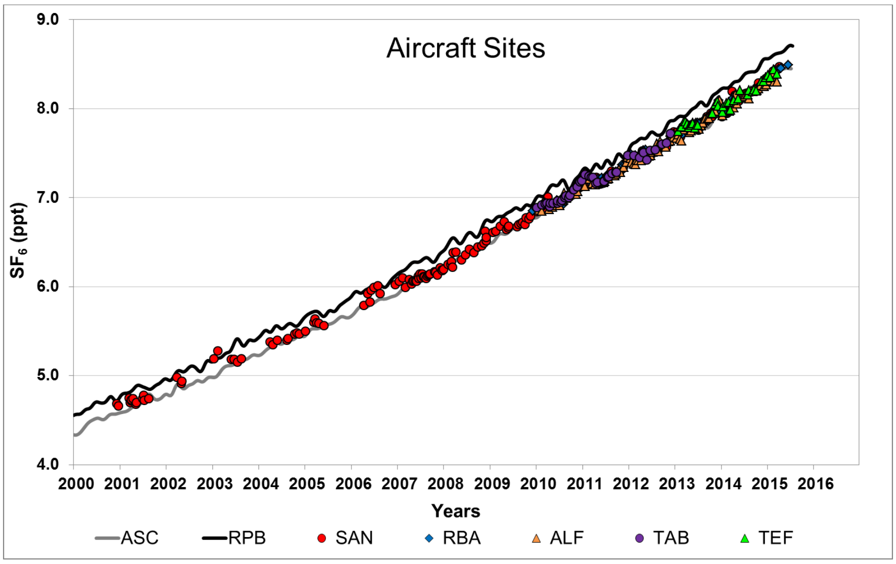

Figure 3. Time series of mean vertical profile from aircraft sites (SAN, RBA, ALF, TAB, TEF) and the Global Stations Ascension and Barbados Island, data from NOAA.

NAT and SAL are coast sites in Brazilian Northeast coast, shown at Figure 4, where 326 and 378 samples were performed, respectively. The annual mean increase found for SAL was 0.29 ppt SF_6/year and for NAT it was found were 0.26 ppt SF_6/year. Since SAL receive air from the North hemisphere (NH) during around 5 months along the year (December to April), the concentrations observed there and the increase rate are influenced by NH, like the aircraft sites SAN, RBA, ALF.

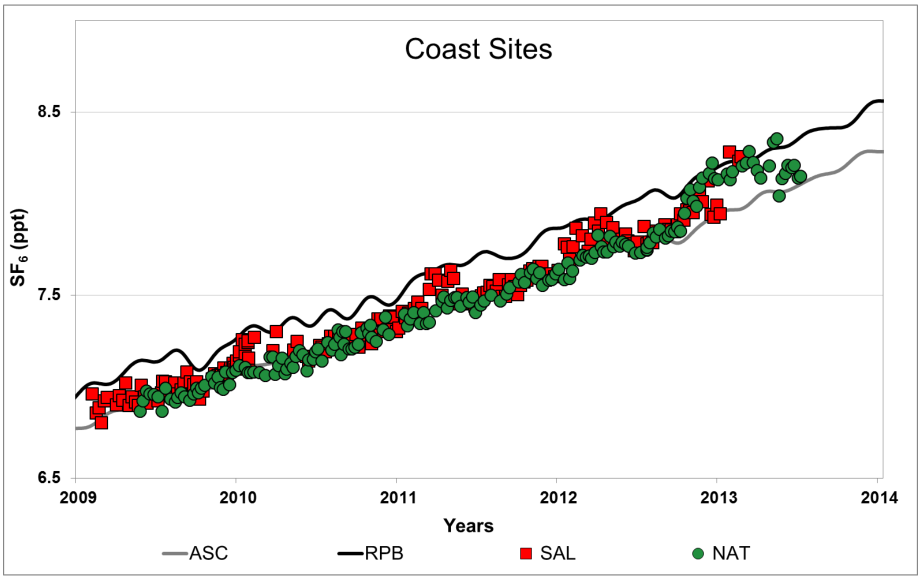

Figure 4. Time series of coast surface sites: SAL (red) and NAT (green)

When we compare the global mean annual increase of 0.27 ppt SF_6/year with the Brazilian sites, we observed a similar behaviour with SAN since 2000, but it is clear that around 2007 the global increase enrichment can be observed.

