20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2019)

Jeju Island, South Korea
2–5 September 2019
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Edited by Andrew Crotwell, Haeyoung Lee and Martin Steinbacher
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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:
https://community.wmo.int/acronyms-and-abbreviations-gaw

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20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2019)

on Jeju Island, South Korea, 2-5 September 2019
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 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2019) took place from 2 to 5 September 2019 and was jointly hosted by the Korea Meteorological Administration (KMA) and National Institute of Meteorological Sciences (NIMS) on Jeju Island in South Korea. 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 2019, 189 participants, including 18 through videoconferencing, from 27 countries and 6 continents attended GGMT-2019. 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.

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, the need to calculate and report uncertainties for all measurements, the need to update the WMO CO$_2$ scale, and associated implications for atmospheric data from the updated scale were discussed.

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.
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. It is the changes in the levels of greenhouse gases in the atmosphere that led to climate changes and these same data serve in supporting the World on the way to resolving the climate crisis. The data from the World Meteorological Organization greenhouse gas community through the common effort converted into one single indicator of the human activities impact on the atmosphere serves as background information for the 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. To reach its objectives, the Paris Agreement 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”. The Subsidiary Body for Scientific and Technological Advice (SBSTA) of the UNFCCC recognized “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.

On 23 September 2019 the Secretary General of United Nations António Guterres convened the UN Climate action summit to motivate and enhance ambitions towards achieving the Paris agreement goal.

In parallel to the increasing political attention to the atmospheric greenhouse gases, there is an increasing interest from the civil society, the media and the general public on this topic. This attention calls for increasing availability, easiness of access, improved timeliness and improved characterization of quality of the greenhouse gas observational data. It also requires additional efforts on bringing in the community that works on greenhouse gas observation in populated areas or the areas with high emissions to be integrated in the global observational effort.

Based on this background, three main objectives justify atmospheric observations of greenhouse gases:

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, for example 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. For example, discussion with the ocean community was launched to agree on the approaches applied to CO₂ observations from ships in the marine boundary layer. The importance of such cooperation was further stressed during the OceanObs’19 conference (Wanninkhof et al., 2019)

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. The improvements are expected to be reached in particular through the benchmarking exercise set up as a cross-cutting research and development activity under the Integrated Global Greenhouse Gas Information System (IG³IS).

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.

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 decades. 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 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. It also needs to make efforts to support general public and civil society by shortening the time of data availability and by providing the outreach materials that help to understand the data in a lay people language.
EXPERT GROUP RECOMMENDATIONS

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

The scientists present at the 20th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (abbreviated as GGMT-2019), 2-5 September 2019, on Jeju Island, South Korea, recommend the following procedures and actions to achieve the goals for network compatibility among GAW laboratories summarized 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, https://www.empa.ch/web/s503/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 persistent it can influence model interpretation of gradients.

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 or other areas of high-density emissions.

Some data quality objectives (for example, repeatability, measurement uncertainty, etc.) are relatively straightforward to quantify by individual laboratories. Network compatibility is not. Network compatibility can only be assessed by comparing measurements of ambient air at a common site (such as 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 (for example 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 travelling 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. Other, on-going comparisons are required in addition to the periodic audits by the WCC. 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Network compatibility goal</th>
<th>Extended network compatibility goal</th>
<th>Range in unpolluted troposphere (approx. range for 2019)</th>
<th>Range covered by the WMO scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.1 ppm (NH) 0.05 ppm (SH)</td>
<td>0.2 ppm</td>
<td>380 - 450 ppm</td>
<td>250 – 520³ ppm</td>
</tr>
<tr>
<td>CH₄</td>
<td>2 ppb</td>
<td>5 ppb</td>
<td>1750 – 2100 ppm</td>
<td>300 – 5900 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>2 ppb</td>
<td>5 ppb</td>
<td>30 – 300 ppm</td>
<td>30 – 500 ppb</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.1 ppb</td>
<td>0.3 ppb</td>
<td>325 – 335 ppb</td>
<td>260 – 370 ppb</td>
</tr>
<tr>
<td>SF₆</td>
<td>0.02 ppt</td>
<td>0.05 ppt</td>
<td>9 – 11 ppt</td>
<td>2.0 – 20 ppt</td>
</tr>
<tr>
<td>H₂</td>
<td>2 ppb</td>
<td>5 ppb</td>
<td>400 – 600 ppb</td>
<td>140 – 1200 ppb</td>
</tr>
<tr>
<td>δ¹³C-CO₂</td>
<td>0.01‰</td>
<td>0.1‰</td>
<td>-9.5 to -7.5‰</td>
<td>(VPDB)</td>
</tr>
<tr>
<td>δ¹⁸O-CO₂</td>
<td>0.05‰</td>
<td>0.1‰</td>
<td>-2 to +2‰</td>
<td>(VPDB-CO₂)</td>
</tr>
<tr>
<td>δ¹³C-CH₄</td>
<td>0.02‰</td>
<td>0.2‰</td>
<td>-51 to -46‰</td>
<td>(VPDB)</td>
</tr>
<tr>
<td>δ²H-CH₄</td>
<td>1‰</td>
<td>5‰</td>
<td>-120 to -63‰</td>
<td>(VSMOW)</td>
</tr>
<tr>
<td>Δ¹⁴C-CO₂</td>
<td>0.5‰</td>
<td>3‰</td>
<td>-80 to 20‰</td>
<td></td>
</tr>
<tr>
<td>Δ¹⁴C-CH₄</td>
<td>0.5‰</td>
<td>3‰</td>
<td>50-350‰</td>
<td></td>
</tr>
<tr>
<td>Δ¹⁴C-CO</td>
<td>2 molecules cm⁻³</td>
<td></td>
<td>0-25 molecules cm⁻³</td>
<td></td>
</tr>
<tr>
<td>O₂/N₂</td>
<td>2 per meg</td>
<td>10 per meg</td>
<td>-900 to -400 per meg</td>
<td>(vs. SIO scale)</td>
</tr>
</tbody>
</table>

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. NH represents northern hemisphere while SH southern hemisphere.

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.

³ The upper limit of the WMO CO₂ X2007 scale is 520 ppm. The upper limit is being increased to 800 ppm as part of the WMO CO₂ X2019 scale revision (expected in 2020) to meet the needs of atmospheric monitoring community engaged in urban measurements.
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 (such as 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 mol 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 the corresponding isotope scales) using the delta notation:

\[ \delta = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \]

- δ-values are expressed in multiples of 0.001 (designated ‰ or "per mil"), e.g. \( \delta = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \times 1000 \) ‰

The international scale for \( \delta^{13}\text{C} \) is VPDB (Vienna Pee Dee Belemnite). IAEA-603 and NBS-19 (now exhausted) calcites are the primary international reference materials used for the realization of the VPDB scale.

For \( \delta^{18}\text{O} \), different scales are in use (VPDB-CO₂, Vienna Standard Mean Ocean Water (VSMOW)). For the \( \delta^{18}\text{O} \) of CO₂ in air samples, the common scale is the VPDB-CO₂ scale (Brand et al., 2010), which is realized through IAEA-603 or NBS-19 by carbonate-H₃PO₄ digestion under controlled conditions. Although the VPDB-CO₂ scale is linked to the VSMOW scale, the 2-point VSMOW-SLAP data normalisation cannot be applied to air-CO₂ \( \delta^{18}\text{O} \) data for practical reasons.

The JRAS-06 realization of the VPDB and VPDB-CO₂ scales is recommended for the WMO/GAW community to improve network compatibility.

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

Abundance variations of O₂/N₂ (and Ar/N₂) ratios in air are also expressed using the delta notation:

\[ \delta(O_2/N_2) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \] 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".

For the O$_2$/N$_2$ ratio, there is no assigned WMO/GAW Central Calibration Laboratory and no international scale or air standard has yet been 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. Current international comparisons of O$_2$/N$_2$ indicate that the network compatibility between any two laboratories is not better than ±5 per meg.

The $^{14}$C of atmospheric CO$_2$ measurements are usually reported in $\Delta^{14}$C notation, the deviation from the absolute radiocarbon reference standard (Stuiver and Polach, 1977):

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

with $R=^{14}$C/C, the corrections are for fractionation and radioactive decay ($\lambda$) of the standard and reported in per mil (‰). 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, 2017a) which relates to the overarching WMO guidance for implementation of a quality management system for national meteorological and hydrological services (WMO, 2017b), 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 data quality and the traceability of network observations to the respective WMO scales (see section 1.3).

In the context of greenhouse gases, relevant WMO/GAW CCLs currently exist for: carbon dioxide (CO₂, at the National Oceanic and Atmospheric Administration (NOAA)), methane (CH₄, at NOAA), nitrous oxide (N₂O, at NOAA), carbon monoxide (CO, at NOAA), sulphur hexafluoride (SF₆, at NOAA), stable isotopes in CO₂ (only for CO₂-in-air measurements, at Max-Planck Institute for Biogeochemistry (MPI-BGC)), and hydrogen (H₂, at MPI-BGC). Respective WCCs are available for CO₂ (split between NOAA and the Swiss Federal Laboratories for Materials Science and Technology (Empa)), CH₄ (split between the Japan Meteorological Agency (JMA) and Empa), N₂O (at the Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Atmospheric Environmental Research (KIT/IMK-IFU), SF₆ (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). The information and previous archived results of the round-robin experiment hosted by NOAA are presented in www.esrl.noaa.gov/gmd/ccgg/wmorr/wmorr_results.php. 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 (2008)). 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 (CO₂, N₂O, SF₆, and other trace species), Tohoku University, Japan (CO₂, CH₄, CO, N₂O, and SF₆), National Institute for Environmental Studies, Japan (CO₂,CH₄, CO, N₂O, and SF₆), University of Heidelberg, Germany (SF₆).
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 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 17034 (2016). 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\textsubscript{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 April 2020):

- WMO CO\textsubscript{2} X2007 (scheduled to update to WMO CO\textsubscript{2} X2019 in 2020)
- WMO CH\textsubscript{4} X2004A
- WMO CO X2014A
The “X” stands for mole fraction.

JRAS-06 is the WMO recommended realization of the internationally recognized VPDB-CO₂ scale to be used for measurements of stable isotopes of atmospheric CO₂.

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 characterised in CO₂ 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 (CO₂, CH₄, N₂O, 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 (for example 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, 2017a)), 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 not all labs were 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, 2017a) available on the WMO/GAW web page. WCC responsibilities can be split between multiple institutions, for example by roles (like for CO$_2$; coordination of round-robins (NOAA) and performance of audits (Empa)) or by regions (like for CH$_4$; Americas, Europe, Africa (Empa) and Asia, South-West Pacific (JMA)).

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-I).

e) 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) Empa, in its role as WCC for CO$_2$, CH$_4$, and CO has demonstrated the benefits of using a travelling instrument for GAW station audits (Zellweger et al., 2016, 2019). 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 General requirements for 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 (for example 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 (that is, standards attached to the operational equipment for regular calibration), and from working standards to atmospheric measurements. The use of an in-house hierarchy and dedicated working standards will extend the lifetime of the highest in-house standards. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retroactive changes in case of scale revisions) 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 participates 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 minimize 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 H₂ in which case stainless steel is recommended. Cylinder head valves should be packless, brass valves with PCTFE or metal seats; for H₂ such valves made either from stainless 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 CO₂, the calibration standards should be replaced once the cylinder pressure has decreased to 20 bar. The maximum acceptable initial pressure for calibration standards is unclear, but is at least 140 bar, with little experience within the community at higher pressures.
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\textsubscript{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\textsubscript{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\textsubscript{2} standards should be analysed and provided with the mole fraction
of CO\textsubscript{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 (for example if the instrument response is fit to a quadratic
function, then at least four standards are needed).

ii. For instruments with relatively variable baseline response, a so-called “zero
tank” (ZT) standard may be required to periodically adjust the offset of the
baseline response.

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 fool proof when poor choices are made with gas handling or data management. A trade-off in instrument stability and complexity versus cost must often be balanced according to the needs, resources and challenges of the measurement programme.

For a more comprehensive discussion of recommendations and guidelines for best practice for in situ measurements, the reader is referred to Measurement Guidelines for CH₄ and N₂O (WMO, 2009) and for CO (WMO, 2010). These guidelines were written prior to the wide application of laser spectroscopic techniques in atmospheric GHG monitoring. However, they still offer relevant information on calibration strategies, scale propagation, traceability to the WMO scales, and general QA/QC concepts.

The following list of best practices is specifically for CO₂ 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. ISO nomenclature (JCGM, 2008) shall be used for uncertainty estimates. See Chapter 2 for guidance. In addition, investigators are encouraged to include with their data an estimate of interlaboratory measurement compatibility based on results from an on-going comparison of atmospheric measurements. Details of how these estimates are calculated and what activities are used to verify them need to be provided.

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 O₂/N₂ observations (see Chapter 6).

d) With respect to drying air samples:
   i. 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. Ideally, water and water vapour would be removed from the sample gas stream, however if that is not possible, understanding its influence on the mole fraction determination must be carefully quantified (see 1.5-d(ii) and 1.5-e below).
   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 CO₂. These requirements are to ensure that WMO/GAW network compatibility goals can be met. Water vapour effects influencing accurate mole fraction determination include mole fraction dilution, transient surface effects from wetting and drying tubing walls, and some instrument specific spectroscopic interference such as pressure broadening. Note that drying to a dew point of -40 °C (127 ppm water vapour) leads to a 0.05 ppm dilution offset in a CO₂ 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 CO₂ 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 CO₂ and are unsuitable. Magnesium perchlorate (Mg(ClO₄)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 CO₂ mole fraction: Studies with Cavity Ring-Down Spectroscopy (CRDS) instruments showed that correction functions can be used (Rella et al., 2013). However, the correction functions must be determined for each individual instrument. Furthermore, additional testing and veriﬁcation studies are needed. These include, but are not limited to: side-by-side comparisons of two instruments, one with comprehensive drying of inlet air streams, the other with no drying and using water vapour correction factors. Side-by-side studies should take place for several months and under a variety of conditions, for example at locations with poor room temperature stability, on airborne or shipboard platforms, and at locations with very high ambient humidity (see for example 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) Due to the poorer signal-to-noise ratio and the more difﬁcult determination of water vapour correction parameters for CO measured with CRDS, it is preferred to dry the sample prior to analysis when using this measurement technique (Zellweger et al., 2019).

g) 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.

h) 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.

i) 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.

j) 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.
k) 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.

l) 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.

m) 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.

n) 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, for example, 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.

o) 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.

p) 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.

q) 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.

r) 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.

s) 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. This is indispensable information for
data processing, quality control and uncertainty estimates (see Chapter 2) and is an integral part of the data management strategy (see Chapter 16).

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. The main objectives are to provide information about the quality of the data to users so that they can understand the limitations in what signals can be reliably detected in the data. 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](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:**

- 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 (that is 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 B uncertainty cannot be reduced by statistical treatment (that is by increasing the number of aliquots under analysis).
- Type A uncertainties are characterized by estimated variances, degrees of freedom and covariances where appropriate. The distribution can typically be determined from the observations (such as 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 (such as 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 inexact
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:

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

  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 (such as standard deviations). If, for particular applications, it is necessary to multiply
  the combined standard uncertainty by a factor to obtain an expanded uncertainty (for example 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
  (that is 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. It is strongly recommended to
  regularly analyse a target gas to estimate reproducibility, even if this measurement
does not cover all sources of uncertainty (see 1.4-r).

**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 (for example 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 (for example 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, it must be properly detailed in a technical report or scientific publication, and 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:

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

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 (for example 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. Large uncertainty or imprecise instruments inhibit reaching the network compatibility goals.

**Reporting of uncertainties:** In order to ensure correct and optimal use of the uncertainties by the data users, it is important that these are well documented by technical reports or peer review publications. It is also essential to move towards a homogenization of the types of uncertainty proposed. In the end, the uncertainties must be provided in the data files in the form of additional columns. The underlying uncertainty determination approach needs to be also documented in the metadata.
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 and short- and long-term repeatability. 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. It is also proposed to explore the possibility of using Jupyter notebooks to illustrate and analyse the data processing and uncertainties calculation through a few cases. This tool could be set up jointly by ICOS and NOAA/ESRL as a community effort (see Chapter 16.7).
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 targets of 0.1 ppm for the northern and 0.05 ppm for the southern hemisphere are intended to address small, globally significant gradients over large spatial scales (for example caused by Southern Ocean fluxes). 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 serves as CCL for CO$_2$ for the GAW Programme. The CCL is in the process of revising the CO$_2$ scale from WMO CO$_2$ X2007 to WMO CO$_2$ X2019. This update is expected in mid-2020. The new X2019 scale is embodied in a set of 19 CO$_2$-in-dried-air mixtures in large high-pressure cylinders (primary standards) covering the nominal range 250 to 800 ppm. Primary standard values are assigned by repeated (approximately every 2 years) manometric determinations (Zhao et al., 1997). 15 of the primary standards, covering the nominal range 250 – 520 ppm, are the same standards that defined the X2007 scale with updated assignments. The scale revision fixes two errors in the manometric calculations used to value assign the primary standards, and result from an improved understanding of the manometric method. The effect of fixing the errors introduces a mole fraction dependent difference between WMO CO$_2$ X2019 and WMO CO$_2$ X2007 ranging from approximately 0.05 ppm at 250 ppm to 0.3 ppm at 520 ppm. In addition, mole fraction and time-dependent biases in X2007 that were introduced due to errors in the implementation of X2007 are removed in X2019. In essence, differences in nominal values on the X2007 and the X2019 scale will be different for each reference tank provided by the CCL, depending on the mole fraction and the time of analysis at the CCL. In consequence, this requires a complete reprocessing of the data, but the community is aware of difficulties that may arise for some laboratories in reprocessing the historic data. Thus, the CCL plans to provide a simplified approximation to correct the data in case laboratories are unable to reprocess their data.

The revised scale will be propagated to all measurements of tertiary standards measured by the CCL and supersedes all historical WMO CO$_2$ scales disseminated by NOAA. Reprocessed results on X2019 for all historical tertiary measurements by the CCL will be made available to the community on the CCL website (https://www.esrl.noaa.gov/gmd/ccl/).

The WMO CO$_2$ X2019 revision expands the upper limit of the scale from 520 ppm to 800 ppm to meet the needs of the atmospheric monitoring community engaged in urban measurements. The expanded range is expressly intended for the purpose of monitoring in urban environments where the more relaxed expanded network compatibility goals are deemed sufficient. The absolute accuracy and the reproducibility of scale propagation will be less constrained by the CCL above ~500 ppm, but are of sufficient quality to meet these demands.

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).
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

1. **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.

2. **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.

3. **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.

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

5. **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 $< \pm 0.03$ ppm (95% confidence level, coverage factor k=2) over the mole fraction range 250 – 500 ppm. Transfer of the CO$_2$ scale above this range is targeted for use in urban measurements, and the requirements for scale transfer uncertainty can therefore be relax. The CCL shall aim to transfer the scale in the 500–800 ppm range with a reproducibility of $\pm 0.1$ ppm (95% confidence level, coverage factor k=2).

6. **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.

7. **g)** The CCL should archive the X2007 assignments of primary and secondary standards.

8. **h)** The CCL should archive and make available to the GGMT community X2007 values for tertiary measurements made prior to the X2019 revision.

9. **i)** The CCL should provide estimates of the uncertainty introduced by using an empirical scale conversion in lieu of fully reprocessing from re-assigned values for tertiary standards.

10. **j)** The CCL should provide estimates of the differences between data tied to historical scales disseminated by NOAA prior to X2007 and X2019.

11. **k)** WMO/GAW measurement laboratories should strive to implement the X2019 scale revision, including historical measurements, within one year of the release of the new scale by the CCL.
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. However, to make the best use of these measurements, datasets from different laboratories must be compatible within small limits. The network compatibility goals for stable isotope measurements of CO$_2$ and CH$_4$ in air are presented in Table 1. These limits are required to assess 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 somewhat (Table 1), even though more precise links to VPDB would minimize uncertainty in these studies.

However, results from a flask-air comparison for $\delta^{13}$C and $\delta^{18}$O of atmospheric CO$_2$ samples for background stations demonstrate that laboratories continue to show persistent offsets that are much larger than those stipulated by network compatibility goals presented in Table 1 (Ernst, 2015). Likewise, in the last WMO round-robin experiment (RR6)$^1$, large discrepancies were observed among laboratories: up to 0.09 ‰ and 0.4 ‰ for $\delta^{13}$C and $\delta^{18}$O respectively, well above the stated compatibility goals of 0.01 and 0.05 ‰. No single source for these discrepancies has been identified but calibration to VPDB-CO$_2$, measurement, and sampling effects (sample collection, drying, storage etc.) are all potential contributors.

Similarly, a recent review of comparison results for methane isotopes (Umezawa et al., 2018) demonstrates interlaboratory discrepancies up to 0.5 ‰ for $\delta^{13}$C and 13 ‰ for $\delta^2$H for ambient air samples, far above 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 interlaboratory compatibility.

Here we outline calibration approaches for stable isotopes of the major greenhouse gas CO$_2$, primarily with mass spectrometric methods but also with optical techniques. We present recommendations for implementing more robust calibration strategies for stable isotope measurements of the important atmospheric trace gases CH$_4$, N$_2$O, and CO. We also note that sampling effects (sample collection, drying, storage, etc.) may cause biases when comparing data; these should 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; therefore, these primary mixtures are SI-traceable. In contrast, stable isotope scales are artefact-based; they are based on established reference materials (RMs) with assigned values for both the definition and the scale realization that are not SI-traceable. Further, isotopic measurement results depend on ion correction procedures (see section 4.3.3), and different methods and parameters can result in different $\delta^{13}$C and $\delta^{18}$O values from the same raw measurement data.

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$^1$ https://www.esrl.noaa.gov/gmd/ccgg/wmorr/wmorr_results.php
Given that, the parameters used for data processing in all laboratories should be standardized to produce the same $\delta^{3}{\text{C}}$ and $\delta^{8}{\text{O}}$ values from the same measurement data, thus helping to achieve the stated network compatibility goals.

Stable isotope data of air-$\text{CO}_2$ ($\delta^{3}{\text{C}}$, $\delta^{8}{\text{O}}$, $\delta^{17}{\text{O}}$), air-$\text{CO}$ ($\delta^{3}{\text{C}}$), and air-$\text{CH}_4$ ($\delta^{3}{\text{C}}$) are expressed on the VPDB-$\text{CO}_2$ scale\(^2\), while $\delta^{3}{\text{H}}$ of air-$\text{CH}_4$ and $\delta^{8}{\text{O}}$ of air-$\text{CO}$ are expressed on the VSMOW/SLAP scale.

It is now recommended that the VPDB-$\text{CO}_2$ scale be established with gaseous CO$_2$ evolved from the primary RM IAEA-603, a marble calcite, which has assigned values of $\delta^{3}{\text{C}}_{\text{VPDB}} = +2.46 \pm 0.01 \text{%}$ and $\delta^{8}{\text{O}}_{\text{VPDB}} = -2.37 \pm 0.04 \text{%}$ (see IAEA website). IAEA-603 replaces the initial VPDB-defining material NBS-19, which defined the VPDB scale at $\delta^{3}{\text{C}} = +1.95 \text{%}$ and $\delta^{8}{\text{O}} = -2.20 \text{%}$ exactly\(^3\). Although supplies of NBS-19 are now exhausted, the VPDB scale definition based on NBS-19 remains valid. If/when other RMs with sufficiently low uncertainty become available they may be used to define other "points" on the VPDB-$\text{CO}_2$ scale.

