The “GOLLUM” O₂ intercomparison programme: Latest results and next steps


23 authors listed – if anyone else should be included, please let me know.
Talk outline

- Historical background and GOLLUM beginnings.
- Details of the GOLLUM programme.
- Some data and results.
- Some suggestions for what next – for open discussion.
WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 148

Report of the Eleventh WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques

(Tokyo, Japan, 25 – 28 September 2001)
3) **O$_2$/N$_2$ CALIBRATION**

Intercalibration activities be undertaken to improve the usefulness of O$_2$/N$_2$ measurements, which are now being conducted by a growing number of laboratories world-wide. At present, there are no absolute standards for atmospheric O$_2$/N$_2$ ratio, and each laboratory has reported results relative to individual laboratory reference gases. The scientific value of O$_2$/N$_2$ measurements would be largely enhanced if measures were taken to bring the observations onto a common scale, with a precision of a few per meg, and if this scale could be tied to absolute standards, with an absolute accuracy of 5 per meg or better. Both tasks are very challenging, however, and it is not clear how best to implement such measures at this time. What is needed at present are creative efforts on the part of individual laboratories or among groups of laboratories to test strategies for intercalibration and to test approaches to standards development. At the Scripps Institution of Oceanography, for example, a program is underway to develop air standards for O$_2$/N$_2$ ratio analysis based on gravimetry. Another identifiable need is having several stations worldwide where samples can be collected in parallel for several laboratories, as this will aid in establishing the offsets between the individual laboratory scales in the absence of a common scale. Two such stations already exist: (1) Cape Grim station, where samples are currently being collected for laboratories at Princeton, Scripps, and CSIRO, and (2) the Scripps Pier in La Jolla, California, where samples are being collected for Princeton and Scripps.
WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 161

12th WMO/IAEA MEETING OF EXPERTS
ON CARBON DIOXIDE CONCENTRATION
AND RELATED TRACERS
MEASUREMENT TECHNIQUES

(Toronto, Canada, 15-18 September 2003)
In considering an ideal calibration and intercomparison programme, the following points were considered:

a) **Ultimately there is a need for a globally standardised calibration scale which all labs/field sites are linked to.**

b) **One or more mechanisms are needed which provide quality assurance that data derived from flask measurements from one lab are comparable to data derived from flask measurements from a second lab.**

c) **One or more mechanisms are needed which provide quality assurance that data derived from continuous measurements from one lab/field site are comparable to data derived from continuous measurements from a second lab/field site.**

d) **Any calibration or intercomparison programme must take into account the fact that many different analyser techniques are currently used within the community to achieve high-precision \( \text{O}_2/\text{N}_2 \) measurements (e.g. interferometric, mass spectrometric, paramagnetic, VUV absorption, gas chromatographic, and electrochemical fuel cell).**

Ten of the twelve \( \text{O}_2/\text{N}_2 \) labs (of Annex 1) were represented at this meeting, and the following recommendations were agreed upon by all participants:

a) **A “Round-Robin Cylinder” intercomparison programme will be initiated.** This will consist of two sets of three high pressure cylinders to be analysed by all participating labs, with the two sets to rotate in opposite direction. At this stage we do not recommend that this programme should result in a common calibration scale, instead it should be used to establish and maintain a link between existing calibration scales. This decision should be reassessed at the 13th WMO/IAEA Experts Meeting in 2005.

b) **For those laboratories which make flask measurements, we will initiate a “Sausage Flasks Matrix” intercomparison programme.** This will involve a primary laboratory simultaneously filling a pair of flasks from each participating laboratory from a high pressure cylinder and distributing to all labs for analysis.
c) Although we did not formalise a programme, we strongly encourage all flask measurement laboratories to initiate or continue “Shared Flasks” intercomparison programmes. That is, programmes whereby two (or more) laboratories analyse sample air from a station site, either from exactly the same flasks, or from flasks filled simultaneously at a given site. The wider community at this meeting discussed the possibility of a “Super-Site”, where a single field station is used to link all flask analysis laboratories in such intercomparison programmes. If such a Super-Site is adopted, it would be wise for the \( \text{O}_2/\text{N}_2 \) community to adopt the same site.

d) Ralph Keeling (SIO) agreed to be the “Primary Lab”, supplying all high pressure gas cylinders for the round-robin cylinder programme, and filling all flasks for the sausage flasks matrix programme.

e) Andrew Manning (MPI-BGC) agreed to collate all data resulting from the two programmes.
Naming the programme

- **ATOMIC**
  - *ATmospheric Oxygen Measurement InterComparison programme*

- **GOLLUM**
  - *Global Oxygen Laboratories Link Ultra-precise Measurements*
Scale of the “GOLLUM” programme

- 23 authors.
- 10 measurement laboratories.
- 7 countries.
- 3 atmospheric species’ compatibility assessed (O₂/N₂; Ar/N₂; CO₂).
- 11+ years of intercomparison measurements.
- 6 high pressure cylinders in 2 loops of 3 cylinders each.
- 29 graphs on the website.