4. Conclusions

From the beginning of the samplings in 2000 at SAN until the present date, an annual increase of 0.26 ppt SF_6/year was observed. From 2007, for all aircraft sites and SAL coast site an annual increase of 0.29 ppt SF_6/year was observed. At NAT, that is not observed NH influence, the annual increase observed was 0.26 ppt SF_6/year.

The SF_6 mixing ratio at the Amazon Basin generally reflects part of the year the southern hemisphere mixing ratios, but when the Intertropical Convergence Zone (ITCZ) bring air masses from North Hemisphere, then the mixing ratios also reflect the NH. This situation can be observed better at the coast site SAL. At the beginning of the year when the ITCZ come down, the mixing ratio show peaks and reaches the RPB concentrations.

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THE RESULT OF THE FIRST SF$_6$ INTER-COMPARISON EXPERIMENT (SICE) 2016-2017

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1. Introduction

WMO/GAW Programme encouraged World Calibration Centre (WCCs) to help improve data quality, homogenize data from different stations and networks through inter-comparison experiment [1]. The Korea Meteorological Administration (KMA) has played a role as the WCC for SF$_6$ (WCC-SF$_6$) since 2012. Under the MoU with the WMO, WCC-SF$_6$ organized the first SF$_6$ inter-comparison experiment (SICE) from 2016 to 2017. Eight countries with twelve labs participated in this experiment and were divided into two circuits for Europe and Asia-Pacific regions.

2. Preparation of SICE cylinders

To prepare the cylinders for SICE, we collected dried natural air in well-mixed conditions at Anmyeondo GAW station in Korea. After diluting and spiking the collected dry air, we certified two cylinders with two-point calibrations method (bracketing). The analysis was conducted in the following order: certified reference material 1, unknown sample, certified reference material 2, and certified reference material 1 again (CRM1-sample-CRM2-CRM1). Here, the certified reference materials were the laboratory standards traceable to WMO-X2014 scale. We duplicated 5 injections at each cylinder, and certified the mole fractions of cylinders with the following formula (Equation 1):

$$C_{sample} = C_{CRM1} + (C_{CRM2} - C_{CRM1}) \times \frac{R_{corr.} - R_{CRM1}}{R_{corr.CRM2} - R_{CRM1}} \qquad (1)$$

Where C represents mole fractions of SF$_6$ (pmol/mol), R responses from GC-μECD (Agilent 7890A), and $R_{corr.}$ and $R_{corr.CRM2}$ corrected responses by the drift factor.

Assuming that equipment drift is linear with time, a drift factor, f_{drift}, can be obtained as follows (Equation 2):

$$f_{drift}\,(i) = \left\{ \frac{(3\times R_{CRM1'})}{3\,R_{CRM1'} + (R_{CRM1''} - R_{CRM1'})i} \right\} \qquad (2)$$

For the analysis uncertainty, we considered the drift increase in the two-point calibration formula (Equation 3).

$$\mathrm{u}\left(C_{sample}\right)^2 = \left[\left|\frac{R_{corr.} - R_{CRM1}}{R_{corr.CRM2} - R_{CRM1}} \times (C_{CRM2} - C_{CRM1})\right| \times \sqrt{\left(\frac{u\left(R_{sample} - R_{CRM1}\right)}{R_{sample} - R_{CRM1}}\right)^2 + \left(\frac{u(R_{CRM2} - R_{CRM1})}{R_{CRM2} - R_{CRM1}}\right)^2 + \left(\frac{u(C_{CRM2} - C_{CRM1})}{C_{CRM2} - C_{CRM1}}\right)^2}\,\right]^2 + u(C_{CRM1})^2$$

Here, $\mathrm{u}\left(\mathrm{R}_i - R_j\right) = \sqrt{\mathrm{u}(\mathrm{R}_i)^2 + \mathrm{u}(R_j)^2}$ (3)

Where u(R) represents the standard deviation of the responses and u(C) uncertainty.
The detailed information was described in [2] and [3].

