

# EXPERT GROUP RECOMMENDATIONS

## 14<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques

(Helsinki, Finland, 10-13 September 2007)



**World  
Meteorological  
Organization**  
Weather • Climate • Water



## Table of Contents

### EXPERT GROUP RECOMMENDATIONS

<b>1.</b>	<b>CALIBRATION of GAW MEASUREMENTS - WMO CENTRAL CALIBRATION LABORATORIES ..</b>	<b>2</b>
1.1	Background.....	2
1.2	General requirements for Central Calibration Laboratories.....	2
1.3	Maintenance of calibration by GAW measurement laboratories .....	3
<b>2.</b>	<b>SPECIFIC REQUIREMENTS for CO<sub>2</sub> CALIBRATION.....</b>	<b>4</b>
<b>3.</b>	<b>SPECIFIC REQUIREMENTS FOR CO<sub>2</sub> STABLE ISOTOPE CALIBRATION .....</b>	<b>4</b>
3.1	Background.....	4
3.2	Current achievements for CO <sub>2</sub> stable isotope calibrations .....	4
3.3	Recommendations for CO <sub>2</sub> stable isotope calibrations .....	5
<b>4.</b>	<b>SPECIFIC REQUIREMENTS for RADIOCARBON in CO<sub>2</sub> CALIBRATION.....</b>	<b>6</b>
4.1	Background.....	6
4.2	<sup>14</sup> CO <sub>2</sub> calibration and intercomparison activities and respective recommendations .....	6
<b>5.</b>	<b>SPECIFIC REQUIREMENTS FOR O<sub>2</sub>/N<sub>2</sub> CALIBRATION.....</b>	<b>6</b>
5.1	Background.....	6
5.2	O <sub>2</sub> /N <sub>2</sub> calibration and intercomparison activities .....	7
5.3	Recommendations .....	7
<b>6.</b>	<b>SPECIFIC REQUIREMENTS FOR CH<sub>4</sub> CALIBRATION .....</b>	<b>7</b>
<b>7.</b>	<b>SPECIFIC REQUIREMENTS FOR N<sub>2</sub>O CALIBRATION.....</b>	<b>8</b>
7.1	Background.....	8
7.2	Recommendations.....	8
<b>8.</b>	<b>SPECIFIC REQUIREMENTS TO SF<sub>6</sub> CALIBRATION .....</b>	<b>8</b>
8.1	Background.....	8
8.2	Recommendations .....	9
<b>9.</b>	<b>SPECIFIC REQUIREMENTS FOR CO CALIBRATION .....</b>	<b>9</b>
9.1	Background.....	9
9.2	CO intercomparison activities .....	9
9.3	Specific recommendations for CO calibration at the WMO-GAW CCL and at GAW stations.....	9
<b>10.</b>	<b>SPECIFIC REQUIREMENTS FOR H<sub>2</sub> CALIBRATION.....</b>	<b>10</b>
10.1	Background.....	10
10.2	Recommendations.....	11
<b>11.</b>	<b>GENERAL RECOMMENDATIONS FOR QUALITY CONTROL OF ATMOSPHERIC TRACE GAS MEASUREMENTS .....</b>	<b>11</b>
11.1	General .....	11
11.2	Flask intercomparison.....	12
11.3	Recommendations for in-situ measurements .....	12
<b>12.</b>	<b>RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING .....</b>	<b>13</b>
12.1	Data management .....	13
12.2	Data archiving .....	13
12.3	Co-operative data products .....	13
<b>13.</b>	<b>SUMMARY OF RECENT INTERNATIONAL PLANNING OF ATMOSPHERIC TRACE GAS MEASUREMENT STRATEGIES.....</b>	<b>14</b>
Annex 1.....		19

## EXPERT GROUP RECOMMENDATIONS

The scientists present at the 14<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, 10-13 September 2007 in Helsinki, Finland, recommend the following procedures and actions, to achieve the adopted WMO goals for the Global Atmosphere Watch (GAW) network comparability among different laboratories and various components as summarised in Table 1. Definitions of terms concerning precision, accuracy etc. are given in Table 2.

