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Review

Global quality control for long-lived trace gas measurements

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Abstract: This report arose from the 10th World Meteorological Organization's (WMO) meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques, Stockholm, 23-26 August 1999, at which a proposal was put forward to address some of the known problems associated with quality control of global trace gas measurements, in particular, carbon dioxide, methane and their respective isotopes, and proposes some changes to significantly improve on current situation. The meeting was also attended by a member of the Research Co-ordination Meeting of the International Atomic Energy Agency's (IAEA) Co-ordinated Research Project on Isotope-aided studies of atmospheric carbon dioxide and other greenhouse gases. The aim of this proposal is greatly improved inter-laboratory comparability for measurement of long-lived atmospheric trace gas species, resulting in improved derivation of source/sink fluxes from spatial and temporal atmospheric composition changes. A network with regional "hubs" responsible for maintaining an efficient means of inter-comparing all laboratories with a much higher frequency than what has been practiced to date is proposed. Mayor needs and components of such a network will be presented. This proposal is supported, in principle, by both WMO and IAEA, and has implications for all scientific groups involved in trace gas measurements.

1. Introduction

There is abundant recent evidence, some examples of which are referred to below, that the differences between laboratory measurements of atmospheric composition often exceed the quoted precision of measurement. This is also true with a given laboratory's programs when several analysis methods (non dispersive infra red [NDIR] *vs.* gas chromatography [GC]) and/or *in situ vs.* grab sampling techniques are used. This limits our confidence in the accuracy of regional sources and sinks that are being derived from the observed spatial and temporal patterns of a trace gas with the help of atmospheric chemical transport models. It also limits the usefulness of individual programs in expanding the global coverage of measurements sorely needed by the models. About 10 years ago a target precision for large-scale spatial and temporal differences was set by WMO to 0.1 μmol per mol for CO_2 in the northern hemisphere, and 0.05 μmol per mol in the southern hemisphere; 0.01 per mil was set for d^{13}C in IAEA/WMO forums. These targets have never been consistently achieved. Secondly, the ongoing process of international negotiations about limiting trace gas emissions in order to avoid or minimize man-made climate change has made the issue more urgent. A third motivation relates to on-going improvements in technology, which are expected to make it easier to achieve the target for the complete measurement system, including methods and procedures, standard reference gases, calibration transfers, and field sampling and measurement systems.

Some of the well documented systematic problems that still require explanation, and remedy or effective allowance are given below:

- Systematic CO_2 discrepancies at the 0.2 μmol per mol level when flask air samples are operated next to a continuously monitoring instrument.
- Similar differences between laboratories at the same site.
- Large and variable CO_2 discrepancies between up to 24 laboratories in the 1991–93 and 1994–97 WMO Round Robin comparisons.
- Clear indication of non-linearity in CO_2 measurement, involving most laboratories reporting to the 1994–97 WMO Round Robin.
- δ^{13}C differences 10 times target inter-comparability in the 1996–98 IAEA CLASSIC circulation between 4 major network laboratories with clear evidence of non-linearity.
- Documented evidence of subtle systematic CO_2 and δ^{13}C offsets caused by high pressure regulators.
- Mounting evidence for pressure dependence in CO_2 from high pressure aluminium containers.
- Flask air-sharing comparisons showing CO_2 differences up to 10 times the differences measured in high pressure cylinders.
- Flask air-sharing comparisons of real samples revealing and documenting both step changes (δ^{13}C, δ^{18}O) and long term drifts (CO, H_2) between two laboratories , not detected by conventional intercalibration activities.
- (Note: while these examples are mainly focussed on CO_2, the most studied trace gas, it is expected that similar problems will influence other trace gas measurements).