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 $\delta^{3}{\text{H}} = 0 \pm 0.3 \text{%}$ and $\delta^{8}{\text{O}} = 0 \pm 0.02 \text{%}$ (based on measurements against the now exhausted VSMOW and SLAP).

For scale realization, IUPAC recommends one primary RM to define the delta-scale origin (zero-point) and a second scale-anchor RM with appreciably different values to define the scale-span (Wieser, 2006; Coplen et al., 2006). From 2006 to 2017, the recommended scale-span RM for all $\delta^{3}{\text{C}}$ data normalisation was LSVEC ($\delta^{3}{\text{C}} = -46.6 \text{%}$, assigned with zero uncertainty; Coplen et al., 2006). In 2017, the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) ceased recommending the use of LSVEC for carbon isotope ratio analysis because it had been demonstrated to have unstable composition (IUPAC, 2018). Although IUPAC recommends using a second RM, a replacement material has not yet been identified for use throughout the community. For $\delta^{8}{\text{O}}$ in carbonates and CO$_2$, the VPDB-$\text{CO}_2$ scale is used without the second RM aimed to define the scale span (Brand et al., 2014). SLAP2 is the scale-span RM for $\delta^{3}{\text{H}}$ data in all materials ($\delta^{3}{\text{H}}_{\text{SLAP2}} = -427.5 \pm 0.3 \text{%}$) and for $\delta^{8}{\text{O}}$ data in waters and solids ($\delta^{8}{\text{O}}_{\text{SLAP2}} = -55.50 \pm 0.02 \text{%}$).

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

The IAEA is recognised as custodian of the stable isotope scales and primary RMs for H, C, N, O, and S ($\delta^{3}{\text{H}}$, $\delta^{3}{\text{C}}$, $\delta^{15}{\text{N}}$, $\delta^{18}{\text{O}}$ and $\delta^{34}{\text{S}}$) (IAEA, 2016) and is responsible for making such materials available and for producing replacements when necessary. The uncertainty assigned to the values of these primary RMs must meet or exceed objectives for the most critical applications, including the WMO network compatibility goals (Table 1).

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\(^2\) For consistency we refer to the VPDB-$\text{CO}_2$ scale for both $\delta^{3}{\text{C}}$ and $\delta^{8}{\text{O}}$ data reporting. Note, $\delta^{8}{\text{O}}$ values for air-$\text{CO}_2$ should be solely expressed on the VPDB-$\text{CO}_2$ scale (Brand et al., 2010). When oxygen isotopes are not included, reporting $\delta^{3}{\text{C}}$ data on the VPDB scale is allowed as $\delta^{3}{\text{C}}$ values are the same for the VPDB and VPDB-$\text{CO}_2$ scales.

\(^3\) Values for NBS-19 were introduced without uncertainty characterization (Hut, 1987).
As mentioned above, the supply of NBS-19 is exhausted but its use and scale-defining role remains valid. There is enough stock of its replacement, IAEA-603, to last an estimated 100 years. IAEA has reported the uncertainty of IAEA-603 characterizing how a single aliquot (out of the first batch of ~5000 units) represents the assigned value; by averaging data obtained on several aliquots one may reduce the uncertainty related to its inhomogeneity. Following the discontinuation of LSVEC, IAEA is working on a spread of new calcium carbonate scale anchors covering a range of $\delta^{13}$C values with low uncertainty (Assonov, presented at GGMT-2019).

Three materials have been prepared, these are sealed in glass ampoules (batches of 3000 or more ampoules of each RM) to prevent any drift during storage; the homogeneity in $\delta^{13}$C is has been confirmed at $\pm 0.006 \permil$ (Assonov et al., 2020). All requirements for RMs laid out by ISO 17034 (2016) and ISO Guide 35 (2017) will be fulfilled: homogeneity and stability assessment, similarity of RM matrix to the matrix of IAEA-603, metrological traceability of values assigned, use of well-tested mass-spectrometric methods, consistent data treatment including $^{17}$O correction, and full uncertainty budgeting. The use of these standards as anchors for the VPDB scale may lead to a revision of the scale in the future; possibly warranting a distinct name for the new version of the scale.

Given the discontinuance of LSVEC and the time required to address LSVEC-replacements, several pure CO$_2$ gases that were prepared as international RMs at NIST (RMs 8562 – 8564; https://www-s.nist.gov/srmors/viewTableV.cfm?tableid=42) may be useful as supplemental RMs. If used, they should be used cautiously as there are only limited amounts of these RMs and they were characterized for $\delta^{13}$C and $\delta^{18}$O in accordance with the initial LSVEC value (see Coplen et al., 2006, and https://www-s.nist.gov/srmors/viewTableV.cfm?tableid=42). Other homogeneous gas standards, such as NARCIS I and NARCIS II (Mukai, 2003), while not international RM’s, could also be useful for scale validation if supplies are adequate (Brand et al., 2009, 2014).

The GGMT participants welcome revision of the VPDB scale realization, and the cooperation between the IAEA, WMO, the Central Calibration Laboratory for CO$_2$ stable isotopes (CCL-isoCO$_2$), BIPM and NMIs for improving metrological traceability and uncertainty evaluation of different reference materials used for atmospheric measurements. In particular, we encourage the creation of CO$_2$-in-air mixtures and the exploration of methods to improve the determination of the absolute stable isotope ratio ($^{13}$C/$^{12}$C)$^5$ of the VPDB-CO$_2$ scale origin, which is part of the EMPIR project SIRS (http://www.vtt.fi/sites/SIRS/).

N$_2$O isotope data are linked to the $\delta^{15}$N$_{Air}$-N$_2$ and VSMOW oxygen scales. The first N$_2$O isotope RMs with provisional delta values were provided by USGS (Ostrom et al., 2018). Given that no international RMs in the form of N$_2$O with stated uncertainty are available from IAEA, efforts to release RMs in the form of pure-N$_2$O gas (in ampoules) or N$_2$O in air (in cylinders or flasks) are encouraged, especially for $\delta^{15}$N and $\delta^{13}$N. GGMT requests that the IAEA assess their capability to produce appropriate N$_2$O RMs, or at least facilitate the distribution thereof.

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4 Uncertainty components are listed in IAEA-603 Reference Sheet (Table 2), available at https://nucleus.iaea.org/rpsr/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 NBS-19); contribution of Type A uncertainty can be reduced when several aliquots of IAEA-603 are analysed.

5 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) do not address the uncertainty required at $\pm 0.01 \permil$. 

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4.1.3 The role of the Central Calibration Laboratory for CO\textsubscript{2} stable isotopes (CCL-isoCO\textsubscript{2})

The role of the CCL-isoCO\textsubscript{2} is to provide or calibrate appropriate CO\textsubscript{2}-in-air mixtures (for example characterized natural air) with values fully traceable to the VPDB-CO\textsubscript{2} scale to be used for stable isotope measurements of atmospheric CO\textsubscript{2}. The most crucial task for the CCL-isoCO\textsubscript{2} is to correctly link CO\textsubscript{2}-in-air mixtures to the artefact-based VPDB-CO\textsubscript{2} scale realized using primary reference materials as discussed above. Appropriate use of CO\textsubscript{2}-in-air mixtures that have been value-assigned on the VPDB-CO\textsubscript{2} scale by CCL-isoCO\textsubscript{2} should improve comparability of measurements in order to achieve network compatibility goals.

An integral aspect of the CCL-isoCO\textsubscript{2} operation is the assignment of uncertainty following sound metrological principles (WMO, 2018a). As recommended by GGMT-2017, uncertainty propagation should be based on the traceability chain to the VPDB-CO\textsubscript{2} scale. All documentation relevant to the development of the scale realization, describing the analytical procedures and the complete uncertainty budget, should be made available and be updated as needed. In addition, details of the tests used to establish relevant corrections and their magnitudes should be provided.

As the CCL-isoCO\textsubscript{2} operates as a provider of RMs to the WMO/GAW network it should (i) develop and maintain appropriate Quality System and Quality Assurance schemes addressing requirements for calibration laboratories (such as ISO/IEC 17025 (2017)), and (ii) address the requirements for RMs producers following ISO 17034 (2016) and ISO guide 35 (2017).

The stable isotope laboratory (BGC-IsoLab) at the Max Planck Institute for Biogeochemistry (MPI-BGC), Jena, Germany, was designated CCL-isoCO\textsubscript{2} in 2009 and has named their realization of the VPDB-CO\textsubscript{2} scale JRAS-06 (JRAS is an abbreviation of Jena Reference Air Set, see pages 71 (Wendeberg, 2013) and Abbreviations). JRAS-06 will be discussed in section 4.3.2.

4.1.4 Uncertainty and scale realization in the absence of a primary method

Application of metrological concepts, consistent with the 3\textsuperscript{rd} Edition of the International Vocabulary of Metrology (VIM 3, 2008), is still under development for stable isotope measurements. The GAW community sets network compatibility targets that require comparability - metrologically traceable to the same scale, such as VPDB-CO\textsubscript{2}. As there is no primary method for realizing the VPDB-CO\textsubscript{2} scale, regular verification against a stable, high-level scale anchor with a low value-assignment uncertainty is required.

The network compatibility goals set by the community dictate the uncertainty objective for each laboratory in its tie to VPDB-CO\textsubscript{2}, whether through the recommended JRAS-06 or an alternate scale realization. It should be noted that this compatibility goal is close to the performance limit of the best dual inlet isotope ratio mass spectrometers (IRMS) and beyond the reach of currently available continuous-flow IRMS and optical techniques. In addition, the transfer of the JRAS-06 scale realization itself brings a non-negligible uncertainty which is comparable to the WMO network compatibility goals, that is each JRAS-06 value assigned tank or flask bears an individual value and uncertainty. As JRAS-06 flasks and air-cylinders

\footnote{Only international RMs in the form of marble carbonates are proven to be stable over a long time (NBS-19, IAEA-603 and NBS 18).}
calibrated by CCL-isoCO₂ are used for calibration transfer in user laboratories, CCL-isoCO₂ must assign these values and uncertainties following best practices.

Visualising the traceability chain allows users to see how each step introduces a component of uncertainty; these affect the ability to achieve long-term compatibility among users of the scale realization. The steps are as follows:

a) **Primary reference materials:** To achieve long-term reproducibility of the 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) **Long-term stability:** The long-term stability of the scale realization can be demonstrated by regular measurements of secondary standards against the primary RMs. For JRAS-06, CO₂ is freshly released from aliquots of primary carbonate RMs using the carbonate/phosphoric acid preparation to demonstrate that the link to VPDB-CO₂ is constant over time. The JRAS-06 scale defining carbonate is MAR-J1 which is linked to the VPDB-CO₂ scale via phosphoric acid reactions of NBS-19 and now IAEA-603.

c) **Scale transfer to user labs:** JRAS flasks and high-pressure cylinders of air used for scale transfer are value assigned using measurements relative to JRAS-06 secondary standards. All related steps (CO₂ extraction and measurements) contribute to the uncertainty and these must be included accordingly.

d) **Scale transfer within user labs:** Transfer of the CCL-isoCO₂ scale calibration from flasks or cylinders to laboratory standards involves additional steps that contribute to the uncertainty budget. These must also be considered accordingly.

Each step in the calibration hierarchy is critical for long-term compatibility, and each has an uncertainty associated with it. Additional uncertainty components can come from sampling and measurement steps not mentioned above. All uncertainties must be included and propagated in the form of

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

Where a σᵢ is associated with each and every measurement or correction step.

To demonstrate and achieve long-term data compatibility across laboratories contributing to the WMO/GAW programme, the calibration hierarchy and traceability to the VPDB-CO₂ scale at each laboratory should be established (preferably through the current CCL-isoCO₂ realization JRAS-06), 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 improvement. This requires close cooperation between analytical laboratories, the CCL-isoCO₂, the WCC-isoCO₂ working group (see 4.1.5) 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

As there is no WMO-designated WCC for CO₂ stable isotopes, GGMT 2019 discussed the possibility of a working group to fulfil the roles of the WCC-isoCO₂. At this time, an official WCC designation does not seem likely, so a working group (whether formal or informal) could
provide some of the activities of the WCC to the community pending WMO action. Members of the group would have to demonstrate expert knowledge of some, if not all aspects of measuring isotopes of atmospheric CO₂, and the standardisation of these measurements. Possible WCC activities could include:

- Validating the scale realisation maintained by the CCL with independent measurements against international RMs.
- Confirming the stability of the scale realisation maintained by the CCL within quoted uncertainties.
- Contributing to the design, planning and coordination of round-robin (RR) and intercomparison (ICP) exercises, so that the results can be used to address specific effects separately.
- Analysing results and metadata from RR and ICP exercises to aid identification of laboratory and instrumental effects.
- Ensuring consistent use of correction algorithms.
- Designing tests for instrumental effects.
- Summarizing the best knowledge and providing recommendations and SOPs to the community.
- Providing expert advice on calibration schemes and uncertainty propagation.

WCC-isoCO₂ could commence with input into the upcoming WMO CO₂ round-robin (RR7) that is scheduled to commence in early 2020. In the reporting of the CO₂ stable isotope data for RR7 there will be additional information requested that will include the local realisation of VPDB-CO₂ in use, traceability to primary RMs, correction algorithms, and uncertainty estimation. The WCC-isoCO₂ could help collect and evaluate this metadata.

4.2 Current challenges for stable isotopes of CO₂

For ensuring comparable and compatible stable isotope ratio measurement results for CO₂ in air, several challenges must be addressed. The major issues are outlined below:

a) Primary and secondary international reference materials: Marble RM IAEA-603 (replacement for NBS-19), with well-characterized uncertainty, was released in 2016. In addition to the LSVEC replacement (see 4.1.1), is the need to establish and maintain several international secondary RMs in the form of pure CO₂ gases with very low uncertainties that cover the δ³C range of interest.

b) Scale contraction (η-effect⁷): During isotope ratio mass spectrometric measurements, cross contamination (ion source “memory”) shrinks the apparent difference between sample and reference CO₂ gas. This effect scales with the difference in isotopic ratio of the two gases and affects IRMS measurements in all laboratories, whether they are measuring primary reference materials, propagating the scale of CO₂-in-air, or measuring samples. All measurement operators need to be aware of this effect and minimise it where appropriate. Any residual scale contraction should be measured and corrected for (see 4.3).

c) Storage effects: Marble calcium carbonates are useful reference materials because they are stable over time. However, air sample measurements are usually measured relative to CO₂ extracted from air mixtures, usually from high-pressure cylinders that provide

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⁷ Following the notation given in (Verkouteren et al., 2003a, b).
the calibration link. Maintaining these laboratory standard gas mixtures, and propagating the local realization of VPDB-CO$_2$ over time, requires careful storage and gas-handling.

d) Water: Oxygen isotope exchange between CO$_2$ and H$_2$O during sample storage is a known problem for $\delta^{18}O$ and can be addressed by drying the air sample during collection and careful flask pre-treatment.

e) Corrections: Inconsistencies between laboratories can arise from different algorithms and/or parameterizations of the necessary corrections (for example $^{17}O$- and N$_2$O corrections). Such algorithms should be standardised following recommended procedures, where possible, to ensure comparability (see section 4.3.3). Deviations from the recommended procedures must be documented.

f) Estimation and reporting of combined uncertainty: Uncertainty estimation (such as typical lab-uncertainty) should accompany sample data reporting, based on the metrological traceability chain to the VPDB-CO$_2$ scale level. Similar treatments of uncertainty should be used in each laboratory to ensure compatibility, compare data quality, and allow comparison of the most critical steps in the measurement process.

g) Quality control: Standardized QA/QC procedures for the stable isotope measurement community are not yet well developed and improvements aimed at achieving better compatibility are urgently needed. ISO/IEC 17025 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

As the custodian of the VPDB scale-defining materials, and the principal RM producer and distributor, IAEA must select, characterize, test, and release a suitable replacement for LSVEC. The replacement material for LSVEC, as well as other materials that could validate the scale, should be stable, homogenous, sufficiently abundant, and cover the $\delta^{13}C$ range of interest. A range of materials could be introduced to help identify drift and other “behaviours” and to provide redundancy should problems with any one material be encountered in the future (Assonov, presentation at GGMT-2019).

GGMT-2019 requests that additional labs develop the capability to validate the JRAS-06 scale realization by evolving CO$_2$ from carbonates by H$_3$PO$_4$ acid reaction and create CO$_2$-in-air mixtures. IAEA, BIPM, NMIs and/or other carbonate specialist laboratories are potential candidates for this work. We also recommend that relevant documents and descriptions of critical steps, for example standard operating procedures (SOPs), be available from labs pursuing this capability.

4.3.2 CCL-isoCO$_2$

The CCL-isoCO$_2$ must maintain a sustainable calibration scheme consistent with the requirements for all CCLs described in section 1.2 and modified to incorporate the specifics of stable isotope measurements as summarized below. While this list specifically targets the CCL for stable isotope work of atmospheric species, it contains “best-practice” components that should be followed by all laboratories that are part of the WMO-GAW community measuring stable isotopes. Following the description of the requirements for CCL-isoCO$_2$ we present a
brief summary of the CCL-isoCO\textsubscript{2} at MPI-BGC IsoLab procedures that have been developed to deliver calibration onto the VPDB-CO\textsubscript{2} scale.

a) **Traceability chain:** The GGMT community requests that the CCL-isoCO\textsubscript{2} provide descriptions of the full measurement traceability chain to the VPDB-CO\textsubscript{2} scale for all calibration measurements. This includes all measurement and preparation steps, all lab and primary standards and their uncertainties, and major instrumental and data corrections. The CCL-isoCO\textsubscript{2} is also asked to verify and demonstrate long-term traceability, and to make all relevant descriptions available upon request and in relevant reports.

b) **Scale-realization/scale-transfer:** The GGMT community request that the CCL-isoCO\textsubscript{2} document and provide all relevant data pertaining to the transfer of the VPDB-CO\textsubscript{2} scale from primary reference materials to CO\textsubscript{2}-in-air standards. We also request that an estimate of the uncertainty introduced by the calibration transfer procedure at each step accompany all values assigned for calibration mixtures, and that end-user laboratories receive full data reports with robust uncertainty quantification.

c) **Long-term stability of the scale realization and recalibrations:** Regular verification and recalibration to the primary RMs are necessary to demonstrate long term stability and integrity of the scale realization. Given that the VPDB-CO\textsubscript{2} scale is artefact-based and that there are very strict requirements for long-term network compatibility in the WMO/GAW community, GGMT-2019 suggests that secondary standards and internal carbonate standards (if used) be regularly verified against primary RMs IAEA-603 and other high level international RMs - including the LSVEC replacement - as they become available. If scale revision occurs, this should be reported to the GGMT community at the earliest time.

d) **Combined uncertainty and uncertainty budget:** The clearly presented traceability chain allows for the identification and evaluation of all uncertainty components. This should include all uncertainty components such as calibration materials, measurements, preparation steps, and data corrections used in the CCL-isoCO\textsubscript{2} scale realization. Combined uncertainties should be provided for each calibrated mixture for use in the user laboratory as a Type B uncertainty. At GGMT 2019 there was extensive discussion on the different approaches to uncertainty budgeting that are currently in use among the stable isotope WMO-GAW community. A solid metrological approach should be developed.

e) **N\textsubscript{2}O-correction:** The N\textsubscript{2}O correction has been the subject of several publications describing different correction methods. Given that the mole fraction and isotopic signature of N\textsubscript{2}O in working standards – which are typically natural air – closely mimic atmospheric samples, biases in the N\textsubscript{2}O corrections used by different laboratories are thought to be extremely small. However, when synthetic N\textsubscript{2}O (produced from NH\textsubscript{4}NO\textsubscript{3} decomposition) is used to make the carbonate CO\textsubscript{2} in air mixtures (JRAS flasks) the isotopic composition of the N\textsubscript{2}O can be quite different from ambient. This can lead to potential bias of 0.01 ‰ (Assonov and Brenninkmeijer, 2006). The isotopic composition of the N\textsubscript{2}O in the synthetic air used by the CCL-isoCO\textsubscript{2} to make CO\textsubscript{2} in air mixtures from carbonates is not known. This may cause potential bias where laboratories receive JRAS-06 mixtures and use those to calibrate their own in-house standards, as the JRAS-06 mixtures may contain isotopically different N\textsubscript{2}O from other labs’ in-house standards. However, this problem only arises where N\textsubscript{2}O is an isobaric contamination that needs to be corrected for. For example, optical instruments will not suffer from this potential bias.

f) **Documentation:** To safeguard the future of the scale realization, the CCL-isoCO\textsubscript{2} is requested to carefully document all updates, developments, technical details and
detailed SOPs involved in the realization and maintenance of the scale realization and to make these available upon request and in regularly updated reports.

g) **Quality Management System and Data Quality:** We recommend that the CCL-isoCO₂ develops a quality management system that uses ISO/IEC 17025 as a guideline with particular attention paid to overall measurement performance and reproducibility documentation. The use of surveillance cylinders measured at different intervals (daily, quarterly, yearly) and regular recalibrations to the primary RMs can be used to evaluate overall measurement reproducibility and realistically estimated uncertainty.

h) **Comparisons:** It is important that the CCL-isoCO₂ participates in comparisons and round-robin and cooperates with other expert labs in the community for scale verification and establishment of best practices, including RR7 and the CCQM Key Comparison Pilot Study on CO₂ isotopes (organised jointly by BIPM-IAEA and planned for 2020).

MPI-BGC IsoLab reports they are working towards meeting all of the specifics above. Development of the CCL-isoCO₂ JRAS-06 realization of the VPDB-CO₂ scale and analysis of isotopes of atmospheric carbon dioxide has been described in several publications (Werner et al. (2001), Ghosh et al. (2005), Brand et al. (2009), Wendeberg et al. (2011), Wendeberg et al. (2013 and references therein) and will be summarized in a future publication that will document the procedure used to transfer the JRAS-06 realization of the VPDB-CO₂ scale to the GAW community (and others). Internally to MPI-BGC IsoLab, the JRAS-06 realization is based on extensive, continual measurements of two laboratory calcium carbonate standards, MAR-J1 ($\delta^{13}C = +1.96 \pm 0.01 \, \text{%o}$, $\delta^{18}O = -2.58 \pm 0.03 \, \text{%o}$) and OMC-J1 ($\delta^{13}C = -4.37 \pm 0.01 \, \text{%o}$ and $\delta^{18}O = -8.93 \pm 0.03 \, \text{%o}$). These carbonates have been value assigned by MPI-BGC IsoLab against the primary RM materials that define the VPDB scale, both NBS-19 and IAEA-603, and have demonstrated stability (Wendeberg et al., 2013). The operational scale used for verification and transfer is based on these measurements of carbonates.