**Table 1: Recommended inter-laboratory (network) comparability of components discussed.**

Component	Inter-Laboratory comparability
CO <sub>2</sub>	± 0.1 ppm (± 0.05 ppm in the southern hemisphere)
δ <sup>13</sup> C-CO <sub>2</sub>	± 0.01 ‰
δ <sup>18</sup> O-CO <sub>2</sub>	± 0.05 ‰
Δ <sup>14</sup> C-CO <sub>2</sub>	± 1 ‰
O <sub>2</sub> /N <sub>2</sub>	± 1 per meg
CH <sub>4</sub>	± 2 ppb
CO	± 2 ppb
N <sub>2</sub> O	± 0.1 ppb
H <sub>2</sub>	± 2 ppb
SF <sub>6</sub>	± 0.02 ppt

**Table 2: Definitions of terms related to data quality.**

(cf. <http://www.empa.ch/gaw/glossary.html> for a more comprehensive glossary)

Term	Definition	Ref.
Accuracy (of a test method)	The closeness of agreement between a test result and the accepted reference value. <sup>(a)</sup>	1
Comparability	Mean difference between two (or more) sets of measurements, which should be within given limits. <sup>(b)</sup>	
Bias	The difference between the expectation of the test results and an accepted reference value.	2
Precision	Degree of internal agreement among independent measurements made under specific conditions. <sup>(c)</sup>	2
Repeatability (of results of measurements)	Closeness of the agreement between the results of successive measurements of the same measure and carried out under the same conditions of measurement. <sup>(d)</sup>	2
Reproducibility (of results of measurements)	Closeness of the agreement between results of measurements of the same measure and carried out under changed conditions of measurement. <sup>(d)</sup>	2
Uncertainty  (Standard uncertainty)	A parameter associated with the result of a measurement that characterises the dispersion of values that could reasonably be attributed to the measurement. <sup>(e,f)</sup>  (Uncertainty of the result of a measurement expressed as a standard deviation)	2  3
Coverage factor	numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty [3] Note: A coverage factor of k=2 typically yields expanded uncertainties that correspond to a 95% confidence interval.	

<sup>(a)</sup> Note that accuracy 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) Precision must not be confused with accuracy or trueness. It is a measure for the dispersion of values.*

*(d) 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  $\pm 1$  standard deviations.*

*(e) The concept of "uncertainty" is explained in detail in ISO Publications 1995.*

*(f) In practice the term "error (measurement error)" seems to be often used when actually "uncertainty" is meant. An error is viewed as having two components, a random and a systematic component. As further stated in ISO Publications (1995), "error" is an idealised concept and errors cannot be known exactly. "Error" and "uncertainty" are not synonyms, but represent completely different concepts.*

*Ref. 1, 2, 3: ISO Publications 1993a & b; 1995.*

## **1. CALIBRATION OF GAW MEASUREMENTS - WMO 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 comparability 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 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, 2007) to achieve and maintain inter-comparability of global observations. WMO-GAW CCLs currently exist for the following trace gases: carbon dioxide (CO<sub>2</sub>, at NOAA/ESRL), methane (CH<sub>4</sub>, at NOAA/ESRL), nitrous oxide (N<sub>2</sub>O, at NOAA/ESRL) and carbon monoxide (CO, at NOAA/ESRL). At the 14<sup>th</sup> WMO Experts Meeting in Helsinki, Finland, the Max-Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, has been asked and agreed to act as the WMO-GAW CCL for stable isotopes in CO<sub>2</sub> (only for CO<sub>2</sub>-in-air measurements).

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

### **1.2 General requirements for Central Calibration Laboratories**

- a) The CCL maintains the WMO Mole Fraction Scale for the respective gas mixing ratio in air by carrying out regular determinations of this primary scale with an absolute method. 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.
- c) While the WMO scale for each trace gas is defined and maintained by an operational designated CCL, WMO and IAEA welcome efforts that monitor, confirm, or improve CCL links to Primary Reference Materials or Fundamental Constants. Such efforts should involve cooperation with National Metrology Institutes (NMI).
- 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 absolute measurements and comparisons. Revisions of the WMO Scale by the GAW CCL must be distinguished by name, such as WMO X2005, 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.
- g) The CCL provides calibrated reference gas mixtures of gas mixtures-in-air (called "transfer standards") at the lowest possible cost.
- h) The CCL provides for a backup in case a catastrophic event occurs.
- i) 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 comparable to the degree that is required (see Section 11).
- j) In order to assure comparability 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-robins 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 CO<sub>2</sub> mole fractions has the highest priority in the round-robins, 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 its link to the WMO Scales by having its laboratory standards regularly re-calibrated by the CCL. It is recommended that the laboratory primary gases are kept 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 maintains a strictly hierarchical scheme of transferring the calibration of its laboratory primary gases ("laboratory 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 minimise the risk of creating offsets that are coherent among laboratories within the same region, each laboratory should maintain the shortest possible direct link to the WMO-GAW 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 and comparability 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 CO<sub>2</sub>, are adjusted in reference air mixtures, the isotopic composition of the cylinder trace gas remains close to that in air. 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.