2. Historical links

WMO has been a strong supporter of the global measurement programs which are now incorporated into the Global Atmosphere Watch program and has sponsored 10 "Experts" meetings since their inception. Initially, these meetings were held approximately every 4 years and focussed on problems of measurement, comparability of scales and interpretation of the data collected in the global networks. While scale and measurement problems remained, the frequency increased to every 2 years and the focus gradually shifted to understanding the problems associated with the use of the global data in inversion models to infer regional sources and sinks in the global carbon cycle. Recognizing that there were on-going problems in merging data sets from different measurement programs, a number of inter-comparison programs were started including the WMO Round Robin set of CO_2-in-Air tanks which were sent to each laboratory, several flask sample inter-comparison projects, such as, the one at Alert, NWT, (WMO, 2001) and another between two of the major labs (NOAA-CMDL and CSIRO) at Cape Grim, Tasmania (Masarie *et al.*, 1999), and the data integration project called GLOBALVIEW initiated by the NOAA-CMDL labs (Masarie *et al.*, 1995). Unfortunately, these are still considered insufficient to bring closure to the integration of the data sets into a common one suitable for inversion modelling on shorter time and space scales than is currently possible.

The proposal presented here is an integration of elements of the IAEA carbon isotope "CLASSIC-AL" inter-comparisons (Collin Allison, an unpublished manuscript), the WMO CO_2 "Round Robin" inter-comparisons (Peterson *et al.*, 1999), the CMDL-CSIRO flask air-sharing inter-comparison (ICP), and culminating in enhanced GLOBALVIEW data assimilations by the Cooperative Atmospheric Data Integration Project.

(Possible interaction with GAW QA/SAC (Quality Assurance/Science Activity Centres) with similar objectives, have not yet been explored).

3. General approach

The essence of quality control is redundancy and frequent scrutiny of the data. Ideally, all reference gases need to be unambiguously traceable to a single common calibration scale. The reference gases may be drifting, however, or a mistake may have been made, and therefore all reference gases need to be checked regularly in an independent way. During the use of reference gases in calibrating measurements systematic errors may be introduced due to procedures and materials. Linearity of measurement instrumentation is often overlooked as a source of inter-calibration error. Finally, errors will be introduced by the measurement or sampling procedures themselves, independent of any calibration problems. Inter-comparisons between different methods and between laboratories are necessary as a means of detecting and addressing such problems. All of these controls need to be exercised on a continuing basis because the experience of many decades shows that unacceptable discrepancies tend to develop over time.

Secondly, too little thought has been given to data management by many laboratories, often resulting in difficult access even to their own data. Improved and transparent access to data is an integral part of this plan.

Thirdly, because of the global nature of many environmental problems, it is essential that access to first-rate quality control needs to be made both easier and affordable for many laboratories.

Note that the plan below does not provide, and should not be used to provide, a link to an international calibration scale! Instead, it is aimed at providing a dynamic monitoring of inter-comparability between measurement laboratories. In so far as the major interpretative studies involve conversion of trace gas composition differences into fluxes, there is an immediate application for improved inter-comparability results. This plan anticipates such application by automatic inclusion of results in enhanced GLOBALVIEW data assimilations.

Also intrinsic to this plan is a two-year international review process that assesses all inter-comparison information and makes recommendations for ongoing operation. These reviews will examine performance in the light of contemporary scientific requirements. Initially, the plan is expected to elucidate many of the systematic errors that have largely prevented merging of past data sets. In the longer term, the plan is expected to be of use in establishing and maintaining globally accessible calibration scales.

The initial focus is on the urgent problems of measuring CO_2 and CO_2 isotopes, but this does not exclude other trace gases that can be measured without compromising cylinder lifetime or circulation frequency (*e.g.* CH_4, CO, N_2O, H_2, $\delta^{13}CH_4$, etc.).

4. The GLOBALHUBS plan

Four globally distributed and tightly linked 'HUB' laboratories that are a source of well-characterised air for laboratories in their region. Two HUB laboratories are identified for special duties, a PREPARATION HUB (nominally GASLAB in CSIRO Atmospheric Research, Australia), and a CALIBRATION HUB associated with the WMO Central CO_2 Laboratory at CMDL, NOAA, USA (Fig. 1).

