15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques

(Jena, Germany, 7-10 September 2009)

Edited by Willi A. Brand
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In situ and ground-based remote sensing measurements of atmospheric CO$_2$ in New Zealand (G.W. Brailsford, V. Sherlock, A. Gomez, K. Riedel, D. Smale, M. Kotkamp, B. Stephens, J. Robinson, B. Connor and S. Mikaloff-Fletcher)

Vertical Profiles of Greenhouse Gas Concentrations via Airborne Measurements (Eric Crosson, Marc Fischer, Anna Karion, Colm Sweeney, Aaron Van Pelt, Tom Sherwood and Suman Saripalli)

NOAA SF6 Measurements from 1987 to 2009 (Brad Hall, Geoff Dutton, Debbie Mondeel, Ed Dlugokencky, David Nance, Pat Lang, Gabrielle Petron, James Butler and James Elkins)

Australian Regional High Precision Greenhouse Gas Observation Network: Southern Ocean Network (CO$_2$ Sink) and New Australian Tropical Atmospheric Research Station (M. V. van der Schoot, L. P. Steele, D. A. Spencer, P. B. Krummel, R. J. Francey, P. Fraser, A.R. Stavert, M. Schmidt, M. Ramonet and B. Wastine)

NOAA/IPEN GHG Inter-comparison and Efforts to start a GHG Network in Brazil (Luciana V. Gatti, Monica T. S. D’Amelio, Thomas J. Conway, John B. Miller, Andrew Crotwell, Luana S. Basso, Alexandre Martinewski, Alaor Dall’Antonia, Netzair Vianna and Pieter Tans)

Understanding Northeast Asian CO$_2$ Emissions from Continuous Monitoring at Gosan Station (Jooil Kim, Lkhagvadorj and Kyung-Ryul Kim)

Recent results from measurements of CO$_2$, CH$_4$, CO and N$_2$O at the GAW station Cape Point (E-G. Brunke, C. Labuschagne, B. Parker and H.E. Scheel)

Continuous CO$_2$/CH$_4$ measurement at Zotino Tall Tower Observatory (ZOTTO) in Central Siberia (Jan Winderlich, Huilin Chen, Annette Höfer, Christoph Gerbig and Martin Heimann)

Long Term Observations of Climate Altering Gases at the Mt. Cimone "O. Vittoni" Research Station (2165 M, Italy) (Michela Maione, Umberto Giostra, Francesco Furlani, Igor Arduini, Francesco Graziosi, Paolo Bonasoni and Paolo Cristofanelli)

Cabauw (NL) station report (A. T. Vermeulen, M. E. Popa, W.C.M. van den Bulk and P.A.C. Jongejan)

Network Observation of Greenhouse Gases and Related Tracers in China (Lingxi ZHOU, Lixin LIU, Shuangxi FANG, Fang ZHANG, Bo YAO, Min WEN, Lin XU, Shuai GU, Kunpeng ZANG, Lingjun XIA, Xiaoqun ZHANG, Yupu WEN, Xuji ZHOU, Guoqing ZHANG, Honghui XU, Zhiquiang MA, Xin DAI, Peng LIU, Qianli MA, Xiaofeng XU, Dajiang YU, Jianqiang HUANG, Xiaoqiang ZHANG, Qingli SONG, Junciang GU and more station colleagues)


Glass Flask Air Sample Analysis through Gas Chromatography in India: Implications for Constraining CO$_2$ surface fluxes (Yogesh K. Tiwari and K. Ravi Kumar)

Performance test of a mobile fossil fuel CO$_2$ monitoring station developed in ATOMKI (M. Molnár, L. Haszpra, I. Major, J. Szádai and I. Svetlik)


Greenhouse gas measurement capability at the Carbon Related Atmospheric Measurement (CRAM) Laboratory at the University of East Anglia, United Kingdom (Philip A. Wilson, Andrew C. Manning, Andrew J. Macdonald, Alex J. Etchells and Elena A. Kozlova)

Improvements in the Carbon Dioxide and Methane Continuous Measurement Programs at Izaña Global GAW Station (Spain) during 2007-2009 (A.J. Gomez-Pelaez and R. Ramos)

First results from the new JRC greenhouse gas monitoring site at Ispra, Italy (H.A. Scheeren, P. Bergamaschi, N. R. Jensen, C. Gruening, I. Goded, and J. van Aardenne)

2. CALIBRATION / PROPAGATION OF SCALES FOR CO₂ IN AIR

The WMO Mole Fraction Scales for CO₂ and other greenhouse gases, and uncertainty of the atmospheric measurements (Pieter Tans, Conglong Zhao and Duane Kitzis)

Recent History of CO₂ Standard Gases in JMA (Kazuto Suda, Hidekazu Matsueda, Kazuhiro Tsuboi and Shinya Takatsuji)

A new CO₂ calibration scale based on gravimetric one-step dilution cylinders in National Institute for Environmental Studies – NIES 09 CO₂ Scale (T. Machida, Y. Tohjima, K. Katsumata and H. Mukai)

Linking Isotopologue Specific Measurements of CO₂ to the Existing International Mole Fraction Scale (Z. M. Loh, L. P. Steele, P. B. Krummel, M. van der Schot, D. M. Etheridge, D. A. Spencer and R. J. Francey)

World Calibration Centre for Carbon Dioxide: Supporting the Quality of the Global Observation System (Jörg Klausen, Christoph Zellweger and Brigitte Buchmann)

3. CALIBRATION / PROPAGATION OF SCALES FOR CH₄, CO, SF₆, N₂O, AND H₂ IN AIR

Nitrous Oxide: Are We Making Progress (Brad Hall, Geoff Dutton, Kirk Thoning and Ed Dlugokencky)

Report of the WCC-N₂O (H.E. Scheel)

Is it time for a WMO Hydrogen calibration scale? (A. Jordan)

Quality Assurance and Quality Control of WDCGG Data (Kazuto Suda, Atsuya Kinoshita, Yukio Kurihara and Rie Nakamura)

4. INTERCOMPARISON ACTIVITIES

Summing Up 14 Years of Intercomparison Activities of the World Calibration Centre at Empa (WCC-Empa): Methane, Carbon Monoxide and Ozone (Christoph Zellweger, Jörg Klausen and Brigitte Buchmann)

New Capabilities for Interpreting Comparison Data (Ken Masarie, D. Chao, P. Novelli and P. Tans)

WMO round-robin inter-comparison: progress and a new website (Lingxi ZHOU, D.R.Kitzis, P.P. Tans, K.Masarie and D.Chao)

Preliminary results from the first inter-comparison of Accelerator Mass Spectrometry atmospheric ¹⁴CO₂ measurements (John Miller, Chad Wolak, Scott Lehman, Collin Allison, Heather Graven, Tom Guilderson, Ralph Keeling, Harro Meijer, T. Nakamura, Takakiyo Nakazawa, Rolf Neubert, Andrew Smith, John Southon and Xiaomei Xu)

5. ISOTOPE CALIBRATION AND MEASUREMENTS


Re-evaluation of isotopic scale for CO₂ in National Institute for Environmental Studies (Japan) and its relation with inter-comparison works (Hitoshi Mukai, Keiko Tohmone, and Yoko Kajita)

JRAS isotope reference: A generalized VPDB scale anchor for CO₂ in air? (Magnus Wendeberg, J. M. Richter, M. Rothe and W.A. Brand)

How accurately do we know ¹³C/¹²C, ¹⁸O/¹⁶O and ¹⁷O/¹⁶O ratios in CO₂ and their corresponding δ values? (Jan Kaiser)

Isobaric correction of mass-spectrometric isotope ratio measurements of O₂, CO, CO₂ and N₂O (Jan Kaiser and Thomas Röckmann)

A robust setup for long-term monitoring of fossil fuel CO₂ and other trace gases, and its test against established conventional monitoring in Heidelberg (Felix Vogel, Jaroslav Jeschka, Bernd Kromer, Axel Steinhof, Samuel Hammer and Ingeborg Levin)
6. GREENHOUSE GAS, O\textsubscript{2}/N\textsubscript{2} AND AR/N\textsubscript{2} MEASUREMENT TECHNIQUES AND COMPARISONS

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FTIR Trace Gas Analyser trial at Cape Grim: comparison with Loflo, AGAGE and IRMS measurements of CO\textsubscript{2}, CH\textsubscript{4}, CO, N\textsubscript{2}O and \(\delta^{13}\)C in CO\textsubscript{2} (David Griffith, Nicholas Deutscher, Paul Krummel, Paul Fraser And Paul Steele)

Field testing of unattended cavity ring-down spectroscopy analyzers measuring carbon dioxide: long-term stability, water vapor effects, and uncertainty analysis (Scott J. Richardson, Natasha L. Miles, Kenneth J. Davis, Eric R. Crosson, Chris Rella, Aaron Van Pelt, Edward Wahl and Arlyn E. Andrews)

Recent developments in instrumentation for greenhouse gases and related tracer measurements (Aaron Van Pelt, Eric Crosson, Natasha Miles, Scott Richardson, Ken Davis, Christoph Thomas and Beverly Law)

Picarro G1301 vs. Licor NDIR and GC systems - first results from comparison running at Pallas GAW Station (J. Hatakka, T. Laurila and Y. Viisanen)

A high accuracy analyzer for airborne measurements of greenhouse gases (CO\textsubscript{2} and CH\textsubscript{4}) (Huilin Chen, Christoph Gerbig, Jan Winderlich and Annette Hoefer)

ICON – A new In-Situ capability for O\textsubscript{2}/N\textsubscript{2} measurements from airborne platforms (Julia Steinbach, Christoph Gerbig, Karl Kübler, Reimo Leppert, Frank Voigt and Bernd Schlöffel)

7. RELATED TRACER OBSERVATIONS AND ANALYSIS

Review of NOAA/GMD CO measurements: Methods and Reference Gases (P.C Novelli, A. Crotwell, K.A. Masarie, B.D. Hall and P.M. Lang)

Re-evaluation of NIES CO Scale using High Concentration Gravimetric CO Standard Gases (Keiichi Katsumata, Toshinobu Machida, Hiroshi Tanimoto, Hideki Nara and Hitoshi Mukai)

Practicality of Using a Dynamic Dilution System for the Calibration of Carbon Monoxide Observations at GAW Stations (Jörg Klausen, Christoph Zellweger and Brigitte Buchmann)

Atmospheric Molecular Hydrogen Measurements in the RAMCES Network (Camille Yver, Martina Schmidt, Michel Ramonet, Philippe Bousquet, Victor Kazan and Mathilde Grand)

Measurements of H\textsubscript{2} vertical profiles at Cabauw tall tower station (NL) (M. E. Popa, A. T. Vermeulen, W.C.M. van den Bulk, P.A.C. Jongejan, T. Röckmann and A. Batenburg)

\(^{14}\text{CO}_2\) measurements in the NOAA/ESRL Global Co-operative Sampling Network: An update on measurements and data quality (Scott Lehman, John Miller, Jocelyn Turnbull, John Southon, Pieter Tans and Colm Sweeney)
Participants attending the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, Jena, Germany, 7-10 September 2009
EXECUTIVE SUMMARY

Understanding the global carbon cycle and taking informed action to mitigate carbon emissions globally requires a well-established Integrated Global Carbon Observing System. Measurements of greenhouse gases come from flask samples taken at about 100 globally distributed surface-based (including ship sampling) sites, while aircraft and approximately 30 observatories make continuous measurements. The implementation of these atmospheric observations is coordinated by the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO). As part of this programme, WMO/GAW experts meet biennially with the International Atomic Energy Agency (IAEA) to review the scientific understanding of greenhouse gas sources and sinks, and to examine data quality objectives and measurement techniques.

The 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques took place from 7 to 10 September 2009 at the Max Planck Institute for Biogeochemistry in Jena, Germany. The meeting reviewed current WMO data quality objectives, covering such topics as carbon dioxide and other greenhouse gases, stable isotopes, radiocarbon in greenhouse gas measurements, calibration, quality control, data management and archiving. The experts also discussed new and emerging technologies, including measurements of greenhouse gases with high-precision spectroscopic methods.

The group made several recommendations on the WMO data quality objectives, as well as on the development of the GAW Programme infrastructure. These recommendations are summarized in the first part of the meeting report. In particular, the Expert group recommended establishing a WMO/GAW Central Calibration Laboratory (CCL) for hydrogen at the Max Planck Institute for Biogeochemistry and a CCL for SF₆ at NOAA/ESRL.

WMO has provided the umbrella for the meetings of experts on carbon dioxide since 1975. International Atomic Energy Agency (IAEA) joined WMO as a co-organizer in 1997 due to the increased use of carbon isotopes in studying the carbon cycle.
An Integrated Global Greenhouse Gas Observations and Analysis System: WMO/GAW

The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) was established in 1989. It has six themes and greenhouse gases are among them. GAW is a partnership of managers, scientists and technical expertise from 80 countries. The international greenhouse gas measurement community that met at this 15th meeting, co-sponsored by WMO and IAEA, is involved in nationally funded measurement programmes that constitute the global long-term greenhouse gas monitoring network supported by GAW partners. The first meeting of this group, held in 1975 at Scripps Institution of Oceanography, was co-sponsored by WMO.

An integrated global greenhouse gas observation and analysis system is required to differentiate between natural and anthropogenic source and sink changes, and to monitor the short- and long-term effects of climate policies at global and national scales. The GAW Programme for greenhouse gases (http://www.wmo.int/gaw) is the core of the GEO atmospheric carbon cycle observational framework. It is recognized by the Global Climate Observing System (GCOS) in its implementation plan to the United Nations Framework Convention on Climate Change (UNFCCC). It implements the recommendations of the Integrated Global Atmospheric Chemistry Observations strategy (IGACO) of the International Global Observing Strategy (IGOS), subsequently adopted by GEO. The WMO/GAW Programme offers a unique integrated approach to coordinating atmospheric carbon cycle observations and research. This is schematically represented in Figure 1.

Figure 1 - Greenhouse gas observations being implemented by WMO/GAW as an atmospheric component of IGACO

Elements of the GAW Programme for greenhouse gases are summarized in Figure 2. GAW coordinates the activities of the observational network via several mechanisms. To ensure the quality (and compatibility) of the measurements within the network, GAW solicits Central Calibration Laboratories (CCLs) that maintain primary standards for key greenhouse gases.
(including CO₂, CH₄ and N₂O). NOAA, which supports mentioned standards, participates in the key comparisons organized by the International Bureau of Weights and Measures (BIPM). CCL activities and gas standard issues are discussed by the expert group at regular Expert meetings, and the recommendations from the last meeting are presented in this report.