## **2. SPECIFIC REQUIREMENTS FOR CO<sub>2</sub> CALIBRATION**

- a) The primary scale for CO<sub>2</sub> shall range from approximately 180 ppm (covering atmospheric values in ice cores) to over 500 ppm. The scale is currently embodied in a set of 15 CO<sub>2</sub>-in-air mixtures in large high-pressure cylinders.
- b) Since the WMO scale was maintained until 1995 by the Scripps Institution of Oceanography, 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.
- c) The CCL is encouraged to make available on its web site 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  $\pm 0.03$  ppm or less among the CO<sub>2</sub> calibration scales of laboratories participating in the WMO-GAW programme, the CCL shall aim to provide the calibrated standards for transfer of the CO<sub>2</sub> scale to secondary and tertiary standards at that level of consistency.
- e) Each WMO-GAW measurement laboratory must actively maintain its link to the WMO Scale by having its laboratory standards for CO<sub>2</sub> re-calibrated by the CCL every three years.

## **3. SPECIFIC REQUIREMENTS FOR CO<sub>2</sub> STABLE ISOTOPE CALIBRATION**

### **3.1 Background**

Efforts for comparing the stable isotopes of CO<sub>2</sub> in air have continued in the last two years and results were reported during the 14<sup>th</sup> WMO Meeting of CO<sub>2</sub> Experts (see contributions in this volume). These intercomparison exercises are indicative of the progress that has been made in CO<sub>2</sub> stable isotope ratio measurements in air. Moreover, more fundamental issues have been addressed like release of CO<sub>2</sub> from carbonates, <sup>17</sup>O and N<sub>2</sub>O corrections. The results and arguments presented allow a number of conclusions to be drawn on the sources of measured isotopic differences between participating laboratories. The implemented intercomparison programmes (e.g. sausage flasks, high pressure cylinder round-robins, pure CO<sub>2</sub> ampoules and whole-air mixtures) are strongly recommended to be continued in the future as a routine surveillance and quality control tool.

### **3.2 Current achievements for CO<sub>2</sub> stable isotope calibrations**

- a) The possible experimental reasons for systematic offsets in measured CO<sub>2</sub> isotopic compositions are different for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . In  $\delta^{13}\text{C}$ , scaling errors seem the most prominent issue whereas  $\delta^{18}\text{O}$  suffers from exchange of oxygen with water as well as from different techniques of generating CO<sub>2</sub> from carbonate reference material.
- b) The possible underlying causes must be addressed separately for clean (pure) CO<sub>2</sub> and for CO<sub>2</sub> in air. Clean CO<sub>2</sub> is developed from carbonates or is available as a calibrated clean gas. In contrast, CO<sub>2</sub> in air is always accompanied by N<sub>2</sub>O. In addition, traces of co-trapped air from the cryogenic separation as well as issues of trapping efficiency and isotopic alterations during trapping can change the measured isotopic ratios.
- c) There is only one internationally recognized isotope scale for  $\delta^{13}\text{C}$ : VPDB. This scale has recently been refined by IUPAC and IAEA via adding a second fixed calibration point (L-SVEC Li<sub>2</sub>CO<sub>3</sub> = -46.6‰ versus VPDB). As a result, a number of international secondary reference materials still must be newly evaluated, including reference materials that have been used for CO<sub>2</sub>-in-air isotopic calibration (see 3.3b)). Intercomparability of  $\delta^{13}\text{C}$  values of air CO<sub>2</sub> in the past has mainly suffered from different amounts of cross contamination during mass spectrometric measurement (eta-effect). The new scaling rule should be able to adequately address this problem. In order to implement this rule into CO<sub>2</sub>-in-air analyses a practical solution (for instance two air standards with <sup>13</sup>CO<sub>2</sub> isotopic ratios similar to NBS19 and LSVEC) is needed and suggestions are welcome.

- d) To establish a tie to the VPDB scale kept by the IAEA, standards for CO<sub>2</sub>-stable isotopes-in-air must be created. MPI-BGC Jena is now able to accurately prepare CO<sub>2</sub> from carbonate material and mix this with CO<sub>2</sub>-free air in a fully automated system. These mixtures can now serve as air reference material ('J-RAS', Jena Reference Air Set) and will provide the required firm link of air-CO<sub>2</sub> measurements to the VPDB scale (Ghosh et al., 2005, Brand et al., this volume). The long-term integrity of CO<sub>2</sub>-in-air isotope results should, however, be based on carbonate material. The future production and dissemination of the J-RAS air-CO<sub>2</sub> anchor to the VPDB scale has been funded by the European Community under the IMMEC project. Given the progress made in the last two years MPI-BGC is asked to take a leading role for unifying the stable isotope scales across the community and act as a WMO-GAW Central Calibration Lab for isotopes (CCL) for these species by providing the JRAS air-CO<sub>2</sub>. BGC Jena has agreed to produce this reference material and provide participating laboratories with a new set of gases at a rate of two per year. Propagation of the scale will be performed only via CO<sub>2</sub>-in-air.
- e) Comparability of δ<sup>18</sup>O data between laboratories remains poor (progress has been made with inter-laboratory precision of close to ±0.2‰, which is still far off the goal of ±0.05‰ (Table 1)). The availability of reference air with assigned isotope values should help to unify reported δ<sup>18</sup>O data, irrespective of their accuracy.
- f) The major cause for the current discrepancies is not scaling (like for δ<sup>13</sup>C) because air-CO<sub>2</sub> is close to VPDB-CO<sub>2</sub>. Progress evidently cannot be made by having the individual laboratories generate CO<sub>2</sub> from NBS19. MSC, NIES and MPI-BGC have reported on progress in our understanding of the underlying causes for the discrepancies. These studies need to be continued and the same partners are asked to further investigate this issue and report on the results during the next meeting. The new findings will enable to establish a more rigorous relation to the VSMOW scale as well.