5. Quality control of calibrations

A key new element, essential for the PREP. HUB, but also arguably for each HUB, is improved NDIR techniques (DaCosta and Steele, 1999; WMO-TD No. 952). The new low-flow system is expected to permit routine quality-assessment of regulators and standards for CO_2 to a precision of around 0.002 μmol per mol (*e.g.* regulators assessed in hours, cylinder drifts detected in weeks/months rather than years, decanting accurately and monitored, etc.). If necessary, cylinder drifts in CO_2 can be accurately and economically tracked over the cylinder lifetime. As the program moves into other trace gas species, modern up-to-date GC systems will also be required.

(1) Annual circulation between the four HUBS of 5 high pressure cylinders ("circulators")
 a) Aluminium cylinders (~5 litres @ 150 bar=800 litres).
 b) Estimated circulator tank lifetime ~10 years.
 c) filled with clean dry Southern Hemisphere air, but with composition of target gases modified to bracket anticipated atmospheric values (*e.g.* for CO_2, 350, 375, 385, 400, 430 μmol per mol; $\delta^{13}C$, 0 to -45‰, etc.)
 d) dedicated high-quality high-pressure regulators, and uniform high-pressure cylinder sampling protocols (addressing identified systematic problems with previous round-robin methods)
 e) A back/up set of 5 cylinders will be prepared, for emergency/redundancy, in addition to the IAEA CLASSIC cylinders.

(2) A new set of non-circulating "primary" high-pressure cylinder air standards (with dedicated regulators) to join the suite of primaries at the Central CO_2 Laboratory.
 a) Aluminium cylinders (~30 litres @ 150 bar=6000 litres).
 b) Estimated lifetime>25 years.
 c) Have particular relevance to CO_2 isotope measurement scales (*e.g.* for CO_2 [μmol per mol], $\delta^{13}C$ (‰): 360, 0; 375, -7.5; 390, -8.5; 405, -9.5; 420, -45). Measure the isotopic composition of the current CCL primaries.
 d) dedicated high-quality high-pressure regulators

(3) Frequent (four times per year) high-precision monitoring of the relative measurement between each of three HUBS and the PREP. HUB ("oscillators") using low pressure 'ambient' air standards in large volume containers (34L stainless steel containers) at$<$4