Another element of the GAW Quality Assurance framework is World and Regional Calibration Centers (WCC/RCC) maintained by WMO partners, which perform station audits, develop standard operating procedures and measurement guidelines. WCC/RCCs are the elements of the quality control that ensure proper scale propagation to in-situ measurements. Proper scale propagation is also ensured by network calibration centres supported by GAW partners. Data quality objectives defining the degree of compatibility of the measurements performed by different partners are regularly reviewed at the Expert meetings. Measurement data, after quality control, are submitted to, archived by, and disseminated by the WMO/GAW World Data Center for Greenhouse Gases (WDCGG). These data are used for global products and assessment preparation.

The atmospheric observational network, including surface and aircraft in situ sampling sites, is shown in Figure 3. It consists of discrete samples collected in flasks, continuous measurements at fixed stations, and observations from mobile platforms (ship and aircraft). It has not changed in spatial coverage recently compared to the large expansion seen in the 1980s and 1990s. However, it contains several new elements, in particular enhanced frequency and quality of the observations. Technological development (e.g., wide application of robust optical analyzers) provides a new challenge in accurate scale propagation. An increase in the number of tall towers equipped with continuous analyzers also contributes to the development of the observational network (e.g., measurements performed in the framework of CarboEurope and further ICOS projects). The development of precise and autonomous CO₂ measuring equipment has made this possible, along with outfitting several commercial airliners with in situ continuous analyzers, providing regular profiles and upper tropospheric transects from various locations.
Figure 3 - CO$_2$ observational network based on data submissions by September 2009 to the WMO/GAW World Data Centre for Greenhouse Gases. Only locations where measurements have continued for more than three years during 2005-2009 and where those data have been reported to the WDCGG are shown in the figure.

The need for satellite data validation and data representation on the WMO scale drove the development of a network of upward looking Fourier Transform Spectrometers (FTS) measuring total column CO$_2$ and CH$_4$. FTS is required as the surface-based in situ network that allows for the measurements of the column integral as measured e.g. by SCIAMACHY, GOSAT and the future OCO-2. The Total Carbon Column Observing Network (TCCON, www.tccon.caltech.edu) is a ground-based network of high resolution FTSs which record the near infrared solar absorption spectrum and retrieve column-average mixing ratios of CO$_2$, CH$_4$, N$_2$O and several other gases with high precision and accuracy. Total column measurements of CO$_2$ are tied to the WMO calibration scale through comparisons of FTS measurements with aircraft profiles measured over TCCON stations with in situ instruments themselves calibrated to the WMO World Reference Scale. In turn, TCCON measurements, once calibrated, serve to validate satellite measurements from GOSAT, SCIAMACHY and in the future OCO-2. TCCON was established in 2004 and joined GAW in 2009. A map of the sites is given in Figure 4.

Figure 4 - TCCON station locations, 2009
The WMO/GAW community with the support of the Secretariat in Geneva issues annually the WMO Greenhouse Gas Bulletin summarizing the state of atmospheric composition from observations up to December of the previous year, in time for the annual Convention of the Parties to the UNFCCC. The Bulletins highlight the global network and in each issue a particular observational or analysis product. These Bulletins can be found at the GAW website (www.wmo.int/gaw). Other products are available at various partnering sites, e.g., http://www.esrl.noaa.gov/gmd/dv/ and http://www.carbontracker.eu/.
EXPERT GROUP RECOMMENDATIONS

The scientists present at the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, 7-10 September 2009 in Jena, Germany, recommend the following procedures and actions, to achieve the adopted WMO goals for the GAW network compatibility among different laboratories and various components as summarised in Table 1. These goals are motivated from the perspective of the required data quality and compatibility for interpretation of global or continental scale atmospheric data, obtained from different laboratories, and e.g. jointly used in atmospheric transport model inversion studies. These compatibility goals should be reached in the respective specified mole fraction ranges observed in the global background troposphere (and where calibration scales are well defined by the WMO/GAW Central Calibration Laboratories).

It is noted that the previously used term "comparability" has been replaced by "compatibility" in agreement with definitions in the 3rd edition of the "International vocabulary of metrology – Basic and general concepts and associated terms (VIM) (JCGM 200, 2008, see reference list)."

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

Currently, some of the terms related to measurements as well as to Quality Assurance & Quality Control (QA/QC) in atmospheric science are used with different meanings and/or on the basis of different definitions. Since a closer link between GAW and BIPM (www.bipm.org) is now being established, as evidenced, for example, by the "WMO-BIPM Workshop on Measurement Challenges for Global Observation Systems for Climate Change Monitoring – Traceability, Stability and Uncertainty" in April 2010, the use of accepted terminology within GAW has become even more important. It is possible that a number of terms and ISO recommendations might not be familiar to the GAW community. Some terms might even require a revision of current usage within GAW.

Some special explanations might be helpful here in the context of the above-mentioned transition from "comparability" to "compatibility". "Comparability" means that results (of different labs) are comparable i.e. can be compared. In a metrological sense this simply means that results being on the same scale can be compared. By consistent use of the same scale for the same compound (in all steps such as measurements, determination of corrections etc), one will have comparability of results. "Compatibility" means that results are compatible, within a specified numerical value. Metrologically this means (an oversimplification): measured once, accepted everywhere (within a chosen value which is not the same as the total combined uncertainty). For instance, the total combined uncertainty in two labs might be ±0.1 permil (for example) and still results can be compatible within 0.01 permil.

Definitions of selected terms concerning recommended ISO terminology are given in Table 2. In particular, reference is made to the 3rd edition of the VIM, which has replaced the 2nd edition. The reader is also referred to the ISO publication "Guide to the Expression of Uncertainty in Measurement" (the abbreviation of this title is GUM, see reference list). For a glossary especially compiled for GAW purposes see http://gaw.empa.ch/glossary.html. More explanations, particularly with respect to the transition from VIM2 to VIM3, can be obtained from a presentation available via http://www.eqalm.org/Symposium09/Presentations/De%20Bievre.pdf. All GAW participants are strongly encouraged to take note of the ISO documents.
Table 1 - Recommended compatibility of measurements of components discussed

<table>
<thead>
<tr>
<th>Component</th>
<th>Compatibility goal</th>
<th>range in the unpolluted troposphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>± 0.1 ppm (± 0.05 ppm in the southern hemisphere)</td>
<td>360 … 420 ppm</td>
</tr>
<tr>
<td>d¹³C-CO₂</td>
<td>± 0.01 ‰</td>
<td>-7.5 … -9 ‰ vs. VPDB</td>
</tr>
<tr>
<td>d¹⁸O-CO₂</td>
<td>± 0.05 ‰</td>
<td>-2 … +2‰ vs. VPDB</td>
</tr>
<tr>
<td>D¹⁴C-CO₂</td>
<td>± 1 ‰</td>
<td>0 … 70‰</td>
</tr>
<tr>
<td>O₂/N₂</td>
<td>± 2 per meg</td>
<td>-250 … -550 per meg</td>
</tr>
<tr>
<td>CH₄</td>
<td>± 2 ppb</td>
<td>1700 … 2000 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>± 2 ppb</td>
<td>30 … 300 ppb</td>
</tr>
<tr>
<td>N₂O</td>
<td>± 0.1 ppb</td>
<td>320 … 335 ppb</td>
</tr>
<tr>
<td>H₂</td>
<td>± 2 ppb</td>
<td>450 … 600 ppb</td>
</tr>
<tr>
<td>SF₆</td>
<td>± 0.02 ppt</td>
<td>5 … 9 ppt</td>
</tr>
</tbody>
</table>

The numbers given in the Table 1 also reflect the currently achievable minimal measurement uncertainty (1 sigma) for individual analyses of most species, except for $^{14}$CO₂ or O₂/N₂ (this also concerns the currently achieved compatibility of measurements in different laboratories for these species). There is no international WMO/GAW CCL for O₂/N₂ measurements and international comparisons indicate that the consistency between any two laboratories is not better than ± 5 per meg. For $\Delta^{14}$CO₂ analyses there is only little experience available on the long-term compatibility of different laboratories, but for global as well as regional applications the reproducibility for individual measurements should be better than ±2‰.

Table 2 - Definitions of selected terms related to data quality (updated according to VIM3)

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>accuracy</td>
<td>closeness of agreement between a measured quantity value and a true quantity value of a measurand #1. A measurement is said to be more accurate when it offers a smaller measurement error.</td>
<td>VIM</td>
</tr>
<tr>
<td>Measurement trueness</td>
<td>closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value #2. Measurement trueness is not a quantity and thus cannot be expressed numerically, but measures for closeness of agreement are given in ISO 5725.</td>
<td>VIM</td>
</tr>
<tr>
<td>Measurand</td>
<td>quantity intended to be measured</td>
<td>VIM</td>
</tr>
<tr>
<td>measurement error</td>
<td>inverse to measurement trueness</td>
<td>VIM</td>
</tr>
</tbody>
</table>

#1 Measurement accuracy is sometimes understood as closeness of agreement between measured quantity values that are being attributed to the measurand.

#2 Measurement accuracy should not be used for ‘measurement trueness’ and vice versa.

#3 Measurement accuracy should not be used for ‘measurement trueness’ and measurement trueness should not be used for ‘measurement accuracy’.
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>metrological traceability</td>
<td>property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty</td>
<td>VIM</td>
</tr>
<tr>
<td>metrological comparability of measurement results</td>
<td>comparability of measurement results, for quantities of a given kind, that are metrologically traceable to the same reference.</td>
<td>VIM</td>
</tr>
<tr>
<td>metrological compatibility</td>
<td>property of a set of measurement results for a specified measurand, such that the absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference b) NOTE 1 Metrological compatibility of measurement results replaces the traditional concept of ‘staying within the error’, as it represents the criterion for deciding whether two measurement results refer to the same measurand or not. If in a set of measurements of a measurand, thought to be constant, a measurement result is not compatible with the others, either the measurement was not correct (e.g. its measurement uncertainty was assessed as being too small) or the measured quantity changed between measurements. NOTE 2 Correlation between the measurements influences metrological compatibility of measurement results. If the measurements are completely uncorrelated, the standard measurement uncertainty of their difference is equal to the root mean square sum of their standard measurement uncertainties, while it is lower for positive covariance or higher for negative covariance.</td>
<td>VIM</td>
</tr>
<tr>
<td>measurement bias</td>
<td>estimate of a systematic measurement error</td>
<td>VIM</td>
</tr>
<tr>
<td>measurement precision</td>
<td>closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions a) NOTE 1 Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement. NOTE 2 The ‘specified conditions’ can be, for example, repeatability conditions of measurement, intermediate precision conditions of measurement, or reproducibility conditions of measurement (see ISO 5725-3:1994). NOTE 3 Measurement precision is used to define measurement repeatability, intermediate measurement precision, and measurement reproducibility. NOTE 4 Sometimes “measurement precision” is erroneously used to mean measurement accuracy.</td>
<td>VIM</td>
</tr>
<tr>
<td>measurement repeatability</td>
<td>measurement precision under a set of repeatability conditions of measurement c)</td>
<td>VIM</td>
</tr>
<tr>
<td>Measurement reproducibility</td>
<td>measurement precision under reproducibility conditions of measurement d) NOTE Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994.</td>
<td>VIM</td>
</tr>
<tr>
<td>measurement uncertainty</td>
<td>non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used NOTE 1 Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated. NOTE 2 The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a specified multiple of</td>
<td>VIM</td>
</tr>
</tbody>
</table>
### Measurement Uncertainty

**NOTE 3** Measurement uncertainty comprises, in general, many components. Some of these may be evaluated by **Type A evaluation of measurement uncertainty** from the statistical distribution of the quantity values from series of measurements and can be characterized by standard deviations. The other components, which may be evaluated by **Type B evaluation of measurement uncertainty**, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.  

**NOTE 4** In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quantity value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard measurement uncertainty</td>
<td>measurement uncertainty expressed as a standard deviation</td>
<td>VIM</td>
</tr>
<tr>
<td>coverage factor</td>
<td>number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty</td>
<td>VIM</td>
</tr>
<tr>
<td>measurement error</td>
<td>measured quantity value minus a reference quantity value</td>
<td>VIM</td>
</tr>
<tr>
<td>systematic measurement error</td>
<td>component of measurement error that in replicate measurements remains constant or varies in a predictable manner</td>
<td>VIM</td>
</tr>
</tbody>
</table>

**a)** Note that accuracy, trueness and precision are qualitative concepts and should be avoided in quantitative expressions.

**b)** 1. For example, difference in a comparison of measurements of a species in a discrete sample with the hourly average for the same hour in which the discrete sample was collected.

2. In the case of significantly different variances of the two sample sets, the difference of the mean may not be meaningful. The Wilcoxon-Mann-Whitney test can be used to test for statistical significance.

**c)** Repeatability and reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results. In practice quantitative expressions of repeatability or reproducibility often refer to a dispersion of ± 1 standard deviation.

**d)** The concept of “uncertainty” is explained in detail in the GUM (see reference list).
The following definitions and units are used throughout this document:

Mole fractions of substances in dry air:

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

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

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

Isotope or molecular ratios:

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

\[
\delta = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \text{ with } R = \frac{[\text{heavy isotope}]}{[\text{light isotope}]}.
\]

\(\delta\)-values are communicated in multiples of 1000 (‰; per mill ‘units’).

The international reference for \(\delta^{13}\text{C}\) is VPDB. For \(\delta^{18}\text{O}\), multiple references are in use (VPDB, VSMOW, air-\text{O}_2).

The delta notation is also used to express relative abundance variations of \(\text{O}_2/\text{N}_2\) (and \(\text{Ar}/\text{N}_2\)) ratios in air:

\[
\delta_{\text{O}_2/\text{N}_2} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \text{ with } R = \frac{\text{O}_2}{\text{N}_2} \text{ (see also Section 5)}
\]

The respective international air standard is not established, yet. The Scripps Institution of Oceanography (SIO) local \(\text{O}_2/\text{N}_2\) scale, based on a set of cylinders filled at the Scripps Pier is the most widely used scale.

\(\delta_{\text{O}_2/\text{N}_2}\) values are expressed in multiples of \(10^6\) or per meg ‘units’.

1. CALIBRATION OF GAW MEASUREMENTS – WMO/GAW CENTRAL CALIBRATION LABORATORIES

1.1 Background

Round-robin comparisons of laboratory standards and comparisons of field measurements and samples over the last decades have regularly shown differences in trace gas measurements larger than the target compatibility for merging data from different field sites (see Table 1). These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements. The WMO/GAW Central Calibration Laboratories (CCL) for important greenhouse and trace gases therefore remain one of the fundamental components of the WMO/GAW network (WMO GAW Strategic Plan, WMO/GAW Report No. 172, 2007) to achieve and maintain compatibility of global observations from different laboratories.

WMO/GAW CCLs currently exist for the following trace gases: carbon dioxide (CO\(_2\), at NOAA/ESRL), methane (CH\(_4\), at NOAA/ESRL), nitrous oxide (N\(_2\)O, at NOAA/ESRL), carbon monoxide (CO, at NOAA/ESRL), and stable isotopes in CO\(_2\) (only for CO\(_2\)-in-air measurements, at Max-Planck Institute for Biogeochemistry (MPI-BGC)). At the 15\(^{th}\) WMO Experts Meeting in Jena, Germany, the Max-Planck Institute for Biogeochemistry (MPI-BGC, Jena, Germany) has been asked and agreed to act as the WMO/GAW CCL for molecular hydrogen (H\(_2\)) measurements. NOAA/ESRL has been asked and agreed to act as the WMO/GAW CCL for sulphur hexafluoride (SF\(_6\)).
In this section, the general requirements for WMO/GAW CCLs and general issues to maintain calibration of observations by GAW laboratories are discussed. Additional trace gas-specific needs are dealt with separately in subsequent sections.

1.2 General requirements for Central Calibration Laboratories

a) For gas species and isotopic ratios, the CCL maintains the WMO Mole Fraction Scale for the respective species in air by carrying out regular determinations of this primary scale with primary methods linking it to fundamental quantities (SI). The scale is embodied in an adequate set of gas mixtures-in-air in large high-pressure cylinders (called “WMO Primary Standards”).

b) The CCL carries out comparisons with independent primary scales, established either through gravimetric, manometric, or other means. For the stable isotope scale of CO$_2$ in air, the CCL establishes the link to the respective international stable isotope scales (e.g. VPDB for $\delta^{13}$C).

c) While the WMO scale for each trace gas is defined and maintained by an operational, designated CCL, WMO and IAEA recommend that all monitoring systems 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 prerequisite for a comprehensive, homogeneous monitoring system in the future.

d) The WMO/GAW and IAEA Expert committees undertake the responsibility for the evaluation of the effectiveness of such measures and for recommending modifications to existing protocols.

e) 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 X2007, and the appropriate version number should be included in each standard calibration report. The CCL archives all earlier versions of the WMO scale.

f) 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, and the mixing ratio and isotopic range of CO$_2$ in standards used for this calibration transfer procedure.

g) The CCL provides calibrated reference gas mixtures (gas mixtures-in-air, called “transfer standards”) at the lowest possible cost.

h) In view of different specific sensitivities of various instrumentation to the isotopic composition of the analytes, the isotopic composition of CO$_2$ in transfer standards should be close to atmospheric levels. If the preparation of the standard gas involves the addition of CO$_2$ the CCL provides information on the isotopic composition of this added CO$_2$ and the approximate fraction of this admixture to the total CO$_2$ in air.

i) The CCL provides for a backup in case a catastrophic event occurs.

j) The CCL, or a designated WMO/GAW World Calibration Centre, 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. 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, comparisons of reference gases by themselves are not sufficient to ensure that atmospheric measurements are compatible to the degree that is required (see Section 11).

k) In order to maximize the usefulness of round-robin results, circulation of cylinders is discontinued after two years at latest, and results are evaluated even if not all labs were able to yet analyse the tanks. A new round-robin will then be started with the labs that had not been included before to be first in line. Tracking tank circulation and data submission will
be more rigorous than in earlier round-robin studies, with the status of tank circulation and data submission being posted online on a Web Page to be installed and maintained by ESRL. Analysis of CO₂ mole fractions has the highest priority in the round-robin studies, but laboratories are encouraged to measure multiple species if time (all analyses must be finished in 4 weeks) and air consumption allow for.

1.3 Maintenance of calibration by GAW measurement laboratories

a) All laboratories that participate in the GAW Programme must calibrate and report measurements relative to a single carefully maintained scale, the WMO Mole Fraction Scale for gas mole fractions in dry air, including its version number. Each GAW measurement laboratory must actively maintain direct traceability to the WMO Scales. This may be maintained by a network calibration centre of GAW partners. This facility must have in-house (secondary) standards regularly re-calibrated by the CCL. Its calibration strategy should avoid additional standard levels in the calibration hierarchy and try to keep the secondary standards for many years so that a calibration history can be built for each of them.

b) It is recommended that each WMO/GAW measurement laboratory or network calibration centre maintains a strictly hierarchical scheme of transferring the calibration of its in-house secondary standards to working standards, and from working standards to atmospheric measurements. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retro-active changes) in the assigned values of higher-level standards all the way to measured values for atmospheric air.

c) In order 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.

d) Because of ongoing improvements in measurement technology it is possible that individual laboratories or groups of laboratories may be able to maintain excellent precision in scale propagation from their laboratory standards to lower level standards, which could be beyond the precision with which laboratory standards can be tied to the WMO scale. Internal scales of this sort must also remain tied to the WMO scale to the extent possible.

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

f) We recommend the use of natural air and that, when trace gases, in particular CO₂, are adjusted in reference air mixtures, the isotopic composition of the cylinder trace gas remains close to that in air to minimize the influence of isotopic composition on calibrations. We recommend further a very thorough process of elimination of leaks, minimization of thermal gradients, and horizontal storage of cylinders in order to minimize the risk of fractionation between the gas components in the cylinder.

g) Acknowledging that greenhouse gas measurements will come under greater scrutiny in coming years and that remote sensing techniques are emerging for measuring greenhouse gases, WMO/GAW CCLs should ensure that calibration scales are and remain traceable to SI units. Working closely with metrology institutes and the BIPM can help ensure such traceability.

h) Engaging the remote sensing community in calibration (and validation) with ground-based measurements is essential for ensuring that this type of data can be used in high resolution analyses without introducing spatial and temporal biases. Such engagement should not be limited to the CCLs alone, as individual scientists or research groups making vertical profiles can contribute significantly to this effort.

2. SPECIFIC REQUIREMENTS FOR CO₂ CALIBRATION

2.1 Background

The general goals for compatibility of measurements of CO₂ in air are stated above in Table 1. The target of 0.1 ppm for the Northern and 0.05 ppm for the Southern Hemisphere is intended to address small, globally significant gradients over large spatial scales (for example Southern Ocean
fluxes). However, also over continental and even densely inhabited and semi-polluted regions such as Europe spatial gradients of free tropospheric (non-boundary layer) CO$_2$ mole fractions may be small so that also for regional networks the compatibility goal for the Northern Hemisphere is still considered to be adequate.

2.2 Current CO$_2$ calibration and comparison activities

The primary scale for CO$_2$ ranges from approximately 70 µmol/mol (covering atmospheric values in ice cores) to 3000 µmol/mol (covering dissolved CO$_2$ in the oceans). The scale is currently embodied in a set of 15 CO$_2$-in-air mixtures in large high-pressure cylinders covering the ambient range 250-520 ppm, and in another 20 cylinders providing both a backup and a larger range.

2.3 Recommendations for CO$_2$ calibration and comparison activities

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

b) The CO$_2$ isotopic composition of distributed reference standards should be kept in the range of ambient atmospheric CO$_2$ to avoid isotopic measurement bias during instrument calibration, with spiking gases as close as possible to ambient CO$_2$. The isotopic composition of distributed standard gases should be roughly determined by the CCL.

c) The CCL is encouraged to make available on its website the calibration results of all GAW laboratory standards based on previous versions of the scale as well as those based on the current scale.

d) In order to make possible a level of consistency of ±0.03 ppm or less among the CO$_2$ calibration scales of laboratories participating in the WMO/GAW Programme, the CCL shall aim to provide the calibrated standards for transfer of the CO$_2$ scale to secondary and tertiary standards at that level of consistency.

e) Each WMO/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 in-house standards for CO$_2$ (covering the measurement range) re-calibrated by the CCL every three years.

3. SPECIFIC REQUIREMENTS FOR CO$_2$ STABLE ISOTOPE CALIBRATION

The general goals for compatibility of stable isotope measurements of CO$_2$ in air are stated above in Table 1. The $\delta^{13}$C target of 0.01 per mill is intended to address small, globally significant gradients over large spatial scales (for example Southern Ocean isotopic disequilibrium fluxes). For ecological or biogeochemical studies of predominantly local or regional significance, a reduced $\delta^{13}$C compatibility goal of 0.05 per mill is considered to be adequate.

3.1 Background

During the two years since the 2007 WMO CO$_2$ Experts Meeting considerable progress concerning the stable isotope calibration of CO$_2$ in air measurements have been made. The introduction of the Jena Reference Air Set (JRAS) - an effort to bring about a unifying scale anchor for $\delta^{13}$C and $\delta^{18}$O measurements of CO$_2$ in air, has reiterated the need for a consistent use of the $^{17}$O correction. JRAS also highlighted uncertainties in the anchoring of local scales to VPDB and gave indications of instrument specific scale contraction issues. This along with results from ongoing inter-laboratory comparison programmes has led to an extension of the role of the Central Calibration Laboratory for stable isotopes of CO$_2$ in air. Starting 2010, MPI-BGC in Jena will, in addition to the JRAS gases also provide calibrated high-pressure air tanks to allow for a common calibration of the CO$_2$ in air scale at atmospheric isotope composition.
3.2 Current CO₂ stable isotope calibration and comparison activities
The major difficulties in bringing stable isotope ratio results closer together have been identified. These are:

a) Scale contraction (‘η’-effect) during mass spectrometric measurements; this affects mostly δ¹³C measurements, arising from the fact that the scale origin (defined by NBS 19) is 10 ‰ away from air isotope values.

b) The ‘η’-effect is not a major problem for δ¹⁸O. Here, exchange with water during sample storage and inconsistent scales between laboratories seem to be the main culprits.

c) Further inconsistencies between laboratories arise from different algorithms and/or parameterizations of the necessary corrections for δ¹⁷O and N₂O.

d) Failure to report assignment uncertainties in the isotopic composition of gas used as a reference.

These problems have now been fully recognized and documented. It is agreed that progress in this area requires the availability of whole-air standards firmly anchored on VPDB-CO₂ scale by the Central Calibration Laboratory. The CCL should make these gases available in glass flasks as well as in high-pressure cylinders, as distribution of calibrated pure CO₂ alone will not be able to resolve the issues. Investigations addressing effects of memory or cross contamination locally may prove more efficient when aspects of sample extraction and mass spectrometric measurement can be studied separately. For a reliable compatibility assessment between laboratories, generation and maintenance of the full traceability chain to the primary (VPDB) scale is necessary and should be provided in the future. Progress in this area can be measured as implemented in the form of the various inter-laboratory comparison programmes.

3.3 Central Calibration Laboratory for stable isotopes of CO₂ in air
MPI-BGC has agreed to continue the role of a CCL for stable isotopes of CO₂ in air. In addition to supplying the community with JRAS gases, the MPI-BGC is asked to provide calibrated high-pressure cylinders filled with either Northern Hemisphere clean air (from Northern Germany) or Southern Hemisphere air (from Australia). These cylinders are intended to provide a working standard (or surveillance gas) in the local laboratories.

Support from participating laboratories to provide a limited number of cylinders containing clean air will be sought (preferably marine Southern Hemisphere air (δ¹³C ≈ -8 ‰)). These will serve as a suite of quasi-primaries in the CCL, calibrated by the MPI-BGC at air-isotope values and marking the ambient atmosphere range independent of availability of other, solid reference materials and associated procedures.

3.4 Recommendations for CO₂ stable isotope calibration and comparison activities

a) ¹⁷O-correction: For removing the ¹²C¹⁶O¹⁷O contribution from the mass spectrometrically measured ¹⁸O results, use of the ratio assumption set provided by Assonov and Brenninkmeijer (2003a, b), as recommended by the 13th and 14th WMO experts meetings is reiterated. Further, to ensure that the effect of the ¹⁷O-correction is kept at a minimum, the use of air references is recommended and the use of reference materials with a large deviation in δ¹⁸O (e.g. NBS 18) should be avoided. In order to provide a consistent link to the VPDB–CO₂ scale (as defined through NBS 19-CO₂) the CCL is advised to apply corrections based on the Assonov-Brenninkmeijer ratio assumption set exclusively. The CCL is asked to assist in linking present day measurements to historical data records, which have been using other corrections to remove the ¹²C¹⁶O¹⁷O isobaric interference.

b) N₂O-correction: The N₂O correction has been the subject of several publications, which through different experimental approaches lead to a common size for the correction. The CCL is asked to implement the required correction and verify its validity over time. With the provision of reference air, ambiguities in the N₂O correction of different laboratories will be extremely small and should not interfere with the quantitative results. As a control measure,
the CCL is asked to provide air with varying N₂O concentration occasionally (also without N₂O) to the participating laboratories and report the results on its web site.

c) **JRAS:** For improving data compatibility at air isotopic composition the Jena Reference Air Set (JRAS) will be expanded to include a reference point at atmospheric CO₂ levels (δ¹³C = -8 ‰). In lieu of a calcite with suitable isotope composition, clean air will be used for this purpose. This will be decanted from Southern Hemisphere air in a high-pressure cylinder (courtesy of CSIRO, Australia). With a single 50-L cylinder filled up to 200 bar, more than 1000 reference flasks can be provided, thus making sure that the distributed air originates from the same source for the foreseeable future. Standardized procedures to use JRAS locally as a scale anchor will be circulated before the next meeting. Initially it is recommended that JRAS be used as a second anchor in parallel to the existing local scale anchor with the intention to switch to the common scale anchor, once a sufficient overlap has been established.

d) **Inter-Laboratory Comparisons:** All laboratories are encouraged to continue their participation in the existing inter-laboratory comparison activities. These are required to monitor remaining scale differences so that possible discrepancies can be addressed as they arise. A comprehensive comparison activity should include all forms of samples, i.e. flasks as well as low- and high-pressure cylinders and very homogeneous pure CO₂ ampoules. Reported values must be accompanied by estimates of uncertainties, including a description of their derivation in accompanying metadata.

e) **Instrument-specific scale contraction:** Further investigation of the indications of instrument-specific influences on scale contraction is needed. Specifically it should be investigated whether there is a scale contraction effect, which might be common or typical for certain instrument brands or batches of them. Analytical protocols to either eliminate or to quantify the scale contraction effect and monitor its magnitude over time should be developed locally. This information should be provided together with communicated data.

f) **Selection of laboratory working gases.** During Isotope Ratio Mass Spectrometer (IRMS) measurements scale contraction and memory effects critically depend on the reference gases in use. More specifically, the results are affected by the isotopic distance between these gases. To minimize such effects, the isotopic composition of the working reference gases should be as close as possible to that of CO₂ in ambient air.