### 3.3 Recommendations for CO<sub>2</sub> stable isotope calibrations

- a) Since δ<sup>13</sup>C of atmospheric CO<sub>2</sub> is close to -8‰ on the VPDB scale, any secondary reference material used for high-precision isotope work around this value needs to be re-evaluated. The generation of two pure CO<sub>2</sub> reference materials (NARCIS 1 and 2) by NIES with a composition of NARCIS 1 close to air CO<sub>2</sub> and NARCIS 2 close to NBS 19 has greatly facilitated intercomparison of isotope measurements on pure CO<sub>2</sub> from different laboratories. For establishing a set of recommended values from the intercomparison, more data are required for NARCIS 2. MSC, NIES and MPI-BGC have presented new results comparing these materials with CO<sub>2</sub> generated from the primary references thereby assigning new delta values with very small error margins.
- b) The availability and careful calibration of other CO<sub>2</sub> reference materials from NIST (carbon dioxide: RM 8562-8564) has proven to be an independent and reliable resource for tracing offsets between individual laboratory scales. These reference materials have already been re-assessed on the 2-point VPDB scale with very small changes to the original values (i.e. RM 8562: δ<sup>13</sup>C = -3.72‰, RM 8564: δ<sup>13</sup>C = -10.45‰, RM 8563: δ<sup>13</sup>C = -41.59‰ (Coplen et al., 2006)). It is recommended to NIST to insure future availability of these materials.
- c) Recent findings of the world water pools related fractionation laws for <sup>18</sup>O/<sup>16</sup>O and <sup>17</sup>O/<sup>16</sup>O require a new ruling for high-accuracy calibration of δ<sup>13</sup>C in air CO<sub>2</sub>. The recommendation of the 13<sup>th</sup> WMO experts meeting to exclusively use the ratio assumption set provided by Assonov and Brenninkmeijer (2003a; 2003b) is endorsed. Mass spectrometry evaluation software as well as individual laboratory software packages should be adapted correspondingly.
- d) The need of a calcite reference material with carbon and oxygen isotopic compositions close to atmospheric CO<sub>2</sub> is re-iterated and emphasized. The material is necessary in order to eliminate ambiguities arising from different mass spectrometric scaling factors and other corrections (<sup>17</sup>O correction, N<sub>2</sub>O correction, etc.).

## 4. SPECIFIC REQUIREMENTS FOR RADIOCARBON IN CO<sub>2</sub> 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 <sup>14</sup>C activity are available and distributed by e.g. IAEA.

For atmospheric measurements of  $\Delta^{14}\text{C}$  in CO<sub>2</sub>, two main sampling techniques are used: High-volume CO<sub>2</sub> absorption in basic solution or by molecular sieve and whole-air flask sampling (typically 1.5-5 L flasks). Two methods of analysis are used: Conventional radioactive counting and Accelerator Mass Spectrometry (AMS). The current level of measurement uncertainty for  $\Delta^{14}\text{C}$  in CO<sub>2</sub> 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 inter-laboratory comparability is recommended (Table 1).

### 4.2 <sup>14</sup>CO<sub>2</sub> calibration and intercomparison activities and respective recommendations

Calibration 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 still solely rely on the Standard Reference Materials distributed by IAEA. But we recommend that laboratories conducting small-volume flask sampling and AMS analysis should use whole air cylinders as reference material that is similar to the air samples measured.

The first intercomparison activity for  $\Delta^{14}\text{C}$  in CO<sub>2</sub> was initiated at the 13<sup>th</sup> WMO/IAEA Meeting of CO<sub>2</sub> Experts in Boulder Colorado (WMO GAW Report # 168, 2006) and is currently underway. The intercomparison is being managed by University of Colorado and NOAA/ESRL/GMD with support from WMO. Six laboratories are currently participating by sending flasks to NOAA to be filled with air from two whole-air reference cylinders. This intercomparison exercise should report results by the 15<sup>th</sup> WMO Meeting of Experts.