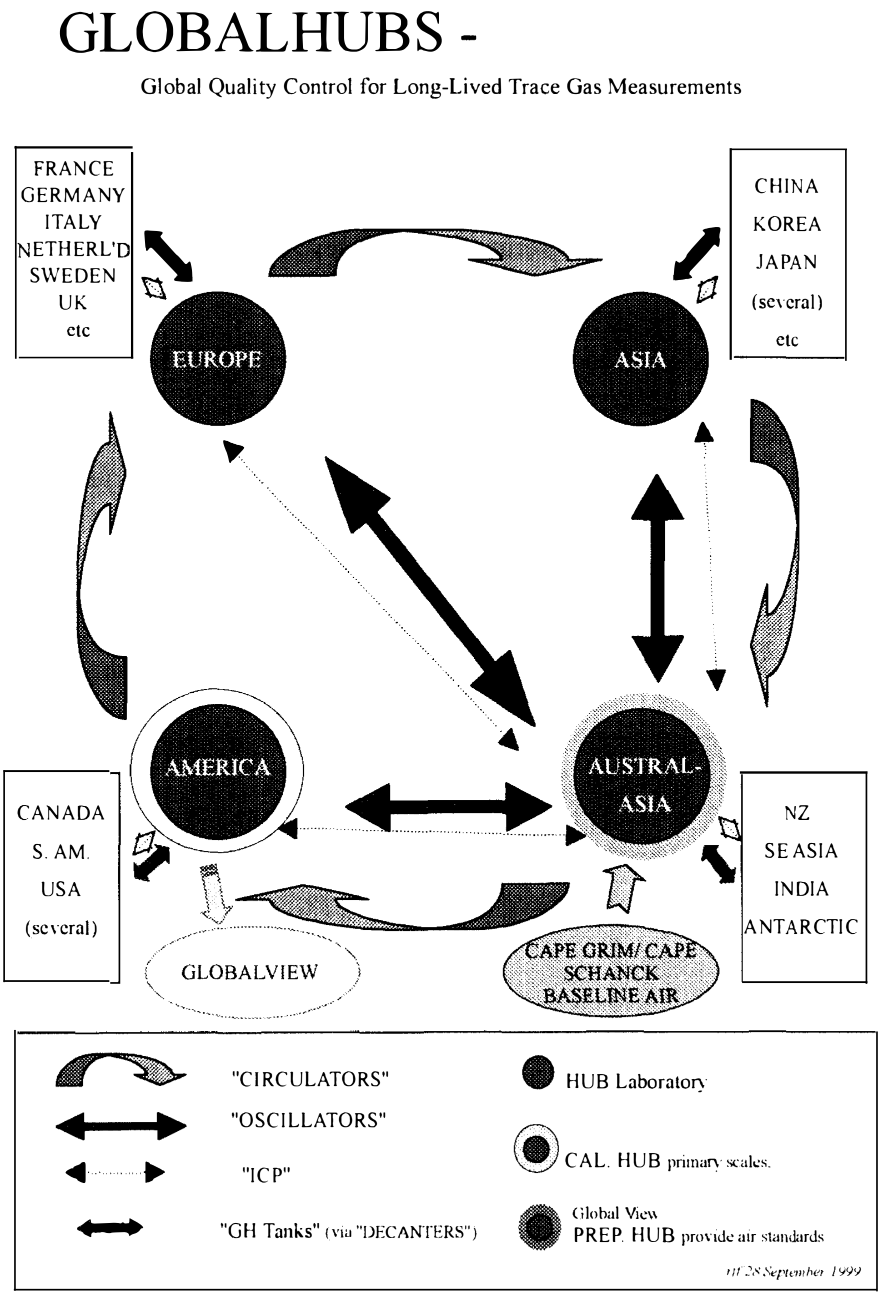

Fig. 1. A schematic outlining the exchange of gases in flasks, low-pressure cylinders and high-pressure tanks between hubs is shown above. A similar pattern of exchange could be developed between the hubs and the client laboratories in their respective regions.

bar.

a) Sufficient air for many repeat measurements, but ~1 year lifetime.
b) Avoids systematic effects often observed with high pressure regulators. These comparisons are half-way between standards and actual samples.
c) Non-hazardous goods, implying reduced freight costs.

6. Quality control of sample measurements

(1) Weekly low-precision monitoring of the relative measurement by the four HUBS on routine sampling network flask samples collected at two sites for all four hub laboratories.

a) This is designed to catch any systematic differences due to sample flask filling/storage/analysis

b) also carries biogeochemical information

(2) Automated and up-to-date logging and presentation of HUB laboratory activities and results (circulators, oscillators, and HUB-ICP comparisons) on a password protected World Wide Web (WWW) site open only to all contributors to GLOBALVIEW.

a) Near real-time electronic access to assigned values and calibration status of the air standard for individual species for participating laboratories.

b) The observed differences between the HUB laboratories will be used in a transparent way to make adjustments to contributed laboratory data when they are brought together into consistent global data sets (GLOBALVIEW) for modeling purposes. The differences are NOT used by any laboratory to adjust its calibration scale or change its data because that would sacrifice the traceability of the calibration scale. When a problem becomes apparent, the laboratory should fix the problem itself, either in its standard reference gases or in its procedures.

(3) Customer service involves a HUB laboratory responding to requests from regional laboratories, (on a cost recovery basis), for regular and ongoing access to characterised air in GLOBALHUBS (GH) tanks. HUB laboratories are expected to stimulate the exchange of melons with regional laboratories.

a) Each HUB will be provided by a SUPERHUB with a maintained supply of aluminium cylinders (~30 litres @ 150 bar=6000 litres, "decanters") filled with ambient whole air standards, for decanting into GH tanks (provided on short-term loan to a laboratory).

b) Activities over and above basic HUB commitments to be negotiated on a commercial basis? (*e.g.* acquisition of more melons, or more frequent access?)

(4) Continuing inter-comparison of actual flask samples between regional laboratories (including their HUB), or between regional laboratories linked to a separate HUB (more expensive), are a final essential part of the integrated quality control of sampling and measurement procedures.

(Note: Automated software for transferring data between CMDL and CSIRO and updating statistical comparisons and plots has been operating for several years, and is being implemented at other sites).

7. Summary of suggested HUB and SUPERHUB commitments

(1) HUB Commitments (not necessarily all in one laboratory).

a) Minimum 5 year institutional commitment?

b) Maintain circulation of HUB circulators, oscillators and ICP comparisons.

c) Ensure prompt registration of results on WWW (software recommendations to be developed/might include assistance).

d) Only adjust internal calibration scales in response to independently identified and quantified systematic error.
e) Ensure and encourage the provision of standard air in GH Tanks (specify maximum frequency) to SUITABLE laboratories in their region.
f) Record transactions and results.
g) Play a key role in the 2-yearly GLOBALHUBS assessment meetings.

(2) PREPARATION HUB Commitments (over and above routine HUB operation) include:
a) Provision of primary, circulator, and decanter air standards in high pressure cylinders.
b) The acquisition and quality assessment of HUB hardware (high pressure and low pressure cylinders, regulators)
c) Filling of high pressure cylinders at a clean-air site (also involves spiking and stripping whole air for specified span ranges).
d) Develop and document decanting from decanters into GH Tanks.
e) Monitor decanting (from high pressure cylinders to GH Tanks) protocols and effectiveness.

(3) CALIBRATION HUB Commitments (over and above routine HUB operation) include:
a) Link GLOBALHUBS primaries to manometric/gravimetric standards at regular intervals.
b) Design and implement consistent software for managing and reporting of results, including graphical presentations, on the WWW.

8. Funding strategy

At this stage we are suggesting a coordinated approach to the three regional networks APN (Asia Pacific Network), ENRICH (Europe Network for Research in Global Change)), IAI (Inter-America Institute for Global Change Research), three funding organisations with a charter to develop regional cooperation on global change research. For example APN supports "global environmental change research projects which cannot be conducted on a national basis and require regional cooperation". Alternatively, part funding might be sought from GEF (Global Environmental Facility) or similar agencies.

Request SUPERHUB and HUB set up costs, and HUB/SUPERHUB basic operating costs over three years.

International set up funding directed at core activities only. Regional funding then requested regionally. After set up, the whole exercise might be best operated on a user pays basis (with developing countries continuing to seek funding aid.

9. Training strategy

The human resources required to operate the GLOBALHUBS program can be partly addressed by the HUBS acting as training and development centres for scientific/technical people from developing laboratories. In addition we should develop a course in high-accuracy trace gas monitoring.

10. Implementation strategy

The initial hurdle is obtaining funding for a SUPERHUB so that preparation of a suitable number and quality of HUB standards can commence. Initial container storage tests will occupy a minimum of 3–6 months. It is expected that different HUBS might take different times to become fully operational (depending also on the availability of HUB establishment costs).

There will clearly be regional politics involved in identifying a HUB and hopefully these can be largely sorted out within each region. The initial criteria for being a HUB will demand a considerable degree of experience and competence. Sharing arrangements might be considered, but would have to demonstrate that they do not compromise the basic integrity, dispatch and lifetime of the circulating and oscillating standards. Some sort of phased implementation needs to be developed once HUBS are identified and committed?

Table 1. GLOBALHUBS Setup Hardware.
A draft estimate of setup costs to be revised when the plan is finally implemented.

	Container volume (L)	Full Pressure/ volume (bar/ L STP)	Lifetime (years)	Number of containers	Number of regulators	Span CO_2 (µmol per mol) $\delta^{13}C$ (‰)	Circulation (year^{-1})
HUB							
PRIMARIES	30	150/6000	>25	5	5	350 to 430 0 to -45	(CAR to CMDL)
CIRCULATORS	5	150/800	~10		2x5	350 to 430 0 to -45	1
OSCILLATORS	34	4/140	~1	2x3	2x3	ambient	4
FLASC/ICP	0.5-2	2/(1-4)	~0.1	-	-	sample	>20
Customer				Per HUB	Per HUB	Per HUB	Per HUB
DECANTERS	30	150/6000	~1 ~5?	3 2	5	~ambient lo&hi	0.5
GH Tanks	34	4/140	~2*	5	-	~ambient lo&hi	~1-4
FLASC/ICP	0.5-2	2/(1-4)	~0.1	-	-	sample	>20

*@300 L per decant/DECANTER Cylinder

Hardware	approximate	costing:	Containers (@$1000)	Regulators (@1500)	Cost
Aluminium	8000L	Primaries	5	5	$12.500 AU
		Decanters	5x4=20	20	$50.000
Aluminium	800 L	Circulators	2x5	10	$25.000
Stainless	Steel 34L	Oscillators	2x3	-	$ 6.000
		GH Tanks	4x5	-	$20.000
					$113.500
					~ $75,000 US

11. Australian SUPERHUB?

As a stimulus for further discussion, here are preliminary considerations of the required support to establish an Australian SUPERHUB (Table 1)

In addition to cylinder hardware in Table 1, an Australasian HUB/SUPERHUB would require: a back-up RIX compressor system, money to construct a dedicated LO FLOW HIGH PRECISION CO_2 analyser, at least one full time technical officer (including overheads) for set up (2 years), at a technical officer position for ongoing HUB commitments (training positions). We would also be seeking all freight and consumable costs for SUPERHUB and HUB activities.

References

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Appendix A - DRAFT RECOMMENDATIONS BY WMO (and IAEA) EXPERTS related to the GLOBALHUBS proposal, Stockholm, August 26, 1999.

1. The meeting unanimously endorsed the proposal as one that:

   a) Recognised the need for this measurement community to react to new demands, particularly in relation to improved estimates of regional trace gas fluxes deduced from measured changes in atmospheric composition.
   b) Identified serious systematic error in current CO_2 and CO_2 tracer measurement both within and across programs that are not adequately addressed with existing calibration and inter-comparison strategies.
   c) Outlined a strategy which would significantly reduce these errors by:

      i. improved access to precisely-characterized standard air for laboratory inter-comparison. (The improvement pertains to existing highly-developed laboratories but is particularly relevant for developing laboratories)
      ii. providing a motivation and framework for rapid integration of the improved inter-comparison information into existing international data repositories (particularly enhancing the value of the output of smaller/regional laboratories)
      iii. providing greatly improved access for the user (modelling) community to globally consistent data sets
      iv. providing greater transparency of methodologies leading to global data assimilations.

2. The meeting agreed with a suggestion that a small working group be formed to further develop the GLOBALHUBS proposal. The responsibilities of the group include:

   a) Survey the expectations of participating (customer) measurement laboratories
   b) Define the interaction with existing inter-comparison activities, e.g. WMO Round Robins, IAEA CLASSIC)
   c) Explore interactive relationships with major clients such as the carbon budget modelling community (TRANSCOM), other international data repositories, in particular GAW QA/SAC, the WMO and CDIAC.
   d) Explore interactions with major science planning groups (IGAC, etc.?)
   e) Define the responsibilities of SUPERHUB and HUB laboratories
   f) Estimate the setup, operating costs and possible implementation schedule
   g) Explore possible funding agencies
   h) Prepare a funding strategy
   i) Prepare appropriate funding proposals
   j) Provide a full on-going record of actions to WMO (Dr John Miller) and IAEA (Dr Manfred Groening).
   k) Provide a full summary to the Experts community and invite comment, prior to implementation of any action with future policy implications.
   l) Aim for a 6-month timeframe to complete these tasks, subject to the availability of a consultant to assist with data collection and summaries.

Roger Francey offered to form a working group and/or co-opt experts, and approach WMO/IAEA with the view of acquiring the services of Dr Neil Trivett as an independent consultant. This offer was accepted by the meeting.