- 11+ year programme has been entirely unfunded!!!
• 2 sets of 3 high pressure cylinders of air
• Travelling in opposite directions around world
• Rapid turnover time (5 weeks)
• About 18 months for full rotation.
Background on Atmospheric oxygen measurement

Atmospheric oxygen (O₂) measurements are used to provide insight and quantitative understanding of the global carbon cycle [Bender et al., 1996; Bender et al., 1998; Keeling and Shertz, 1992]. More recently they have been used in other applications such as understanding air-sea gas exchange [Keeling et al., 1998] and critiquing ocean biogeochemical and atmospheric transport models [Battle et al., 2006; Stephens et al., 1998].

Atmospheric O₂ measurements were first established in 1988 by Professor Ralph Keeling at Scripps Institution of Oceanography [Keeling, 1988], and are now made at 13 laboratories around the world, and at 25 field stations. The
Excel logsheet for submitting data

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<td>Email a copy of this logsheet to Andrew Manning (<a href="mailto:a.manning@uea.ac.uk">a.manning@uea.ac.uk</a>) within 4 weeks of making your analyses.</td>
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<td>Please describe any damage you have observed to the cylinders or boxes:</td>
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New ASCII text file for submitting data

- Allows automated generation of files for submission by participants.
- Should result in less errors and mistakes.
- And big reduction in manual labour requirements.
Results: Scripps: $O_2$
Results: Scripps: Relative $O_2$

GOLLUM: Scripps Institution Of Oceanography relative to SIO reference

Δ $O_2/N_2$ (per meg)

Bilbo
CC178269
CC177811
CC180655

Frodo
CC177841
CC177837
CC178444

WMO intercompatibility goal ($\pm 2$ per meg)
Results: Scripps: CO$_2$
Results: Scripps: Relative CO$_2$

GOLLUM: Scripps Institution Of Oceanography relative to SIO reference

Created 11 Sep 15 11:36

WMO intercompatability goal (± 0.1 ppm)
Results: Scripps: Ar

GOLLUM: History at Scripps Institution Of Oceanography

Bilbo
CC177811
CC178269
CC180655

Frodo
CC177841
CC178444
CC177837

Ar/N₂ (per meg)
Results: Scripps: Relative Ar
Results: NIES: Relative $O_2$

- Note: $y$-axis scale of next few graphs is not constant; but WMO goal gives some indication.
Results: Tohoku University: Relative $O_2$
Results: NIWA: Relative O$_2$
Results: University of Bern: Relative O$_2$

Collum: University of Bern relative to Sl0 reference (minus 590 offset)

- Bilbo: CC178269, CC177811, CC180655
- Frodo: CC177841, CC177837, CC178444

Δ O$_2$/N$_2$ (per meg)

Created 11 Sep 15 11:38

----- WMO intercompatibility goal (± 2 per meg)
Results: Groningen University: Relative $O_2$
Results: University of East Anglia: Relative $O_2$
Results: NCAR: Relative O$_2$

GOLLUM: National Center for Atmospheric Research relative to SIO reference

Δ O$_2$/N$_2$ (per meg)

- Dec05
- Nov06
- Oct07
- Sep08
- Aug09
- Jul10
- Jun11
- May12
- Apr13
- Mar14
- Feb15

Bilbo
CC178269
CC177811
CC180655

Frodo
CC177841
CC177837
CC178444

WMO intercompatibility goal (± 2 per meg)
Results: Max Planck: Relative $O_2$
Results: Max Planck: Relative Ar

GOLLUM: Max Planck Institute for Biogeochemistry relative to SIO reference (minus 130 offset)
Results: Princeton University: Relative O$_2$
Results: Everyone: Relative $O_2$

GOLLUM: Average Differences From SIO reference values

- Bilbo
- Frodo
- SIO
- NCAR
- PU\((-70)\)
- UEA
- CIO–RUG\((-340)\)
- UBERN\((-590)\)
- MPI–BGC
- TU\((-160)\)
- NIES\((-195)\)
- CMAR
- NIWA

Created 11 Sep 15 1:38

--- WMO intercomaptability goal (± 2 per meg)
Results: Everyone: Relative Ar
Results: Everyone: Relative CO$_2$
WMO Round Robin results, 2015

WMO RR: 6; Circuit: all

Lab minus NCAR (Δ O₂/N₂, per mg)

-100 0 100 200 300 400 500 600

UEA  RUG  AIST  TU

Global Atmosphere Watch

Created: 2015-09-09
Maintaining the momentum from this Workshop: Part 1: Third APO Workshop

- I’ve done some extensive research on where we might want to hold the next workshop...
Alpha Phi Omega Fall Rush 2012

Rush
Co-ed Service Fraternity

Join the nation’s largest collegiate fraternity and become part of a brotherhood that is passionate about service!

Formal Rush
Tuesday 8/28 & Wednesday 8/29
Bobo Spiritual Life Center
7:00 p.m.

Social Rush
Wednesday 9/5
Laser tag & roller skate with APO
Meet at 4:30 p.m.

Dinner with Exec
Thursday 9/6
Come eat dinner and get to know the members of exec.
6:45 p.m.

Informal Rush
Friday 9/7
Bear Park
4:00 p.m.