As the current intercomparison excludes the laboratories using high-volume sampling techniques, we propose the following potential methods for future intercomparison that could include laboratories using either type of sampling technique:

- a) Splitting and dissemination of high-volume pure CO<sub>2</sub> samples to the laboratories.
- b) Co-located sampling at observation stations.

## 5. SPECIFIC REQUIREMENTS FOR O<sub>2</sub>/N<sub>2</sub> CALIBRATION

### 5.1 Background

Measurements of the changes in atmospheric O<sub>2</sub>/N<sub>2</sub> ratio are useful for constraining sources and sinks of CO<sub>2</sub> and testing land and ocean biogeochemical models. The relative variations in O<sub>2</sub>/N<sub>2</sub> ratio are very small but can now be observed by at least six techniques. These techniques can be grouped into two categories: (1) those which measure O<sub>2</sub>/N<sub>2</sub> ratios directly (mass spectrometry and gas chromatography), and those which effectively measure changes in the O<sub>2</sub> 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 O<sub>2</sub>/N<sub>2</sub> ratio. For the mole-fraction type measurements, this requires accounting for dilution due to variations in CO<sub>2</sub> and possibly other gases. If synthetic air is used as a reference material, corrections may also be needed for differences in Ar/N<sub>2</sub> ratio. By convention, O<sub>2</sub>/N<sub>2</sub> ratios are expressed as relative deviations compared to a reference

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

where  $\delta(\text{O}_2/\text{N}_2)$  is multiplied by  $10^6$  and expressed in “per meg” units. 1 per meg is a dimensionless unit equivalent to 0.001 per mille. The  $\text{O}_2/\text{N}_2$  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 reports on its own scale.

## 5.2 $\text{O}_2/\text{N}_2$ calibration and intercomparison activities

At the 12<sup>th</sup> WMO  $\text{CO}_2$  Experts Meeting in Toronto (WMO GAW Report # 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, a “sausage flasks” intercomparison programme, and a “round-robin cylinder” intercomparison 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 air from high-pressure gas cylinders.

Details of the GOLLUM programme can be found in the WMO Technical Document No. 1275. A document was prepared and distributed to the participating laboratories in the GOLLUM programme outlining the required laboratory protocols. The GOLLUM programme has been coordinated by A. Manning at the University of East Anglia, with the  $\text{O}_2$  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.

The round robin cylinders (2 sets of 3 aluminium cylinders) were prepared in 2004 at SIO and started their worldwide rotations in 2005. At the time of the 14<sup>th</sup> WMO Experts meeting, two circuits of the round-robin cylinders were completed and three 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  $\pm 3$  per meg, the estimated precision of a trend measurement in the SIO lab.

In addition to preparing cylinders for the GOLLUM programme, the  $\text{O}_2$  lab at SIO has prepared high-pressure cylinders for a number of laboratories. These cylinders have provided another means to assess laboratory scale differences.

## 5.3 Recommendations

- a) Continue both, the round-robin cylinder and sausage flask components of the GOLLUM programme for at least two more years.
- b) Establish a web page for logistical support and for dissemination of results of the GOLLUM programme.
- c) Encourage SIO to continue to provide reference gases to laboratories on request at reasonable cost.
- d) Encourage additional efforts, such as overlapping flask sampling from different programmes, to compare  $\text{O}_2/\text{N}_2$  scales and methods between programmes.
- e) Encourage the standardisation of existing  $\text{O}_2/\text{N}_2$  techniques, and particularly to identify and correct weaknesses in laboratories’ current techniques in sample collection, sample analysis, and in defining and propagating calibration scales.

## 6. SPECIFIC REQUIREMENTS FOR $\text{CH}_4$ CALIBRATION

At the 12<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, it was agreed that NOAA would assume the role of the WMO-GAW Central Calibration Laboratory (CCL) for methane. 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  $\text{nmol mol}^{-1}$ , 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  $\text{CH}_4$  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. The CCL will transfer the CH<sub>4</sub> scale to calibrated CH<sub>4</sub>-in-air standards with an uncertainty of <1 nmol mol<sup>-1</sup>. All laboratories that participate in the GAW programme must calibrate measurements to relative to the WMO CH<sub>4</sub>-in-air mole fraction scale and report them to the WMO World Data Centre for Greenhouse Gases in Japan.

Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its laboratory standards for CH<sub>4</sub> re-calibrated by the CCL every six years.