3. The result of SICE

The first SICE results are shown in Figure 2. Final SF_6 mole fractions of cylinders certified by WCC-SF_6 are 7.89 tions of cylinders certified by W circuit 1 while those were 7.88±0.01 ppt and 9.2 ± 0.02 ppt in circuit 2. Referring to the recommendations [1], we included Central Calibration Laboratory (CCL) managed by National Oceanic and Atmospheric Administration, Earth System Research Laboratory in each circuit and showed good agreements with them. There are three labs that analysed the cylinders with their own scale, such as Heidelberg University, METAS, and KRISS. Among the labs with WMO scales, seven labs analysed SF_6 with WMO-X2014 scale while two labs with WMO-X2006. UEA, one of two labs of WMO-X2006 updated the value with WMO-X2014 scale after the SICE. Here, we used the latter value of UEA, showing the differences decreased -0.01 ppt in both of levels compared to the previous results with WMO-X2006. Overall, nine labs are in the extended compatibility goal for high while eight labs in low levels (Figure 1).

When we compared between the labs that used WMO scale, most of the labs (five of eight) were in the extended compatibility goal at both high and low levels except for three (Figure 2). In this analysis CCL was excluded since they are the standard under the GAW umbrella. This result emphasizes the importance of using the same scale for the data harmonization. One lab used WMO-X2006 scale that would show better results if they updated the value with WMO-X2014. For another lab, which was out of the goals, the range of prepared standards could not cover the SICE cylinders that high level would be behind the DQO according to their report.

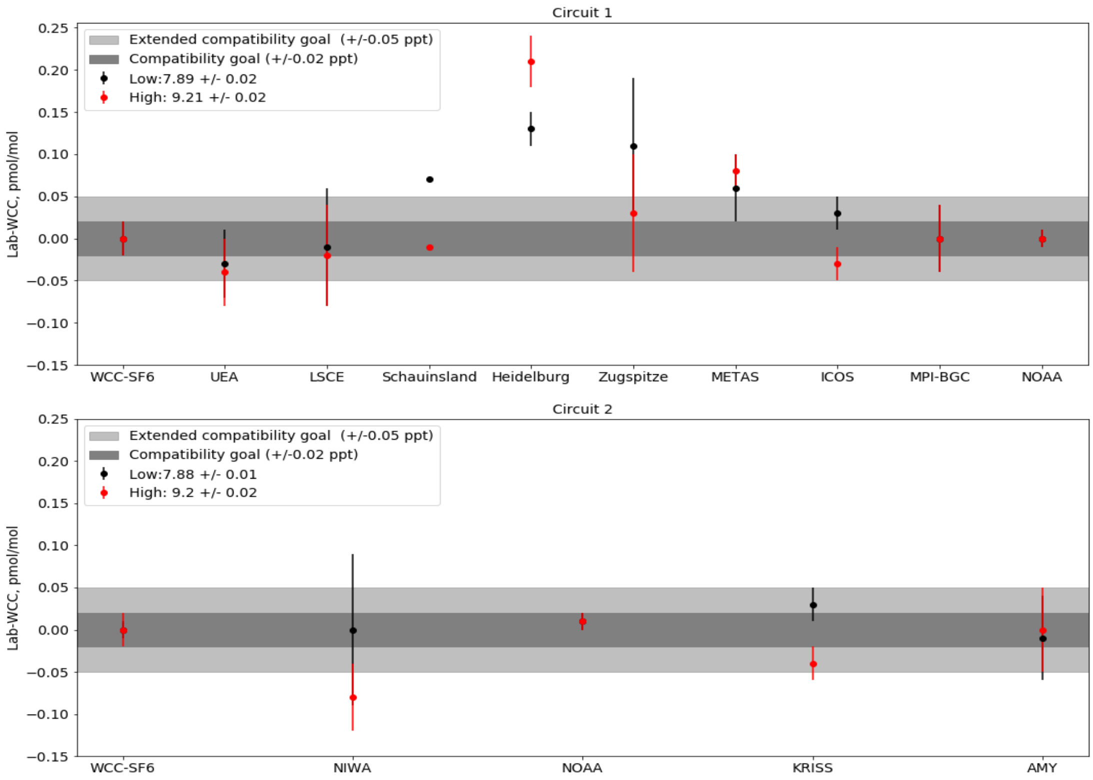

Figure 1. The result of first SICE, the differences between laboratories and WCC-SF$_6$, in circuit 1: Europe (top) and circuit 2: Asia-Pacific (bottom). The error bar indicates the reported repeatability from each laboratory. Red dots indicate high level and black dots low levels.

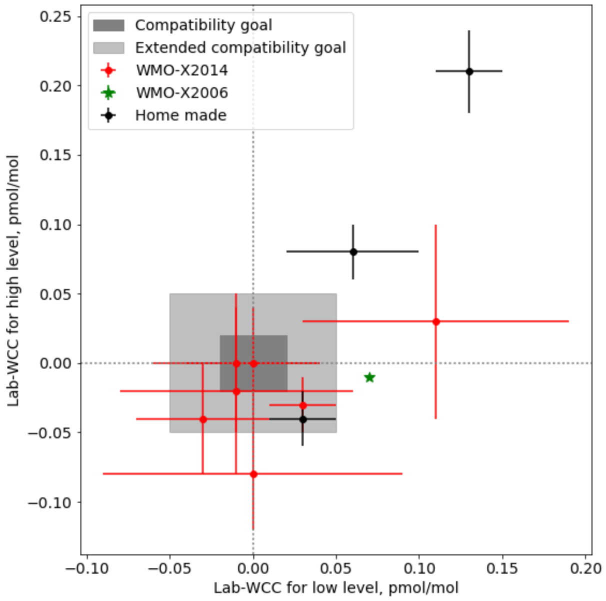

Figure 2. The Youden plot of differences between participated laboratories and WCC-SF$_6$. Red dots indicate WMO-X2014 scale, green dot WMO-X2006 scale, and black dots Laboratory's own scale. X-axis means the differences for low level cylinders and y-axis for high level. CCL and WCC-SF$_6$ are excluded here.

4. Inter-comparison experiment between WCC-SF_6 and CCL

WCC-SF_6 also has implemented biennial comparison activities with CCL since 2013 to confirm the traceability and compatibility (Figure 3). In most cases, two labs showed good agreements without the high level of SF_6 in 2015. Since we analysed the cylinders using one calibration tank without bracketing, the high level is behind the compatibility goal due to the non-linear characteristic of micro-ECD. We have a plan to do this experiment in 2019 again.

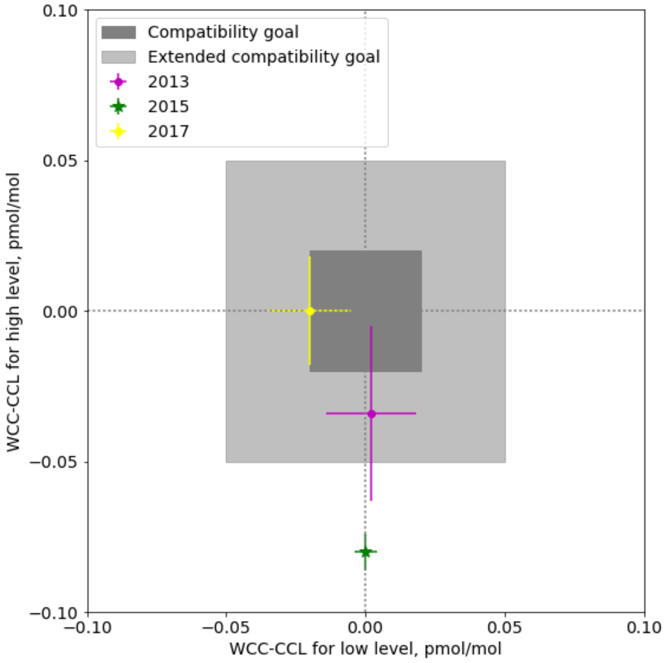

Figure 3. The Youden plot of the differences between WCC-SF_6 and CCL in 2013 (magenta), 2015 (green) and 2017 (yellow). The bar indicates analysis uncertainty of the WCC-SF_6. X-axis means the differences between two labs for low level cylinders and y-axis for high level.

5. Summary

WCC-SF_6 organized the first SF_6 inter-comparison experiment (SICE) from 2016 to 2017. Eight countries with twelve labs participated in this experiment and nine labs (75%) are in the extended compatibility goal for high while eight labs (67%) in low levels. When we compared the labs which used WMO scale, five of eight labs (64%) were in the extended compatibility goal, indicating the importance of same standard scale for data harmonization. The SICE result and the cylinder preparation method were described in the final report (www.wmo.int/pages/prog/arep/gaw/documents/FinalreportofSICE_2016.pdf) [2].

We also conducted the inter-comparison experiment with CCL biennially to keep the traceability and compatibility. Most cases showed the good agreements except for the case when we analysed SF_6 with one standard tank. Based on this experience, WCC-SF_6 published the relevant technical report [3] to help labs which would like to calibrate the instrument and certify the atmospheric SF_6 correctly.

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