Presently BGC-IsoLab provides measurement data of cylinders that are calibrated at the CCL-isoCO₂, or JRAS-06 flasks prepared from the MAR-J1 and OMC-J1 carbonates, to “customer” laboratories. Uncertainty estimation is also provided for each calibration and BGC-IsoLab is making a concerted effort to meet users’ expectations for uncertainty quantification. The CCL-isoCO₂ is an active participant in WMO round-robin exercises and other same-air comparisons to help improve the community approach to a robust calibration onto the VPDB-CO₂ scale. Full details of how MPI-BGC IsoLab meets the requirements for operation as CCL-isoCO₂ and the operational scale transfer are beyond the scope of this document and will be presented in the future publication.

### 4.3.3 Analytical laboratories

Since long-term network compatibility of CO₂ stable isotopic composition is the primary objective of the WMO/GAW community, we encourage laboratories to use the JRAS-06 realization provided by the CCL-isoCO₂, or to have an option of reporting data on the JRAS-06 realization of VPDB-CO₂ scale. If laboratories are not on the VPDB-CO₂ scale as realized by JRAS-06, they should be explicit about which realization of the VPDB-CO₂ scale is in local use and provide details regarding its traceability to primary reference materials. If possible, they should provide data showing how this realization compares with the JRAS-06 scale realization. This is especially important in comparison exercises such as the round-robin, where laboratories that do not report data on JRAS-06 will be asked to provide information on their discrepancy with JRAS-06 realization.
Specific attention should be paid to the following for IRMS measurements (specifics relating to optical techniques are covered in section 4.4):

a) **Scale transfer to JRAS-06**: The scale transfer can be realized by one of two methods:
   (a) high-pressure cylinders of natural (or synthetic) air provided by participating laboratories and calibrated by the CCL-isoCO$_2$ on the JRAS-06 scale, or (b) a set of JRAS-06 5L glass flasks of air with CO$_2$ derived from the MAR-J1 and OMC-J1 materials. Cylinders are preferred, due to the limited volume of the flasks. Ideally, a lab moving to JRAS-06 would have at least two and preferably 3 cylinders calibrated by the CCL. One of the cylinders should be different from ambient by several per mil to validate the scale span. An additional cylinder would serve both for redundant in case of tank failure, and for drift monitoring and for surveillance purposes. These cylinders should be re-calibrated by BGC-Isolab intermittently. Every two years is ideal; however if this time frame is not possible, additional comparisons are advised to check for compatibility. Transfer of historical data will involve calibrating local standards to JRAS-06 standards and careful data reprocessing.

b) **IRMS-specific scale contraction**: Investigations of instrument-specific influences on scale contraction ($\eta$ or eta effect, see footnote-7) 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). Laboratories are encouraged to characterize the $\eta$ effect where no second scale anchor is available, and minimize it as much as reasonably possible. The magnitude of $\eta$ can be determined for dual inlet systems (Francey and Allison, 1994; Verkouteren et al., 2003a, b; Allison and Francey, 2007), and the data can then be corrected for the remaining $\eta$-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 as a critical component of data quality control. Monitoring the raw data of two lab references with a large difference in delta value between each other (Huang et al., 2013) is a feasible method to monitor and quality-control for the degree of cross contamination. The lab references could be carbonates, air-CO$_2$ or pure CO$_2$.

c) **Selection of laboratory working gases**: During IRMS measurements, the magnitude of scale contraction and memory effects critically depend on the reference gases in use. 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.

d) **$^{17}$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 should be applied by numerical solution of all equations (Assonov and Brenninkmeijer, 2003a, b) rather than the 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 air-CO$_2$ is recommended, and the use of reference materials with a large deviation in $\delta^{18}$O should be avoided.

e) **N$_2$O-correction**: The N$_2$O correction has been the subject of several publications, which lead to a common correction algorithm dependent on a correct assessment of the relative ionisation efficiency of N$_2$O and CO$_2$. Laboratories should make appropriate corrections for N$_2$O 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 and N₂O relative ionisation efficiency re-determined on a regular basis.

f) **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 N₂O, ¹⁷O and for η-effect), revision of JRAS-06 or other relevant changes. Final processed data should be submitted to WMO/GAW World Data Centre for Greenhouse Gases and include appropriate metadata and uncertainty estimations. Furthermore, laboratories are encouraged to include with their data an estimate of interlaboratory measurement compatibility based on results from an ongoing comparison of actual atmospheric measurements (that is the mean difference between laboratory measurements over a specific period).

g) **Quality Assurance:** Appropriate QA/QC procedures should be established in each laboratory. ISO/IEC 17025 (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 monitored for drift, and recalibrated by the CCL-isoCO₂ at appropriate intervals (see 4.3.3 a) or replaced by a newly characterized high-level calibration cylinder with appropriate cross measurement of calibration cylinders.

h) **Uncertainty:** It is recommended that all reported measurement results be accompanied with the combined uncertainties (for example evaluated as the typical combined uncertainty of quality-control mixtures). This should include scale realization to primary RM (based on the uncertainty given by CCL-isoCO₂ to each JRAS-06 flask or air cylinder), CO₂ extraction, and data corrections. The atmospheric community, IAEA, BIPM and the NMIs have been collaborating on developing a template to aid in this process. Note: There may be two levels of uncertainty reported by a laboratory: an internal uncertainty, where common components of the uncertainty budget have been removed (for example to compare measurements over a time series at two sites by a single lab), as well as a total uncertainty, which would include all of the uncertainty components back to the common point in the traceability (such as for comparing data from sites measured by different laboratories).

i) **Interlaboratory Comparisons:** All laboratories are encouraged to participate in comparison activities, particularly the WMO round-robins organized by NOAA, as well as co-located or same-air comparisons of atmospheric flask samples (intercomparisons). 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 working group as it develops. If the sources/causes of discrepancies cannot be found, uncertainties should be re-evaluated using the comparison data as a guide. Comparison activities should also include diverse forms of samples, for example flasks, low- and high-pressure cylinders, or pure CO₂ ampoules (such as NARCIS sets 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 (and re-submit) their comparison data considering present recommendations regarding corrections and calibration scales, if they have not already done so.
4.4 Isotopic measurements of CO₂ using optical techniques

Optical analysers that report mole fractions of individual isotopically substituted molecules, commonly referred to as "isotopologues" or "isotopocules", are now in routine use. Calculations using these mole fractions allows isotopic composition to be expressed as delta values with a precision, after processing, of around 0.1‰ or better for δ¹³C of atmospheric CO₂. These are valuable for continuous measurements.

Delta values from such instruments are normally calculated from the ratios of reported individual isotopocule mole fractions. These have been derived from measured spectra using tabulated absorption line strengths and reference isotopic abundances from a spectral parameter database (typically HITRAN, http://hitran.org/, and see notes on HITRAN in section 4.4.1). Some corrections that are applicable to mass spectrometric methods, such as those for ¹⁷O and N₂O are not required, but other corrections specific to the applied spectroscopic technique may be needed. For example, raw calculated isotopic ratios (given as delta values) may be subject to instrumental factors such as spectral interference from other atmospheric components, gas matrix effects (for example N₂, O₂, Ar) and total CO₂ concentration. Calibration and drift-correction for optical instruments are typically done using CO₂-in-air reference mixtures characterized by the traditional IRMS methods.

An approach for calibrating optical instruments has been developed by several groups (Wehr et al., 2013; Flores et al., 2017; Tans et al., 2017; Griffith, 2018 and references therein). The method is based on the mole fractions of major isotopocules, and thus has the advantage of not requiring a range of isotopic ratios in calibration mixtures. The approach calibrates the instrument response for isotopocules of interest independently (for example for CO₂: ¹²C¹⁶O¹⁶O, ¹³C¹⁶O¹⁶O, ¹²C¹⁸O¹⁶O) based on air mixtures with well-characterised CO₂ mole fractions (WMO CO₂ scale) and isotopic composition assigned on the VPDB-CO₂ scale (preferably the JRAS-06 realization thereof) using IRMS. This information is used to calculate the mole fraction of each isotopocule in the calibration mixture in order to obtain the corresponding calibration function of the instrument for each isotopocule. If the (total) CO₂ mole fraction in calibration-mixtures spans the range of ambient air samples, the mole fraction of each isotopocule in the mixtures will span that of the samples as well.

The precision (repeatability) of optical isotopic measurements of δ¹³C due to random error is determined by the relative precision of the spectroscopic analyses of the isotopocules, typically better than 0.1‰ and approaching 0.01‰ for isotopocule ratios in newer instruments. Absolute accuracy is determined by the measurement of reference standards (similarly 0.1 – 0.01‰ for random error) and the systematic uncertainty in their assigned total CO₂ and delta values as provided by the relevant calibration laboratory. Spectral interferences, gas matrix effects, and instrument drift should be accounted for when assessing accuracy and precision.

This approach has been demonstrated for FTIR (Fourier-transform infrared) spectroscopy and is applicable to optical methods in general. It avoids the complexities of a calibration scheme based directly on raw or uncalibrated isotope ratios (delta values) which have a total mole fraction dependence that also needs to be either characterised or eliminated by making measurements at a constant mole fraction. 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 value) differences⁶.

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⁶ Presently, calibration based on isotope ratios (delta values) is the most common approach used by manufacturers of optical isotopic analysers.
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 N₂O and CH₄ measurements. Practical details on how to implement the novel approach using CO₂ as an example 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, the CCLs should provide both the total mole fraction of CO₂ and its isotopic composition for each calibration gas. For mixtures produced by NOAA with calibrated CO₂ mole fraction, the isotope composition on the VPDB-CO₂ scale may be provided by CCL-isoCO₂ or INSTAAR. Both labs will report on the JRAS-06 realization of the VPDB-CO₂ scale.

b) If the data are provided by other laboratories, traceability and uncertainty budgets should be documented.

c) As no calibrated measurement of δ²⁷O is available at this time, it can be determined with sufficient accuracy for most purposes from δ¹⁸O by assuming a mass dependent relationship.

d) Developers and providers of isotopic optical analysers should follow an open philosophy, making the primary measurements and relevant algorithms used in the calculation of calibrated delta values available to the users. The aim is to ensure comparability across instrument types, manufacturers and measurement laboratories, and to enable verification of procedures and corrections by individual operators. Measurement information may include pressures, temperatures, optical path lengths, spectra, absorption line peak heights, and 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 mole fraction of each isotopically substituted molecule.

e) When referencing spectral databases such as HITRAN, users should be aware that the reference isotopic abundances incorporate relative abundances of isotopic species based on assumed isotope ratios that do not necessarily relate directly to VPDB-CO₂ and may not be in agreement with the IUPAC accepted values (Brand et al., 2014).

f) 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 CH₄ isotope calibration and comparison activities

#### 4.5.1 Historic to current situation

The stable isotopic composition of atmospheric methane has been regularly measured for nearly three decades, involving at least 16 laboratories in eight countries (Umezawa et al., 2018). While the primary focus for most laboratories has been δ³⁴C-CH₄, δ¹³H-CH₄ has been measured to a lesser extent. All δ³⁴C data are reported on the VPDB scale (the same scale as used for reporting δ³¹C of air-CO₂) and δ¹³H on the VSMOW/SLAP scale. The long-term monitoring of atmospheric δ³⁴C-CH₄ in background air is challenged by the very small seasonal and long-term variations. The currently available δ³¹C-CH₄ data show seasonal cycles with amplitudes between 0.2 ‰ and 0.8 ‰ in southern and boreal northern hemispheric background air, respectively, and those for δ¹³H-CH₄ were up to 10 ‰ at northern hemispheric
sites. In comparison, the interpolar gradient for $\delta^{13}$C-CH$_4$ ranges around 0.5 ‰, and that of $\delta^3$H-CH$_4$ is approximately 10 ‰.

The small variability requires a careful design of the calibration strategy for methane isotopes. However, this is complicated because RMs in the form of CH$_4$-gas or CH$_4$-in-air mixtures are not available. Laboratories have developed calibration strategies and practical solutions that enabled them to pursue their atmospheric monitoring programmes by reporting data on the VPDB scale for $\delta^{13}$C, and they performed comparisons to assess analytical offsets between laboratories. While the internal precision and reproducibility within labs is generally relatively good, lab-to-lab discrepancies exceed the network compatibility goals significantly (Umezawa et al., 2018). This implies the presence of significant inconsistencies across labs in calibration approaches, use of available RMs, accounting for instrumental effects and in the data treatment (see 4.5.3).

4.5.2 Assessing current laboratory effects with round-robin and co-located observations

INSTAAR and NIWA have prepared a round-robin to precisely measure the current laboratory offsets for $\delta^3$H-CH$_4$ and $\delta^{13}$C-CH$_4$ measurements. For that purpose, four high-pressure cylinders were prepared with natural and semi-synthetic CH$_4$-in-air mixtures that were targeted to identify instrumental and data correction effects. The round-robin began in 2019. The cylinders include: 1) northern hemispheric air, 2) northern hemispheric air mixed with CH$_4$-free air to a CH$_4$ mole fraction of ~1000 ppb, 3) southern hemispheric air with doubled krypton mole fraction, 4) southern hemispheric air with negative isotope spike, balanced with CH$_4$-free air to a CH$_4$ mole fraction of ~1850 ppb.

The round-robin gases will test the ability of laboratories to address a range of analytical challenges such as scale contraction, CH$_4$-amount dependence and Kr interference. First results of the round-robin and a detailed comparison between MPI-BGC and NIWA have been presented and discussed at the GGMT-2019. While those results generally support the laboratory offsets as reconstructed by Umezawa et al., 2018, they also highlight that some offsets and analytical effects have not been accurately captured or have changed over time.

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 where feasible. There are several sites where multiple laboratories are measuring samples, and these intercomparison activities are also useful for assessing lab offsets and their consistency over time.

4.5.3 Potential causes and remedies for interlaboratory differences

a) Primary reference material: Since no CH$_4$-specific RMs were available when these measurements commenced several decades ago, individual laboratories have developed in-house procedures to relate their measurements to the international VPDB and VSMOW/SLAP isotope scales. Historically, the RMs used for $\delta^3$H-CH$_4$ scale realizations were predominantly waters (VSMOW2 – SLAP2 and respective precursors). However, a range of RMs with very different chemical properties and revised isotope values have been used for the $\delta^{13}$C-CH$_4$ scale realizations (overview in Sperlich et al., 2016 and Umezawa et al., 2018). Data users need to be aware of potential data-set biases, reflecting the fact that there is no unifying scale realization for $\delta^{13}$C-CH$_4$ or $\delta^3$H-CH$_4$
measurements and they should be in close contact with the laboratories to discuss the use of available data.

b) **Transfer of calibrations from one lab to another:** Local $^{13}\text{C}$-$\text{CH}_4$ or $^{17}\text{O}$-$\text{CH}_4$ scale realizations have been transferred from one laboratory to another by transferring gas mixtures with well measured isotopic values. Thus, the calibration traceability to the scale level includes multiple laboratories (see Umezawa et al., 2018 for examples). This makes it more difficult to apply accurate offset corrections retrospectively. It is of crucial importance that the complete history of the scale realization is documented and propagated in an uncertainty budget. This includes the values and uncertainties of the applied RMs, the uncertainty of the scale realization, the uncertainty of the scale transfer and the uncertainty of dependent measurements of the newly established reference frame.

c) **Inconsistent use of $^{17}\text{O}$ correction (for $^{13}\text{C}$-$\text{CH}_4$):** Measurements of $^{13}\text{C}$-$\text{CH}_4$ in air have predominantly been made using isotope ratio mass spectrometers (IRMS), including the oxidation of $\text{CH}_4$ to $\text{CO}_2$ prior to IRMS analysis. IRMS measurements of $^{13}\text{C}$ in $\text{CH}_4$-derived $\text{CO}_2$ include a $^{17}\text{O}$-correction algorithm, which has been revised in the past. Laboratories currently measuring $^{13}\text{C}$-$\text{CH}_4$ use different $^{17}\text{O}$-correction algorithms (Umezawa et al., 2018), which may cause a significant bias between laboratories. The effect of inappropriate $^{17}\text{O}$-correction is most pronounced when the measurements include large isotope ranges, as is the case for measurements of relatively $^{13}\text{C}$ depleted $\text{CH}_4$ in comparison to measurements of $\text{CO}_2$ evolved from RMs such as NBS-19. Inconsistent combination of different $^{17}\text{O}$-correction algorithms during $^{13}\text{C}$-$\text{CH}_4$ scale realization transfer from one lab to another may be another reason for $^{17}\text{O}$-correction related biases. It is recommended for all laboratories measuring $^{13}\text{C}$-$\text{CH}_4$ using IRMS to apply the $^{17}\text{O}$-correction after Assonov and Brenninkeijer 2003 (a,b) or Brand et al., 2010.

d) **Instability of LSVEC:** Due to the depleted $^{13}\text{C}$ value of $-46.6$ ‰, the instability in LSVEC (see above) may be most impactful for measurements of $^{13}\text{C}$-$\text{CH}_4$. As soon as a second scale anchor is available for the $^{13}\text{C}$-VPDB scale it will need to be incorporated into the calibration scheme for $^{13}\text{C}$-$\text{CH}_4$ of atmospheric methane. All laboratories making measurements of $^{13}\text{C}$ in atmospheric $\text{CH}_4$ are advised to maintain their calibration strategies as already established and be ready to apply corrections retrospectively when new RMs are released.

e) **Krypton effect:** The interference of krypton with $^{13}\text{C}$-$\text{CH}_4$ measurements in air samples using gas chromatography - isotope ratio mass spectrometer (GC-IRMS) systems has been identified by Schmitt et al. (2013), where the interference causes an artefact that varies with the $\text{CH}_4$:Kr ratio in the sample. Because atmospheric Kr mole fractions are rather stable, this effect scales directly with variations of $\text{CH}_4$ mole fractions. The authors demonstrate that the implementation of a post-combustion chromatographic column to separate $\text{CH}_4$-derived $\text{CO}_2$ from krypton prevents this interference. Analytical systems other than GC-IRMS are not affected by this interference.

f) **Scale contraction effects:** Scale contraction is an underestimation of isotopic differences. For example, this effect may potentially be large when air samples contain variable amounts of $\text{CH}_4$ from local, isotopically distinct sources or in the analysis of ice core samples. Scale contraction has often been described as an artefact in dual inlet IRMS analysis (see section 4.3.3). However, scale contraction effects (or potentially an overestimation of scale span) may also occur in GC-IRMS analysis where they have different origins, including mass spectrometric effects, $\text{CH}_4$ blank effects, and more. It is strongly recommended to thoroughly assess and eliminate analytical scale span effects where possible, or carefully estimate their magnitudes and correct for them. If a scaling correction has to be applied, details of that correction should be supplied within the
data publication. These effects should be accounted for using suitable working gases and QA/QC procedures.

g) \textit{CH}_4 \textit{amount effect}: Automated systems to measure $\delta^{3}\text{C-CH}_4$ or $\delta^{2}\text{H-CH}_4$ in air samples often analyse constant amounts of air, i.e. the sample volume is controlled via sample loop or sample flow-rate. The analysis of samples with variable \textit{CH}_4 mole fractions would result in the analytical processing of variable amounts of \textit{CH}_4, which potentially creates \textit{CH}_4-amount dependent isotope effects. For example, non-linearity effects in IRMS instruments may affect the final data during the evaluation of sample peaks with different peak sizes. This is particularly important for the analysis of $\delta^{2}\text{H-CH}_4$, where an accurate $H_2$-factor correction must be applied. Also, the cryogenic pre-concentration of \textit{CH}_4 on an adsorbent may be limited to an instrument-specific maximum \textit{CH}_4 amount. Isotopic fractionation may occur when this \textit{CH}_4 amount is exceeded. Furthermore, the analytical steps of \textit{CH}_4 oxidation or \textit{CH}_4 pyrolysis may be limited to instrument-specific amounts of \textit{CH}_4. Isotope fractionation effects may then arise when this \textit{CH}_4 amount is exceeded and incomplete \textit{CH}_4 conversion occurs. Instrument design should minimize the effect of different \textit{CH}_4 amounts on measured isotope ratios where possible. If an analytical system requires a \textit{CH}_4-amount correction, it is strongly recommended to document the details of that correction within the publication of the data as scientific literature and/or in data-bases. It is strongly recommended to apply suitable working reference gases and QA/QC gases, covering the range of \textit{CH}_4-amount variation that is expected in the measured samples.

h) \textit{Long-term stability and QA/QC}: Long-term stability of analytical systems should be monitored using an appropriate number of working reference gases as well as suitable QA/QC gases for quality-control. It is recommended to create a critical redundancy with the applied QA/QC gases so that future replacements of analytical components, working reference gases and updates to working reference gases as well as RMs can be reliably performed and documented. In the light of an upcoming revision of the VPDB-scale for $\delta^{3}\text{C}$ and related RMs (even if potential shifts of RM’s values may be very small), it is recommended to archive a sufficient number of historic and current laboratory standard gases for future scale revisions.

i) \textit{Developing new capabilities for the analysis of $\delta^{3}\text{C-CH}_4$ or $\delta^{2}\text{H-CH}_4$ in air samples}: Laboratories starting isotope measurements in atmospheric \textit{CH}_4 may seek to get a suitable range of air mixtures (see round-robin mixtures) in high-pressure cylinders “calibrated” as their highest local reference gases by a laboratory with a well-established referencing history. In the absence of RMs in the form of \textit{CH}_4 (or \textit{CH}_4-mixtures), laboratories may decide to base their calibrations on existing $\delta^{3}\text{C-CH}_4$ or $\delta^{2}\text{H-CH}_4$ scale realizations of a well-established laboratory as intermediate solution. It is advised to ensure all relevant documentation is available that enables the transition to updated RMs in future. It is recommended for local scale realizations to be verified and updated in regular intervals to prevent laboratory-specific biases and drifts.

### 4.5.4 Outlook

The need for consistent $\delta^{3}\text{C-CH}_4$ and $\delta^{2}\text{H-CH}_4$ scale realizations has been recognized at previous GGTM meetings. A practical approach for preparing isotopically characterized methane-in-air mixtures linked to the accepted international isotope scales (VPDB and VSMOW/SLAP) has been presented at GGTM-2015 and published by Sperlich et al. (2016). An update of this strategy was presented at the GGTM-2019 by Sperlich et al., which proposes a framework to develop a Community Reference Gas Scale realization of the VPDB and VSMOW/SLAP scales, improving comparability and compatibility between labs. Several pure \textit{CH}_4 gases were analysed under identical analytical conditions directly against available RMs, so
that known effects (for example consistent use of $^{17}$O-correction, potentially incomplete conversion of RMs and CH$_4$) were minimized. These CH$_4$ gases will be re-characterized once a successor for LSVEC is determined.

4.6 N$_2$O isotope calibration and comparison activities

The need for N$_2$O isotope standard reference materials has been recognized by previous GGMT meetings. New technology is increasing the ability to measure N$_2$O isotopocules and clumped isotopes. GGMT-2019 welcomes the effort to develop new international reference materials for $\delta^{15}$N, $\delta^{18}$O, $\delta^{13}$N and $\delta^{18}$O in N$_2$O with target uncertainties of 1.0 ‰ ($\delta^{15}$N and $\delta^{13}$N) and 0.5 ‰ ($\delta^{18}$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 (project website: http://www.vtt.fi/sites/SIRS/). The N$_2$O work is 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$_2$O with stated uncertainty are available, particularly crucial for $\delta^{15}$N and $\delta^{13}$N, efforts to release RMs in the form of pure N$_2$O gas (in ampoules) or N$_2$O-in-air (cylinders or flasks) are encouraged. GGMT recommends that IAEA be requested to assess their capability to prepare suitable materials.

We recommend that future GGMT meetings discuss the scientifically required network compatibility for isotopic measurement of atmospheric N$_2$O, which are likely to be very demanding due to the long atmospheric lifetime of N$_2$O.

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 compared to CO$_2$. $\delta^{13}$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 (two-point data normalisation 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 (for example Mak and Yang, 1998; Tsunogai et al., 2002). In brief, CO is either extracted from air by CO-oxidation on I$_2$O$_5$ 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$_2$O$_5$-oxidation reactor (iv) calibration or elimination of CO produced within the extraction system (that is “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 CO₂ be eventually transferred to stable isotopes of CO.
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 $\Delta$ in this reference):

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

with $R=^{14}$C/$^{12}$C, the corrections are for fractionation and radioactive decay ($\lambda$) 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 (such as 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 normalisation 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 13$^{th}$ 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 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 21$^{st}$ 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-2021.

d) We recommend the continuation of regular whole-air and pure-CO$_2$ comparison exercises to increase the statistical robustness of the results.

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 standardisation 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 (such as optical $^{14}$C measurement techniques) which could potentially make in situ atmospheric $^{14}$C measurement realistic in the future.
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 O₂/N₂ CALIBRATION

6.1 Background

Measurements of the changes in the atmospheric O₂/N₂ ratio are useful for constraining sources and sinks of CO₂ and testing land and ocean biogeochemical models. The relative variations in the O₂/N₂ 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 O₂/N₂ ratios directly (mass spectrometry and gas chromatography), and (2) those which effectively measure the O₂ 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 O₂ to N₂. For mole-fraction type measurements, this requires accounting for dilution due to variations in CO₂ and possibly other gases. If synthetic air is used as a reference material, corrections may also be needed for differences in Ar/N₂ ratio. By convention, O₂/N₂ ratios are expressed as relative deviations compared to a reference

\[ \delta(O₂/N₂) = \frac{(O₂/N₂)_{\text{sample}}}{(O₂/N₂)_{\text{reference}}} - 1 \]

in which \( \delta(O₂/N₂) \) is multiplied by \( 10^6 \) and expressed in per meg. Per meg is a dimensionless quantity and is equivalent to 0.001 per mil (‰), 0.01 per cent (%) or 1 ppm (Coplen, 2011).

The O₂/N₂ reference is typically tied to natural air delivered from high-pressure gas cylinders. There is currently no common source of reference material, nor is there a CCL for O₂/N₂. Most laboratories either report relative to their own internal reference or relative to references which were analysed and given \( \delta(O₂/N₂) \) values at the Scripps Institution of Oceanography (SIO).

Calibration of measurements of O₂/N₂ also typically requires a determination of instrument sensitivity to changes in O₂/N₂ ratio, that is establishing the instrument span. This can be done, for example, by introducing samples which have a known deviation in O₂/N₂ ratio from a reference. Span difference between labs can also be identified by the sharing of reference gases.

There is considerable scientific value to be gained from different laboratories reporting O₂/N₂ measurements on a common scale. The O₂/N₂ measurement community recognizes the SIO O₂ scale as the best candidate for a common reference. With a goal of establishing this as the common scale for reporting and comparing O₂/N₂ measurements, we recommend that all O₂/N₂ measuring laboratories participate in the Global Oxygen Laboratories Link Ultra-precise Measurements (GOLLUM) comparison exercise (see section 6.2 for more information), and we recommend that laboratories take steps to link their internal laboratory scales directly to the SIO O₂ scale. In support of this, we recommend that the SIO O₂ laboratory continue to provide measurements for other laboratories on a cost-recovery basis, with a targeted turn-around time of five weeks for existing tanks, and also continue to provide service for filling and calibration of new tanks with a target turn-around time of six months.

The practice of basing O₂/N₂ measurements on natural air stored in high-pressure cylinders appears acceptable for measuring changes in background air, provided the cylinders are handled according to certain best practices, including orienting cylinders horizontally to minimize thermal and gravitational fractionation, and taking care to dry cylinders to 1 ppm of H₂O 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. For the diagnosis of fractionation processes, many laboratories have found it useful to make simultaneous measurements of the Ar/N$_2$ ratio, which has atmospheric variations much smaller than O$_2$/N$_2$ but which has amplified responses to most fractionation processes.

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, for example 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).

### 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 original 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 SIO serving as the point of origin for the round-robin programme. Following recommendations from GGMT-2017 the GOLLUM project has been restarted. The next round of GOLLUM tanks is in preparation at SIO with the next circuit expected to start by summer 2020.

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 interlaboratory 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. In 2017, SIO retrospectively revised earlier measurements to reflect a change in the span calibration factor of the interferometric method used at SIO, which had an impact at the level of 2% of span. This revision included retrospective revision of values of GOLLUM and other tanks measured at SIO for other groups. This new scale is designated the SIO 2017 O$_2$/N$_2$ scale.
An important recent development was the development of high-accuracy (~ ± 5 per meg) gravimetric standards by Nobuyuki Aoki and colleagues at the National Institute of Advanced Industrial Science and Technology (AIST) in Tsukuba, Japan (Aoki et al., 2019), which has proved valuable for identifying differences in span calibration between several laboratories and is an important step towards achieving a long-term calibration independent of air stored in high-pressure cylinders.

### 6.3 Recommendations for O₂/N₂ 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:
   i. An additional suite of circulating cylinders equipped with “dip-tubes” to minimize the influence of thermal fractionation.
   ii. An additional suite of circulating cylinders that incorporates those field stations making in situ measurements of atmospheric O₂ and which are not presently included in any O₂ comparison programme.
   iii. An additional suite of tanks with large changes in O₂/N₂ ratio, for example spanning +/- 2000 per meg around ambient. The goal is to more accurately characterize scale contraction/expansion issues between labs.

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 O₂/N₂ scales and methods between programmes.

g) Encourage the sharing of information on well-tested O₂/N₂ 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 O₂ measurements such as developing intake and “tee” designs that do not fractionate O₂ relative to N₂, and to investigate the influence of dip-tubes installed in high-pressure cylinders.

i) Continue and expand efforts to produce gravimetric standards for O₂/N₂. We recognize the value in having several laboratories engaging in this activity.

j) Encourage efforts by the relevant laboratories to assess the influence on their O₂/N₂ measurements (using different analytical techniques) of variations in CO, H₂, CH₄, N₂O, H₂O, and any other species that are commonly present in air samples with the potential to interfere at the per meg level.

k) Continue evaluation of the SIO O₂ scale for future implementation as the common scale for reporting and comparing O₂/N₂ measurements, and establish named versions of this scale for tracking updates.

l) Encourage those laboratories which report relative to tanks calibrated at SIO to retrospectively convert to the SIO 2017 O₂/N₂ scale, with assistance from SIO on conveying the tank revisions.

m) Encourage laboratories to employ an error model for O₂/N₂ measurements that allows for uncertainty in span calibration.
7. **SPECIFIC REQUIREMENTS FOR CH\textsubscript{4} CALIBRATION**

7.1 **Background**

NOAA 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 (April 2020) version of the WMO mole fraction scale for methane is WMO CH\textsubscript{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\textsubscript{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\textsubscript{4} values between 300 and 3000 ppb).

7.2 **Recommendations for CH\textsubscript{4} calibration and comparison activities**

a) The CCL will transfer the CH\textsubscript{4} scale to calibrated CH\textsubscript{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\textsubscript{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\textsubscript{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 N₂O 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 N₂O mole fractions reported by different laboratories are still large compared to atmospheric gradients. The mean inter-hemispheric difference in N₂O mole fraction is around 1 ppb and the pole-to-pole difference is 2 ppb. These differences are 0.3-0.6% of the recent global mean mole fraction of N₂O in the troposphere. This necessitates not only high measurement precision, but also high consistency among assigned values for standards. Network compatibility of measurements from different laboratories of 0.1 ppb is needed.

NOAA serves as the CCL for nitrous oxide. The current (April 2020) version of the WMO mole fraction scale for nitrous oxide is WMO N₂O X2006A. The scale consists of 13 gravimetrically-prepared N₂O-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 N₂O calibrations is estimated to be 0.2 ppb at the 95% confidence level.

8.2 Recommendations for N₂O calibration and comparison activities

a) Each GAW measurement laboratory or network calibration centre of GAW partners must actively maintain its link to the WMO scale by having a subset of its highest level standards for N₂O re-calibrated by the CCL every four years.

b) The CCL and the WCC (Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, KIT/IMK-IFU) should work together to establish more frequent comparisons among GAW stations and other key laboratories that measure N₂O. The CCL should strengthen collaborations with Empa and KMA, since N₂O can sometimes be incorporated in CO₂ audits performed by Empa and SF₆ audits performed by KMA.

c) The use of a travelling N₂O instrument during audits by the WCC-N₂O 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 the GGMT community.

f) The CCL should investigate differences between observations linked to the WMO N₂O scale and those linked to the Advanced Global Atmospheric Gases Experiment (AGAGE) N₂O scale.
9. SPECIFIC REQUIREMENTS FOR SF₆ CALIBRATION

9.1 Background

Sulphur hexafluoride (SF₆) is a very long-lived trace gas with strong infrared absorbance. SF₆ is ~22500 times more effective as a climate forcing agent than CO₂ on a per-mass basis over a 100-year time scale. The tropospheric mole fraction of SF₆ has increased steadily, with a growth rate of 0.2-0.3 ppt/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".

SF₆ is typically measured using gas chromatography with electron capture detection (GC-ECD), similar to N₂O. NOAA serves as the WMO/GAW Central Calibration Laboratory (CCL) for atmospheric SF₆. The current (April 2020) version of the WMO mole fraction scale for sulphur hexafluoride is WMO SF₆ 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). Scale propagation uncertainty (reproducibility, see Chapter 2) is estimated at ±0.02 ppt (95% C.L.).

The Korea Meteorological Administration (KMA), assisted by Korea Research Institute of Standards and Science (KRISS), serves as a World Calibration Centre for SF₆ (WCC-SF₆). A SF₆ comparison was initiated by the WCC-SF₆ in 2016 and the first comparison report is available on the WMO website (https://community.wmo.int/other-gaw-related-publications).

9.2 Recommendations for SF₆ calibration and comparison activities

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

b) The WCC-SF₆ is encouraged to organize round-robin comparisons of SF₆ working standards among WMO participants and to implement audits for assessing SF₆ measurements in the GAW community.

c) The CCL and WCC-SF₆ should compare their laboratory standards on a regular basis.

d) 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 SF₆ 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 is the WMO/GAW CCL for carbon monoxide. The current (April 2020) version of the WMO mole fraction scale for CO is WMO CO X2014A. Due to growth 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).

In the latest scale revision (WMO CO X2014A, introduced in December 2015) the gravimetric standards made in 2011 have been designated as the Primary Standards and all measurements made since 2011 are related to their values in a strict hierarchal calibration scheme. There are 14 primary standards covering the nominal range 30–1000 ppb. The WMO CO X2014A scale covers the range 30–500 ppb. Calibrations from 500–1000 ppb by the CCL are on an extended scale that is closely tied to the WMO scale but has higher uncertainty of scale propagation.

Growth of CO in the primary standards is occurring. With the WMO CO X2014A scale revision the CCL decided to change the method used to define the scale with the goal of improving the ability to track drift in the primary standards to allow a single set of primary standards to define the scale. 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\textsubscript{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\textsubscript{4} ratio. CH\textsubscript{4} is measured in each dilution standard and used with the known CO:CH\textsubscript{4} ratio of the parent to assign a CO value to the dilution standard. The drift in the primary standards was determined between 2011 and 2015 by a series of repeated comparisons of the primary standards to fresh sets of dilution standards made from the stable parent tanks. These drift rates define the time dependent assigned values of the primary standards. Over time, more comparisons have been made and show that the drift corrections applied to the primary standards for the X2014A
scale are generally too high leading to a time-dependent bias in the scale. The CCL is investigating further with the goal of another scale revision in 2021. (See CCL website for more detailed information and periodic updates 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 (Zellweger et al., 2019). This has helped the international in situ CO measurement community enormously, but also has exposed some drift and inconsistency in the NOAA 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 verify that the CO mole fractions in primary standards are not changing, or ensure that they 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) 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.

f) In addition to regular re-calibrations by the CCL laboratories are encouraged to develop techniques to monitor cylinders for drift. Options include a comparison to well-characterized target tanks, ongoing comparison with other laboratories, and static and dynamic dilution techniques using an internal tracer. If drift is suspected in the laboratories highest level standards, then they should be directly returned to the CCL for recalibration to maintain traceability to the WMO scale.

g) The CCL shall further investigate the discrepancy between the drift corrections fixed in 2015 and the experimentally observed growth rates since then. It shall also examine the small biases between the two analytical methods used to propagate the scale with the goal of another scale revision in 2021 which addresses these biases.
11. SPECIFIC REQUIREMENTS FOR H₂ CALIBRATION

11.1 Background

Molecular hydrogen plays a significant role in global atmospheric chemistry due to its role in CH₄ – 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 H₂ calibration and comparison activities

MPI-BGC serves as the WMO/GAW CCL for atmospheric molecular hydrogen. The current (April 2020) scale is WMO H₂ 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, H₂ growth in two of the primary standards was detected that were stored in one specific steel cylinder type. In 2015, increases in hydrogen at rates of 0.3 ppb/year have been detected in two additional primary standards in another, but similar type of steel cylinder. In consequence, all standards stored in these type of cylinder were disregarded and replaced by alternative standards with 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. Experimental results to control the stability of the scale (see 11.3a) have suggested a mole fraction related bias in the scale of about 2 ppb in the atmospheric H₂ mole fraction 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 H₂ calibration and comparison activities

a) 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.

b) 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).

c) 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 superior to the common HgO reduction detectors (with respect to precision and non-linearity) are available (Novelli et al., 2009) and should be considered for new installations.
d) Due to the strong non-linearity of the HgO reduction detectors, it is particularly important for \( \text{H}_2 \) measurements that the mole fraction of the working standard gas is close to the mean annual \( \text{H}_2 \) level observed at the site. In contrast, the target standard gases used for quality control purposes are recommended to have \( \text{H}_2 \) mole fractions that are at the high end of the observed values to provide good diagnostic.

e) 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.
12. RECOMMENDATIONS FOR GREENHOUSE GAS NETWORKS IN URBAN AREAS AND OTHER 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 network sites reasonably represent the region of interest. Network compatibility between sites within a regional network is required over the often large range of observed dry air mole fractions.

Frequently it is also of central importance to reliably 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 air 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.

Observations of Δ$^{14}$C in CO$_2$ represents a special case where reproducibility of 30-50% for individual measurements of the regional Δ$^{14}$C offset from the local boundary condition may be sufficient to be useful, although precision of 5% or better is ultimately desirable.

Progress is expected particularly to be made by projects under the umbrella of the Integrated Global Greenhouse Gas Information System (IG$^3$IS), which is promoted by WMO and its partners. IG$^3$IS will provide a common platform, co-developed with stakeholders, for establishing benchmarks, good practices utilizing diverse measurement and analysis approaches inside a reliable framework. The IG$^3$IS Science Implementation Plan (WMO, 2019a)
lists "Support of Mitigation Efforts of Cities" as one of its key objectives. It is planned to make use of above-mentioned observations and associated modelling to identify emitters, quantify emissions, and to understand the underlying processes.

12.2 Recommendations

a) We recommend the IG³IS working group for urban greenhouse gas emissions continues to interact with the WMO/GAW Urban Research Meteorology and Environment (GURME) Project and the group working on Integrated Urban Services (IUS).

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. Current experiences should be collected in an effort towards developing improved recommendations on background definitions/methodologies at GGMT-2021.

c) 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, 2018b) following a lost-cost sensor experts meeting in February 2018.

d) In recent years, mobile surveys of GHGs in urban areas have become more widely used (especially for methane). The general recommendations of a signal to noise ratio of 5% still applies. However, additional care should be given to the collection of important metadata like, inlet height on vehicle, flow rates and sample residence time in the system, etc. It is also critical to ensure the careful synchronisation for additional data streams for example GPS coordinates, meteorological conditions collected on the same mobile platform.
13. RECOMMENDATIONS FOR GROUND-BASED TOTAL COLUMN REMOTE SENSING TECHNIQUES

13.1 Background

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

To avoid station-to-station biases 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). The protocols are fully described in two network papers by Wunch et al. (2010, 2011).

For practical comparisons 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 calibrated 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. Chapter 15 on emerging techniques provides 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 with greater portability than TCCON have recently become available. These have the potential to expand the global coverage of this type of atmospheric measurement. The precision, accuracy, drift, susceptibility to interference and general performance of these sensors is being assessed and quantified through co-located and coincident measurements at TCCON sites; only then can these measurements be related to validated TCCON measurements.

The most advanced such approach is the Collaborative Carbon Column Observing Network (COCCON), which uses a smaller, portable, lower resolution FTIR spectrometer with integrated suntracker. The lower resolution limits the ability to retrieve vertical information and makes 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., 2019).

A separate side-by-side study of several low resolution solar infrared spectrometers (including COCCON) has recently been carried out with coincident TCCON and Aircore measurements and the performance of each system assessed (Sha et al., 2019).

Low resolution portable spectrometers may also be used for long-term observations in 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, low
resolution spectrometers can potentially be used for verification of the site-to-site consistency of TCCON measurements.

### 13.2 Compatibility goals

The ESA Report for Mission selection: Carbonsat (ESA 2015, p 54) and US National Academies of Sciences, Engineering and Medicine Decadal Survey (NAS, 2018, p 601) have evaluated compatibility goals for total column measurements of CO₂ and CH₄ from satellites in space with near-global coverage, analogous to those given for in situ measurements in Table 1. For ground-based total column measurements such as those from TCCON to act as a “calibrated ground truth” for satellite measurements, random and systematic errors should be significantly smaller than those of the space-based measurements, say by a factor of three. The compatibility goals for space-based measurements are summarized in Table 2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Random (Goal/Threshold)</th>
<th>Systematic (Goal/Threshold)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XCO₂</td>
<td>1/3 ppm</td>
<td>0.2/0.5 ppm</td>
</tr>
<tr>
<td>XCH₄</td>
<td>6/12 ppb</td>
<td>2.5/5 ppb</td>
</tr>
</tbody>
</table>

### 13.3 Recommendations

a) Ground-based remote sensing measurements of CO₂, CH₄, N₂O and CO from TCCON sites must follow the formal TCCON data protocols and be accepted in the TCCON network and to be acceptable to GAW.

b) Future networks of more affordable and portable FTIR spectrometers (such as COCCON and others currently being assessed) 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, standardised spectrum analysis protocols should be followed to minimize the risk of bias in derived total columns and mole fractions. Once in operation, each spectrometer contributing to the network or measurement campaigns should undergo regular re-verification of its characteristics (for example in side-by-side validation at a TCCON site).

c) 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.
14. RECOMMENDATIONS FOR AIR MEASUREMENTS OF CO2 ON SHIPS

14.1 Background

Measurement of the partial pressure of CO2 (pCO2) in surface water throughout the global oceans is an important constraint on the role that oceans play in absorbing anthropogenic CO2 that has been released into the atmosphere. These measurements are being made on a combination of research ships and ships of opportunity that, in many cases, can also make measurements of atmospheric CO2 with the same system. Provided that these air measurements meet the basic requirements of the GGGM community, the more than 300 ship transects that contribute to the global ocean surface water pCO2 database (Surface Ocean CO2 ATlas – SOCAT, https://www.socat.info) each year can provide a valuable addition to the currently available atmospheric CO2 datasets.

On Wednesday, September 4, 2019, a presentation and discussion was convened as part of the GGGM-2019 meeting to examine the results of ongoing efforts to improve and expand atmospheric CO2 measurements from ships with the ultimate aim of incorporating these measurements into the Cooperative Air Sampling Network. It was pointed out in this discussion that verification of the comparability for ship-based atmospheric CO2 will ultimately help verify the compatibility and comparability of contemporaneous surface ocean pCO2 measurements by providing an independent reference for the mole fraction of CO2 measurement needed to calculate pCO2. The discussion also highlighted the results of a comparison of atmospheric CO2 measurements made from an underway pCO2 system and a dedicated surveillance system that was installed on the RV Ron Brown from February to May of 2019.

14.2 Recommendations

Benefits

The global atmospheric CO2 community will benefit from high-accuracy ship-based atmospheric measurements of CO2 mole fractions because of the unique spatial coverage that ships offer. Owing to the complexity of CO2 land-based emissions, additional ocean measurements, over open-ocean and ocean regions adjacent to land, could provide the boundary conditions for inversion models focused on constraining continental-scale uptake of atmospheric CO2 by land and ocean (fluxes).

The ocean carbon community will also benefit from additional atmospheric measurements in several ways. First, many ocean flux estimates are based on measurements of the air-sea CO2 difference, typically using a smoothed product such as the zonally-averaged NOAA Marine Boundary Layer (MBL) Reference (GLOBALVIEW-CO2, 2013) for the atmospheric value. Although atmospheric CO2 over the ocean is generally less variable by an order of magnitude than ocean pCO2, the use of smoothed atmospheric CO2 products can lead to significant regional biases in flux estimates, particularly along continental margins where short-term and seasonal fluctuations may be large. As shown from an analysis of the difference between NOAA’s CarbonTracker and NOAA’s MBL product, biases in basin-scale air-sea fluxes arise because of the lack of east-west gradients in NOAA’s GlobalView MBL product. More reliable fluxes could be obtained if, instead of using the interpolated NOAA MBL product, atmospheric CO2 measurements from the ships themselves were used to characterize longitudinal variability, provided that these measurements are sufficiently comparable to other measurements in the Cooperative Air Sampling Network. Additionally, these ship-based measurements could be ingested into data assimilation systems such as NOAA’s CarbonTracker.
to create atmospheric CO\textsubscript{2} products that more accurately capture spatiotemporal variability over the ocean. Lastly, as discussed in more detail below, an improvement in the quality control of atmospheric measurements on ships will improve the traceability of contemporaneous surface ocean pCO\textsubscript{2} measurements to the WMO scale.

**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\textsubscript{2} scale is similar to other land-based in situ CO\textsubscript{2} measurements discussed in this document. These include a set of standards that are:

- Clearly traceable to the latest WMO CO\textsubscript{2} scale
- Span the expected range of atmospheric values
- Numerous enough in concentration-space and temporal frequency to account for non-linearity and drift of the CO\textsubscript{2} analysis system.

This also includes meta-data that can document:

- Procedures for identifying measurements contaminated by ship engine exhausts in dataset.
- Fully document hardware installations of air inlet lines.
- Numerical procedures for deriving the dry mole fraction of CO\textsubscript{2}.
- Uncertainty assessment of the data that accounts for all the major sources of error (for guidelines see Chapter 2).