## **7. SPECIFIC REQUIREMENTS FOR N<sub>2</sub>O 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, also in the frame of the global nitrogen cycle. Systematic differences between mole fractions reported by different laboratories are large compared to atmospheric gradients. The mean interhemispheric difference in N<sub>2</sub>O 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 N<sub>2</sub>O in the troposphere. This necessitates not only high measurement precision, but also high consistency among assigned values for standards. Inter-laboratory comparability of 0.1 ppb is needed.

### **7.2 Recommendations**

- a) NOAA/ESRL/GMD serves as the CCL for nitrous oxide. It maintains a gravimetrically-prepared N<sub>2</sub>O-in-air standard scale consisting of 13 WMO Primary Standards covering the range of 260 – 370 nmole mol<sup>-1</sup> (Hall et al., 2007). The reproducibility of NOAA N<sub>2</sub>O calibrations is estimated to be 0.2 ppb at the 95% confidence level. Efforts to improve precision and reproducibility are ongoing.
- b) The CCL will include N<sub>2</sub>O calibration results in the web-based database maintained by the NOAA Carbon Cycle Greenhouse Gases group.
- c) Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its laboratory standards for N<sub>2</sub>O re-calibrated by the CCL every three years.
- d) We encourage the development of new or improved techniques, such as optical techniques, that would lead to improvements in precision and reproducibility.

## **8. SPECIFIC REQUIREMENTS TO SF<sub>6</sub> CALIBRATION**

### **8.1 Background**

Sulfurhexafluoride (SF<sub>6</sub>) is a long-lived trace gas with strong infrared absorbance properties. Emissions of SF<sub>6</sub> are 22800 times more effective than CO<sub>2</sub> on a per-mass basis over a 100-year time scale. The tropospheric mixing ratio of SF<sub>6</sub> has increased steadily, with a current growth rate of about 0.22 ppt yr<sup>-1</sup>. The steady growth rate and long lifetime (~3000 years) make it a useful tracer of atmospheric transport, including stratospheric “age-of-air determination”. Because SF<sub>6</sub> 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.

SF<sub>6</sub> is typically measured using GC-ECD techniques in a manner similar to that of N<sub>2</sub>O. There are currently three scales in use: NOAA, Univ. of Heidelberg, and SIO. Although there have been few formal SF<sub>6</sub> comparisons, informal comparisons show that scale comparability is generally good. 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. The formation of a WMO-GAW CCL for SF<sub>6</sub>, responsible for maintaining a scale and facilitating the distribution of standards, would benefit the atmospheric (SF<sub>6</sub>) measurement community.

## **8.2 Recommendations**

- a) Establish a WMO-GAW CCL for SF<sub>6</sub>.
- b) Include SF<sub>6</sub> in WMO-GAW round-robin experiments when possible.
- c) Investigations are encouraged to explore advanced techniques to improve measurement precision.

## **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 provides column abundances; wide geographical coverage of CO with some limited vertical resolution is becoming available from several satellite-based sensors (MOPITT-TERRA, SCIAMACHY-ENVISAT, TESS-AURA). 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.

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  $\pm 2$  ppb ( $k=2$ ). Unlike CO<sub>2</sub>, 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: a) Available measurement techniques can be non-linear and do not have the stability or precision for long-term measurements of low drift rates. b) 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. c) 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 inter-comparison with diluted gases from high-concentration cylinders (10 ppm) is regularly required.

### **9.2 CO intercomparison activities**

NOAA ESRL's Carbon Cycle Group has on two occasions organized round-robin tests involving 5 to 10 laboratories. This has helped "the international insitu CO measurement community" enormously, but also exposed some drift and inconsistency in the NOAA ESRL calibration scale, as well as the gravimetric technique.

WMO through EMPA and its WMO-GAW WCC for CO has endeavoured to improve the international comparability 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 Specific recommendations for CO calibration at the WMO-GAW CCL and at GAW stations**

- a) Inter-laboratory comparability for global GAW stations to  $\pm 2$  ppb (mean bias) and standards to  $\pm 1$  ppb or 0.5% (whichever is greater, expanded uncertainty,  $k=2$ ) are needed. Comparisons of CO measurements among laboratories (through round-robins, and other intercomparison 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 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. Based upon several sets of gravimetric standards this scale was revised in 2000. The WMO-2000 scale still underwent some adjustments, and NOAA ESRL is encouraged to 'freeze' the current scale prepared in 2006 as WMO-2006 scale. It is this WMO-2006 scale that GAW stations should refer to. 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.