4. **SPECIFIC REQUIREMENTS FOR RADIOCARBON IN CO₂ CALIBRATION**

4.1 **Background**

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

For atmospheric measurements of Δ¹⁴C in CO₂, two main sampling techniques are used: High-volume CO₂ absorption in basic solution or by molecular sieve and whole-air flask sampling (typically 1.5-5 L flasks). Two methods of analysis are used: conventional radioactive counting and Accelerator Mass Spectrometry (AMS). The current level of measurement uncertainty for Δ¹⁴C in CO₂ is 2-5‰, with a few laboratories at slightly better than 2‰ uncertainty. As atmospheric gradients in background air are currently very small, a target level of 1‰ for compatibility of measurements from different laboratories is recommended (Table 1).

4.2 **Current ¹⁴CO₂ calibration and comparison activities**

The first comparison activity for Δ¹⁴C in CO₂ was initiated at the 13th WMO/IAEA Meeting of CO₂ Experts in Boulder Colorado (WMO/GAW Report No. 168, 2006). Preliminary results were reported (see Miller et al., this volume). Six laboratories participated by sending flasks to NOAA/ESRL/GMD to be filled with air from two whole-air reference cylinders for CO₂ extraction, target preparation and ¹⁴C AMS analysis.
Calibration and comparison with whole-air standards is difficult in the case of large-volume sampling and conventional counting techniques as sample volume is generally larger than 20 cubic meters of air. Therefore, these techniques will generally rely on the Standard Reference Materials distributed by IAEA. However, in one particular case it was possible to perform an ongoing comparison over more than two years by AMS and conventional measurements that yielded very promising results (see Vogel et al., this volume).

4.3 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 that is similar to the air samples measured and, potentially, as a secondary standard.

b) We recommend a workshop to discuss the use of whole-air cylinders as reference material for $\Delta^{14}$C in CO$_2$.

c) We recommend continuation of the whole-air comparison at a frequency of once per year or more.

d) As the current comparison excludes the laboratories using high-volume sampling techniques, we propose the following potential methods for future comparison that could include laboratories using either type of sampling technique: (1) Splitting and dissemination of high-volume pure CO$_2$ samples to the laboratories, (2) Co-located sampling at observation stations.

5. SPECIFIC REQUIREMENTS FOR O$_2$/N$_2$ CALIBRATION

5.1 Background

Measurements of the changes in atmospheric O$_2$/N$_2$ ratio are useful for constraining sources and sinks of CO$_2$ and testing land and ocean biogeochemical models. The relative variations in O$_2$/N$_2$ ratio are very small but can now be observed by at least six analytical techniques. These techniques can be grouped into two categories: (1) those which measure O$_2$/N$_2$ ratios directly (mass spectrometry and gas chromatography), and those which effectively measure the O$_2$ mole fraction in dry air (interferometric, paramagnetic, fuel cell, vacuum ultraviolet photometric). A convention has emerged to convert the raw measurement signals, regardless of technique, into equivalent changes in mole ratio of O$_2$ to N$_2$. For mole-fraction type measurements, this requires accounting for dilution due to variations in CO$_2$ and possibly other gases. If synthetic air is used as a reference material, corrections may also be needed for differences in Ar/N$_2$ ratio. By convention, O$_2$/N$_2$ ratios are expressed as relative deviations compared to a reference

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

where $\delta$($O_2/N_2$) is multiplied by 10$^6$ and expressed in “per meg” units. Per meg is a dimensionless unit equivalent to 1 per meg = 0.001 per mille. The O$_2$/N$_2$ reference is typically tied to natural air delivered from high-pressure gas cylinders. As there is no common source of reference material, each laboratory has employed its own reference, and hence it has not been straightforward to report measurements on a common scale.

The practice of basing O$_2$/N$_2$ measurements on natural air stored in high-pressure cylinders appears acceptable for measuring changes in background air, provided the cylinders are handled according to certain best practices, including orienting cylinders horizontally to minimize thermal and gravitational fractionation. Nevertheless, improved understanding of the source of variability of measured O$_2$/N$_2$ ratios delivered from high-pressure cylinders is an important need of the community. An independent need is the development of absolute standards for O$_2$/N$_2$ calibration scales to the level of 5 per meg or better.

The appropriateness of using the “per meg” unit to describe 10$^{-6}$ changes in relative ratios has recently been questioned by terminology experts of the International Union of Pure and Applied Chemistry (IUPAC) who recommend instead using the term “part per million” (ppm).
Unfortunately, the IUPAC recommendation is not acceptable to our community as long as the “ppm” is used to describe simple mole fractions, a practice which is too deeply engrained in the language of our community, and indeed the wider public, to be easily changed. Expressing observed $\text{O}_2$ changes in mole fractions would cause widespread confusion and interpretation difficulties, because the $\text{O}_2$ mole fraction can be significantly influenced by changes in other species. For example, a 1 ppm increase in $\text{CO}_2$ in an air parcel (with no other changes) would, simply by dilution, decrease the $\text{O}_2$ mole fraction by $\sim 0.21$ ppm, and could be erroneously interpreted as an $\text{O}_2$ flux change. The same dilution process also occurs for every other species, but is negligible in almost all applications. For example, a 1 ppm increase in $\text{CH}_4$ in an air parcel would dilute the $\text{CO}_2$ mole fraction by $\sim 0.0004$ ppm. Thus, expressing atmospheric $\text{O}_2$ changes as $\text{O}_2/\text{N}_2$ ratios was explicitly established because of the unique situation of needing to quantify changes for a gas species which is not a trace gas.

The relationship between changes in $\text{O}_2/\text{N}_2$ ratio and equivalent changes in $\text{O}_2$ mole fraction has been discussed in peer-reviewed literature. However, confusion does still exist. Adding 1 µmol of $\text{O}_2$ per mole of dry air increases the $\text{O}_2/\text{N}_2$ 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 $\text{O}_2$ 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/mol of dry air increases the mole fraction by almost exactly 1 ppm. The factor 4.77 per meg per ppm relates the change in $\text{O}_2/\text{N}_2$ ratio to the equivalent change in a trace gas, and is thus the relevant factor for most applications, e.g. calculating changes in $\text{O}_2/\text{N}_2$ ratios in an air parcel resulting from $\text{O}_2$ fluxes. The alternate factor of $4.77/0.79 = 6.04$ per meg per ppm can also be relevant in certain applications, however, such as for calculating instrument response functions (Kozlova et al., 2008, p. 4).

5.2 Current $\text{O}_2/\text{N}_2$ calibration and comparison activities

At the 12th WMO CO$_2$ Experts Meeting in Toronto (WMO/GAW Report No. 161, 2005) the Global Oxygen Laboratories Link Ultra-precise Measurements (GOLLUM) programme was initiated to provide constraints on the offsets between the different laboratory scales and to clarify the requirements for placing measurements on a common scale. There are two components to this programme, each of which has been running since 2005: a “sausage flasks” comparison programme, and a “round-robin cylinder” comparison programme. The sausage flask programme compares the laboratories’ ability to extract and analyse air from a small flask sample, whereas the round-robin cylinder programme compares the laboratories’ calibration scales, and their methods for extracting and analysing air from high-pressure gas cylinders.

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

At the time of the 15th WMO Experts meeting, three circuits of the two sets of round-robin cylinders were completed and four sets of sausage flasks had been distributed. The repeated analyses at SIO, two years after their initial measurement, showed the change in the cylinders was zero to within ±3 per meg, the estimated precision of a trend measurement in the SIO lab. All results are shown in detail on the web site. Data are shown on the web page within 1 week of being received; however, as is often the case with comparison programmes, some participants are not providing their data in a timely fashion.

In addition to preparing cylinders for the GOLLUM programme, the Keeling lab at SIO has been preparing high-pressure cylinders for a number of laboratories. These cylinders have provided another means to assess laboratory scale differences and may assist in developing a common scale.
5.3 Recommendations for O$_2$/N$_2$ calibration and comparison activities

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

b) Expand the round-robin cylinder programme to include:
   - an additional suite of circulating cylinders equipped with “dip-tubes” to minimize influence of thermal fractionation.
   - an additional suite of circulating cylinders that incorporate those field stations making in situ measurements of atmospheric O$_2$ and which are not presently included in any O$_2$ comparison programme.

c) Sustain the web page for logistical support and for rapid dissemination of results of the GOLLUM programme. Expand the web page by adding results of the sausage flask programme, and including pressure histories of the round-robin cylinders.

d) Encourage the timely delivery of comparison results by all participants.

e) Encourage SIO to continue to provide reference gases to laboratories on request at reasonable cost.

f) Encourage additional efforts, such as overlapping flask sampling from different programmes, to compare O$_2$/N$_2$ scales and methods between programmes.

g) Encourage the standardisation of existing O$_2$/N$_2$ techniques, and particularly to identify and correct weaknesses in laboratories’ current techniques in sample collection, sample analysis, and in defining and propagating calibration scales.

h) It is recommended that an effort be undertaken to produce gravimetric standards for O$_2$/N$_2$ to solidify the long-term calibration of O$_2$/N$_2$ measurements.

i) Continue using the per meg unit to report O$_2$/N$_2$ ratios.

6. SPECIFIC REQUIREMENTS FOR CH$_4$ CALIBRATION

6.1 Background
At the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques it was agreed that NOAA/ESRL would assume the role of the WMO/GAW Central Calibration Laboratory (CCL) for methane.

6.2 Current CH$_4$ calibration and comparison activities
The NOAA04 scale was designated as the official calibration scale consisting of 16 gravimetrically prepared primary standards which cover the nominal range of 300 to 2600 nmol/mol, so it is suitable to calibrate standards for measurements of air extracted from ice cores and contemporary measurements from GAW sites. This new scale results in CH$_4$ mole fractions that are a factor of 1.0124 greater than the previous scale (now designated CMDL83) (Dlugokencky et al., 2005). The range of secondary transfer standards is the same as the range of the WMO Primary Standards.

6.3 Recommendations for CH$_4$ calibration and comparison activities

a) The CCL will transfer the CH$_4$ scale to calibrated CH$_4$-in-air standards with an uncertainty of $<1$ nmol/mol.

b) All laboratories that participate in the GAW Programme must calibrate measurements relative to the WMO CH$_4$-in-air mole fraction scale and report them to the WMO/GAW World Data Centre for Greenhouse Gases in Japan.

c) Each GAW measurement laboratory or network calibration centre of GAW partners must actively maintain its link to the WMO Scale by having its in-house secondary standards for CH$_4$ re-calibrated by the CCL every six years.

d) CH$_4$ isotope calibration: The need for a standardized calibration of methane in air is also being recognized. A group will be formed to investigate strategies for providing a calibration of isotopes of methane in air ($^{13}$C and $^2$H) to the accepted IAEA scales (V-PDB and V-SMOW), and also for preparing and providing secondary standards of CH$_4$-in-air to be distributed to interested labs for comparisons.
7. SPECIFIC REQUIREMENTS FOR N₂O CALIBRATION

7.1 Background

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

7.2 Current N₂O calibration and comparison activities

NOAA/ESRL/GMD maintains a gravimetrically-prepared N₂O-in-air standard scale consisting of 13 WMO Primary Standards covering the range of 260 – 370 nmol/mol (Hall et al., 2007). The reproducibility of NOAA N₂O calibrations (2 sigma) is estimated to be 0.16 nmol/mol at the 95% confidence level (k=2).

7.3 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 its laboratory standards for N₂O re-calibrated by the CCL every three years.

b) We encourage the development of new or improved techniques that would lead to improvements in precision and reproducibility, including the amount of calibration gases required. Experience with new techniques should be shared with the community through newly formed web-based discussion groups.

c) The CCL and the WCC should work together to establish more frequent comparisons among GAW stations and other key laboratories that measure N₂O. Given the difficulties involved in N₂O measurement, the frequency of current round-robin activities is insufficient for quality control purposes.

8. SPECIFIC REQUIREMENTS FOR SF₆ CALIBRATION

8.1 Background

Sulfurhexafluoride (SF₆) is a long-lived trace gas with strong infrared absorbance properties. Emissions of SF₆ are 23900 times more effective than CO₂ on a per-mass basis over a 100-year time scale. The tropospheric mixing ratio of SF₆ has increased steadily, with a growth rate of 0.2-0.3 ppt yr⁻¹. The steady growth rate and long lifetime (~3200 years) make it a useful tracer of atmospheric transport, including stratospheric "age-of-air determination". Because SF₆ is almost entirely anthropogenic in origin, used primarily in electrical power distribution, it is a potentially powerful tracer of anthropogenic activity on global and regional scales.

SF₆ is typically measured using GC-ECD techniques in a manner similar to that of N₂O. There are currently three scales in use: NOAA, Univ. of Heidelberg, and SIO. Although there have been few formal SF₆ comparisons, informal comparisons show that scale compatibility is generally good (see e.g. www.cucumbers.uea.ac.uk). However, to be optimally useful as a tracer of atmospheric transport, consistency of scale must be exceptionally good (on the order of 0.02 ppt). In this regard, a commonly accepted scale does not exist.

At the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, NOAA/ESRL has agreed to serve as the WMO/GAW Central Calibration Laboratory (CCL) for atmospheric sulphur hexafluoride. NOAA/ESRL currently maintains a gravimetrically-prepared SF₆-in-air standard scale consisting of
16 standards covering the range of 1 – 10 pmol/mol. Recent improvements in SF₆ analysis have been made, such that 0.02 ppt reproducibility (1 sigma) of SF₆ calibrations is now achievable.

8.2 Recommendations for SF₆ calibration and comparison activities

a) Include SF₆ in WMO/GAW round-robin experiments when possible.

b) Investigations are encouraged to explore advanced techniques to improve measurement precision.

c) Investigators with NOAA-assigned SF₆ values dating prior to 2007 are encouraged to have their cylinders re-calibrated by NOAA/ESRL.

9. SPECIFIC REQUIREMENTS FOR CO CALIBRATION

9.1 Background

CO is an important component in tropospheric chemistry due to its high reactivity with OH. It is the major chemically active trace gas resulting from biomass burning and fossil fuel combustion, and a precursor gas of tropospheric ozone. Most atmospheric measurements are based on collected air samples or in-situ analysis, although systematic measurements from satellites, aircraft and surface-based FTIRs are improving (WMO GAW/ACCENT Workshop, 2005). Differences among reference scales and drift of standards have been a serious problem for these in-situ CO measurements in the past. Spectroscopic retrieval of CO principally provides column abundances; wide geographical coverage of CO with some limited vertical resolution is becoming available from ground-based remote sensing as well as several satellite-based sensors (MOPITT-TERRA, SCIAMACHY-ENVISAT, TESS-AURA, AIRS-AQUA, GOSAT). The TCCON network of ground-based remote-sensing instruments provides both total column as well as vertically resolved information. The present recommendations will, however, pertain to the calibration of in-situ observation only; the validation of remote sensing data is a complicated separate issue not treated here.

9.2 Current CO calibration and comparison activities

Experience has shown that the accurate calibration of in-situ CO measurements is far from trivial. Mole fractions between 40 and 250 nmol/mol (and higher) should be determined with an expanded uncertainty of ±2 nmol/mol (k=2). The NOAA scale currently covers a range up to 500 nmol/mol and the CCL is gradually expanding the range up to 1000 nmol/mol with an estimated uncertainty of about 0.8% at those levels. Unlike CO₂, for CO there is a low degree of standardization in analytical techniques deployed (WMO/GAW Report No. 168 (2006)). Specific calibration problems for CO are: (1) Some of the more traditional measurement techniques are non-linear and do not have the stability or precision for long-term measurements with low drift rates. (2) Gravimetric mixtures must be diluted to environmental levels, and at these levels CO mixing ratios in high-pressure cylinders may not be stable over time periods of several years. (3) The preparation of a gravimetric standard does not a priori guarantee that the actual CO mole fraction corresponds to the assumed one. Careful maintenance of the gravimetric scale and/or comparison with diluted gases from high-concentration cylinders (10 ppm) is regularly required.

NOAA ESRL’s Carbon Cycle Greenhouse Gases Group has on two occasions’ organized round-robin tests involving 10 to 15 laboratories. This has helped “the international in situ CO measurement community” enormously, but also exposed some drift and inconsistency in the NOAA/ESRL calibration scale, as well as in the gravimetric technique. New analytical techniques have helped to eliminate most of these issues during the past years.

WMO through EMPA and its WMO/GAW WCC for CO has endeavoured to improve the international compatibility by implementing an audit system for CO measurements at Global GAW stations. Combining all experience gained so far, it is realistic to expect CO data to be expressed on one single scale that is traceable to a single source. For establishing global trends, and to get a sufficiently accurate estimate of the tropospheric burden, it seems that 1% expanded uncertainty (k=2) is now becoming both analytically attainable and scientifically sufficient.
9.3 Recommendations for CO calibration at the WMO/GAW CCL and at GAW stations

a) Compatibility of measurements at Global GAW stations of ±2 ppb (mean bias) and of standards with ±1 ppb or 0.5% repeatability (whichever is greater, expanded uncertainty, k=2) are needed. Comparisons of CO measurements among laboratories (through round-robbins and other comparison sample exchanges) have documented differences in measurements among laboratories. They have proven useful in identifying inconsistencies and/or drift in CO standards and therefore are strongly encouraged.

b) NOAA ESRL is the WMO/GAW CCL for carbon monoxide. In this capacity, they provide calibrated standards to GAW laboratories, and CO calibrations should be traceable to the scale maintained by NOAA ESRL. The CCL maintains 12 primary standards with CO mole fractions between 20 ppb and 500 ppb. Standards are contained in Luxfer cylinders fitted with brass valves obtained from Scott-Marin, Inc. Eight of these cylinders (50 to 300 ppb) have calibration histories since 2002, four more since 2008. All standards have been stable to within 1 ppb. The stability of the lowest standard (20 ppb) may slightly exceed this limit. The WMO-2000 scale was established based on several sets of gravimetric standards using the GC-HgO technique. Later on, the WMO-2004 scale was established based on Vacuum-UV Resonance Fluorescence (VURF) measurements. The CCL expects to prepare another set of gravimetric standards in 2010, creating the WMO-2010 scale. After consolidation, the CCL is expected to re-assign for all cylinders distributed since 1990 the mole fraction, including best estimates of uncertainty on this WMO-2010 scale.

c) The CCL is encouraged to include the calibrations of CO in the NOAA database and make this available on the internet.

d) The CCL is responsible for documenting the evolution of the WMO CO scale and for communicating all revisions to the stations as well as to WCC-EMPA.

e) The frequency of the preparation of gravimetric Primary Standards should be increased to a triennial to quadrennial interval to determine any long term drift of the scale. The CCL is presently in the process of establishing a capability of making accurate dilutions as a second means of assuring the stability of the WMO Primary Scale.

f) Standard drift remains a serious issue for CO measurements at the stations. Therefore an annual recalibration of at least one of the in-house station standards is strongly recommended.

g) The WMO/GAW SAG Reactive Gases’ Subgroup on Carbon Monoxide should be reconstituted and should continue to work on resolving issues of the calibration scale, in particular by giving guidance to stations on how to re-process older data. A SAG Guidance Document on CO measurements is expected by mid 2010.

h) Currently, no laboratory is conducting absolute volumetric measurements of CO. These measurements would be an extremely useful alternative to dynamic dilution of high-concentration gases for confirming the consistency and potential drift in the WMO primary scale.

i) EMPA is the designated World Calibration Centre (WCC) for carbon monoxide and is in charge of conducting system and performance audits including comparisons at Global GAW stations. Evaluation of CO audits by the WCC should be limited to the average range covered by the seasonal variability of daily means. Audit results and other comparison results should be archived along with CO data at the WDCGG or with GAWSIS.

j) Within the GAW Programme, regular comparisons or calibrations by designated calibration centres (with global or regional scope) are necessary to ensure traceability of the observations. Furthermore, regular audits by the WCC are needed as an independent check of the measurements on-site.

k) It should be explored if, in this particular case of a trace gas with large danger of drifting standards, regional round-robbins could help to maintain the link to the CCL.

l) For many stations, a dynamic dilution system may be an additional means of calibrating their instruments, in particular in cases where non-linear instrument response may be an issue (Zellweger et al., this issue).

m) There is a large number of stations (some of which are regional GAW stations) that are equipped with less sophisticated (or calibrated) CO analysers. These measurements are currently poorly exploited, in part because some of these data (e.g., from environmental
agencies) are not easily accessible and the quality of these observations is not well assessed. There is a need for identification, comparison and improved accessibility of these observations.

10. **SPECIFIC REQUIREMENTS FOR H₂ CALIBRATION**

10.1 **Background**

Molecular hydrogen plays a significant role in global atmospheric chemistry due to its interference in CH₄ – CO - OH cycling. The balance of hydrogen could change with the implementation of a new H₂ energy carrier. Therefore, it is important to establish its global budget and atmospheric trend. There is currently no internationally accepted standard scale available for measurements of atmospheric molecular hydrogen nor is there any institution to distribute such standards.

There are different networks of monitoring stations that are linked to independent scales (NOAA, CSIRO-AGAGE, EuroHydros, NIES). These scales have been prepared using different methods, and known biases between these scales exist that have not always been constant in time and include concentration dependencies. Efforts to integrate data from different networks have been undertaken based on results from long-term inter-laboratory comparison activities (Xiao et al. 2007). While this documents the need to achieve transparent and consistent scales, the reliability of this approach depends on a solid evaluation of these differences. There is a clear need to get consistent data from independent networks and therefore harmonisation of the scale still remains a task of high priority. Molecular hydrogen is recognized as an important target variable to be measured in the WMO/GAW global network and specific tasks are outlined for implementation by the global research community (WMO/GAW Report No.172, 2007)

10.2 **Current H₂ calibration and comparison activities**

At the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, MPI-BGC has offered to serve as the WMO/GAW Central Calibration Laboratory (CCL) for atmospheric molecular hydrogen. The MPI2009 scale consisting of 13 primary standards of hydrogen in air ranging from 140 to 1200 nmol/mol was designated as the WMO calibration scale.

10.3 **Recommendations for H₂ calibration and comparison activities**

a) It is recommended that the CCL produces, on an annual basis, additional standards that provide a check for the stability of the WMO scale.

b) Long time series of atmospheric hydrogen have been generated by the NOAA and CSIRO/AGAGE monitoring networks. To enable a collaborative global network for hydrogen measurements a concerted effort to harmonize these sets of data is urgently needed. In the course of this process the measurement groups are encouraged to link to the new WMO scale. The CCL is requested to cooperate closely with NOAA and CSIRO to facilitate an exact adjustment of their proper calibration scales to the WMO scale.

c) In addition, temporal changes of inter-laboratory biases that have not always been related to scale changes, underline the necessity to continue comparison of hydrogen data. These exercises will be a valuable tool to monitor the success of a future scale harmonization and shall be continued at regular intervals.

d) A major problem most laboratories that measure hydrogen encompass is to ensure the stability of their standards. It is recommended that every laboratory develops a strategy to account for this. This includes appropriate choice of standard gas containers that have been tested successfully (mostly stainless steel cylinders). A set of standard gases in large low pressure glass flasks has proved to be an easy and useful approach. Aluminium cylinders commonly used for other trace gas standard mixtures often show significant growth of hydrogen. Thus, the long-term use of aluminium cylinders as in-house secondary standards is discouraged.
e) Appropriate characterization of the detector response in the ambient range is required at an interval of four times per year and at any change of configuration of the detection system, given the strong non-linear response of the commonly used HgO reduction detectors. A combination of a dilution series and a set of in-house laboratory standards have proven to be a useful approach to characterize the detector response over larger ranges of mixing ratios. Analysis techniques with characteristics superior (i.e. precision and non-linearity) to the common HgO reduction detectors have been described recently and should be considered for new installations.

f) Due to the strong non-linearity it is particularly important for H₂ measurements that the mixing ratio of the working standard gas is close to the mean annual H₂ level observed at the site. In contrast, the target standard gases used for quality control purpose are recommended to have H₂ mixing ratios that are at the high end of the observed values to provide good diagnostic information.

11. GENERAL RECOMMENDATIONS FOR QUALITY CONTROL OF ATMOSPHERIC TRACE GAS MEASUREMENTS

The Group of WMO Experts nominates Ken Masarie (NOAA/ESRL) to review the recommendations summarized below at least six months before the next meeting, and remind laboratories to prepare summaries of their current intercomparison (ICP) activities as they relate to the respective recommendations.

11.1 General Recommendations

a) Relating standards to the WMO Mole Fraction Scales: Investigators should follow practices outlined in Section 1.3 of this report for obtaining a sufficient number and range of calibration gases from the respective WMO/GAW CCL (laboratory standards) and transferring those calibrations to working and field standards. The data management system in use should allow for easy reprocessing and easy propagation of scale changes from laboratory standards to final measurements.

b) Real-air and modern-CO₂ (and other trace gas) standards: Working standards must have natural levels of N₂, O₂, and Ar to avoid biases e.g. due to different pressure-broadening effects between sample and calibration gases. CO₂ standards should have CO₂ with ambient δ¹³C ratios to avoid isotopic interference in specific analysers.

c) Besides round-robin comparisons, more frequent and ongoing comparison activities between pairs of laboratories which incorporate the analyses of actual air samples are strongly recommended. The tremendous benefit of ongoing same-air comparisons has been demonstrated (Masarie et al., 2001) and is reinforced. Mutual exchange of air in glass flasks is encouraged as a means to detect experimental deficiencies. The comparison experiment at Alert involving multiple laboratories at a single site has proven to be extremely valuable. Similar multi-lab comparisons have been conducted at Cape Grim. Comparisons of measurements from co-located in-situ instruments and co-located discrete samples and in-situ instruments are also strongly recommended.

d) 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 sole reason for sharing preliminary data is for detection of problems.

e) Data comparisons (or eventually merging) require sufficient metadata to identify methodology differences that potentially influence quantitative comparisons. These metadata should be provided by the ICP participants and will allow to independently quantifying bias, and/or specifically state assumptions in comparisons.

f) To better understand the effectiveness of various comparison strategies, laboratories with ongoing comparison experiments are encouraged to report at the next WMO/IAEA CO₂ Experts meeting what they have learned, how the comparison has affected measurement
quality and compatibility and the benefit of redundant or complementary comparisons. This will be needed to develop a comprehensive quality control strategy.

g) Flask sampling programmes shall be implemented where possible at observational sites making continuous measurements. This will provide ongoing quality control and help determine measurement uncertainty and eventually allow merging data sets from different laboratories.

h) An assessment will be performed to evaluate the feasibility of a “travelling” CO2 measurement system to operate for a period of weeks to months in parallel to existing station systems. ICOS will coordinate this effort.

i) As part of its tasks as World Calibration Centre for CH4 and CO, EMPA will investigate the use of a travelling instrument for GAW station audits. Picarro Inc. offered to provide one of their instruments for this exercise.

j) Clear protocols and reports of experience gained in comparison projects should be provided. Results should be published and readily accessible via internet. The evaluation of such activities and recommendations for refinement, co-ordination and expansion of such activities has been accepted as a key responsibility of future WMO/IAEA Expert meetings.

k) Traceable uncertainty estimates: 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. Details of how these estimates are calculated and what activities are used to verify them (data reporting) need to be provided. ISO nomenclature (see details in introduction) shall be used for uncertainty estimates and discussions.

l) Deviations from recommendations: We recognize the value of innovation and experimentation with new approaches. In this context instruments based on Cavity Ring Down Spectroscopy (CRDS) seem to be particularly promising for a number of trace gases. 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. Furthermore, the results of such experimentation should be reported at future WMO/IAEA CO2 Experts meetings and similar venues, and published in the peer-reviewed literature whenever possible.

11.2 Recommendations for in-situ measurements

a) Continuous in-situ measurements of CO2 and other trace gases can greatly improve our understanding of regional-scale fluxes. For this reason, and in response to recent advances in technology, the number of investigators and sites carrying out in-situ trace gas measurements is rapidly increasing. Many sound principles for conducting in-situ CO2 measurements have been described in detail in WMO/GAW Report No. 134 (1999). The group recommends that the SAG-GHG initiates a timely update of Report 134 well before the next WMO Experts Meeting in 2011. Preliminary recommendations for CO2 measurements have been summarized in the 13th WMO/IAEA Experts meeting recommendation (WMO/GAW Report No. 168, 2006).

b) It is recommended that new robust analytical technologies (e.g., laser-based optical analyzers, closed-cell Fourier spectrometers) are tested. The envisaged ICOS Atmospheric Thematic Centre will initiate a web-based forum to distribute the results and generate discussion among “experts”. New techniques should meet the scientific requirements of accuracy and precision as stated in GAW reports. Specific areas that need to be investigated are calibration frequency and ability to correct for water vapour dilution or interference with other trace substances, and other artefacts besides sample drying. Manufacturers are encouraged to offer detailed training, perhaps through GAWTEC. The community should identify species for which new technologies are needed and specify which instruments should be available for new observables.

c) Besides recommendations on the greenhouse and associated trace gases mentioned above the WMO Experts identified a strong need for expert guidance to establish an adequate calibration process and comparison activity for atmospheric 222Rn observations. WMO and IAEA will contact respective specialists to give advice. The outcome should be communicated as early as possible, however, during the 16th Meeting of Experts at the latest.
12. RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING

12.1 Data management

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

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

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

12.2 Data archiving

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

12.3 Co-operative data products

All laboratories making high-quality greenhouse gases measurements are strongly encouraged to participate in the Co-operative Atmospheric Data Integration Project which produces the GLOBALVIEW data products. The majority of current participants provide updates in August that include data through December of the preceding year. Data contributed to the GLOBALVIEW project are used to derive the data product. The product includes no actual data.
13. SUMMARY OF RECENT INTERNATIONAL PLANNING OF ATMOSPHERIC TRACE GAS MEASUREMENT STRATEGIES

This report is prepared in the context of widespread governmental acceptance of climate change (United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto protocol), and leads to new and urgent challenges to the carbon cycle community. Two main objectives justify the deployment of atmospheric observations:

(1) To monitor and assess the effectiveness of emission control and/or reduction activities on atmospheric levels, including attribution of sources and sinks by region and sector.
(2) To quantify the present state of the fluxes of greenhouse gases and better understand the controlling processes.

An overview of the observational needs for validating GHG emissions and reductions is given in Marquis and Tans (2008) and NRC (2010). Recently, new GHG measurement data streams from satellites with global coverage have become available based on a variety of instruments (SCIAMACHY, AIRS, IASI, GOSAT) and are being integrated into global data assimilation systems (e.g. the GEMS project). However, these new observations lack long-term continuity, are subject to various biases and do not cover with sufficient accuracy the full suite of GHG and associated tracers defined by WMO/GAW. Hence a complementary, long-term, high-quality network of surface-based in-situ, tall tower and total column as well as systematic aircraft observations are indispensable, in order to reliably detect and quantify long-term changes in GHG sources and sinks. Furthermore, these measurements allow an independent assessment of regional trends, as needed by local policymakers.

In addition to the WMO/GAW global programme and its predecessor BAPMoN operating since 1975 and targeting the coordination of systematic atmospheric greenhouse gases observations, there have been international research efforts on understanding the carbon cycle. One has been co-ordinated by the Global Carbon Project (GCP) (http://www.globalcarbonproject.org/) combining the efforts of International Geosphere-Biosphere Project (IGBP), World Climate Research Project (WCRP) and International Human Dimensions Programme (IHDP). The GCP produced in 2003 a Science Implementation Plan dealing with the patterns and variability of carbon fluxes, the associated processes and feedbacks, and the management of the carbon cycle. GCP identified both systematic observations of concentrations in the atmosphere and oceans and process-oriented carbon cycle observations.

In parallel, the former Integrated Global Carbon Observing Strategy Partnership (IGOS-P) produced a Theme Report on Integrated Global Carbon Observations (IGCO). This theme has been subsumed into the Global Earths Observation System of Systems as one of three GEO tasks contributing to a Global Carbon Observation and Analysis System. The IGCO plan outlined a strategy to coordinate systematic global carbon observational networks that can form the backbone of an integrated carbon cycle monitoring system and is currently being updated and revised to address emerging carbon and greenhouse gas issues. The plan acknowledges GAW for atmospheric measurements and builds upon earlier planning by GTOS/TCO (Terrestrial Carbon Observations: http://www.fao.org/gtos/TCO.html), GOOS (Global Ocean Observing System: http://ioc.unesco.org/goos/), and GCOS (Global Climate Observation System). (The Atmospheric Observation Panel for Climate (AOPC) of GCOS has acknowledged the GAW network for CO₂ and CH₄ as a Comprehensive Network of GCOS in 2006.)

The main role of the IGCO is to establish data requirements, design network configurations, and develop advanced algorithms for carbon observations, which will be the core of a future, sustained observing system by 2015 sees the long term efforts of GAW through this WMO/IAEA Expert team and other components of GAW complementing parallel efforts in terrestrial and marine reservoirs. The GAW greenhouse gas observations were also part of a second IGOS-P strategy on Integrated Global Atmospheric Chemistry Observations (IGACO) which includes not only greenhouse gases, but also a number of other atmospheric constituents, including aerosols and...
The IGACO strategy (WMO/GAW Report No. 159, 2004) is being implemented through the WMO/GAW Programme and its Strategic Plan for 2008-2015.

In both GCP and IGCO strategies, a strong atmospheric observing component is outlined as indispensable to link land and ocean observing components and to integrate across spatial heterogeneities and temporal variability. A modelling strategy for developing Carbon Cycle Data Assimilation schemes that will interpret observations in terms of fluxes is also outlined, based upon a combination of data and models for the different domains: atmosphere, ocean and land, where results from one domain place valuable constraints on the workings of the other two ("multiple constraint").

Two major regional programmes have received funding to increase the density of atmospheric trace gas observations in GAW and terrestrial carbon observations over North America (NACP: http://www.nacarbon.org/nacp/), and Europe (CarboEurope-IP: http://www.carboeurope.org/, ICOS: http://icos-infrastructure.eu). It is important that those regional programmes remain tightly linked to the international WMO/GAW effort and produce regional data sets that can be merged safely into an enhanced global picture of carbon sources and sinks. Lessons from such regional initiatives should be valuable to formulate future atmospheric observing strategies for the remaining under-sampled regions, in particular in the tropics. The strong commitment to build expertise in developing countries by WMO and IAEA, including the establishment of high-quality measurement capabilities, remains a critical issue for achieving adequate spatial coverage of the globe in the coming decade.

Finally, it is acknowledged that society will need more comprehensive and better coordinated information as it begins to address the problem of rising greenhouse gases in the atmosphere. There likely will be international treaties, national policies, and regional strategies (i.e., emission reduction, efficiency improvements, offsets, etc.) applied to a number of economic, social, and environmental sectors. Some will work better than others and some will not work at all. Providing independent, globally coherent information on the success of these efforts will give considerable strength to these treaties, policies, and strategies. The closest thing the world has to build a globally consistent greenhouse gas observation network is WMO's Global Atmospheric Watch and the scientists who support it. However, providing coherent, regional-scale information requires not only enhanced observations, but also improved modelling and ensemble reanalysis. These challenges are emerging and it is not known what shape greenhouse gas management strategies will take, though it is certain there will be many factors contributing to it. WMO/GAW needs to be positioned to provide the atmospheric basis for such an observation and analysis system and to engage with other communities to ensure reliable analyses. In support of these activities, the WMO Commission for Atmospheric Sciences adopted the following statement at the 15th quadrennial meeting, held in November 2009 in Incheon, Korea:

“8.3 The lead role of WMO in global partnerships for air quality/environmental forecasting and tracking carbon dioxide and other greenhouse gases

8.3.3 The Commission endorsed the recommendation of the CAS Management Group (2008) that WMO work towards establishing an Integrated Global Carbon Observation Prediction and Assessment System, acknowledging that monitoring requirements may be forthcoming to support global emission reduction and mitigation policy, and recognizing that CO₂ interacts strongly with the biosphere and hydrosphere, that considerable research is necessary to support such a system, and that such research would need to be compatible with what might ultimately become operational – that is, aiming at operational implementation:

(a) Integrating and expanding existing observing systems and validating and incorporating satellite and aircraft measurements to produce a global, near real time database of atmospheric CO₂;
(b) Developing and implementing an ensemble-based reanalysis for research and operational applications that includes surface-atmosphere interactions; and
(c) Applying model-based systems to analysis and prediction of the transport and evolution of CO₂. These systems should be linked to operational frameworks to insure reliable access to data, production of forecasts, and delivery of services."

The following observational strategies seem to be most promising in this context:

a) Expand aircraft flights over vegetated areas not sampled or under-sampled, with priority to tropical South America, Africa, and South East Asia. Higher altitude flights shall be needed to cope with vigorous convective mixing up to 10 km in the tropics. For that purpose, the use of passenger aircraft such as pioneered in atmospheric chemistry (CARIBIC, MOZAIC programmes) should be promoted.

b) Make the effort to recruit scientists from the under-sampled continents/areas to join the WMO Experts group.

c) Carry out continuous measurements in the boundary layer, in particular on top of high towers, and further pursue the option to use eddy flux towers as a platform for additional precise CO₂ mixing ratio observations. These observations will help us to quantify regional sources and sinks by means of inverse modelling.

d) Carry out in the vicinity of continuous tower-based boundary layer measurement sites frequent vertical profiles if possible under all weather conditions, which will quantify the vertical mixing of surface sources and sink fluxes.

e) Develop and implement long-term measurements of total column Greenhouse Gases at a number of sites in WMO/GAW and its partner stratospheric network NDAAC recognising the need for satellite calibration/validation and modelling.

f) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes (¹³CO₂, O₂/N₂, ¹⁸OCO, stable isotopes in CH₄ and CO) and separate fossil fuel emissions (¹⁴CO₂, CO...). Along these lines it is absolutely essential that detailed spatially and temporally resolved fossil fuel CO₂ and CO emissions inventories be developed and pursued.

g) Add measurements of characteristic chemical trace substances to the measurement programme or suite of components analysed in flask samples to sort out source contributions of the various GHGs.

h) Develop high-quality measurements of transport tracers (SF₆, ²²⁡Rn, C₂Cl₄...) to validate numerical models of atmospheric transport (in particular their vertical mixing) including aircraft sampling.

i) Report actual uncertainties on individual data where available. In particular, pursue the development of data products (e.g. GLOBALVIEW) that can include wherever possible information on representativeness, calibration offsets, etc. Take into account station characteristics and catchment area description.

j) Plan atmospheric measurements jointly with terrestrial and oceanic process communities to optimise the link of atmospheric composition change to surface processes. For example, the development of the “virtual tall tower” concept to use short towers as part of atmospheric networks, and the synergetic use of ocean ΔpCO₂ survey programmes to make atmospheric measurements.

k) Encourage and facilitate the development of improved atmospheric tracer transport models. Among the identifiable needs are improving the representation of atmospheric convection, the representation of the atmospheric boundary layer and the need to improve spatial and temporal resolution to better account for sources and sinks variability. Equally as important for assessing the distribution of fluxes is the use of several independently developed models and their frequent intercomparison. Finally, it is important to develop and maintain community models which are numerically efficient, which can run from standard computer platforms with a modest amount of training, and which are made available to the scientific community as a whole.
References


International vocabulary of metrology - Basic and general concepts and associated terms (VIM), 3rd Edition, Joint Committee for Guides in Metrology (JCGM), (2008), (available on the BIPM's website, www.bipm.org)


ABBREVIATIONS AND ACRONYMS USED IN THIS REPORT

AGAGE Advanced Global Atmospheric Gases Experiment
AVD Absolute Volumetric Determination
BIPM International Bureau of Weights and Measures
CARBOEUROPE Programme regrouping ecosystem and atmospheric research on the carbon balance of Europe (EU funded project)
CARIBIC Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrument Container
CCL Central Calibration Laboratory
CDIAC Carbon Dioxide Information Analysis Centre
CLASSIC Circulation of Laboratory Air Standards for Stable Isotope inter Comparisons
CMDL Climate Monitoring and Diagnostics Laboratory, Boulder, CO, U.S.A. (now NOAA ESRL GMD)
CRDS Cavity Ring Down Spectroscopy
CSIRO Commonwealth Scientific & Industrial Research Organisation
DBMS Data Base Management Strategy
ECD Electron Capture Detector
EMPA Eidgenössische MaterialPrüfungsAnstalt
ESRL Earth System Research Laboratory (NOAA, Boulder, CO U.S.A.)
FID Flame Ionisation Detector
GAW Global Atmosphere Watch (WMO Programme)
GAWTEC GAW Training and Education Centre
GCP Global Carbon Project
GG or GHG Greenhouse Gases
GLOBALVIEW Co-operative Atmospheric Data Integration Project
GOOS Global Ocean Observing System
GOSAT Greenhouse gas Observing SA.tellite by the Japan Aerospace Exploration Agency (JAXA)
GMD Global Monitoring Division (NOAA ESRL, Boulder, CO, U.S.A.)
GTOS Global Terrestrial Observing System
IAEA International Atomic Energy Agency
ICP InterComParison (experiment)
ICOS Integrated Carbon Observation System (EU-funded project)
IGACO Integrated Global Atmospheric Chemistry Observations
IGBP International Geosphere-Biosphere Programme
IGCO Integrated Global Carbon Observation
IGOS Integrated Global Observing Strategy
IHALICE International HALocarbon in Air Comparison Experiment
IHDP International Human Dimensions Programme
ISO International Organization for Standardization
IUPAC International Union of Pure and Applied Chemistry
JCGM Joint Committee for Guides in Metrology
JRAS Jena Reference Air Set
MOPITT-TERRA Measurements Of Pollution In The Troposphere
MOZAIC Measurement of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus in-service aircraft
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
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<tr>
<td>MPI-BGC</td>
<td>Max-Planck Institut für Biogeochemie, Jena, Germany</td>
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<td>MSC</td>
<td>Meteorological Service of Canada</td>
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<td>NACP</td>
<td>The North American Carbon Programme</td>
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<tr>
<td>NCAR C-DAS</td>
<td>National Centre for Atmospheric Research Carbon Data-Model Assimilation</td>
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<tr>
<td>NIES</td>
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<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<tr>
<td>NOAA</td>
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<tr>
<td>OCO</td>
<td>Orbital Carbon Observatory</td>
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<tr>
<td>OSSE</td>
<td>Observing System Simulation Experiment</td>
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<tr>
<td>PI</td>
<td>Principal Investigator</td>
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<tr>
<td>QA/SAC</td>
<td>Quality Assurance/Science Activity Centre</td>
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<tr>
<td>RGD</td>
<td>Reduction Gas Detector</td>
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<tr>
<td>SAG</td>
<td>Scientific Advisory Group</td>
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<tr>
<td>SCIAMACHY</td>
<td>SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY</td>
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<tr>
<td>SIO</td>
<td>Scripps Institution of Oceanography</td>
</tr>
<tr>
<td>SRM</td>
<td>Standard Reference Material</td>
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<tr>
<td>TACOS</td>
<td>Terrestrial and Atmospheric Carbon Observing System -Infrastructure (EU funded project)</td>
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<td>TCO</td>
<td>Terrestrial Carbon Observations</td>
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<tr>
<td>TCCON</td>
<td>Total Carbon Column Observing Network</td>
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<tr>
<td>TDLAS</td>
<td>Tunable Diode Laser Absorption Spectroscopy</td>
</tr>
<tr>
<td>UEA</td>
<td>University of East Anglia</td>
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<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
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<tr>
<td>VPDB</td>
<td>Vienna Pee Dee Belemnite (Isotope Standard)</td>
</tr>
<tr>
<td>VSMOW</td>
<td>Vienna Standard Mean Ocean Water (Isotope Standard)</td>
</tr>
<tr>
<td>VURF</td>
<td>Vacuum-UV Resonance Fluorescence</td>
</tr>
<tr>
<td>WCC</td>
<td>World Calibration Centre</td>
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<tr>
<td>WCRP</td>
<td>World Climate Research Programme</td>
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<tr>
<td>WDCGG</td>
<td>World Data Centre for Greenhouse Gases</td>
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<tr>
<td>WMO</td>
<td>World Meteorological Organization</td>
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PREVIOUS EXPERT MEETINGS

The first meeting of the Experts on Carbon Dioxide Measurement was held in La Jolla, California, United States of America, and sponsored by the World Meteorological Organization (WMO). WMO has sponsored all subsequent meetings. These meetings have provided a quasiregular communication among all national CO2 monitoring programmes, which has ensured that CO2 is monitored with the best current techniques available, that advantage is taken of new methodologies as they become available, and that all programmes are intercalibrated by accepted international standards.

The following is a list of meetings in this series:

<table>
<thead>
<tr>
<th>LOCATION</th>
<th>DATE</th>
<th>PUBLICATION</th>
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<tbody>
<tr>
<td>1. La Jolla, California, USA</td>
<td>3-7 March 1975</td>
<td>4*</td>
</tr>
<tr>
<td>2. Geneva, Switzerland</td>
<td>8-11 September 1981</td>
<td>6†</td>
</tr>
<tr>
<td>3. Lake Arrowhead, California, USA</td>
<td>4-8 November 1985</td>
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<tr>
<td>4. Gaithersburg, Maryland, USA</td>
<td>15-17 June 1987</td>
<td>51†</td>
</tr>
<tr>
<td>5. Hilo, Hawaii, USA</td>
<td>24-26 March 1988</td>
<td>‡</td>
</tr>
<tr>
<td>6. Lake Arrowhead, California, USA</td>
<td>14-19 October 1990</td>
<td>77‡</td>
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<tr>
<td>7. Rome, Italy</td>
<td>7-10 September 1993</td>
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</tr>
<tr>
<td>8. Boulder, Colorado, USA</td>
<td>6-11 July 1995</td>
<td>121†</td>
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<td>9. Aspendale, Australia</td>
<td>1-4 September 1997</td>
<td>132†</td>
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<td>10. Stockholm, Sweden</td>
<td>23-26 August 1999</td>
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<tr>
<td>11. Tokyo, Japan</td>
<td>25-28 September 2001</td>
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<td>12. Toronto, Canada</td>
<td>15-18 September 2003</td>
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<tr>
<td>14. Helsinki, Finland</td>
<td>10-13 September 2007</td>
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<tr>
<td>15. Jena, Germany</td>
<td>7-10 September 2009</td>
<td>194†</td>
</tr>
</tbody>
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* Number of reports in the WMO Executive Panel-I/Document 5, 13.3.1975.
† Number of reports in the WMO Research Department/GAW Report Series.
List of Participants

Colin Allison  
CSIRO Marine and Atmospheric Research  
Aspendale, Victoria,  
Australia  
Email: colin.allison@csiro.au

Nobuyuki Aoki  
National Metrology Institute of Japan  
Ibaraki  
Japan  
Email: aoki-nobu@aist.go.jp

Sergey Assonov  
MPI fuer Chemie  
Mainz  
Germany  
Email: assonov_sergey@yahoo.com

Douglas Baer  
Los Gatos Research  
Mountain View  
USA  
Email: d.baer@lgrinc.com

Leonard A. Barrie  
World Meteorological Organization  
1211 Geneva 2  
Switzerland  
Email: lbarrie@wmo.int

Gordon Brailsford  
NIWA  
Wellington,  
New Zealand  
Email: g.brailsford@niwa.co.nz

Willi A. Brand  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: wbrand@bgc-jena.mpg.de

Ernst-Guenther Erich Brunke  
South African Weather Service  
Stellenbosch  
South Africa  
Email: ernst.brunke@weathersa.co.za

George Burba  
LI-COR Biosciences  
Lincoln  
Nebraska  
USA  
Email: george.burba@licor.com

James H. Butler  
NOAA Earth System Research Laboratory  
Boulder, Colorado  
USA  
Email: james.h.butler@noaa.gov

Huilin Chen  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: hchen@bgc-jena.mpg.de

Eric Crosson  
Picarro, Inc.  
Sunnyvale  
California  
USA  
Email: ecrosson@picarro.com
Roger Curcoll Masanes
Institut Català de Recerca del Clima (IC3)
Barcelona
Spain
Email: rcurcoll@pcb.ub.cat

Marc Delmotte
CNRS / LSCE
Gif sur Yvette
France
Email: marc.delmotte@lsce.ipsl.fr

Edward Dlugokencky
NOAA ESRL
Boulder, Colorado
USA
Email: ed.dlugokencky@noaa.gov

Rebecca Fisher
Department of Earth Sciences,
Royal Holloway, University of London
Egham
United Kingdom
Email: r.fisher@es.rhul.ac.uk

Roger James Francey
CSIRO Marine and Atmospheric Research
Aspendale, Victoria
Australia
Email: roger.francey@csiro.au

Wolfgang Fricke
Deutscher Wetterdienst
Hohenpeißenberg
Germany
Email: Wolfgang.Fricke@dwd.de

Luciana Gatti
IPEN
Sao Paulo
Brazil
Email: lvgatti@gmail.com

Heike Geilmann
Max Planck Institute for Biogeochemistry
Jena
Germany
Email: geilmann@bgc-jena.mpg.de

Heike Graven
ETH Zurich
Zurich
Switzerland
Email: heather.graven@env.ethz.ch

David Griffith
University of Wollongong
School of Chemistry
Wollongong
Australia
Email: griffith@uow.edu.au

Brad Hall
NOAA Earth System
Boulder, Colorado
USA
Email: Bradley.Hall@noaa.gov

Robert Claire Hamme
University of Victoria
School of Earth and Ocean Sciences
Victoria
Canada
Email: rhamme@uvic.ca

Samuel Hammer
Institut für Umweltphysik,
Heidelberg
Germany
Email: Samuel.Hammer@iup.uni-heidelberg.de

László Haszpra
Hungarian Meteorological Service
Budapest
Hungary
Email: haszpra.l@met.hu
Juha Hatakka  
Finnish Meteorological Institute  
Helsinki  
Finland  
Email: juha.hatakka@fmi.fi

Martin Heimann  
Max-Planck-Institute for Biogeochemistry  
Jena  
Germany  
Email: martin.heimann@bgc-jena.mpg.de

Susanne Hermsmeier  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: sherms@bgc-jena.mpg.de

Lin Huang  
Environment Canada  
Toronto  
Canada  
Email: lin.huang@ec.gc.ca

Nuggehalli Kesavamurthi Indira  
C-MMACS  
Bangalore  
India  
Email: indira@cmmacs.ernet.in

Theo Manuel Jenk  
Centre for Ice and Climate  
Copenhagen  
Denmark  
Email: tjenk@gfy.ku.dk

Armin Jordan  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: ajordan@bgc-jena.mpg.de

Jan Kaiser  
University of East Anglia  
School of Environmental Sciences  
Norwich  
United Kingdom  
Email: J.Kaiser@uea.ac.uk

Keiichi Katsumata  
National Institute for Environmental Studies  
Tsukuba  
Japan  
Email: katsumata.keiichi@nies.go.jp

Ralph F. Keeling  
Scripps Institution of Oceanography  
San Diego  
California  
USA  
Email: rkeeling@ucsd.edu

Jooil Kim  
Seoul National University  
Seoul  
Rep. of Korea  
Email: kji2080@gmail.com

Jörg Klausen  
Empa, GAW QA/SAC  
Dübendorf  
Switzerland  
Email: joerg.klausen@empa.ch

Elena Kozlova  
University of East Anglia  
School of Environmental Sciences  
Norwich  
United Kingdom  
Email: e.kozlova@uea.ac.uk

Paul Krummel  
CSIRO Marine and Atmospheric Research  
Aspendale, Victoria  
Australia  
Email: paul.krummel@csiro.au

Jost Valentin Lavric  
LSCE  
Gif sur Yvette  
France  
Email: Jost-Valentin.Lavric@lsce.ipsl.fr

Jeonsoon Lee  
Korea Research Institute of Standards and Science (KRISS)  
Daejeon  
Republic of Korea  
Email: leejs@kriss.re.kr
Scott Lehman  
University of Colorado  
INSTAAR  
Boulder, Colorado  
USA  
Email: Scott.Lehman@Colorado.edu

Markus Leuenberger  
University of Bern  
Bern  
Switzerland  
Email: leuenberger@climate.unibe.ch

Ingeborg Levin  
Institut für Umweltphysik  
Heidelberg  
Germany  
Email: Ingeborg.Levin@iup.uni-heidelberg.de

Petra Linke  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: plinke@bgc-jena.mpg.de

Zoe Miranda Loh  
CSIRO Marine & Atmospheric Research  
Aspendale, Victoria  
Australia  
Email: Zoe.Loh@csiro.au

Ingrid Theodora Luijkx  
University of Groningen,  
Centre for Isotope Research  
Groningen  
The Netherlands  
Email: i.t.luijkx@rug.nl

Toshinobu Machida  
National Institute for Environmental Studies  
Tsukuba  
Japan  
Email: tmachida@nies.go.jp

Michela Maione  
University of Urbino,  
Institute of Chemical Sciences  
Urbino  
Italy  
Email: michela.maione@uniurb.it

Andrew Manning  
University of East Anglia  
School of Environmental Sciences  
Norwich  
United Kingdom  
Email: a.manning@uea.ac.uk

Swagath Navin Manohar  
Centre for Isotope Research  
Groningen  
The Netherlands  
Email: s.n.manohar@rug.nl, swagathnavin@gmail

Peter Martín  
LI-COR Biosciences  
Bad Homburg  
Germany  
Email: peter.martin@licor.com

Ken Masarie  
NOAA Earth System Research Laboratory  
Boulder, Colorado  
USA  
Email: kenneth.masarie@noaa.gov

Frank Meinhardt  
Federal Environmental Agency  
Kirchzarten  
Germany  
Email: frank.meinhardt@uba.de

Natasha Miles  
Pennsilvaniya State University  
University Park  
USA  
Email: nmiles@met.psu.edu

Charles Miller  
Jet Propulsion Laboratory,  
Pasadera  
USA  
Email: charles.e.miller@jpl.nasa.gov

Mihály Molnár  
MTA ATOMKI  
Debrecen  
Hungary  
Email: mmol@atomki.hu
Josep-Anton Morguí  
Institut Català de Recerca del Clima (IC3)  
Barcelona  
Spain  
Email: jamorgui@ic3.cat

Hitoshi Mukai  
National Institute for Environmental Studies  
Tsukuba  
Japan  
Email: lmukaih@nies.go.jp

Rolf Neubert  
Centre for Isotope Research  
University of Groningen  
Groningen  
The Netherlands  
Email: r.e.m.neubert@rug.nl

Euan Nisbet  
Department of Earth Sciences  
Royal Holloway, University of London  
Egham  
United Kingdom  
Email: e.nisbet@es.rhul.ac.uk

Justus Notholt  
University Bremen  
Bremen  
Germany  
Email: notholt@uni-bremen.de

Paul Novelli  
NOAA/ESRL  
Boulder, Colorado  
USA  
Email: paul.c.novelli@noaa.gov

Salvatore Piacentino  
ENEA  
Palermo  
Italy  
Email: salvatore.piacentino@enea.it

Elena Popa  
Energy Research Centre of the Netherlands  
The Netherlands  
Email: popa@ecn.nl

Michel Ramonet  
LSCE  
Gif sur Yvette  
France  
Email: michel.ramonet@lsce-ipsl.fr

Scott Richardson  
Pennsylvania State University  
University Park  
USA  
Email: srichardson@psu.edu

Juergen Richter  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: jrichter@bgc-jena.mpg.de

Thomas Röckmann  
Utrecht University  
Utrecht  
The Netherlands  
Email: t.roeckmann@uu.nl

Christian Rödenbeck  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: croeden@bgc-jena.mpg.de

Michael Rothe  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: mrothe@bgc-jena.mpg.de

Celia Sapart  
University of Utrecht  
Utrecht  
The Netherlands  
Email: C.J.Sapart@phys.uu.nl

Hans-Eckhart Scheel  
Forschungszentrum Karlsruhe  
Garmisch-Partenkirchen  
Germany  
Email: hans-eckhart.scheel@imk.fzk.de
Alex Vermeulen  
ECN - Energy research Centre of the Netherlands  
Petten  
The Netherlands  
Email: a.vermeulen@ecn.nl

Ivan Vigano  
University of Utrecht  
Utrecht  
The Netherlands  
Email: I.Vigano@uu.nl

Yrjö Viisanen  
Finnish Meteorological Institute  
Helsinki  
Finland  
Email: yrjo.viisanen@fmi.fi

Felix Robert Vogel  
Ruprecht-Karls- Universität Heidelberg,  
Heidelberg  
Germany  
Email: fvogel@iup.uni-heidelberg.de

Benoit Wastine  
LSCE / EPA  
Dublin  
Ireland  
Email: benoit.wastine@lsce.ipsl.fr

Magnus Wendeberg  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: magnus.wendeberg@bgc-jena.mpg.de

Roland A. Werner  
ETH Zürich  
Zürich  
Switzerland  
Email: rwerner@ipw.agrl.ethz.ch

James White  
University of Colorado  
INSTAAR  
Boulder, Colorado  
USA  
Email: james.white@colorado.edu

Philip Wilson  
University of East Anglia  
Dereham  
United Kingdom  
Email: p.wilson1@uea.ac.uk

Jan Winderlich  
Max Planck Institute for Biogeochemistry  
Jena  
Germany  
Email: jwinder@bgc-jena.mpg.de

Douglas Worthy  
Environment Canada  
Toronto  
Canada  
Email: doug.worthy@ec.gc.ca

Xiaomei Xu  
University of California,  
Irvine  
USA  
Email: xxu@uci.edu

Camille Yver  
LSCE/IPSL  
Gif-sur-Yvette  
France  
Email: camille.yver@lsce.ipsl.fr

Christoph Zellweger  
Empa  
Dübendorf  
Switzerland  
Email: christoph.zellweger@empa.ch

Lingxi Zhou  
CAMS, CMA  
Beijing  
China  
Email: zhoulx@cams.cma.gov.cn
ANNEX IV

15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracer Measurement Techniques
(September 7–10, 2009, Jena, Germany)

Meeting agenda

Monday, 7 September

8:00–9:00 Registration
9:00–9:10 Organizers Information on general aspects of the meeting

General presentations

9:10–9:20 Martin Heimann, Welcome to MPI-BGC Jena


Greenhouse gases observations I: measurement networks (Chair: Martina Schmidt)

9:40–10:00 Jim Butler, Observation System Requirements to Support Greenhouse Gas Management Strategies

10:00–10:20 Justus Notholt, Thorsten Warneke, Paul Wennberg, Janina Messerschmidt, The TCCON network for the calibration of greenhouse gas column data and satellite validation

10:20–10:50 Coffee Break

10:50–11:10 Marcel van der Schoot, L. P. Steele, D. A. Spencer, P. B. Krummel, R. J. Francey, M. Schmidt, M. Ramonet, B. Wastine, Australian regional high precision GHG observation network : Southern Ocean network (CO2 sink) and Australian tropical atmospheric research station.


11:30–11:50 Ingeborg Levin et al., The planned European ICOS network including Central Analytical Laboratory

11:50–12:15 Discussion on ICOS and other regional network calibration strategies (Chair: D. Worthy / J. Butler)

12:15–13:30 Lunch

Calibration / propagation of scales for CO2 in air (Chair: Jim White)

13:30–13:50 Pieter P. Tans, Do we need the WMO Mole Fraction Scale for CO2 and other gases?

13:50–14:05 Kazuto Suda, Hidekazu Matsueda, Kazuhiro Tsuboi and Shinya Takatsuji, Recent history of CO2 standard gases in JMA
**Tuesday, 8 September**

**Intercomparison activities (Chair: H. Mukai)**


8:50–9:10 **Ken Masarie**, D. Chao and P. Tans, New Capabilities For Interpreting Comparison Data


9:30–9:50 **Andrew C. Manning**, What have we learnt from global intercomparison programmes and what should we do next?

9:50–10:20 Coffee Break

10:40–11:20 Various short contributions (~ 3’, max 10’) on flask / in situ intercomparison results at individual stations not already presented within national reports

11:20–11:40 General Discussion on intercomparison programmes (Chair: K. Masarie / B. Stephens)

Isotope calibration and measurements (Chair: Lingxi Zhou)

11:40–12:00 Jim White, C. B. Alden, B.H. Vaughn, S.E. Michel, J. Winokur, and V. Claymore: Uses and Limitations for Isotopes of Carbon Dioxide and Methane

12:00–12:20 Thomas Röckmann, Robina Shaheen, Christoph Janssen, Isotope exchange between CO₂ and O₃ in the stratosphere: atmospheric and laboratory measurements

12:20–13:30 Lunch

High precision CO₂ isotope analyses of air samples from the free tropical troposphere and upper troposphere-lowermost stratosphere region: The CARIBIC project


14:10–14:30 Jan Kaiser, How accurate do we know ¹³C/¹²C, ¹⁸O/¹⁶O and ¹⁷O/¹⁶O ratios in CO₂ and their corresponding delta values?

14:30–14:50 Magnus Wendeberg, J. M. Richter, M. Rothe, W.A. Brand, JRAS Isotope reference: A generalized VPDB scale anchor for CO₂ in air?

14:50–15:20 Coffee Break

15:20–15:40 Bruce Vaughn, J.W.C. White, S.E. Michel, J. Winokur and V. Claymore: Calibrations, Corrections, and Challenges for isotopes of Methane and Carbon Dioxide

15:40–16:00 Colin Allison, Jim White, Merging atmospheric δ¹³C data sets

16:00–16:30 General discussion on isotope calibration and measurements (Chair: R. Francey / M. Wendeberg)

16:30–18:00 Poster Session I
Wednesday, 9 September

**Measurement techniques and comparison (Chair: Doug Worthy)**

8:30–8:50  **David Griffith**, Nicholas Deutscher, Paul Fraser, Paul Krummel, FTIR analyzer for simultaneous high precision measurements of CO₂, d13-CO₂, CH₄, CO and N₂O: intercomparison measurements at Cape Grim

8:50–9:10  **Doug Baer**, Manish Gupta, Tom Owano, Robert Provencal, Ian McAlester, Feng Dong, Novel Instrumentation for Real-time Measurements of N₂O, CO, CO₂ and CH₄

9:10 –9:30  **Scott Richardson**, Natasha Miles, Kenneth Davis, Eric Crosson, Field testing of cavity ring-down spectroscopy instruments measuring CO₂

9:30–9:50  **Aaron Van Pelt**, Eric Crosson, Natasha Miles, Scott Richardson, Ken Davis, Christoph Thomas, Beverly Law, Recent developments in instrumentation for greenhouse gases and related tracer measurements


10:10–10:40  Open discussion on measurement techniques (Chair M. Ramonet / G. Brailsford)

10:40–11:00  Coffee Break

11:00-12:30  **Side Event**: TTorch (ESF RNP) Steering Committee meeting (please contact Alex Vermeulen)

11:00-12:30  Poster Session II

12:30–13:50  Lunch

**Measurements and techniques for O₂/N₂ and Ar/N₂ (Chair: A. Manning)**


14:10–14:30  **Markus Leuenberger**, Chiara Uglietti and Peter Nyfeler, Tracing local natural gas oxidation by means of oxygen to carbon dioxide ratio measurements


14:50–15:20  Open discussion on O₂/N₂ (Chair R. Keeling / M. Leuenberger)

15:20–15:50  Coffee

**Related Tracer Observations and Analysis (Chair: Paul Krummel)**

15:50-16:10  Jocelyn Turnbull, **Scott Lehman**, Pieter Tans, John Miller, John Southon, ¹⁴CO₂ Measurements in the NOAA/ESRL Co-operative Air Sampling Network: An update on measurements and data quality


16:50–17:10  **Camille Yver**, Martina Schmidt, Michel Ramonet, Mathilde Grand, Tropospheric hydrogen measurement in the RAMCES network

17:10–17:30  **Ingeborg Levin**, Tobias Naegler, Renate Heinz, Daniel Osusko, Emilio Cuevas, Andreas Engel, Johann Limberger, Ray L.Langenfelds, Bruno Neininger, Christoph v. Rohden, L. Paul Steele, Rolf Weller, Douglas E. Worthy, Sergej A. Zimov, Atmospheric observation-based global SF₆ emissions – comparison of top-down and bottom-up estimates

17:30–19:30  **Side Event**: ICOS Atmospheric stations instrumentation. For participation please contact Leo Rivier.

**Thursday, 10 September**

**Greenhouse gas observations II: Vertical distribution (L. Haszpra)**

8:30–8:45  Colm Sweeney, Anna Karion, Pieter Tans, Validation of high altitude measurements of CO₂ and CH₄ using the AirCore

8:45–9:00  **Charles Miller**, Challenges for Validating Space-based XCO₂ Data

9:00–9:15  **Gordon Brailsford**, V Sherlock, A Gomez, K Riedel, D Smale, M Kotkamp, J Robinson, B Connor, B Stephens, S Mikaloff-Fletcher, In situ and ground-based remote sensing measurements of atmospheric CO₂ in New Zealand

9:15–9:30  Open discussion on gaps and future needs in integrated observation systems (Chair: C. Gerbig / A. Vermeulen)

**Greenhouse gas observations III: national and site reports (Chair: H.E. Scheel)**

9:30–9:45  **Luciana V. Gatti**, Monica T. S. D’Amelio, John B. Miller, Andrew Crotwell, Luana S. Basso, Alexandre Martinewski, Ed Dlugokencky, Pieter Tans, GHG Inter-comparison NOAA/IPEN and Efforts in to start a GHG Network in Brazil

9:45–10:00  **Jooil Kim**, Bayarmaa Lkhagvadorj, Kyung-Ryul Kim, Understanding Northeast Asian CO₂ emissions from continuous monitoring at Gosan station

10:00–10:15  **E-G. Brunke**, C. Labuschagne, B. Parker and H-E. Scheel, Recent results from measurements of CO₂, CH₄, CO and N₂O at the GAW station Cape Point

10:15–10:30  **Jan Winderlich**, HuiLin Chen, Annette Höfer, Christoph Gerbig, Martin Heimann, Continuous CO₂/CH₂ measurement at Zotino Tall Tower Observatory (ZOTTO) in Central Siberia

10:30–11:00  Coffee Break

11:00–11:15  **Michela Maione**, Umberto Giosa, Francesco Furlani, Jgor Arduini, Francesco Graziosi, Paolo Bonasoni, Paolo Cristofanelli, Rocco Duchi, Angela Marinoni, Long term observations of climate altering gases at the "O. Vittori" observatory at Monte Cimone (Italy)
11:15–11:30  Alex Vermeulen, Elena Popa, Pim van den Bulk, Piet Jongejan, Cabauw station report

11:30–11:45  Martina Schmidt, Greenhouse gas measurements at Trainou Tower (France)

11:45–12:00  Lingxi Zhou, Lixin LIU, Shuangxi FANG, Fang ZHANG, Bo YAO, Min WEN, Lin XU, Shuai GU, Kunpeng ZANG, Lingjun XIA, Xiaochun ZHANG, Yupu WEN, Xiuji ZHOU, Network Observation of Greenhouse Gases and Related Tracers in China

12:00–12:15  N.K. Indira, Efforts in measuring greenhouse gases by setting up stations in India

12:15–13:30  Lunch

13:30–16:00  Plenary discussion and approval of the draft recommendations
                (Chair: I. Levin)

14:30 - 15:00  Coffee Break

16:00  End of the meeting
GLOBAL ATMOSPHERE WATCH REPORT SERIES

8. Review of the Chemical Composition of Precipitation as Measured by the WMO BAPMoN by Prof. Dr. Hans-Walter Georgii, February 1982.
14. Effects of Sulphur Compounds and Other Pollutants on Visibility by Dr. R.F. Pueschel, April 1983.
19. Forecasting of Air Pollution with Emphasis on Research in the USSR by M.E. Berlyand, August 1983.


26. Sulphur and Nitrogen in Precipitation: An Attempt to Use BAPMoN and Other Data to Show Regional and Global Distribution by Dr. C.C. Wallén. April 1986 (WMO TD No. 103).


29. Recommendations on Sunphotometer Measurements in BAPMoN Based on the Experience of a Dust Transport Study in Africa by Dr. Guillaume A. d'Almeida. September 1985 (WMO TD No. 67).


43. Recent progress in sunphotometry (determination of the aerosol optical depth). November 1986.


58. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the years 1986 and 1987 (WMO TD No. 306).


62. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the year 1988 (WMO TD No. 355).


69. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1989 (WMO TD No. 400).


72. Integrated Background Monitoring of Environmental Pollution in Mid-Latitude Eurasia by Yu.A. Izrael and F.Ya. Rovinsky, USSR (WMO TD No. 434).


75. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1990 (WMO TD No. 447).


77. Report of the WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, Lake Arrowhead, California, 14-19 October 1990.


84. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at GAW-BAPMoN sites for the year 1991 (WMO TD No. 543).

85. Chemical Analysis of Precipitation for GAW: Laboratory Analytical Methods and Sample Collection Standards by Dr Jaroslav Santroch (WMO TD No. 550).


89. 4th International Conference on CO₂ (Carqueiranne, France, 13-17 September 1993) (WMO TD No. 561).

91. Extended Abstracts of Papers Presented at the WMO Region VI Conference on the Measurement and Modelling of Atmospheric Composition Changes Including Pollution Transport, Sofia, 4 to 8 October 1993 (WMO TD No. 563).


97. Quality Assurance Project Plan (QAPjP) for Continuous Ground Based Ozone Measurements (WMO TD No. 634).


104. Report of the Fourth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the First Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE, Garmisch-Partenkirchen, Germany, 13 to 17 March 1995 (WMO TD No. 689).


113. The Strategic Plan of the Global Atmosphere Watch (GAW) (WMO TD No. 802).


120. WMO-UMAP Workshop on Broad-Band UV Radiometers (Garmisch-Partenkirchen, Germany, 22 to 23 April 1996) (WMO TD No. 894).


129. Guidelines for Atmospheric Trace Gas Data Management (Ken Masarie and Pieter Tans), 1998 (WMO TD No. 907).


131. WMO Workshop on Regional Transboundary Smoke and Haze in Southeast Asia (Singapore, 2 to 5 June 1998) (Gregory R. Carmichael). Two volumes.

133. Workshop on Advanced Statistical Methods and their Application to Air Quality Data Sets (Helsinki, 14-18 September 1998) (WMO TD No. 956).
135. Sixth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Zurich, Switzerland, 8-11 March 1999) (WMO TD No.1002).
139. The Fifth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Halkidiki, Greece, September 1998)(WMO TD No. 1019).
149. Comparison of Total Ozone Measurements of Dobson and Brewer Spectrophotometers and Recommended Transfer Functions (prepared by J. Staehelin, J. Kerr, R. Evans and K. Vanicek) (WMO TD No. 1147).
150. Updated Guidelines for Atmospheric Trace Gas Data Management (Prepared by Ken Maserie and Pieter Tans (WMO TD No. 1149).
154. WMO/IMEP-15 Trace Elements in Water Laboratory Intercomparison. (WMO TD No. 1195).


170. WMO/GAW Expert Workshop on the Quality and Applications of European GAW Measurements (Tutzing, Germany, 2-5 November 2004) (WMO TD No. 1367).


176. The Tenth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Northwich, United Kingdom, 4-8 June 2007) (WMO TD No. 1420), 61 pp, March 2008.


182. IGACO-Ozone and UV Radiation Implementation Plan (WMO TD No. 1465), 49 pp, April 2009.


193. Guidelines for Reporting Total Ozone Data in Near Real Time (WMO TD No. 1552).