Interviews
Friday 9/7
Cashion 103
7:00 p.m.

Service Rush
Saturday 9/8
Meet at 7th & James Church
10:00 a.m.

For more information contact:
junaid_gilani@baylor.edu
khadija_lalani@baylor.edu
www.apoonline/zetaomega
@BaylorAPO
CONQUER THE PHILIPPINES’ HIGHEST

MT. APO
Kidapawan city, North Cotabato

Mt. Apo
Davao and North Cotabato

FOR MORE DETAILS PLEASE CONTACT:
Miguel "MIQS" Mapalad - 0905 268 8275
Email: miguel.mapalad@yabag.org

The Mount APO
CONQUER THE PHILIPPINES' HIGHEST

MT. APO

Kidapawan

FOR MORE DETAILS PLEASE CONTACT:
Miguel "MIQS" Mapalad - 0905 268 8275
Email: miguel.mapalad@yabag.org

The Mount APO
APO ISLAND
DAUIN, ORIENTAL NEGROS, PHILIPPINES

9°4′N 123°16′E
AREA: 0.74 km² (0.29 sq mi)
Population (2007): 745
Time zone: PST (UTC+8)
Zip code: 6217
Area code: 35

Home to over 650 documented species of fish and estimated to have over 400 species of corals. Most of the Philippines' 450 species of coral can be found in Apo Island.
Maintaining the momentum from this Workshop: Part 2

- EOS article
  - Short report from this Workshop

- GOLLUM mailing list (maintained by myself at UEA)
  - Expand to modelling community too?
    - Currently only ~20 emails per year, so will not be inundated with ‘spam’

- GOLLUM website
  - Expand to include other information?
    - E.g. PDFs of all talks from this Workshop?
      - (Can be placed behind a password)
    - E.g. list of APO-relevant papers?
Maintaining the momentum from this Workshop: Part 3: GOLLUM programme

- **GOLLUM cylinders**
  - Re-hydrotest and refill
    - What concentrations? (Better with range in all 3 cylinders?)
    - Do we want with dip tubes? (previous WMO Recommendations said yes!!)
    - Dew point measured and less than 2 ppm
  - Other participants (CMAR?; AIST?)
  - Produce tables of quantified offsets as in ‘Cucumbers’ programme
    - 5-year time frames?

- **GOLLUM flasks**
  - Do we want to resurrect this programme?

- **Shared flasks programmes – more?**

- **Flask sampling co-located with in situ stations?**
  - Gives Ar/N₂
  - Provides validation, verification, quality control, intercomparison, etc, etc

- **Peer-reviewed paper in 2016/7**
Maintaining the momentum from this Workshop: Part 4a: UK funding opportunity

International Opportunities Fund

- Programme overview

The aim of the International Opportunities Fund (IOF) Scheme is to provide resources to NERC-supported research groups to allow them to forge long-term partnerships with overseas scientists that add value to existing NERC-funded science.

NERC’s usual funding schemes encourage international project partnerships and the IOF is not intended to simply support international collaborative research. It has a specific aim of adding value to existing NERC-funded research, data and knowledge through international collaboration. Furthermore, the IOF seeks to provide a foundation for long-term partnership and added value that will continue beyond the lifetime of the grant. As such, the IOF aims to support collaborations that are not typically supported through NERC’s usual funding schemes.

...should promote excellent research that cannot be delivered by the UK alone.

...some aspects of the research will be more speculative and exploratory than is typical.

...promote UK leadership of international research agenda’s and initiatives.
Maintaining the momentum from this Workshop: Part 4b: UK funding opportunity

- **Funds available:** ~£300,000, i.e. US$450,000 or 410.000 Euro or A$650,000 or NZ$730,000

- **Complication:** call is for international partnerships/collaboration, but can’t give funds to non-UK organisations.
  - But can support travel for foreigners, scientist exchange programmes, workshop, etc.

- Some draft suggestions from me (influenced by both APO needs and meeting call criteria):
  - GOLLUM programme coordination support and expansion
  - Observational Data sets:
    - Develop Obspack O₂
    - Coordinate for community to submit data to WDCGG
    - But first, improve QC of existing data sets
  - Third APO Workshop (in 3 years)
  - Progress on calibration scales
    - Towards WMO scale?? CCL/WCC??
      - Gravimetric standards work?
      - Pay for postdoc to work at Scripps??
Maintaining the momentum from this Workshop: Part 4c: UK funding opportunity

- More draft suggestions from me (influenced by both APO needs and meeting call criteria):
  - Research O₂ measurement issues such as intake and ‘tee’ designs that don’t fractionate; other examples mentioned in WMO Recommendations
  - Modelling progress that could be done via exchange programmes?
    - Garcia and Keeling update?
  - Help Lingxi and others starting up new O₂/N₂ programmes (exchange programmes)
  - Impact related activities, e.g. human physiology impacts paper
  - Produce ‘Best practices’ paper for flask sample collection, analysis, and in situ analysis
  - Stimulate more/speedier publications.
  
  - More precise, more stable instruments that consume less calibration gases.
  - Instability in cylinders...