- c) The frequency of the preparation of gravimetric Primary Standards should be increased to a biannual interval to determine any long term drift of the scale. Furthermore the CCL should improve its capability of making accurate dilutions as a second means of assuring the stability of the WMO Primary Scale.
- d) Standard drift remains a serious issue for CO measurements. Therefore an annual recalibration of at least one of a station's laboratory standards is strongly suggested.
- e) In order to be able to use CO as a tracer for fossil fuel CO<sub>2</sub> at regional GAW or even moderately polluted sites, the CCL should extend its primary scale towards higher mole fractions (up to 1000 ppb).
- f) The WMO SAG Reactive Gases' Subgroup on Carbon Monoxide 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 being developed.
- g) 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.
- h) EMPA is the designated World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA) and is in charge of conducting system and performance audits including intercomparisons at global GAW stations. Audit results and other inter-comparison results should be archived along with CO data at the WDCGG or with GAWSIS.
- i) Within the GAW programme, regular inter-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.
- j) It should be explored if, in this particular case of a trace gas with large danger of drifting standards, regional round robins could help to maintain the link to the CCL.
- k) 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. WCC-EMPA should take the lead in establishing the practicality of such an approach and in assessing the resulting uncertainties for the ambient CO measurements.
- l) There is a large number of stations (some of which are regional GAW stations) that are equipped with less sophisticated (or calibrated) CO monitoring equipment. 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, inter-comparison and improved accessibility of these observations.

## **10. SPECIFIC REQUIREMENTS FOR H<sub>2</sub> CALIBRATION**

### **10.1 Background**

Molecular hydrogen plays a significant role in global atmospheric chemistry due to its interference in CH<sub>4</sub>-CO-OH cycling. The balance of hydrogen could change with the implementation of a new H<sub>2</sub> 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 intercomparison 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 (see the GAW Strategic Plan: 2008-2015; section 7.3.6 referenced in footnote1).

## 10.2 Recommendations

- a) A concerted effort to consolidate the NOAA, CSIRO/AGAGE, EuroHydros and other calibration activities is urgently needed to enable a collaborative global network for hydrogen measurements. These measurement groups are strongly encouraged to establish a common calibration scale. This scale should cover the range from 350-1000 ppb. As part of this effort the existing scales need to be harmonized and the history of their agreement needs to be documented. Links to the BIPM should be explored.
- b) In addition, temporal changes of inter-laboratory biases that have not always been related to scale changes, underline the necessity to continue intercomparison of hydrogen data. These exercises have already been made use of and should be expanded with more high-frequency (i.e. at least monthly) comparisons.
- c) 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 primary standards is discouraged.
- d) Appropriate characterization and regular check of the detector response is required given the strong non-linear response of the commonly used HgO reduction detectors.
- e) There is currently no WMO-GAW CCL for atmospheric molecular hydrogen. In the course of the scale harmonisation process institutions that are in the position of taking this role should be identified and proposed to attend WMO Experts meetings. The decision on this future CCL should be based on documentation on internal and external measurement consistency of the respective laboratory, its ability to assure the stability of the H<sub>2</sub> primary standards, and its ability to supply standards to the community.

## 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 ICP activities as they relate to the respective recommendations.

### 11.1 General

- 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 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-CO<sub>2</sub> (and other trace gas) standards: Working standards must have natural levels of N<sub>2</sub>, O<sub>2</sub>, and Ar to avoid biases e.g. due to different pressure-broadening

effects between sample and calibration gases. CO<sub>2</sub> standards should have CO<sub>2</sub> with ambient δ<sup>13</sup>C ratios.

- c) Besides round-robin comparisons, more frequent intercomparison activities between pairs of laboratories which incorporate the analyses of actual air samples, such as flask air intercomparison (ICP) experiments or collocated in-situ instruments are strongly recommended. The tremendous benefit of routine intercomparison 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 at an early stage and identify discrepancies in the results quickly.
- d) Flask sampling programmes should be implemented at observational sites making continuous measurements as well as automated data processing for these intercomparison projects. A detailed comparison of collocated continuous and flask measurements will be performed until the next WMO Experts meeting which will form the basis to assess the usefulness of such a programme and to decide if audits also for CO<sub>2</sub> need be performed at GAW stations. This would require an instrumental set-up which is easy to ship around.
- e) Clear protocols and reports of experience gained in intercomparison projects should be provided. Results should be published and readily accessible. 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.
- f) Defensible uncertainty estimates: Investigators should report uncertainty estimates for their data and provide details of how these estimates are calculated and what activities are used to verify them. ISO nomenclature shall be used for uncertainty estimates and discussions.
- g) Deviations from recommendations: We recognize the value of innovation and experimentation with new approaches. However, we stress that deviations from established practices should be fully tested to confirm that the new approach does not introduce bias into the measurements. Furthermore, the results of such experimentation should be reported at future WMO CO<sub>2</sub> Experts meetings and similar venues, and published in the peer-reviewed literature whenever possible.