**Audit system**

Because the primary purpose of ship underway pCO\textsubscript{2} systems is to monitor ocean surface pCO\textsubscript{2} which is more variable than atmospheric CO\textsubscript{2} by about an order of magnitude, it has been instructive to deploy an audit system on ships for month long periods to evaluate the atmospheric measurements. This audit system uses independent calibration gases, as well as a separate inlet line and sample drying system to both evaluate the multiple potential biases of a ship-based system’s atmospheric CO\textsubscript{2} measurements and evaluate procedures for identification and elimination of contamination signals from gases emitted by ship operations.

Ideally, this independently calibrated system should have the following characteristics:

- Independent set of calibration gases to test comparability and compatibility of underway pCO\textsubscript{2} system.
- Separate inlet line to test for any contamination of the atmospheric air sample line of the ship-based underway pCO\textsubscript{2} system.
- Frequent (>0.1 Hz) measurements to provide an optimal statistical filter for stack gas contamination.
- Carbon monoxide measurement capability to help detect ship stack gas and test statistical stack gas contamination filter for the existing ship-based pCO\textsubscript{2} system.
- Be compact and easily assembled for quick set up, disassembly and transport.
- Low drift and motion insensitive.
- Set up to independently dry sample air before measurement or have a proven ability to make water corrections to better than 0.1 ppm at 3% relative humidity.
Recent comparison tests suggest that comparisons between an independent calibrated system and atmospheric measurements from an ocean pCO$_2$ system can be done to better than 0.15 ± 0.2 ppm (Wanninkhof et al., 2019). It should be noted that in many cases where it is not possible to have a second inlet line for an independent system; it is still possible and valuable to test instrument compatibility even though such a setup cannot guarantee compatibility with the global network.

A system operated by NOAA is currently circulating among different ships of opportunity to evaluate the compatibility of this rich database of marine boundary layer atmospheric CO$_2$ mole fraction measurements. This prototype system has enabled the use of high resolution measurements of both CO$_2$ and CO to evaluate ship exhaust contamination and it confirms that the standard deviation of a set of 5 atmospheric measurements made over a 5 to 15 minute period, as commonly done by ocean pCO$_2$ systems, is a valid way to flag and filter measurements affected by ship exhaust for the installation on the RV Brown.

**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 i) guide the ocean community in making high precision, traceable measurements of atmospheric CO$_2$ dry mole fraction on ships, and ii) 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 theSurface Ocean CO$_2$ Reference Network (SOCONET) and SOCAT websites.

c) Maintain an ocean community presence at the next GGMPA meeting for further input and report on progress to date.

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 (OSE) and Observing System Simulation Experiment (OSSE).

f) In addition to the surveillance system described above, encourage flask sampling on ships to provide additional independent comparisons and evaluation of atmospheric measurements from underway pCO$_2$ systems, and establish protocols for flask sampling to verify air measurements from underway pCO$_2$ systems.

g) Continue comparisons from ships that currently have atmospheric CO$_2$ measurement systems with participation from both the ocean and atmospheric communities to assess the feasibility of including existing ocean community measurement systems in the atmospheric CO$_2$ network, and for determining key technical challenges that must be overcome to achieve 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.

15.1 General recommendations

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 standardisation, 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 for each new or emerging technique 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, scientific publications and participation in GGMT meetings.

b) We recommend that new analytical technologies (for example laser-based optical analysers, closed-cell Fourier Transform spectrometers) are tested against existing, accepted techniques (for example 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, sensitivity to temperature variations, 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:

i. Noise: Instrument noise should be characterized using dry air of known composition from cylinders. 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.

ii. 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.

iii. 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.

iv. 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.

v. 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 N₂, O₂, 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.
15.2 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 CO₂, CH₄ and other trace gases

Driven in particular by the need to monitor urban emissions at high spatial resolution, low-cost CO₂ sensors have increasingly been developed and evaluated. It is important to point out a few specific requirements for such sensors:

a) The measurements should be reported as dry mole fractions, which requires either correction for ambient water vapour or drying of ambient air.

b) Accuracy must be assessed – accurate measurements are required to derive unbiased surface fluxes from the urban areas.

c) 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.

d) Careful work is needed to characterize the performance of the low-cost sensors themselves following the general guidelines in 15.1 and to continuously monitor the sensor performance over time.

e) The low-cost sensor network requires verification with medium or higher cost reference sensors in the field.

f) 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, 2018b) 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 O₂ measurements

Besides the six traditional analytical techniques (see Chapter 6), laser-based O₂ measurements (QCLS, CRDS) are emerging, although they are currently less precise than the established techniques. The laser-based techniques measure O₂ mole fractions, potentially in humid air with water correction instead of drying the ambient air. To convert O₂ mole fractions to O₂/N₂ ratios, the dilution by CO₂ must be taken into account. Thus, concurrent CO₂ measurements in the same instrument are highly desired on the laser-based analysers.

Open-path measurements

In recent years systems that allow horizontal open path GHG mole fraction observations have become available (such as Waxman et al., 2017; Griffith et al., 2018 and references therein). Pathlengths of several hundred meters up to several kilometres are possible. 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).
Given the variability of mixing ratios over open path 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 challenging. 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 the special case of total column 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 those of 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 they are susceptible to spatial-temporal variability and at this time are 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, such as 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, for example 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 (such as Andersen et al., 2018). 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 expected 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) Maximize users’ ability to assess data quality.
g) Facilitate data and metadata exploration.
h) Minimize the risk of data loss or corruption due to theft, misuse, or hardware/software failure.
i) Maximize security of primary data (such as 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.

Laboratories with demonstrated expertise in data management are encouraged to share their expertise. During the GGMT 2017 meeting, John Mund from NOAA ESRL illustrated how these recommendations are implemented at NOAA using a (conventional) relational database management system.

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 GAW Implementation Plan for the period 2016-2023) (WMO, 2017a). 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 required 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.
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) 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. WDCGG is requested to add the necessary three data columns to the data format (long term target bias estimate, short term repeatability, calibration and scale transfer uncertainty).

The GGMT attendees strongly recommend that the WDCGG together with GAW Expert Team on World Data Centres (ET-WDCs) explore ways in which GAW data can be discoverable and accessible from any WDC, most likely realisable by making use of the WMO Integrated Global Observing System (WIGOS) and the WMO Information System (WIS). ET-WDCs and WDCGG should further integrate GAW Station Information System (GAWSIS) with the Observing Systems Capability Analysis and Review (OSCAR) platform as the hub for ensuring seamless data access to the GAW WDC and archiving centres of the contributing networks.

16.3 Co-operative data products

All laboratories making high-quality greenhouse gases measurements are strongly encouraged to participate in cooperative data projects. Value-added products such as GLOBALVIEW+ (https://www.esrl.noaa.gov/gmd/ccgg/obspack/our_products.php) 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 (for example GLOBALVIEW and now GLOBALVIEW+ distributed through the ObsPack framework) 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 (such as Digital Object Identifier (DOI)). NOAA and ICOS have already performed considerable work in this area, as for example 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

The new WDCGG website has become operational during the course of 2018. The new setup provides an enhanced user experience for submission and editing of metadata. 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.

16.6 Roadmap to improved FAIRness of the data lifecycle

The FAIR data management principles seek to ensure that scientific data is Findable, Accessible, Interoperable, and Reusable (Wilkinson et al., 2016). The community recommends assessing the current level of FAIRness of the GAW GHG data management system and to evaluate the possible improvements, to be discussed at the 2021 GGMT meeting and to be developed into a long-term road map for implementation in the period 2021-2025. Part of the improvements would be:

- The implementation of a persistent identifier system and DOIs.
- Adoption of a clear and open data license, like for example the Creative Commons Attribution 4.0 International (CC4BY).
- Integration of WDCGG with WIGOS and WIS and their metadata schemes.
- Improvement of the data lifecycle and provenance metadata. See item 16.7.

16.7 Development of a data processing cookbook

ICOS and NOAA are requested to implement a data processing cookbook using tools like Jupyter notebooks to demonstrate a well-documented and reproducible approach of a data processing chain from raw data into correctly calibrated data, including the generation of uncertainty and bias estimates and provenance metadata. Other labs are invited to contribute to this and adapt the cookbook to their specific setup. An open mail list will be setup for interested parties to coordinate the information flow. Progress on this development will be announced through the GGMT mailing list.
17. RECOMMENDATIONS FOR THE COOPERATIVE WMO/GAW NETWORK

The eighteenth World Meteorological Congress (Cg-18, Geneva, 3–14 June 2019) adopted a historical reform of the WMO constituent bodies to embrace a more comprehensive Earth system approach, with a stronger focus on water resources and the ocean, more coordinated climate activities and a more concerted effort to translate science into services for society.

The Paris agreement is one of the key drivers of the WMO Strategic Plan for 2020-2023 (WMO, 2019b) adopted by the Congress. One of the strategic objectives refers explicitly to the work related to greenhouse gases:

“Objective 3.3 Advance policy-relevant science
In the next decade science is expected to provide tools and solutions for suitable use in the implementation of national and international policies and actions. WMO key research initiatives, working closely with its partners, will advance scientific assessments and climate projections, authoritative global reports on greenhouse gases and other atmospheric constituencies, and new technologies to better quantify the carbon, energy and water cycles.

Focus in 2020-2023:
Implement an integrated global greenhouse gas information system to enable Members to improve the quality and confidence in national greenhouse gas emission inventories.”

Several other decisions of the eighteenth World Meteorological Congress in June 2019 refer to the value of the greenhouse gas observations. In particular Resolution 67 (Cg-18) WMO scientific and technological support to the Intergovernmental Panel on Climate Change and climate policy states:

Decides to enhance WMO scientific support to climate policy through:
(1) Coordination of annual WMO assessments on the State of the Global Climate, Greenhouse Gas concentrations and other relevant atmospheric constituents, and climate observations and associated data with IPCC assessments and other complementary reports regularly released by other entities using the mechanism established through Resolution 20 (Cg-18);

The GAW Implementation Plan (WMO, 2017a) for 2016-2023 also 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 analysis (including inverse modelling techniques) as promoted by the Integrated Global Greenhouse Gas Information System (IG³IS).

The seventeenth World Meteorological Congress adopted a resolution on IG³IS in 2015, while the Executive Council 70 in 2018 adopted the IG³IS Science Implementation Plan (WMO, 2019a). IG³IS was mentioned as a framework to improve estimates of GHG concentrations and fluxes by the 50th session of Subsidiary Body for Scientific and Technological Advice (SBSTA) and in the 2019 Refinement to the 2006 Guidelines for National Greenhouse Gas Inventories adopted and accepted during the 49th Session of the IPCC in May 2019 (Volume I, Chapter 6).
The new Implementation Plan of the Global Climate Observing System (GCOS) (WMO, 2016) 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.

<table>
<thead>
<tr>
<th>Action A33: Maintain WMO GAW CO₂ and CH₄ monitoring networks</th>
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<td><strong>Action</strong></td>
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<td><strong>Benefit</strong></td>
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<td><strong>Who</strong></td>
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<td><strong>Time frame</strong></td>
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<th>Action A34: Requirements for in situ column composition measurements</th>
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<tr>
<th>Action A36: N₂O, halocarbon and SF₆ networks/measurements</th>
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<td><strong>Benefit</strong></td>
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<td><strong>Who</strong></td>
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<td><strong>Time frame</strong></td>
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The role of the in situ observations is indispensable for the operational system being developed by the European Commission for the evaluation of the global, regional and local emission as articulated in Pinty et al. (2019).

We, the Expert Group convened at GGMT-2019, recommend the following observational strategies:

a) 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 and improve the timeliness and availability of the observational data. 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 should be further encouraged.

b) 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.

c) Develop and implement long-term total column measurements of Greenhouse Gases at a number of sites within the WMO/GAW Programme and its partners, the Total Carbon Column Observing Network (TCCON), and the Collaborative Carbon Column Observing Network (COCCON). 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.

d) WMO recognizes the importance of independent measurement methods, calibration scales, SI traceability 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.

e) Develop high-quality measurements of carbon cycle tracers (that is $\text{O}_2/N_2$, $\text{^{14}CO}_2$, and stable isotopes in CO$_2$, CH$_4$ and CO, COS) 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. The technical cooperation project of IAEA plays an important role in building the capacity in the measurements of the stable isotopes of greenhouse gases. Measurements of additional tracers such as hydrocarbons (such as ethane) and halocarbons are useful for attribution of fluxes and due to their own contributions to radiative forcing.

f) 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.

g) 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.

h) Similarly, measurements of atmospheric composition at flux towers (such as ICOS, NEON, Ameriflux, AsiaFlux, etc.) should continue being linked to WMO calibration scales. Investigators at key laboratories in these networks should continue taking 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.

i) 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. The community should make an effort to connect the research efforts with the operational capability, especially in the institutions that do possess such capabilities, for provision of the emission estimates utilizing atmospheric observations. 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.

Considering the important role that greenhouse gas observations play in support of climate actions, a broader community should be engaged in GHG observations and the value of the GAW GHG observations must be better communicated to stakeholder communities to ensure continued support to existing observations and the network extension. The role of private sector in this context should be evaluated.
18. ORGANIZATION OF GGMT-2021

There was general agreement among all that it would be desirable to convene the next meeting, the 21\textsuperscript{th} WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, in Brazil. Luciana Gatti from the National Institute for Space Research (INPE) has agreed to organize and host this meeting.
REFERENCES


Francey, R.J., and C.E. Allison, 1994: The trend in atmospheric δ¹³CO₂ over the last decade. In Report of the Final Meeting of the Coordinated Research Programme on Isotope Variations of Carbon Dioxide and Other Trace Gases in the Atmosphere, (Ed. K. Rozanski), IAEA, Vienna (pp. 7-10).


WMO, all WMO references below (unless indicated otherwise) are available from https://community.wmo.int/gaw-reports


## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AGAGE</td>
<td>Advanced Global Atmospheric Gases Experiment</td>
</tr>
<tr>
<td>AIST</td>
<td>National Institute of Advanced Industrial Science and Technology</td>
</tr>
<tr>
<td>AMS</td>
<td>Accelerator Mass Spectrometry</td>
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<tr>
<td>AOPC</td>
<td>Atmospheric Observation Panel for Climate</td>
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<tr>
<td>AV</td>
<td>Atmospheric variability</td>
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<tr>
<td>BGC-IsoLab</td>
<td>Stable isotope laboratory at the Max Planck Institute for Biogeochemistry</td>
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<tr>
<td>BIPM</td>
<td>International Bureau of Weights and Measures</td>
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<tr>
<td>CC4BY</td>
<td>Creative Commons Attribution 4.0 International</td>
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<td>CCL</td>
<td>Central Calibration Laboratories</td>
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<tr>
<td>CCL-isoCO₂</td>
<td>Central Calibration Laboratory for CO₂ stable isotopes</td>
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<td>CCQM</td>
<td>Consultative Committee for Amount of Substance – Metrology in Chemistry</td>
</tr>
<tr>
<td>CIAAW</td>
<td>Commission on Isotopic Abundances and Atomic Weights</td>
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<tr>
<td>CIPM</td>
<td>International Committee for Weights and Measures</td>
</tr>
<tr>
<td>COCCON</td>
<td>Collaborative Carbon Column Observing Network</td>
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<tr>
<td>CONTRAIL</td>
<td>Comprehensive Observation Network for Trace gases by Airliner</td>
</tr>
<tr>
<td>COP22</td>
<td>22nd session of the Conference of Parties, Marrakesh, Morocco, November 2016</td>
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<tr>
<td>CRDS</td>
<td>Cavity Ring-Down Spectroscopy</td>
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<tr>
<td>DBMS</td>
<td>Database Management Strategy</td>
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<tr>
<td>DOAS</td>
<td>Differential Optical Absorption Spectroscopy</td>
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<tr>
<td>DOI</td>
<td>Digital Object Identifier</td>
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<tr>
<td>Empa</td>
<td>Swiss Federal Laboratories for Materials Science and Technology</td>
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<tr>
<td>EMPIR</td>
<td>European Metrology Programme for Innovation and Research</td>
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<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
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<td>GAW</td>
<td>Global Atmosphere Watch</td>
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<td>GAWSIS</td>
<td>GAW Station Information System</td>
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<td>GAWTEC</td>
<td>GAW Training and Education Centre</td>
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<td>GC-ECD</td>
<td>Gas chromatography with electron capture detection</td>
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<td>GC-FID</td>
<td>Gas chromatography with flame ionization detection</td>
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<td>Greenhouse Gases and Measurement Techniques</td>
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<td>HITRAN</td>
<td>High-resolution transmission molecular absorption database</td>
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<td>IAEA</td>
<td>International Atomic Energy Agency</td>
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<td>IAEA-603</td>
<td>Primary reference material (marble Ca-carbonate, with δ¹³C=2.46 ±0.01‰ and δ¹⁸O=-2.37 ±0.04‰) used for the realization of the VPDB scale and VPDB-CO₂ scale, by means of IAEA-603 CO₂ gas produced by reaction with H₃PO₄ under specified standard conditions. This primary RM was introduced by IAEA in 2016 as a replacement for the exhausted RM NBS-19.</td>
</tr>
<tr>
<td>IAGOS</td>
<td>In-Service Aircraft for a Global Observing System</td>
</tr>
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ICOS  Integrated Carbon Observation System
ICP  Intercomparison Programmes
IEC  International Electrotechnical Commission
IGIS  Integrated Global Greenhouse Gas Information System
INPE  National Institute for Space Research
INSTAAR  Institute of Arctic and Alpine Research, University of Colorado Boulder
IPCC  Intergovernmental Panel on Climate Change
IRMM  Institute for Reference Materials and Measurements
IRMS  Isotope ratio mass spectrometry
ISO  International Organization for Standardization
IUS  Integrated Urban Services
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
KRIS  Korea Research Institute of Standards and Science
LSVEC  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 synchronising the $\delta^{13}C$ scale-calibration over the range $+1.95 \%$ to $-46.6\%$.
MAR-J1  Laboratory calcium carbonate standard used by CCL_isoCO$_2$
MBL  Marine Boundary Layer
MPI-BGC  Max Plank Institute for Biogeochemistry
NACP  North American Carbon Program
NARCIS  Pure CO$_2$ in glass ampoules prepared by H. Mukai (Mukai, 2003)
NAS  National Academies of Sciences
NBS-19  Primary reference material (marble Ca-carbonate, with $\delta^{13}C=1.95\%$ and $\delta^{18}O=-2.20\%$) used for the realization of the VPDB scale and VPDB-CO$_2$ scale, by means of NBS-19 CO$_2$ gas produced by reaction with H$_3$PO$_4$ under specified standard conditions. In 2016, a replacement for NBS-19, IAEA-603 (also a marble Ca-carbonate) was released by the IAEA. Some amounts of NBS-19 remaining at the IAEA and potentially at some user labs are still valid as RM.
NDIR  Non-Dispersive Infrared (spectroscopy)
NEON  National Ecological Observatory Network
NIMS  National Institute of Meteorological Sciences
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
OMC-J1  Laboratory calcium carbonate standard used by CCL_isoCO$_2$
OSCAR  Observing Systems Capability Analysis and Review
OSE  Observing System Experiment
OSSE  Observing System Simulation Experiment
pCO₂  partial pressure of CO₂ in surface water
PCTFE  Polychlorotrifluoroethylene
QA  Quality Assurance
QC  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
SD  Standard deviation
SI (units)  Système international (d'unités)
SIO  Scripps Institution of Oceanography
SIRS  Metrology for stable isotope reference standards
SLAP / SLAP2  Standard Light Antarctic Precipitation - RM water to be used for 2-point data normalisation at negative δ²H and δ¹⁸O.
SOCAT  Surface Ocean CO₂ ATlas
SOCONET  Surface Ocean CO₂ Reference Network
SOP  Standard operating procedure
SRM  Standard Reference Material
TCCON  Total Carbon Column Observing Network
TT  Target Tank
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 δ¹³C and δ¹⁸O measurement results relative to the (non-existing) artefact VPDB. The VPDB δ¹³C and δ¹⁸O scale is realized through the metrological reference material NBS-19 (now replaced by IAEA-603), see above. The VPDB-CO₂ scale is used to express δ¹⁸O of CO₂ gases.
VSMOW/VSMOW2  Vienna Standard Mean Ocean Water - the international conventional scale used to express δ²H and δ¹⁸O measurement results (excluding δ¹⁸O of carbonates and CO₂ gases).
VURF  Vacuum Ultraviolet Resonance Fluorescence Spectroscopy
WCC  World Calibration Centre
WCC-isoCO₂  World Calibration Centre for CO₂ stable isotopes
WDC  World Data Centre
WDCGG  World Data Centre for Greenhouse Gases
WDC  World Data System
WIGOS  WMO Integrated Global Observing System
WIS  WMO Information System
WMO  World Meteorological Organization
ZT  Zero Tank
ANNEX I

20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019)
(Jeju, South Korea, 2-5 September 2019)

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*Excursion was cancelled due to a typhoon (Lingling).

**Sunday, 1 September 2019**

18:00-20:00  Ice Breaker

**Monday, 2 September 2019**

8:00-9:00  Registration

9:00-9:15  Welcome speech & Introduction of NIMS GHG activities by Sangwon Joo

9:15-9:35  Updates from WMO by Oksana Tarasova

9:35-10:00  Group photo & Coffee break

**Quality assurance of greenhouse gas measurements (including reference standards, comparison activities and good practices)**

(Chair: Oksana Tarasova)

10:00-12:00  T1 (20’) Towards an International Reference Network for Greenhouse Gases by Arlyn Andrews

T2 (20’) Labelling process in ICOS atmosphere and quality control steps towards the first official data releases by Leonard Rivier

T3 (20’) Can your network stand the test of time? by Colm Sweeney

T4 (20’) Update on CO₂, CO, and N₂O calibration scales by Brad Hall

T5 (20’) Implementation of the WMO CO₂ X2019 scale revision by Andrew Crotwell

T6 (20’) Towards an on-going comparison on the accuracy of standards and scales for atmospheric CO₂ measurement by Robert Wielgosz

12:00-13:20  Lunch

**Quality assurance of greenhouse gas measurements (including reference standards, comparison activities and good practices)**

(Chair: Alex Vermeulen)

13:20-14:00  T7 (20’) Training, twinning, and capacity building in support of greenhouse gas observations in data sparse regions by Martin Steinbacher

T8 (20’) Recent Activities and Achievements of WCC-Empa by Christoph Zellweger

14:00-15:00  Discussion

Chapter 1: CALIBRATION OF GAW MEASUREMENTS (Lead: Martin Steinbacher)
Tuesday, 3 September 2019

Quality assurance of greenhouse gas measurements (including reference standards, comparison activities and good practices)
(Chair: Christoph Zellweger)

8:30-9:50
T9 (20’) Comparison of in situ measurements of CO₂ and CH₄ at the Cape Grim Baseline Station by Zoe Loh
T10 (20’) Comparisons of non-CO₂ trace gas measurements between AGAGE and NOAA at common sites by Paul Krummel
T11 (20’) Standard of greenhouse gases measurement by Jeongsoon Lee
T12 (20’) Breakthrough in Negating the Impact of Adsorption in Gas Reference Materials by Paul Brewer

9:50-10:30
Discussion
Chapter 8: SPECIFIC REQUIREMENTS FOR N₂O CALIBRATION (Lead: Brad Hall)
Chapter 9: SPECIFIC REQUIREMENTS FOR SF₆ CALIBRATION (Lead: Hae-young Lee)
Chapter 10: SPECIFIC REQUIREMENTS FOR CO CALIBRATION (Lead: Andrew Crotwell)

10:30-10:40
Discussion
The 7th Round Robin Experiment (Lead: Brad Hall)

10:40-11:00
Coffee Break
Data products and utilization of the observations
Chair: Zoe Loh

11:00-12:00
T13 (20’) Potential Bias in Preliminary Estimates of Global LLGHG Trends by Edward Dlugokencky
T14 (20’) Taking in situ greenhouse gas information into the big data era by Alex Vermeulen
T15 (20’) ObsPack 5 Years Later: Where Are We Now and Where Are We Going? By Kenneth Schuld

12:00-13:20
Lunch, Two vendor’s presentations from 13:00 (each 10’)

13:20-14:00
Discussion
Chapter 2: RECOMMENDATIONS FOR THE DETERMINATION OF UNCERTAINTY (Lead: Armin Jordan and Andrew Crotwell)
Chapter 16: RECOMMENDATIONS FOR DATA MANAGEMENT, ARCHIVING, AND DISTRIBUTION (Lead: Alex Vermeulen)

Advances in the traditional greenhouse gas measurement techniques
(Chair: Doug Worthy)

14:00-15:00
T16 (20’) The evolution of AGAGE: Overview of improved measurement technologies for the quantification of GHG and ODS emissions by Ray Weiss
T17 (20’) A Detachable Trap Preconcentrator with a Gas Chromatograph-Mass Spectrometer for the Analysis of Trace Halogenated Greenhouse Gases by Jeong-Sik Lim
T18 (20’) Methane Source Localisation and Emission Quantification at Facility Scale Using Multi-beam Open Path Laser Dispersion Spectroscopy by Mohammed Belal

Emerging Observation Techniques including low-cost sensors, Remote Sensing and Integration of Observations
(Chair: Ann Stavert)
15:00-16:20 T19 (20’) Open path FTIR measurements of greenhouse gas concentrations and fluxes in the atmosphere over kilometre pathlengths by David Griffith
T20 (20’) Study of error and sensitivity of short-term variation in XCO2 observed by Anmyeondo station by Young-Suk Oh
T21 (20’) Principle, calibration and preliminary results of ground-based atmospheric CO2 monitoring instrument using spatial heterodyne spectroscopy by Zhiwei Li
T22 (20’) Trace gas measurements at the U.S. Southern Great Plains DOE Atmospheric Radiation Measurement Facility using an in situ FTIR: lesson learned after a 6-year deployment by Sebastien Biraud

16:20-18:00 Coffee break & Poster session at Lobby
18:00-20:00 Banquet at Cristal Ballroom

Wednesday, 4 September 2019
8:30-9:00 Discussion Agenda
Chapter 13: RECOMMENDATIONS FOR GROUND-BASED REMOTE SENSING TECHNIQUES (Lead: David Griffith)
Chapter 14: RECOMMENDATIONS FOR AIR MEASUREMENTS OF CO2 ON SHIPS (Lead: David Griffith)
Chapter 15: NEW AND EMERGING TECHNIQUES (Lead: David Griffith)

Measurements and quality assurance for 14C, O2/N2 and related tracers (Chair: Anna Karion)
9:50-10:30 T23 (20’) Atmospheric 14CO2 southern hemisphere latitudinal gradient over recent decades by Rachel Corran
T24 (20’) Inter-comparison of O2/N2 scales among AIST, NIES, TU, and SIO using primary standard mixtures with less than 5 per meg uncertainty for δ(O2/N2) by Nobuyuki Aoki
T25 (20’) Quantifying the span sensitivity of interferometric oxygen measurements by Ralph Keeling
T26 (20’) Outline of the UEA/ENV & CAMS/CMA Collaborative Research Project: Establishing a high Precision atmospheric Oxygen network in China (EPOCH) by Lingxi Zhou

10:20-10:40 Coffee break
Quality assurance of the measurements of the stable isotopes (including reference standards, comparison activities and good practices) (Chair: Paul Brewer)
10:40-12:00 T27 (20’) Challenges in maintaining the artefact-based stable isotope scale for δ13C with the aim to address GAW-WMO uncertainty requirements by Sergey Assonov
T28 (20’) Assuring quality in the measurement and reporting of stable isotope measurements of atmospheric carbon dioxide by Colin Allison
T29 (20’) Comparison of isotope ratio measurement capabilities for CO2 isotopes: Sample preparation and characterization by isotope ratio infrared spectroscopy and mass-spectrometry by Joelle Viallon
T30 (20’) Strategies to assess and reduce current interlaboratory differences in δ 13C-CH4 and δ 2H-CH4 measurements in air samples by Peter Sperlich

12:00-13:20 Lunch, Two vendor’s presentations from 13:00 (each 10’)
Quality assurance of the measurements of the stable isotopes (including reference standards, comparison activities and good practices) (Chair: Jinho Ahn)
13:20-14:00 T31 (20’) JRAS-06: Scale maintenance and keeping up with changing stable isotopic reference materials by Heiko Moossen
T32 (20’) JRAS-06 or bust! The INSTAAR Stable Isotope Lab revises its ties to primary reference materials and releases a revised dataset of stable isotopes of CO2 by Sylvia Michel

14:00-15:00 Discussion
(Parallel) Chapter 4: SPECIFIC REQUIREMENTS FOR STABLE ISOTOPE CALIBRATION (Lead: Sylvia Michel)
Chapter 5: SPECIFIC REQUIREMENTS FOR THE CALIBRATION OF RADIOCARBON IN TRACE GASES (Lead: Jocelyn Turnbull)

Chapter 6: SPECIFIC REQUIREMENTS FOR O₂/N₂ CALIBRATION (Lead: Ralph Keeling)

Chapter 11: SPECIFIC REQUIREMENTS FOR H₂ CALIBRATION (Lead: Armin Jordan)

Sites and network update (Chair: Jocelyn Turnbull)

15:00-16:20
- T33 (20’) Design and implementation of an enhanced observation network in New Zealand by Gordon Brailsford
- T34 (20’) Evolving Greenhouse gases observational network in India by Yogesh Tiwari
- T35 (20’) Collection of CO₂ measurements in Europe for the study of the drought of Summer 2018 by Michel Ramonet
- T36 (20’) Observation of atmospheric carbon monoxide at the background stations in China by Shuangxi Fang

16:20-18:00
- Coffee break & Poster session at Lobby
- Side meeting Capacity development towards wider use of stable isotopic techniques for source attribution of greenhouse gases in the atmosphere

Thursday, 5 September 2019

Urban Observations and Networks (Chair: Luciana Gatti)

8:30-09:50
- T37 (20’) CO₂ and air quality over megacity: a case study of Seoul, Korea by Sojung Sim
- T38 (20’) Carbon Dioxide Enhancement over Seoul Capital Area from Space and Surface Measurements by Chaerin Park
- T39 (20’) High precision CO₂ measurement at Beijing-Tianjin-Hebei city cluster in China by Bo Yao
- T40 (20’) Updates from the Los Angeles Megacities Carbon Project by Jooil Kim

09:50-10:10 Coffee Break

Urban Observations and Networks (Chair: Jooil Kim)

10:10-11:30
- T41 (20’) Development of A Full Carbon Budget for Auckland, New Zealand by Jocelyn Turnbull
- T42 (20’) Progress from the Indianapolis Flux (INFLUX) tower-based urban greenhouse gas network by Natasha Miles
- T43 (20’) Greenhouse gas observations from the Northeast Corridor tower network by Anna Karion
- T44 (20’) Long-term monitoring and modelling of atmospheric CH₄ to track its trend and to assess a detailed spatially explicit emission mapping the Greater Toronto and Hamilton Area, Canada by Felix Vogel

11:30-12:10 Discussion

Chapter 12: RECOMMENDATIONS FOR GREENHOUSE GAS NETWORKS IN AREAS OF HIGH-DENSITY EMISSIONS (Lead: Felix Vogel)

12:10-13:30 Lunch

Observations from the mobile platforms (aircraft, drone, balloon, etc) and over/in the ocean (Chair: Dagmar Kubistin)

13:30-15:30
- T45 (20’) Comparisons of AirCore vertical profiles of greenhouse gases from an intensive RINGO campaign at Sodankylä, Finland by Huilin Chen
- T46 (20’) Continuous airborne measurements of CO₂, CH₄, H₂O and CO in South Korea by Shanlan Li
- T47 (20’) Light Rail-Based Monitoring of Greenhouse Gases Across an Urban Area by Edward Orr
- T48 (20’) Mobile real-time measurement of methane in Beijing: methodology development and application by Wanqi Sun
- T49 (20’) Statistical characterization of atmospheric CO₂ in airport proximity from the CONTRAIL commercial aircraft measurements by Taku Umezawa
- T50 (20’) Implementing Atmospheric CO₂ Measurements from Ships of Opportunity by Rik Wanninkhof

15:30-16:00 Discussion
Chapter 17: RECOMMENDATIONS FOR THE COOPERATIVE WMO/GAW NETWORK
(Lead : Oksana Tarasova)

16:00-17:00 Expert group recommendation
(Lead : Andrew Crotwell, Haeyoung Lee, Martin Steinbacher)

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ANNEX III

20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019)

(Jeju, South Korea, 2-5 September 2019)

POSTER SESSIONS

Quality assurance of greenhouse gas measurements (including reference standards, comparison activities and good practices)

P01 The intercomparison activities of WCC-SF6 during 8 years by Haeyoung Lee
P02 Travelling cylinders as a quality control tool in ICOS atmospheric station network by Hermanni Aaltonen
P03 WCC and QA/SAC activities by JMA by Teruo Kawasaki
P04 Uncertainty analysis of calibration measurements made by the ICOS Flask and Calibration Laboratory by Armin Jordan
P05 Development of dimethyl sulfide primary reference gas mixtures for global atmospheric monitoring by Mi Eon Kim
P06 New calibration system for methane and carbon dioxide at JMA by Kentaro Ishijima
P07 Influences of thermal fractionation and adsorption on CO2 standard mixture gravimetrically prepared using multiple steps by Nobuyuki Aoki
P08 GHGs data comparison between NIES observation network (aircrafts, stations and ships) in the Asian-Pacific region and GOSAT by Shohei Nomura
P09 The Atmospheric Pressure Effect on N2O Analysis and the Use of an Exhaust Chamber to Minimize this Effect by Caio Correia
P10 Ambient air performance of N2O Los Gatos analysers at Hohenpeissenberg by Dagmar Kubistin
P11 Results of a Long-Term International Comparison of Greenhouse Gas and Isotope Measurements at the Global Atmosphere Watch (GAW) Station in Alert, Nunavut, Canada by Doug Worthy
P12 How to deal with water vapor for Greenhouse gas dry mole fraction measurement with Cavity Enhanced Spectrometer: water vapor correction vs Nafion dryer by Olivier Laurent
P13 Metrological performance assessment of different Cavity Enhanced Spectrometer to measure atmospheric nitrous oxide by Olivier Laurent
P14 Laboratory Investigation of CO2 Biases Related to Water Vapor Surface Adsorption in Air Samples Stored in Glass Flasks by Don Neff

Data products and utilization of the observations

P15 Estimation of greenhouse gas emission factors based on observed covariance of CO2, CH4, N2O and CO mole fractions by Laszlo Haszpra
P16 Operation of new WDCGG website and started of satellite data collection by Atsuya Kinoshita
P17 Enhanced terrestrial carbon uptake over South Korea revealed by atmospheric CO2 measurements by Jeongmin Yun
P18 Comparison of regional simulation of terrestrial CO$_2$ flux from the updated version of CarbonTracker Asia (CTA) with FLUCOM and other inversions over East Asia by Samuel Takele Kenea

P19 Recent GAW activities of KMA by Yuwon Kim

P20 Abrupt changes of atmospheric CO$_2$ during the last glacial termination and the Common Era by Jinho Ahn

P21 Introduction of Ganseong Global Climate Change Monitoring Station of Ministry of Environment, Korea by Taekyu Kim

**Advances in the traditional greenhouse gas measurement techniques**

P22 The Macquarie Island high precision CO$_2$ record - Calculating uncertainties and exploring trends by Ann Stavert

P23 Development of Novel Trace Methane and Trace Carbon Dioxide Analyzers - Performance Evaluation Studies and Results of Field Deployment by Graham Leggett

P24 Development of a new flask-air analysis system for the Global Greenhouse Gas Reference Network by Andrew Crotwel

P25 Working standard gas saving system for in situ CO$_2$ and CH$_4$ measurements and calculation method for concentrations and their uncertainty by Motoki Sasakawa

P26 The ICOS automated flask sampler by Markus Eritt

P27 Update on measurements of N$_2$O and CO at the Cape Grim Baseline Air Pollution Station: commissioning of a new high precision in situ analyser by E-A. Guerette

**Emerging Observation Techniques including low-cost sensors**

P28 Performance analysis of Spatial Heterodyne Spectroscopy on column-averaged carbon dioxide observation by Ye Hanhan

**Remote Sensing & Integration of Observations**

P29 Contrasting the differences in CO$_2$ atmospheric growth over Korea with global patterns by Lev Labzovskii

P30 Quality analysis of on-orbit observation data of Greenhouse gases Monitoring Instrument on GaoFeng-5 satellite by Hailiang SHI

P31 Observing patterns of CO$_2$ and air pollutants of cities using satellite data by Hayoung Park

**Measurements and quality assurance for $^{14}$C, O$_2$/N$_2$ and related tracers**

P32 $^{14}$CO$_2$ observations in atmospheric CO$_2$ at Anmyeondo GAW station, Korea: implication for fossil fuel CO$_2$ and emission ratios by Haeyoung Lee

P33 Distinguishing Artifacts from Real Variability in Airborne Measurements of $\delta$(Ar/N$_2$) by Eric Morgan

P34 Trend in atmospheric CO$_2$ concentrations and carbon isotopic compositions observed at a regional background site in East Asia by Hyeeri Park

P35 European atmospheric $^{14}$CO$_2$ activities within the ICOS RI network by Samuel Hammer
### Quality assurance of the measurements of the stable isotopes (including reference standards, comparison activities and good practices)

- **P36** Five years of $\delta^{13}$C(CO$_2$) measurements from an in situ Fourier transform infrared trace gas and isotope analyser at Lauder, New Zealand by Dan Smale
- **P37** The effect of phosphoric acid on carbon dioxide standard gas evolution by Jun Sonobe
- **P38** Assessment of an Isotope Ratio Infrared Spectrometer to measure isotope ratios of carbon dioxide in air under laboratory conditions and at Baring Head, New Zealand by Peter Sperlich
- **P39** Development of a Quality Assurance Scheme for stable isotope measurements in agreement with the GAW Quality Assurance Principles by Sergey Assonov
- **P40** Characterisation of optical isotope analysers for carbon dioxide in the framework of EMPIR project SIRS by Ivan Prokhorov
- **P41** Isotope Ratio Stability of CO$_2$ Mixtures in Natural Air by Megumi Isaji
- **P42** Development of international N$_2$O reference materials for site preference measurements by Joanna Rupacher
- **P43** How good are our measurements of $\delta^{13}$C-CH$_4$? By Sylvia Michel
- **P44** Calibration Methodology for the Scripps $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O stable isotope program 1992-2018 by Keeling Ralph
- **P45** NIWA's $\delta^{13}$C-CO$_2$ measurement programme: Twenty years of monitoring in New Zealand and Antarctica by Rowena Moss
- **P46** Multipoint normalization of $\delta^{18}$O of water against the VSMOW2-SLAP2 scale with an uncertainty assessment by Taewan Kim

### Isotope Measurement Techniques

- **P47** Developing a system to measure nitrous oxide isotopomers in air by Peter Sperlich
- **P48** Optical method for clumped isotope measurements - the case of carbon dioxide by Ivan Prokhorov
- **P49** A cryogen-free automated measurement system of stable carbon isotope ratio of atmospheric methane by Taku Umezawa
- **P50** Measuring stables isotopes of CO$_2$ ($^{13}$C and $^{17,18}$O) in vertical profiles over the Amazon by Raiane A.L.Neves
- **P51** On the performance of simultaneous measurements of $\delta^{13}$C-CO$_2$, $\delta^{18}$O-CO$_2$ and $\delta^{17}$O-CO$_2$ by Quantum Cascade Dual-Laser Absorption Spectrometry in whole air atmospheric samples from Lutjewad station, the Netherlands by Bert A. Scheeren

### Sites and network update

- **P52** Pha Din GAW regional station and development orientation of climate change observing network in VietNam by Thi Quynh Hoa Vu
- **P53** Where is the missing CO$_2$? A regional multi-species approach to trace the fate of atmospheric CO$_2$ in Fiordland National Park, New Zealand by Peter Sperlich
- **P54** Atmospheric trace gas observations: Latest update from the Cape Point station by Casper Labuschagne
- **P55** High frequency measurements of atmospheric HFCs at a regional monitoring site in East Asia and the implications for regional emissions by Sunyoung Park
- **P56** GHG Vertical Profiles Measurement Program in the Amazon by Luciana Gatti
- **P57** Background Concentrations of CO$_2$, CO and N$_2$O in Brazilian Coast by Luciano Marani
- **P58** Study of long term SF$_6$ mole fractions in Amazon and Brazilian Coast by Luana Basso
- **P59** Long Term CH$_4$ measurements in Amazon and Brazilian Coast by Luana Basso
Urban Observations and Networks

P60 Observed and simulated urban CO$_2$ behavior around Jakarta megacity by Masahide Nishihashi

P61 MExico city’s Regional Carbon Impacts (MERCI- CO$_2$): combining high precision surface monitoring, with low-costs sensors, and total column measurements by Michel Ramonet

Observations from the mobile platforms (aircraft, drone, balloon, etc)

P62 Characterising Methane Emissions using a Twin-Otter Airborne Platform by James France

P63 The Aircore system and campaign for vertical profile measurements of greenhouse gases in China by Miao Liang

P64 IAGOS-CORE and IAGOS-CARIBIC greenhouse gas observations from commercial airliners by Christoph Gerbig

P65 Pilot study of Unmanned Aerial Vehicles for sampling water vapor and water isotopes at high-latitudes provides implications for other trace gas sampling by Bruce Vaughn
ANNEX IV

20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019)

(Jeju, South Korea, 2-5 September 2019)

WORKSHOP PROCEEDINGS
LONG TERM CH$_4$ MEASUREMENTS IN AMAZON AND BRAZILIAN COAST

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1. Introduction

Methane is the second most important anthropogenic greenhouse gas, with natural and anthropogenic sources$^{[1]}$. After a period of CH$_4$ growth rate was near zero, since 2007 the atmospheric CH$_4$ has been increasing again. Until now are not completed understand what factors is causing this increase, but one of possible reasons is an increase in wetlands emissions in tropical areas, like Amazon, due anomalies in precipitation during La Niña events$^{[2,3]}$. To improve the understand of the Amazon CH$_4$ balance and the climatic variation effect on this balance, we developed a scientific strategy of GHG measures involving different scales, since local until regional scales, using measures in flasks and small aircrafts to perform vertical profiles.

2. Methodology

The LaGEE (Laboratory of Greenhouse Gases located at National Institute for Space Research/INPE, Brazil) activities starting in 2003, constructing a replica of NOAA/ESRL/GMD GHG Laboratory and installing in Brazil in 2004. Since this time the places studied and the types of measures taken have grown to reach our goal. CH$_4$ atmospheric measurements were started with vertical profiles using small aircrafts, since 2000 in Santarém (SAN; 2.86°S; 54.95°W), 2010 in Rio Branco (RBA; 9.38°S, 67.62°W), Alta Floresta (ALF; 8.80°S, 56.75°W), Tabatinga (TAB; 5.96°S, 70.06°W) and Tefé (TEF; 3.31°S, 65.8°W, which started in 2013 to replace TAB, results from these sites will be named TAB_TEF), all these sites located in Brazilian Amazon. In 2006, we started flasks measurements at Arembepe (ABP; 12.75°S, 38.15°W; between 2006-2009) located at the Brazilian Atlantic coast and since 2010 in more two locations in Brazilian coast, Salinópolis (SAL; 0.60°S, 47.37°W, between 2010-2017) and Natal (NAT; 5.48°S, 35.26°W). In 2014 started another Brazilian coast site, Camocim (CAM; 2.51°S, 40.51°W).

The samples from the Brazilian coast were collected weekly by using a pair of glass flasks (2.5L) and a portable sampler. At Amazon sites samples from vertical profiles were collected, generally fortnightly, using a semi-automatic sampling system, which consists of separate compressor and flask units, developed by ESRL/NOAA.

3. Results and Discussion

We are presenting in this study results of 688 vertical profiles distributed in four sites in Brazilian Amazon, between 2000 and 2018 and a total of 1700 samples from four sites located at Brazilian Northeast coast between 2006 to 2018.
Figure 2 shows the results obtained during 2000 until 2018 in SAN region (Northeast of Brazilian Amazon), and the CH$_4$ mean mole fractions from the south and north hemisphere, respectively, for this period from NOAA database. It was observed that mole fractions from SAN are between the observed in North and south hemisphere and follow the global increase.

Figure 3 shows a comparison between the four sites located at Brazilian Amazon during 2010 and 2018 and the CH$_4$ mean mole fractions from the south and north hemisphere, respectively, for this period. It was observed that mole fractions from all Amazon sites are similar and between the observed in north and south hemisphere, following the global increase.

Analysing the results from Brazilian coast sites (Figure 3), can be observed that ABP, NAT and CAM mole fractions area similar to the south hemisphere mean, while SAL results have a clear seasonality throughout the year, indicating that part time is influenced by north hemisphere (with higher mole fractions), when ITCZ (Intertropical Convergence Zone) is above this region.

4. Conclusions

Results of this long-term measurements showed that all sites had a continuous increase in CH$_4$ concentrations, with an annual growth ratio between 7.2 and 7.6 ppb/year (2010-2018), that is lower than the global increase in this period (7.8 ppb/year using the NOAA data).

Considering only the SAN measurements (2000-2018) the annual growth ratio is 5.8 ppb/year, higher than the observed for the global mean concentration during this period (4.9ppb/year), suggesting higher emissions in this area. Analyzing this long time series of SAN is evident the stable period of CH$_4$ concentrations until 2005 and a clear increase in the concentrations after the middle of 2006, following the CH$_4$ global concentration increase.

Acknowledgments


References


Figure 1. Sample sites located in Brazilian Amazon and NOAA stations

Figure 2. CH$_4$ Temporal series for SAN region (green) and CH$_4$ mean mole fractions of south hemisphere (black line) and north hemisphere (grey line) from NOAA, between 2000-2018
Figure 3. CH$_4$ Temporal series of CH$_4$ for Amazon sites (ALF, RBA, SAN, TAB_TEF) and CH$_4$ mean mole fractions of south hemisphere (black line) and north hemisphere (grey line) from NOAA, between 2010-2018

Figure 4. CH$_4$ temporal series for Brazilian Northeast coast sites (ABP, NAT, CAM, SAL) and CH$_4$ mean mole fractions of south hemisphere (black line) and north hemisphere (grey line) from NOAA, between 2006-2018
1. Introduction

SF$_6$ is one of the most potent greenhouse gases known, having a very high global warming potential of 23,500 (relative to CO$_2$). Its surface fluxes include anthropogenic emissions from applications in industry and very minor uptake by the oceans. SF$_6$ is inert throughout the troposphere and stratosphere and is slowly photolyzed in the mesosphere, resulting in an estimated atmospheric lifetime of 3200 years, so its emissions accumulate in the atmosphere and can be estimated directly from its observed rate of increase$^1$. Its global mole fraction was around 9.5 ppt in 2016, almost twice the level observed in the mid-1990s$^2$. Since it is a very stable gas in the atmosphere, its annual growth rate has been relatively constant since the 1980s, and has been increasing in a very linear way$^3$. Brazil is not an SF$_6$ producer, therefore, the emissions reported in the Brazilian inventory are due only to leaks in equipment installed in the country due to its maintenance or disposal.

2. Methodology

SF$_6$ atmospheric measurements were started with vertical profiles using small aircrafts, since 2000 in Santarém (SAN; 2.86°S; 54.95°W), 2010 in Rio Branco (RBA; 9.38°S, 67.62°W), Alta Floresta (ALF; 8.80°S, 56.75°W), Tabatinga (TAB; 5.96°S, 70.06°W) and Tefé (TEF; 3.31°S, 65.8°W), which started in 2013 to replace TAB, results from these sites will be named TAB_TEF, all these sites located in Brazilian Amazon Basin. In 2006, we started flasks measurements at Arembepe (ABP, 12.75°S, 38.15°W; between 2006-2009) located at the Brazilian Atlantic coast, and since 2010 started two more locations, Salinópolis (SAL; 0.60°S, 47.37°W) and Natal (NAT; 5.48°S, 35.26°W). The samples from the Brazilian coast were collected weekly by using a pair of glass flasks (2.5L) and a portable sampler. At Amazon sites samples from vertical profiles were collected, generally fortnightly, using a semi-automatic sampling system, which consists of separate compressor and flask units, developed by ESRL/NOAA.

3. Results and Discussion

The SF$_6$ growth rate obtained for each study site are shown in Table 1, it was observed that in all sites SF$_6$ mole fractions showed an increase over the studied period, following the global growth rate. SAN results show that SF$_6$ mole fractions increased since 2000, by nearly 5.3 ppt between 2000 and 2018 (Figure 2), and by a mean increase rate of 0.28 ppt per year.
Figure 3 shows the results obtained during 2010 until 2018 in the four Amazon sampling sites, and the SF$_6$ global mean mole fractions for this period. It was observed during all these years that mole fractions at all our stations are generally similar to the global mean, with an annual growth ratio between 0.32 and 0.33 ppt/year. Can be observed an annual seasonality, with higher values between January to beginning of May. This seasonality can also be observed in SAL (located in the Brazilian coast). Examination of air parcel paths using HYSPLIT\textsuperscript{[4,5]} for these periods confirmed that some air parcels arriving at these stations have travelled from the northern hemisphere to the sites. The mean position of Intertropical Convergence Zone (ITCZ) shows variation along the year. Between January and beginning of May the ITCZ is below SAL position, therefore the air masses for SAL and Amazon sites coming from north hemisphere. While in NAT and ABP cannot be observed this seasonality. The air masses back trajectories calculated for NAT and ABP show that the air masses arriving entirety from the South Atlantic Ocean (Figure 3).

4. Conclusions

Results of this long-term measurements showed that all sites had a continuous increase in concentrations, with an annual growth ratio between 0.32 and 0.33 ppt/year (2010-2018), that is similar to the global increase in this period (0.32 ppt/year using the NOAA data). Considering only the SAN measurements (2000-2018) the annual growth ratio is 0.28 ppt/year, the same observed for the global mean concentration during this period.

These results indicate that Amazon and Brazilian northeast coast do not have significant emissions of SF$_6$ and its mole fractions following the global growth ratio.

Acknowledgments


References


Figure 1. Sample sites located in Brazilian Amazon and Brazilian coast

Table 1. SF₆ growth rate to Brazilian Amazon sites and Brazilian coast sites

<table>
<thead>
<tr>
<th>Period</th>
<th>Site</th>
<th>growth rate (ppt/year)</th>
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<tbody>
<tr>
<td>Brazilian Coast Sites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006-2009</td>
<td>ABP</td>
<td>0.27</td>
</tr>
<tr>
<td>2010-2016</td>
<td>SAL</td>
<td>0.32</td>
</tr>
<tr>
<td>2010-2018</td>
<td>NAT</td>
<td>0.33</td>
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<tr>
<td>Brazilian Amazon Sites</td>
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</tr>
<tr>
<td>2000-2018</td>
<td>SAN</td>
<td>0.28</td>
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<tr>
<td>2010-2018</td>
<td>ALF</td>
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<tr>
<td>2010-2018</td>
<td>RBA</td>
<td>0.33</td>
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<tr>
<td>2010-2018</td>
<td>SAN</td>
<td>0.33</td>
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<tr>
<td>2010-2018</td>
<td>TAB_TEF</td>
<td>0.32</td>
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</tbody>
</table>
Figure 2. Temporal series of SF₆ measurements for SAN region (green) and SF₆ global mean mole fractions (black line) from NOAA, between 2000-2018.

Figure 3. Temporal series of SF₆ measurements for Amazon sites (ALF, RBA, SAN, TAB_TEF) and SF₆ global mean mole fractions (black line) from NOAA, between 2010-2018.

Figure 4. Temporal series of SF₆ measurements for Brazilian Northeast coast sites (ABP, NAT, SAL) and SF₆ global mean mole fractions (black line) from NOAA, between 2006-2018.
MEASUREMENT PROGRAM OF GHG VERTICAL PROFILES AT AMAZON

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2 Atmospheric Chemistry Laboratory, Nuclear and Energy Research Institute, IPEN–CNEN/SP, Brazil; 3 GMD/ESRL, NOAA, Boulder, United States; 4 University of Leeds, Leeds, United Kingdom; 5 Energy and Sustainability Research Institute Groningen, The Netherlands; 6 IFRO, Instituto Federal Rondonia

Amazon is the major tropical land regions and is still been poorly comprehend, with only very few regular greenhouse gas measurements available in the tropics, and mostly not of a suitable nature for estimating carbon balances. Amongst the land regions in the tropics of particular importance for the global carbon cycle is the Amazon, by far the largest region hosting the largest carbon pool in vegetation and soils (~200 PgC). Net carbon exchange between tropical land and the atmosphere is potentially important because it holds large amounts of carbon in forests and soils which can be released on short time-scales e.g. via deforestation or changes in growing conditions, like increased heat and the extension of dry season. Such changes may thus cause feedbacks on global climate.

Figure 1. Since 2000 SAN aircraft site, 2010 added more 3 sites TAB, RBA, ALF (0.3 to 4.4km) and more 2 sites until 7.3km RBA and SAL with 3 coast sites SAL (10-17), CAM (14 to now) and NAT (2010 to now). TEF is the substitute of TAB site (TAB was substituted by TAB at 2013)

Actually there are strong pressures over Amazon for agriculture, livestock, mining, logging, etc. The estimated deforestation for Brazilian Legal Amazon is 9,762 km² for the period August 2018 to July 2019. The area of Brazilian Legal Amazon is 5,217,423 km² and represents 9 states, where 40% of deforestation happens at Para state. The deforestation this year represents an increase of 29.5% compared to deforestation rate determined by PRODES 2018, which was 7,536 km². Since 2012 the deforestation is growing, after a very successful programme in reduction. In 2004 the deforested area was 27,772 km² and at 2012 was 4,571 km², representing a reduction of 65.5% (Figure 1).
The fires in August 2019 were very abundant and surpassed historical averages since 1998. The Figure 3 shows Fire counts at Amazon, where around 70% of the fire is inside Biome Amazon. The international political pressure was very helpful in make the government take action to control fires. Understand the roles of Amazon in the Global Carbon Balance and the impact of Climate change is promoting it is very important. Also what the impact of Amazon in the climate change?

To understand the role of the Amazon in the global carbon balance, we developed a scientific strategy of GHG measures, using small aircraft to perform vertical profiles. The aircraft measurement programme was started in 2000 with monthly/biweekly vertical profile sampling at SAN (2.86S 54.95W). From December 2004 to December 2007 we performed vertical profiles at MAN (Dec 2004 / Dec 2007). In 2010, a new step in our programme was started. We added three more aircraft sites: TAB (5.96S 70.06W), RBA (9.38S 67.62W) and ALF (8.80S 56.75W). In 2013 TAB site was moved to TEF (3.39S 65.6W) and we 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 to compare with GOSAT. In 2017 we started a new place at Pantanal, the biggest flooded area in Brazil. During this time, until now, it was performed 910 vertical profiles (Table 1).
According the Brazil’s Third Biennial Update Report to UNFCC (2019), related to 2015 from the Ministry of Science, Technology and Innovation. The total anthropogenic emissions in 2015 were 2,133,180 Gg CO\textsubscript{2} eq, and according the MCTIC the removals was 774,724 Gg CO\textsubscript{2}, considering the regrowth of vegetation, in areas considered managed (2019). Changing the LULUCF participation from 52% to 23%, Agriculture from 20 to 34% and Energy from 21% to 31%, industry is 7%.

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 consistent trade winds that enter Amazonia from the Atlantic coast, permit us use a column integration technique 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 correspond to biomass burning season at Amazon, where it is more intense between Augusts to October. The time series are showed in Figure 4.

The efforts to construct a Brazilian network are very important, considering actual Amazon degradation, the changes in temperature and precipitation are great and have an important impact in the Amazon Carbon Balance, that are presenting a strong impact in the left side of Amazon that are showing a consistent source of carbon to the atmosphere. Also it is an important tool to verify the inventories and compare the emissions and the supposed uptake from the forest.

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<td>17</td>
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<td>18</td>
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<td>24</td>
<td>22</td>
<td>19</td>
<td>5</td>
<td>20</td>
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<td>21</td>
<td>24</td>
<td>20</td>
<td>22</td>
<td>194</td>
</tr>
<tr>
<td>TAB/TEF</td>
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<td>14</td>
<td>9</td>
<td>9</td>
<td>15</td>
<td>16</td>
<td>4</td>
<td>14</td>
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<td>8</td>
<td>8</td>
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<td></td>
<td></td>
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<td>19</td>
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<td>MAN</td>
<td>35</td>
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<td></td>
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<td>59</td>
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<tr>
<td>Total</td>
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<td>73</td>
<td>69</td>
<td>79</td>
<td>89</td>
<td>75</td>
<td>31</td>
<td>41</td>
<td>90</td>
<td>85</td>
<td>87</td>
<td>910</td>
</tr>
</tbody>
</table>
Figure 5. Vertical Profiles Time Series at RBA, ALF, SAN e TAB/TEF. Blue mean above 3.8km height and red mean below 1.5km height.

Acknowledgments

NOAA, NERC, FAPESP, Marinha do Brasil, INPE/CRN, CNPq, CAPES, IPEN, MCT/Brazilian Government.

References


1. Introduction

The sources of greenhouse gases partly overlap. The ratios of their emissions are characteristic for the source. These substances are rather inert chemically, the atmospheric transport affects them uniformly, and therefore, their ratios do not change during the transport time. Consequently, the correlation between their concentrations at a monitoring site gives information on the sources.

Taking advantage of three cold-air pool episodes formed in the Pannonian Basin in January - February 2017, and in situ greenhouse gas measurements at Hegyhátsál tall tower GAW monitoring station (46°57’ N, 16°39’ E, 248 m a.s.l.), covariance of the concentrations of carbon dioxide, methane, nitrous oxide and carbon monoxide was studied. The monitoring site is located in a rural environment in a dominantly agricultural region in West Hungary.

The cold-air pool episodes were caused by persistent high-pressure situations over Central Europe. The weak air movements and the radiative cooling resulted in stable vertical stratification of the lower troposphere limiting the dispersion of air pollutants emitted at the surface. During the episodes, air masses arrived at the monitoring site from the southwest–southeast sector.

2. Covariance between greenhouse gases

High correlation (0.88-0.99) between the concentrations of the greenhouse gases allows the determination of relative emission factors. The three episodes show different emission regimes: high ratios to CO$_2$ in the first period (20-23 Jan), the same CO:CO$_2$ ratio but lower ratios for the other two gases in the second (26-31 Jan), and reduced CO:CO$_2$ ratio but increased N$_2$O:CO$_2$ ratio relative to the previous episode during the last episode (11-17 Feb) (Table 1).

<table>
<thead>
<tr>
<th>period</th>
<th>CH$_4$:CO$_2$ nmol mol$^{-1}$</th>
<th>N$_2$O:CO$_2$ nmol mol$^{-1}$</th>
<th>CO:CO$_2$ nmol mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-23 Jan</td>
<td>13.8</td>
<td>0.31</td>
<td>25.6</td>
</tr>
<tr>
<td>26-31 Jan</td>
<td>6.7</td>
<td>0.15</td>
<td>25.8</td>
</tr>
<tr>
<td>11-17 Feb</td>
<td>8.0</td>
<td>0.31</td>
<td>15.0</td>
</tr>
</tbody>
</table>
The high CO:CO$_2$ ratio characterizing the episodes in January indicates ineffective burning from domestic heating. The relatively high N$_2$O:CO$_2$ ratio and $\Delta^{14}$CO$_2$ measurements revealed in a previous study suggest a high ratio of biomass among the fuels used. Fluctuations in N$_2$O:CO$_2$ and CH$_4$:CO$_2$ ratios are open questions yet.

3. **Estimation of the absolute emission**

For the estimation of the emission, a simple box model consisting of three vertically aligned boxes was compiled where the boxes represented the planetary boundary layer, the residual layer, and the free troposphere. For the determination of the emission, the boundary-layer budget method was used: the surface emission was calculated so that it maintained the measured concentration change in each time-step (1 h). The resulted CO$_2$ emission (7.3 g m$^{-2}$ day$^{-1}$) does not differ significantly from the bottom-up estimation.

Accepting the CO$_2$ emission calculated by the model for the three episodes studied and using the measured GHG to CO$_2$ ratios the emission ranges for CH$_4$, N$_2$O and CO can be estimated for the given geographical region and environmental conditions. The inferred emission ranges for CH$_4$, N$_2$O and CO are 17.9-37.9 mg m$^{-2}$ day$^{-1}$, 1.1-2.2 mg m$^{-2}$ day$^{-1}$, 69.9-120.4 mg m$^{-2}$ day$^{-1}$, respectively. These values are somewhat higher than the officially reported bottom-up annual national averages for Hungary, which are explained by the winter conditions and intensive domestic heating.

**Acknowledgment**

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**References**


WCC AND QA/SAC ACTIVITIES BY JMA

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2. National Institute for Environmental Studies (NIES), Tsukuba, Japan
3. National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
4. Meteorological Research Institute (MRI), Tsukuba, Japan

1. World Calibration Centre for methane in Asia and the South-West Pacific

The Japan Meteorological Agency (JMA) serves as the World Calibration Centre (WCC) for methane (CH₄) and the Quality Assurance/Science Activity Centre (QA/SAC) for carbon dioxide (CO₂) and methane (CH₄) in Asia and the South-West Pacific within the framework of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO). As part of the WMO/GAW quality assurance system, the WCC-JMA has a fundamental role in helping to ensure the traceability of GAW network measurements to the WMO primary standard through comparison campaigns.

1.1 CH₄ Intercomparison (round-robin) experiments

The WCC-JMA organized five rounds of the CH₄ reference gas intercomparison experiments from 2001 to 2019 for the purpose of understanding the differences between CH₄ standard scales of each laboratory as well as to monitor the long-term stability of standard gases in Asia and the South-West Pacific in collaboration with NOAA (WMO/CCL, USA), CSIRO (Australia), NIWA (New Zealand), CMA (China), KMA/KRISS (Republic of Korea), IITM (India), MRI (Japan), NIES (Japan), AIST (Japan), NIPR (Japan), and Tohoku University (Japan); the sixth round is still in progress. WCC-JMA web site: https://ds.data.jma.go.jp/wcc/

Figure 1. Conceptual diagram of the CH₄ reference gas intercomparison experiments. In these experiments, two cylinders of reference gas with different CH₄ mole fractions are circulated in turn to each laboratory for measurement of their mole fractions; the measured values are reported to the WMO/GAW Secretariat through the WCC-JMA.
1.2 Results of CH$_4$ intercomparison experiments

Figure 2. The differences between WCC-JMA and each participant reported in the 6 round-robin experiments from 2001 to 2019 (left). The results converted to the WMO mole fraction scale using the conversion coefficient for each laboratory (right).

Figure 3. Temporal variations of the differences from WCC-JMA for cylinders CPB13002 (nominal value at 1740 ppb) (a) and CPB13003 (nominal value at 1900 ppb) (b) in the 5th round-robin experiment. The measurement results by each institution are converted to the WMO mole fraction scale using conversion coefficients.

2. JMA (In situ) and JMA/AIST/NIES flask air intercomparison at MNM

In addition to the GAW-centre activities, the JMA has made long-term continuous observations of atmospheric mole fractions of major greenhouse gases such as CO$_2$ and CH$_4$ at Minamitorishima GAW Global station (MNM) since 1993 (Figure 4). Other major observation laboratories in Japan also began systematic measurements of atmospheric CO$_2$ and CH$_4$ mole fractions using a flask sampling method in cooperation with JMA at MNM in the 2010s (Table 1). For the purpose of evaluating the consistency of observation data from different methods and laboratories, we compared observation data of JMA and other laboratories at the same station. This presentation focuses on CH$_4$ observation.
Table 1. Observation methods of each laboratory

<table>
<thead>
<tr>
<th>Lab</th>
<th>Sampling type</th>
<th>Sampling frequency</th>
<th>Measurement method</th>
<th>Instrument</th>
<th>Measurement Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>JMA</td>
<td>In-situ</td>
<td>Analyzed every 10 minutes</td>
<td>GC/FID</td>
<td>Round Science Inc. RGC-1</td>
<td>WMO CH₄ X2004A Scale</td>
</tr>
<tr>
<td>JMA</td>
<td>Flask</td>
<td>Fill the flask with ambient air up to 0.3 MPa in minutes once a month</td>
<td>CRDS</td>
<td>G2301, Picarro</td>
<td>WMO CH₄ X2004A Scale</td>
</tr>
<tr>
<td>AIST</td>
<td>Flask</td>
<td>Fill the flask with ambient air up to 0.3 MPa in minutes once a week</td>
<td>GC/FID</td>
<td>GC-14BPF (FID), Shimadzu</td>
<td>AIST Scale</td>
</tr>
<tr>
<td>NIES</td>
<td>Flask</td>
<td>Fill the flask with ambient air up to 0.15 MPa in minutes twice a month</td>
<td>GC/FID</td>
<td>HP7890 (FID), Agilent</td>
<td>NIES 94 CH₄ Scale</td>
</tr>
</tbody>
</table>

Each laboratory collects air samples independently and ships flask samples to their laboratories for analysis. (AIST: National Institute of Advanced Industrial Science and Technology, NIES: National Institute for Environmental Studies)

2.1 Observation data of each laboratory

Figure 5. Temporal variations of CH₄ mole fractions observed by each laboratory at MNM
2.2 Data screening and analysis method

Step 1 - Extract “JMA In situ data” observed at the closest time to the flask sampling.

Step 2 - Calculate the differences between “flask data of each laboratory” and “JMA In situ data”.

Step 3 - Calculate the mean and the standard deviation ($\sigma$) of the differences calculated in step 2.

Step 4 - Select data within the three standard deviations (3$\sigma$) of the mean calculated in step 3.

Step 5 - Calculate the mean of differences for the data selected in step 4.

2.3 Comparison results

![Graphs](https://via.placeholder.com/150)

Figure 6. Comparison results of greenhouse gas observation data from different institutions and different methods at the same station. The upper three graphs show the temporal variations of methane mole fractions observed by each laboratory. The middle three graphs show the temporal variations of differences between “flask data of each laboratory” and “JMA In situ data”. The lower three graphs show the mole fraction dependence of the differences between “flask data of each laboratory” and “JMA In situ data”. The green squares show the differences of standard gas scales between laboratories, which are derived from the iceGGO cylinder comparison [7].

2.4 Future plan

We will continue to evaluate the consistency of CH$_4$ observations by different laboratories at MNM to maintain reliability of the observations. In addition, we plan to compare observation data for other gas species such as CO$_2$, N$_2$O, CO.
3. **Summary**

The WCC-JMA organized five rounds of the CH₄ reference gas intercomparison experiments from 2001 to 2019. Focusing on the results of the last decade, almost all laboratories have shown a good agreement within the GAW compatibility goal of ±2ppb after applying conversion factor. The fifth round-robin demonstrated the better compatibility in the measurements among the laboratories compared to the previous round-robins. We compared the methane observation data from different methods and laboratories at Minamitorishima. The differences between flask data of each laboratory and JMA In situ data are about -0.1±2.3 ppb, +3.6±3.3 ppb, +3.6±2.7 ppb for JMA, AIST and NIES, respectively. These values agree well with the differences between the standard gas scales used for atmospheric observations, which are derived from Inter-Comparison Experiments for Greenhouse Gases Observation (iceGGO) conducted during the period from 2012 to 2016. There are no time-dependent trend of the differences with 95% confidence interval. These results indicate that JMA, AIST, and NIES have maintained quality of the methane observation for a long time.

4. **Acknowledgments**

We thank all the laboratories for their cooperation and contribution to these intercomparison experiments.

**References**


DEVELOPMENT OF NOVEL TRACE METHANE AND TRACE CARBON DIOXIDE ANALYZERS - PERFORMANCE EVALUATION STUDIES AND RESULTS OF FIELD DEPLOYMENT

Graham Leggett

Co-authors: Kristen Minish, Israel Begashaw, Ryan Walbridge, Derek Trutna, Mark Johnson, Anatoly Komissarov

Affiliations: 1. LI-COR Biosciences, Lincoln, Nebraska, USA

We report on the development, performance evaluation, and field deployment of recently commercially available trace gas analysers for the measurement of atmospheric methane and carbon dioxide. Based on Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS), the analysers offer both the sensitivity and stability necessary for long-term atmospheric monitoring measurements, meeting the measurement compatibility goals as defined by WMO/GAW and other measurement networks. The first two analysers released on this common platform are the LI-7810 CH₄/CO₂/H₂O and LI-7815 CO₂/H₂O Trace Gas Analysers.

We introduce the now commercially available trace gas analysers and implementation of the OF-CEAS technology. Performance characterization, including results from long-term measurement stability tests for methane and carbon dioxide at approximately atmospheric background concentration, is given. These results, along with Allan deviation plots for measurements of methane and carbon dioxide, at similar concentrations, are also presented; see Figure 1. In addition, we present data supporting stable operation from -25 oC to +45 oC, as well as an integrated water correction delivering dry mole fraction data.

To make the LI-7810 and LI-7815 ready for laboratory deployment for atmospheric measurement applications, we worked in collaboration with GCWerks, resulting in a new version of the software tailored to these analysers. We summarize how the software is used to manage data acquisition, instrument calibration, and system diagnostics.

The introduction of the LI-7810 and LI-7815 analysers also provides the sampling rate, response time, and dynamic range needed for multiple applications in mobile and agile deployment. Field results of a mobile area survey are presented, where the LI-7810 was installed in a car and driven to locations of interest to determine the presence of methane emissions. Potential sources included a landfill site, an anaerobic digester, and intensive agricultural operations. Open source tools were used to process concentration and geospatial data to visualize data using Google Earth.

In conclusion, the work presented here has resulted in two commercially available trace gas analysers, the LI-7810 and LI-7815 analysers, for the measurement of methane and carbon dioxide. These portable and rugged instruments exceed requirements for both long-term atmospheric background measurements and offer a versatile platform for a range of mobile and agile measurements relevant to the better understanding of greenhouse gas emissions from anthropogenic and natural sources.

¹The initial principles and some portions of the new technology presented herein were developed in part based on the grant from the MONITOR Program by the U.S. Department of Energy Advanced Research Projects Agency - Energy (ARPA-E), under award number DE-AR0000537.
Figure 1. Long-term stability data and Allan deviation plots for LI-7810 CH₄/CO₂/H₂O and LI-7815 CO₂/H₂O Trace Gas Analysers
BACKGROUND CONCENTRATIONS OF CO₂, CO AND N₂O IN BRAZILIAN COAST

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¹Earth System Science Center (CCST), National Institute for Space Research (INPE), São José dos Campos, Brazil
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1. Introduction

There are few measures on background greenhouse gases (GHG) in the tropical areas, mainly in the Atlantic Ocean coast, so these areas are underrepresented in the actual global greenhouse gases (GHG) monitoring network. Understand the characteristic GHG concentrations in Tropical Global range on Atlantic Ocean is an important task for many studies to determine GHG balances and the contribution of Amazon area to the regional and global budget. The Amazon Forest represent around 50% of the world’s rainforest (Gloor et al., 2012). In this work, we present the observations of CO₂, N₂O and CO at four coastal stations located on North and Northeast Brazilian Coast in the period of 2006 to 2018.

1.1 Scientific reasons for Coastal GHG measurement

A better understand of the typical GHG background for the Amazon analysing the air masses that arrived on North and Northeast Brazilian coast, come from the Atlantic Ocean in the period 2006 to 2018 is the motivation of this study.

2. Geographic, material and methods considerations

The GHG background measurements on Brazilian Coast start in Arembepe (ABP: 12º45’46.79“S; 38º10’08.39“W, 15 meters above sea-level) in 2006 and goes to 2010. From 2010 up to 2017, air samples were collected on Salinopolis (SAL: 00º36’15.03“S; 47º22’25.02“W, 10 m a.s.l). Since 2010, samples are collected at Natal (NAT: 05º29’21.83“S; 35º15’39.42“W, 15 m a.s.l. from 2010 to 2015 and 05º47’43.12“S; 35º11’07.27“W, 87 m a.s.l. since 2015). In 2014, the sampling starts in Camocim (CAM: 02º51’47.00“S; 40º51’36.70“W, 21.5 m a.s.l.).

The samples were collected weekly by using a pair of glass flasks (2.5L) and a portable sampler, totalling 1700 samples. The air samples were analysed to quantify carbon dioxide (CO₂), nitrous oxide (N₂O) and carbon monoxide (CO) on the Greenhouse Gas Laboratory (at IPEN until April 2015 and later at LaGEE/CCST/INPE).

Backward trajectories of air masses that arrived at the sites were simulated by HYSPLIT model (DRAXLER, R.R. and ROLPH, G.D. HYSPLIT- HYbrid Single-Particle Lagrangian Integrated Trajectory <http://ready.arl.noaa.gov/hypub-bin/trajtype.pl?runttype=archive>) for each sample by using the location and altitude of the sample point and 240h retroceding, to determine the origin and seasonality of air masses for all sites (Figure 1).
3. Results and discussion

The GHG results showed on Figures 2, 3 and 4 evidence that each study site presented seasonality when compared to the WMO GHG Monitoring Global Stations of Ascension Island (ASC: 07°96'67.00"S; 14°00'00.00"W, South Atlantic Ocean) and Ragged Point Barbados (RPB: 13°16'50.00"N, 59°43'20.00"W, North Atlantic Ocean). The stations of SAL and CAM showed highest GHG concentrations between January and May, a behaviour similar to RPB, when the air masses come from North Hemisphere, while in the rest of the year the concentrations were similar to that observed in ASC, when the simulations track their origin in the south hemisphere. In ABP and NAT the concentrations were lowest and more homogeneous throughout the all year, more similar to ASC, and their origin were tracked only to the south hemisphere. The influence of the displacement of the Intertropical Convergence Zone (ITCZ) on the GHG concentrations at SAL and CAM was confirmed by backward trajectories simulations by HYSPLIT model (using 240 hours) of the air masses (Souza et al., 2009; Rolph, 2017). Mean GHG concentrations for 2018 obtained from CAM and NAT sites (Table 1) increased over 2016 values following the global growth rate, with exception for CO concentrations, which showed a decrease during the period of this study. The trends of increase of all GHG concentrations in the Brazilian coast stations showed a similar behaviour of the global average concentrations during the period of this study.

References


Acknowledgments

Figure 1. Backward trajectories of air masses that arrived in ABP, SAL, NAT and CAM simulated by HYSPLIT model. The percentage of air masses from north (HN) and south (HS) hemispheres are highlighted.

Figure 2. Time series in ABP, SAL, NAT and CAM for CO₂ and the CO₂ background for the WMO GHG Monitoring Global Stations of ASC and RPB.
Table 1. Mean concentration of CO₂, CO and N₂O for CAM and NAT in 2016 and 2018

<table>
<thead>
<tr>
<th></th>
<th>Mean GHG Concentration</th>
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<tr>
<td></td>
<td>CO₂ (ppm)</td>
</tr>
<tr>
<td>Site</td>
<td>Code</td>
</tr>
<tr>
<td>Camocim</td>
<td>CAM</td>
</tr>
<tr>
<td>Natal</td>
<td>NAT</td>
</tr>
</tbody>
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MEASURING STABLES ISOTOPES OF CO₂ (¹³C AND ¹⁷,¹⁸O) IN VERTICAL PROFILES OVER THE AMAZON

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1. Introduction

The most abundant Greenhouse gas (GHG) in our atmosphere is carbon dioxide (CO₂) and in 2017 its concentration reached 146% of pre-industrial levels¹[1]. In the period 2007-2016 around 44% of total CO₂ emissions from human activities accumulated in the atmosphere, while 22% was stored in the ocean and 28% on land¹[1], but important questions remain on the processes behind this partitioning, and their persistence under climate change. The study of the stable isotopologues of CO₂ – ¹³CO₂, C¹⁷OO and C¹⁸OO – can provide new insights, for example on the efficiency of water use during photosynthesis²[2]. They also can be helpful in determining the temporal and spatial distribution of sources and sinks, and to estimate the contributions of C₃ and C₄ to total primary productivity³[3].

2. Methodology

The Greenhouse gas measurements were started with vertical profiles using small aircrafts, since 2010 in SAN (2.86ºS; 54.95ºW), RBA (9.01ºS, 64.72ºW), ALF (98.80ºS, 56.75ºW) and TEF (3.31ºS, 65.8°W), which started in 2013 to replace TAB (5.96ºS, 70.06ºW), all these sites located in Brazilian Amazon Basin (Figure 1).

Samples from vertical profiles were collected, generally fortnightly, using a semi-automatic sampling system, which consists of separate compressor and flask units, developed by ESRL/NOAA. The first unit contains two rechargeable batteries and compressors, and remains at the sampling site. The second unit containing 17 glass flasks (used in SAN) or 12 flasks (used in ALF, RBA and TEF) (Figure 2), a microprocessor that controls the sampling and storage of information about it conditions. Small aircraft were used for collecting, in which were installed a collector tube (inlet), a temperature and relative humidity sensor and GPS (Global Positioning System) to record the position and altitude of each sample. Samples were taken between 12 pm and 2 pm local time, a period of greater stability in the troposphere, and therefore with better repeatability of atmospheric conditions, where the height of the boundary layer is close to its maximum height. The inlet was connected to the compressor unit that transfers the air to the unit containing the flasks which was connected to a device, called the pilot’s display, indicating the pre-programmed altitude determined to sample the first to the last flask. The trajectory of the airplane was made in descending helical profile with a diameter of around 5 km, so there is no influence of the gas emitted by the engine of the aircraft in the sampling, starting at 4420 m and finishing at 427 m in ALF, 308 m in RBA, SAN and TEF.

Since June 2016, 700 ml of air from each flask has been used to extract pure CO₂ in glass vials, to determine d¹³C ratios in CO₂ at the stable isotope laboratory in Groningen, the Netherlands. We currently have close to 1500 vials ready for analysis. In addition, direct
analysis on air in each flask started in Feb-2017 at LaGEE. CO₂ and its stable isotopes (d\textsuperscript{13}C, and Excess-\textsuperscript{17}O, derived from d\textsuperscript{17}O and d\textsuperscript{18}O) are measured on a TILDAS-D CO\textsubscript{2} Analyser from Aerodyne Inc (Figure 3), through a limited number (12-16) repeat measurements of 15ml aliquots of air, interspersed with a measurement of a known reference gas for normalization.

Note that a useful measurement of the oxygen isotopes necessitated rigorous drying (< 2 deg d\textsuperscript{ewpoint T) of very humid tropical air (2-4% H\textsubscript{2}O), using a custom built Nafion drying system (Paul et al., 2019, in preparation).

3. Results and discussion

Figure 4 shows the analysis system. The pressure in valve V2 is six times higher than in Sample Cell. The PFP is connected to a tube containing Magnesium Perchlorate Mg (ClO\textsubscript{4})\textsubscript{2} to minimize the amount of water present in the collected sample.

To inject the sample into valve V2, valves E9 and E12 must be opened. Then the sample should go to Sample Cell, where the analysis will be performed, for this the valves E20 and E23 must be opened. Synthetic air is used to open and close the valves. When the analysis is being performed on Sample Cell, a vacuum is made on the valve V2 line by opening valves E20 and E22. In addition to these, valves E9 and E12 must also be open to “clear” the line for a second sample to be analysed. The analysis of the sample is carried out simultaneously with a reference cylinder (REF), also calibrated in Germany with high accuracy, of 393.03 ppm concentration. 16 measurements are taken for each vial, totaling 192 measurements for each PFP version III and 272 measurements for each PFP version II. The WS1, WS2, and WS3 standards are measured twice: once before starting the analysis and after analysis, for a 12-vial PFP. The TARGET is measured once during the analyse. The sample is taken together with reference so that any changes during the analysis can be tracked, which increases measurement accuracy. Two calibration curves are constructed, so the analysis of the standards is made. There are patterns with low, medium and high concentration, as already reported (WS1, WS2 and WS3). All this procedure is performed in order to verify the stability of the equipment and to give greater precision to the analysis results.

The calibration of TARGET (Table 1) shows a result similar to the observed by NOAA indicating a good precision and stability of the measurements.

4. Conclusion

The stables isotopes will help us to understand better the changes in forest function in Amazonia, since measuring CO₂ in the atmosphere, since it is not possible to separate CO₂ from anthropogenic source from natural, and also inside the natural sources: photosynthesis, respiration and decomposition.

References

Figure 1. Vertical profiles and sampling sites

Figure 2. Portable Flask Package – PFP
Figure 3. TILDAS-D CO₂ Analyser from Aerodyne Inc connected in PFP (version II, with 12 flasks)

Figure 4. Analysis system

Table 1. Calibration TARGET TILDAS-D CO₂ and NOAA

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<tr>
<th>ASICA_TARGET</th>
<th>MEASURED</th>
<th>ASSIGNED NOAA</th>
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<tr>
<td>CO₂</td>
<td>402.85±0.06 ppm</td>
<td>403.3 ppm</td>
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FIVE YEARS OF Δ^{13}C(CO\textsubscript{2}) MEASUREMENTS FROM AN IN SITU FOURIER TRANSFORM INFRARED TRACE GAS AND ISOTOPE ANALYSER AT LAUDER, NEW ZEALAND (45S)

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1. Introduction

We present a five-year time series (2014-2018) of in situ δ\textsuperscript{13}C (CO\textsubscript{2}) measurements made at the NIWA Lauder atmospheric research station using a Fourier transform infrared trace gas and isotope analyser. Individual isotopologue measurements of CO\textsubscript{2} (\textsuperscript{12}CO\textsubscript{2}, \textsuperscript{13}CO\textsubscript{2} and CO\textsubscript{18}O) are calibrated prior to isotopic ratio calculations using the methodology set out in Griffith, AMT, 2018. We assess the long-term performance of the analyser and compare the calibrated measurements to that of collocated δ\textsuperscript{13}C (CO\textsubscript{2}) flask samples.

2. CO\textsubscript{2} isotopologue measurements at Lauder, New Zealand

An in situ Fourier transform infra-red spectrometer (FTIR) trace gas analyser has been operating at Lauder, New Zealand (45S, 170E, 370m) since August 2006 (Smale et al., 2019). Continuous 10-minute measurements of CO\textsubscript{2}, CH\textsubscript{4}, CO and N\textsubscript{2}O are made from air drawn from a 10-metre mast. Regular measurements of reference and working standard (WS) tanks allows calibration of the atmospheric sample to the WMO trace gas scales. Spectra taken from October 2014 to July 2019 have been reanalysed to fit and retrieve CO\textsubscript{2} isotopologues.

Lauder is in the middle on the South Island of New Zealand, surrounded by pastoral farmland with low stock density and with no nearby industrial emission sources. Atmospheric footprint analysis (see fig. 1) show that much of the sampled air originates (since last boundary layer contact) from the western coast of the South Island, a heavily native forested region. We expect CO\textsubscript{2} and δ\textsuperscript{13}C(CO\textsubscript{2}) ‘baseline’ measurements at Lauder to be indicative of southern hemisphere mesoscale background concentrations, with the localised δ\textsuperscript{13}C(CO\textsubscript{2}) source signature dominated by biogenic emissions.

3. CO\textsubscript{2} isotopologue retrievals

Analysis of spectra acquired by the FTIR is conducted using the MALT retrieval algorithm (Griffith, 1996). MALT processing allows individual retrieval of the CO\textsubscript{2} isotopologues: \textsuperscript{12}CO\textsubscript{2}, \textsuperscript{13}CO\textsubscript{2} and CO\textsubscript{18}O. Required inputs to MALT include spectra, instrument specific parameters (instrument field of view, White cell path length) and the white cell pressure and temperature. The retrieved CO\textsubscript{2} isotopologues concentrations are converted into dry mole fractions (mole fraction abbreviations: ppm => µmol mol\textsuperscript{-1}) using the measured cell pressure, temperature and water vapour content (Griffith, 1996). The spectral regions used in MALT for CO\textsubscript{2} isotopologue retrievals are the same as that used by Vardag et al., 2016. \textsuperscript{13}CO\textsubscript{2} and CO\textsubscript{18}O are retrieved in spectra region 1 and \textsuperscript{12}CO\textsubscript{2} in spectral region 2, as shown in figure 2.

4. Precision

Repeatability experiments were performed by taking consecutive 2-minute measurements in standard unvarying operating conditions of cylinder (ambient) dry air. The resultant species
dry mole fraction (and isotopologues) time series were then analysed using the Allan variance technique (Allan, 1966) to characterise precision over differing temporal ranges (see Fig 3).

The CO₂ precision of 10-minute averaged spectra is ~0.025 ppm and ~0.06 ‰ for δ¹³C(CO₂). A Spectronus FTIR system (has a metal white-cell with upgraded FTIR electronics) located at the University of Wollongong (UoW), Australia has a 10-minute precision of ~0.024 ‰ for δ¹³C(CO₂), so there are improvements that can be made to the Lauder FTIR to increase precision.

5. Accuracy and calibration

Measurement accuracy is obtained by calibrating the instrument using WS tanks traceable to WMO trace gas and isotope scales. For CO₂ isotopologue calibration, NIWA currently uses the accepted isotope ratios in VPDB (and VSMOW) stated in Werner and Brand, 2001. Since the FTIR measurements can distinguish the individual CO₂ isotopologues, these are first calibrated before isotope ratios (δ¹³C, δ¹⁸O) are calculated. The methodology of this approach is set out in Griffith, 2018.

Yearly multi-tank suite calibrations are used to characterise the instrument calibration curves. Each isotopologue calibration curve has been shown to be highly linear with a stable gradient. Weekly WS measurements are used to apply an additive correction to the calibrated sample data. This is to account for instrument offset drift between full linear calibrations. Figure 4 shows the weekly correction factors for ¹²CO₂ and ¹³CO₂, note the drift in the correction factor, and step on instrument maintenance (pressure sensor recalibration) or WS change.

6. Reproducibility

Regular measurements of a target tank (surveillance cylinder) over timescales longer than a day allow us to assess instrument reproducibility (as opposed to short term repeatability). Weekly Target tank (TT) measurements started in early 2014. The TT measurements were reanalysed to retrieve CO₂ isotopologues and calibrated the same way as sample measurements. TTs are prepared and assigned (including CO₂ isotopologues) in the same manner as WS tanks. Having the TTs assigned allows accuracy (mean difference between measurement and assignment), as well as reproducibility (spread/standard deviation of difference) to be diagnosed.

Figure 5 displays the difference between the TT measured and assigned values for CO₂ and δ¹³C(CO₂). There are large step changes in the bias upon WS and TT changes. The reproducibility (with bias removed by interval, 1-σ S.D.) of CO₂ is 0.07 ppm and for δ¹³C(CO₂) it is 0.1 ‰.

7. Comparison to flask samples

Flask samples have been taken regularly (~weekly) at Lauder since 2009. So far priority collection has been in baseline conditions. We define measurements taken between 15-16 NZST when the mean wind speed > 5 ms⁻¹ as ‘Baseline’. Baseline conditions are representative of a well-mixed planetary boundary layer with minimum trace gas variability.

Flask sample CO₂ and δ¹³C(CO₂) abundances were measured using Gas Chromatograph (GC) methods at NIWA’s GASLAB facility. GC precision for CO₂ is ~0.06 ppm and ~0.04‰ for δ¹³C(CO₂), comparable precisions to that of the Lauder FTIR. FTIR-flask bias and spread are
greater than the GAW-recommended compatibility goal of 0.01 ‰. A single night time flask shows good agreement with the FTIR (Fig 6, A). Reasons for the FTIR flask differences needs to be investigated.

8. **Baseline trends and seasonal cycles**

Baseline FTIR CO₂ and δ¹³C(CO₂) were analysed to find linear trends and seasonal cycles (Fig 7). A linear trend of 2.02 +/- 0.02 ppm/year was found for CO₂. No statistically significant linear trend from 2014.75 to 2019.6 in δ¹³C(CO₂) was deduced. A CO₂ seasonal cycle is seen (Fig 8, 3-4 ppm peak to peak, three Fourier pairs gave best fit). Springtime CO₂ drawdown is seen. There is no statistically significant δ¹³C(CO₂) seasonal cycle but there appears to be a small negative correlation in the CO₂ and δ¹³C(CO₂) detrended monthly averages.

9. **Source mix using the Keeling plot method**

Assuming a single source mix at Lauder (assumed to be “δbio”, due to the lack of local anthropogenic sources), we can determine the mean isotopic source signature (δ¹³Cs) using the Keeling plot method. Fig 9A shows the calculated δ¹³Cs using data over a 3-day period (data seen in Fig 6D) from two methods: Keeling and Miller-Tans plots. The Keeling plot method was then applied to the FTIR 5-year timeseries (similar to the methodology in Vardag et al., 2016). For each day (centered at midnight +/- 12hrs), δ¹³Cs was calculated. Filtering was applied: daily CO₂ range > 20 ppm, over a time span > 3 hours, with δ¹³Cs uncertainty < 2‰, and linear fit correlation > 0.9. The filtered δ¹³Cs ~-27‰ is within the expected range of C3-C4 plant mixes (Vardag, et al., 2016) and expected from a pastural measurement site (such as Lauder).

10. **Summary**

- We present a ~5-year δ¹³C(CO₂) timeseries (Oct 2014 – Jul 2019) from an FTIR in situ analyser at Lauder, NZ.
- Individual CO₂ isotopologues (¹²CO₂, ¹³CO₂ and CO¹⁸O) are measured with the FTIR.
- The ¹²CO₂, ¹³CO₂ and CO¹⁸O measurements are calibrated individually prior to the calculation of isotopic ratios (δ¹³C, δ¹⁸O).
- Precision: The CO₂ precision of 10-minute averaged spectra is ~0.025 ppm and ~0.06 ‰ for δ¹³C(CO₂).
- Reproducibility: Long-term measurement reproducibility for CO₂ is ~0.07 ppm and for δ¹³C(CO₂) ~ 0.1 ‰.
- Accuracy: Is limited by working standard tank assignment uncertainties.
- There are already improvements that can be made to the analyser to increase precision and reproducibility.
- A seasonal cycle is seen in baseline CO₂ measurements (3-4 ppm peak to peak), along with a possible baseline δ¹³C(CO₂) seasonal cycle.
- A mean carbon isotopic source signature (δ¹³Cs) of ~-27‰ is measured at Lauder. We see no trend or seasonal cycle in δ¹³Cs.

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Figure 1. 2011–2013 mean footprint for Lauder, based on twice daily air history maps at 13-14 
NZST and 15-16 NZST (Steinkamp et al., ACP, 2017)
Figure 2. A: Spectral region 1 B: Spectral region 2. The spectrum is from a repeatability experiment conducted in August 2018 (Individual trace gas and CO₂ isotopologue spectra are consecutively shifted upwards by 0.05 for clarity).

Figure 3. CO₂ and δ^{13}C(CO₂) Allan deviations calculated from a repeatability experiment conducted in August 2018. Overlaid are Allan deviations of δ^{13}C(CO₂) and δ^{18}O(CO₂) from repeatability experiment made on the UoW Spectronus system (light and dark grey lines respectively). The dashed lines represent the Gaussian-noise-limited Allan deviation.

Figure 4. $^{12}$CO₂ (A) and $^{13}$CO₂ (B) correction factors calculated from weekly WS measurements.
Figure 5. TT CO₂ and δ¹³C(CO₂) differences. Vertical lines indicate an interval, on WS or TT change.

Figure 6. Panels A,B,C: Comparison of δ¹³C(CO₂) FTIR and flask samples. D: Measurements over a 3-day span (Nov 2018).
Figure 7. Baseline CO$_2$ and $\delta^{13}$C(CO$_2$)

Figure 8. CO$_2$ and $\delta^{13}$C(CO$_2$) detrended monthly means

Figure 9. A: Keeling and Miller-Tans plots using 3 days of data (Nov 2018, see Figure 6D). B: Filtered time series of calculated $\delta^{13}$Cs, with 2-month smoothing.
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