## **11.2 Flask intercomparison**

- a) Intercomparison programmes distributing to a larger number of laboratories flasks filled in series from tank air as a “sausage” as initiated by the European TACOS project (Levin et al., 2003) are able to increase the benefit of mutual flask exchange.
- b) Another possibility to link several laboratories in one single intercomparison exercise is the establishment of Trace Gas Comparison Sites which will take on the task to fill a larger number of flasks regularly and simultaneously with ambient air and distribute them to participating laboratories. The Alert, Mauna Loa and Cape Grim stations have been recommended as such sites. At Alert station this activity has already started with 6 laboratories. At Cape Grim there are 9 labs participating in such a programme.

## **11.3 Recommendations for in-situ measurements**

- a) Continuous in-situ measurements of CO<sub>2</sub> 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 CO<sub>2</sub> 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 2009. Preliminary recommendation for CO<sub>2</sub> measurements have been summarized in the 13th WMO Experts recommendation (WMO GAW Report No. 168 (2006)).
- b) It is recommended that new robust analytical technologies (e.g., laser-based optical analyzers) are tested. The envisaged new European Infrastructure ICOS (Atmospheric Thematic Centre) may be able to support this activity. A forum should be established 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 observables should be available for new instruments.

- 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 intercomparison activity for atmospheric <sup>222</sup>Rn observations. WMO will contact respective specialists to give advice.

## **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, 2007) A co-ordinated annual submission of data, with clearly identified version number of submitted data and calibration scale, as well as supporting details is strongly recommended. The same recommendation holds to other public-access data archive centres such as the Carbon Dioxide Information Analysis Centre (CDIAC).
- b) A new version of the WDCGG Guide that includes new data categories, new data submission formats, data submission procedures, and distribution ways of data and products has been published. The adherence to this WDCGG Guide is requested.
- c) The WDCGG distributes data in versions consistent with the annual CD-ROM Report and keeps old versions.

### **12.3 Co-operative data products**

All laboratories making high-quality GHG 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 May 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 this report (Tans et al.). Recently, new GHG measurement data streams from satellites with global coverage have become available based on a variety of instruments (SCIAMACHY, AIRS, IASI,) 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). It outlined a strategy to coordinate systematic global carbon observational networks that can form the backbone of an integrated carbon cycle monitoring system. It includes GAW for the atmosphere and builds upon earlier planning by GTOS/TCO (Terrestrial Carbon Observations <http://www.fao.org/gtos/TCO.html>) and GOOS (Global Ocean Observing System <http://ioc.unesco.org/goos/>). The main role of the IGCO 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 aerosols and ozone. The IGACO strategy (WMO GAW Report #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.esig.ucar.edu/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.

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 CO<sub>2</sub> mixing ratio observations. These observations will help us to quantify regional sources and sinks by means of inverse modelling.
- d) 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.
- e) 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.
- f) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes (<sup>13</sup>CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, <sup>18</sup>OCO, stable isotopes in CH<sub>4</sub> and CO) and separate fossil fuel emissions (<sup>14</sup>CO<sub>2</sub>, CO...). Along these lines it is absolutely essential that detailed spatially and temporally resolved fossil fuel CO<sub>2</sub> 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 (SF<sub>6</sub>, <sup>222</sup>Rn, C<sub>2</sub>Cl<sub>4</sub>...) 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 ΔpCO<sub>2</sub> 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 surface 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.

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## 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)
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
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)
IGBP	International Geosphere-Biosphere Programme
IGCO	Integrated Global Carbon Observation
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
MOPITT-TERRA	Measurements Of Pollution In The Troposphere
MOZAIC	Measurement of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus in-service aircraft
MPI-BGC	Max-Planck Institut für Biogeochemie, Jena, Germany
MSC	Meteorological Service of Canada
NACP	The North American Carbon Programme

NCAR C-DAS	National Centre for Atmospheric Research Carbon Data-Model Assimilation
NIES	National Institute for Environmental Studies, Tsukuba, Japan
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration (USA)
OCO	Orbital Carbon Observatory
OSSE	Observing System Simulation Experiment
PI	Principal Investigator
QA/SAC	Quality Assurance/Science Activity Centre
RGD	Reduction Gas Detector
SAG	Scientific Advisory Group
SCIAMACHY	SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY
SIO	Scripps Institution of Oceanography
SRM	Standard Reference Material
TACOS	Terrestrial and Atmospheric Carbon Observing System -Infrastructure (EU funded project)
TCO	Terrestrial Carbon Observations
TDLAS	Tunable Diode Laser Absorption Spectroscopy
UEA	University of East Anglia
UNFCCC	United Nations Framework Convention on Climate Change
VPDB	Vienna Pee Dee Belemnite (Isotope Standard)
VSMOW	Vienna Standard Mean Ocean Water (Isotope Standard)
WCC	World Calibration Centre
WCRP	World Climate Research Programme
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization