# GOLLUM

**G**lobal **O**xygen **L**aboratories **L**ink **U**ltra-precise **M**easurements

# Alternative acronyms considered in 2003

**AT**mospheric **OX**ygen **I**nter**C**omparison programme
**(A TOXIC programme)**

**AT**mospheric **O**xygen **M**easurements **I**nter**C**omparison programme
**(ATOMIC programme)**

**INTER**comparisons **F**or **E**xperimenters **R**ecording **O**xygen **M**easurements **E**nabling **T**remendously **E**xciting **R**esearch

**(INTERFEROMETER)**

**K**eep **E**very **E**xperimenter **L**inked and **I**ntercompared in a **N**etworking **G**roup
**(KEELING)**

# Results from the "GOLLUM" $O_2$ intercomparison programme

## (Global Oxygen Laboratories Link Ultra-precise Measurements)


**Andrew C. Manning[1], Marica Hewitt[1], Alex J. Etchells[1], Mai Hong[1], Penelope A. Pickers[1], Karina E. Adcock[1], R. F. Keeling[2], Eric Morgan[2], Shigeyuki Ishidoya[3], Nobuyuki Aoki[3], Yasunori Tohjima[4], Heiko Moossen[5], Daisuke Goto[6], Shinji Morimoto[7], Markus Eritt[8], Gordon Brailsford[9], Sylvia Nichol[9], Harro Meijer[10], Ingrid Luijkx[11], Kim Faassen[11], Britt Stephens[12], Markus Leuenberger[13]**



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*Carbon Related Atmospheric Measurement Lab*

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University of East Anglia
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*Carbon Related Atmospheric Measurement Lab*

# Affiliations

**1 = UEA:** Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK

**2 = SIO:** Scripps Institution of Oceanography, University of California, San Diego, California, USA

**3 = AIST:** Environmental Management Research Institute, National Institute of Advanced Industrial Science and Technology, Japan

**4 = NIES:** National Institute for Environmental Studies, Ibaraki, Japan

**5 = MPI-BGC:** Stable Isotope Laboratory (BGC-IsoLab), Max Planck Institute for Biogeochemistry, Germany

6 = National Institute of Polar Research, Tokyo, Japan

**7 = TU:** Tohoku University, Sendai, Japan

**8 = ICOS:** ICOS, Flask and Calibration Laboratory, Technologie Center Felsenkeller (TCF), Germany

**9 = NIWA:** National Institute for Water and Atmospheric Research, Wellington, New Zealand

**10 = CIO-RUG**: Centre for Isotope Research, Energy Academy Europe, University of Groningen, The Netherlands

11 = University and Research, Meteorology and Air Quality, The Netherlands

**12 = NCAR:** National Center for Atmospheric Research, Boulder, Colorado, USA

**13 = UBERN :** University of Bern

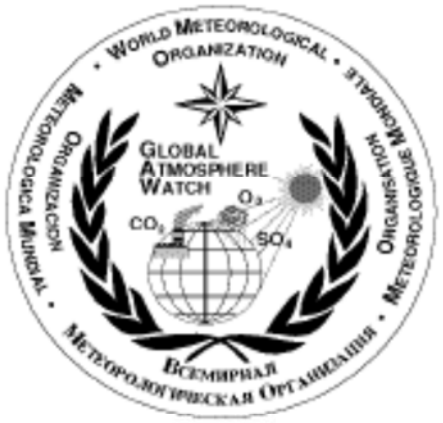
# Talk outline

- Introduction and historical background
- Details of the GOLLUM programme
- Submitting data
- Viewing data live
- Provisional results:
  - 2021-2023
  - 2004-2014
    - Coping with seemingly drifting cylinders
- Other $O_2$ intercomparison programmes
- Future outlook: suggestions and plans

# Introduction

- There is no official WMO calibration scale for $O_2/N_2$ measurements
  - Mostly because of a lack of resources (money, people, time) for anyone to maintain such a scale
- Many (but not all) labs are unofficially on the "Scripps $O_2$ scale"
  - But "Scripps $O_2$ scale" means different things for different labs
  - There are no established protocols for maintaining one's links to this scale
- As a result, combining atmospheric $O_2/N_2$ datasets from different labs is problematic, and even impossible
  - This stymies scientific progress and collaboration
- The GOLLUM programme was initiated in 2003 (by Andrew Manning and Ralph Keeling) to **start** to address these deficiencies
  - Following agreement at the GGMT-2003 meeting in Toronto, Canada

# 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**

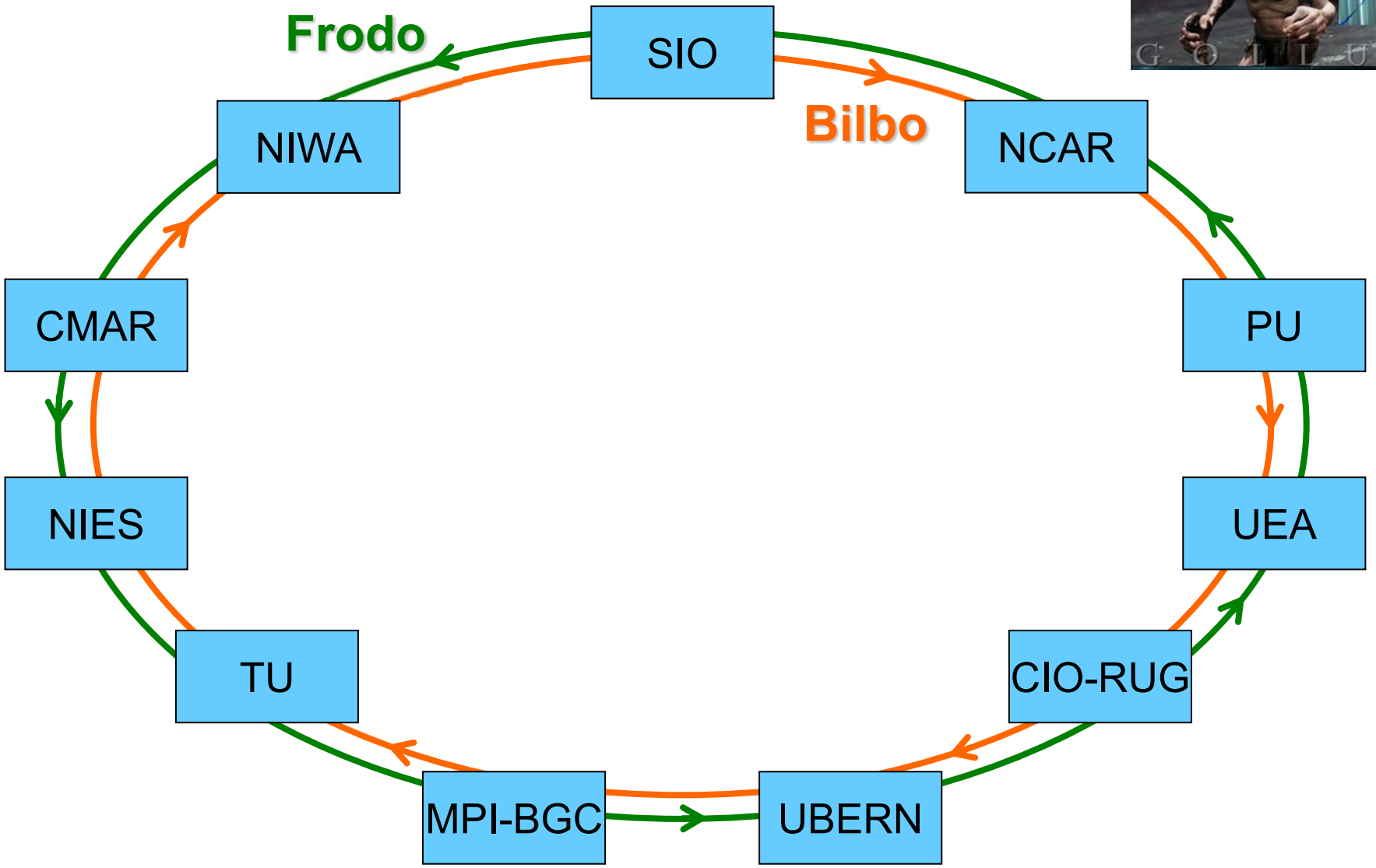
# 12th WMO/IAEA MEETING OF EXPERTS ON CARBON DIOXIDE CONCENTRATION AND RELATED TRACERS MEASUREMENT TECHNIQUES

(Toronto, Canada, 15-18 September 2003)

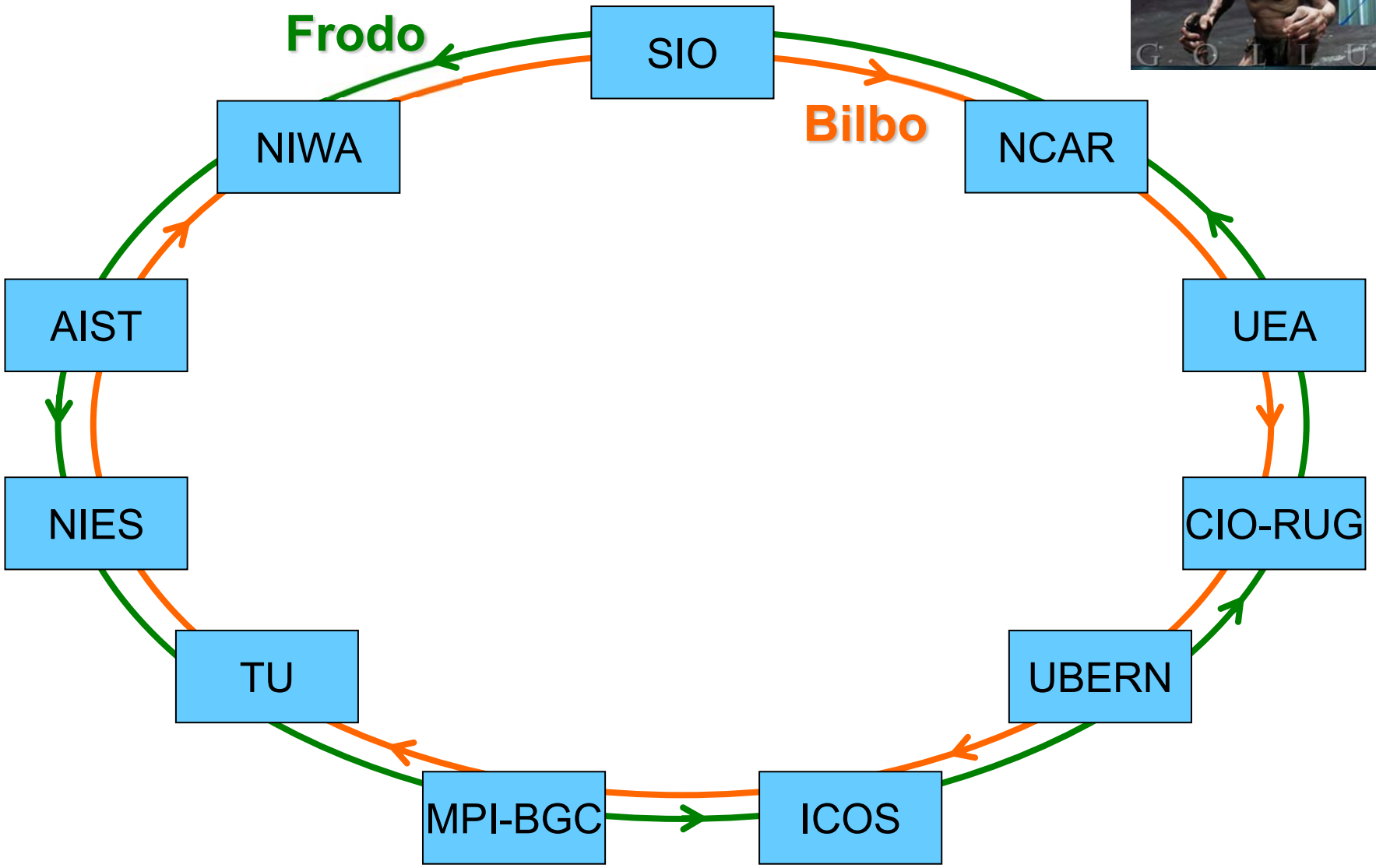
# Details of the GOLLUM programme

- Rotation of cylinders started in 2004, for 11 years
  - Stopped in 2014 as cylinders needed to be refilled
  - Refilling did not happen until 2020 – Tim Lueker has guaranteed this will never reoccur
- Rotations resumed in 2021, continuing indefinitely
- Rotations consist of 2 sets of 3 cylinders, referred to as “Bilbo” and “Frodo” sets
  - The two sets rotate in opposite directions around the world
  - NOTE: The same 6 cylinders are used in both time periods
    - BUT 2 CYLINDERS HAVE SWITCHED THEIR AFFILIATION between Frodo and Bilbo!
    - Do not let this confuse you!
- Species included: $O_2/N_2$, $CO_2$, $Ar/N_2$
- 2004-2014:
  - 10 participating laboratories
- 2021-present:
  - 11 participating laboratories in 7 countries
    - AIST + ICOS added; PU stopped
- **GOLLUM programme has never had any source of funding!!**

# GOLLUM rotations – 2004-2014

# GOLLUM rotations – 2021-present

# http://gollum.uea.ac.uk/

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CRAM Laboratory

GOLLUM

Global Oxygen Laboratories Link Ultra-precise Measurements

Home | Rotations 2004–14 (PDF) | Rotations 2021 – present (PDF) | Shipping Information | Participants (PDF) | Stations Map | Protocols (PDF)
View Data (password required) | Submit Data (password required) | 2010 Royal Society GHG Talks | 2015 APO Workshop Talks | 2020 APO Workshop Talks

## Background on Atmospheric oxygen measurement

Atmospheric oxygen ($O_2$) 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 $O_2$ measurements were first established in 1988 by Professor Ralph Keeling at Scripps Institution of Oceanography [*Keeling*, 1988], and are now made at ~12 laboratories around the world, and at ~25 field stations. The measurements are extremely challenging. For example, the relative precision required, as stipulated by the World Meteorological Organisation Global Atmosphere Watch (WMO/GAW), is 0.0001%. By contrast, the WMO/GAW-required precision for $CO_2$, also considered challenging, is only 0.03%.

## Disclaimer:

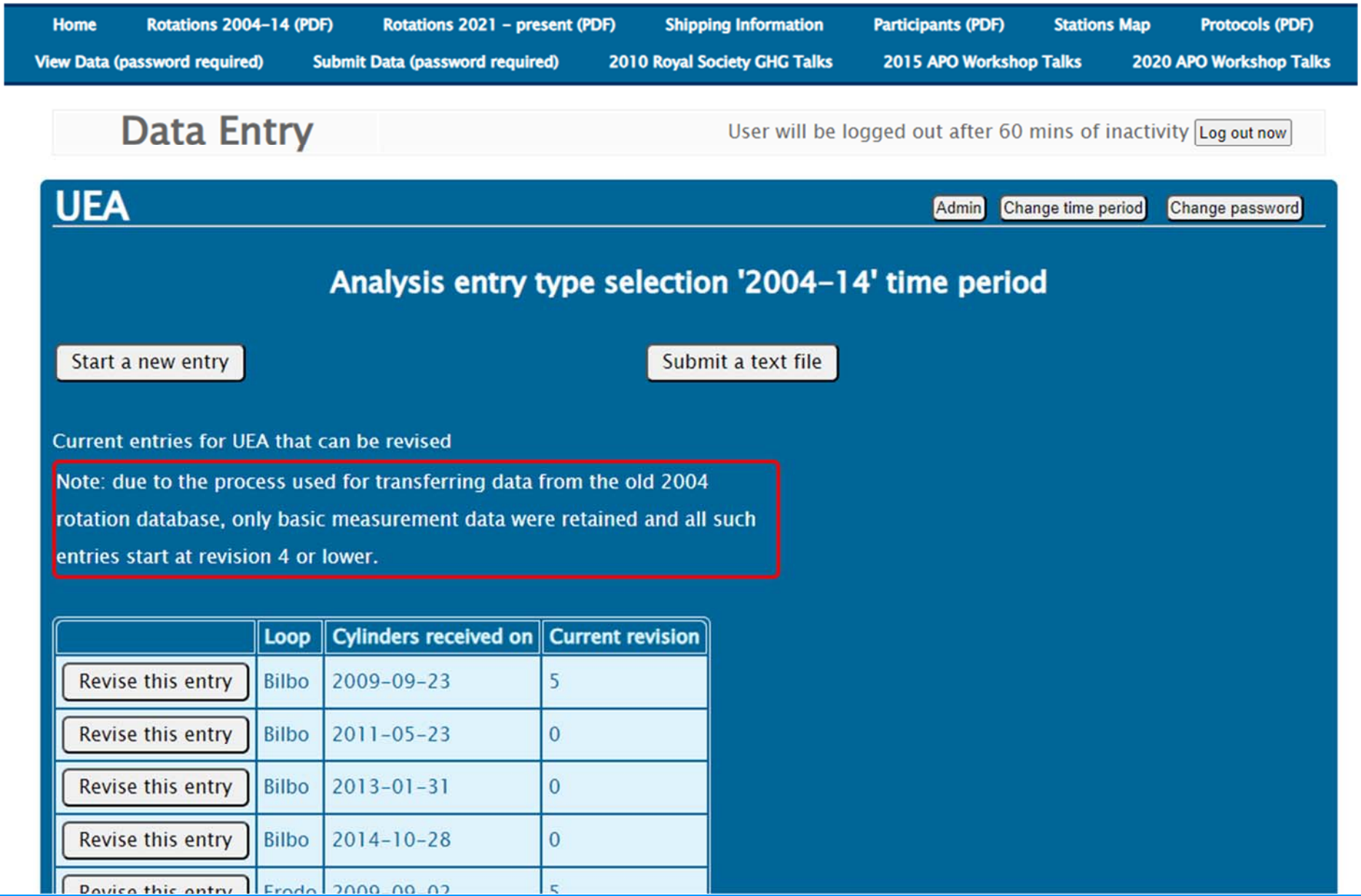
1. All results here are preliminary and provisional

2. These data must NOT be used to adjust any laboratory's calibration scales.

3. If you wish to use or present these data for any reason, please contact Andrew Manning:
A.Manning@uea.ac.uk

## Other Intercomparison

# Submitting data (i)



# Submitting data (ii)

| | |
|---|---|
| Revision number (0 if original, unrevised data): | 6 |
| Loop: | ○ Frodo<br>◉ Bilbo |
| Averaged data: | ○ Data averaged from analyses made over several days<br>◉ Data from single day's analysis |

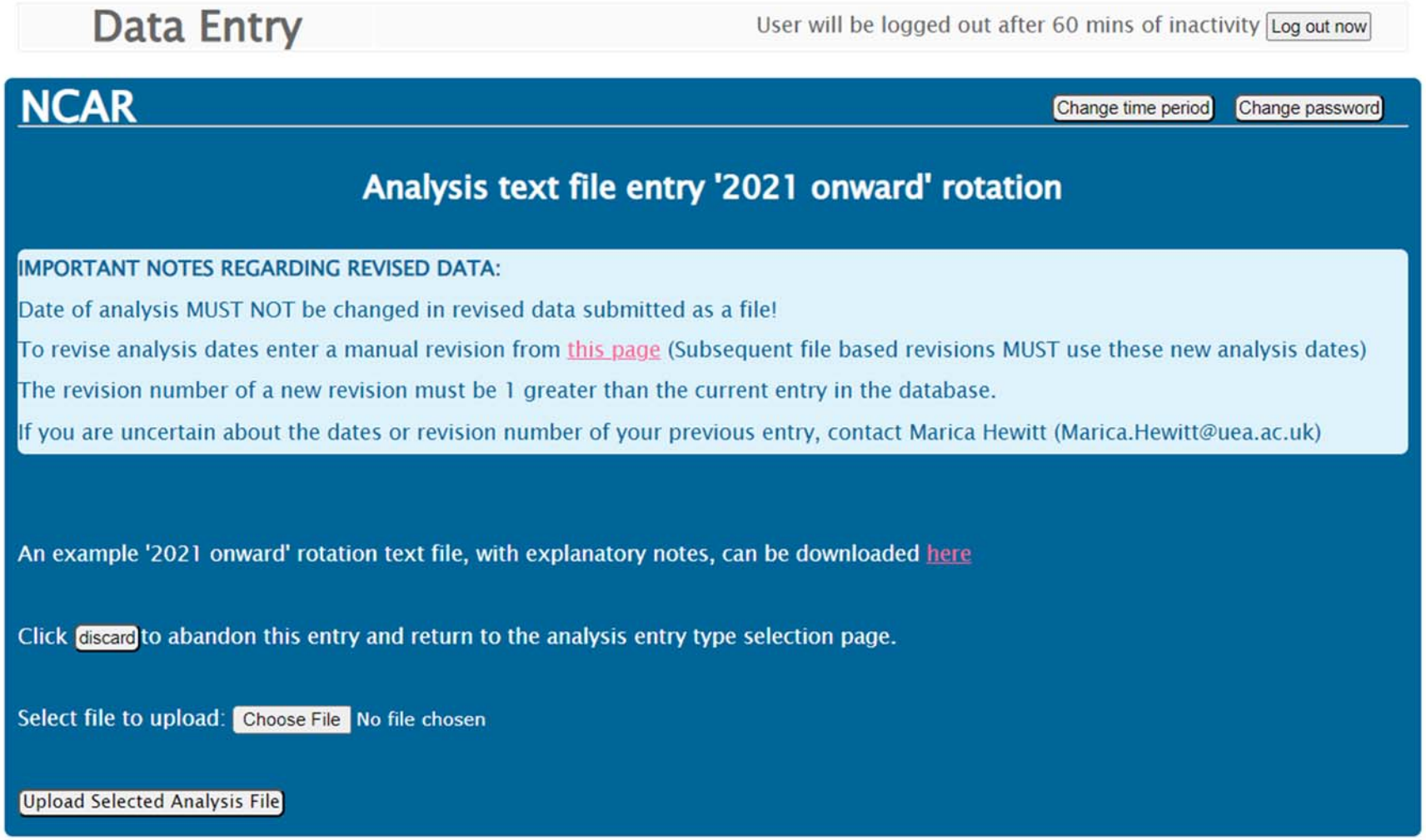
**PLEASE NOTE:**

**If text file uploads may be used in the future to revise this data, it is CRITICAL that the 'received pressure' date is the same as the earliest of the three dates for analysis of $O_2$, $CO_2$ and Ar!**

| Participant: **UEA** | Analysis date | Bilbo Cylinders | | | Calibration scale info<br>for each gas:<br>• supplied by who?<br>• name of scale? |
|---|---|---|---|---|---|
| | | CC178269 | CC177811 | CC180655 | |
| received pressure (bar) | 23/09/2009 | 88 | 65 | 91 | |
| final pressure (bar) | 23/09/2009 | 85 | 63 | 89 | |
| $O_2/N_2$ ratio (per meg) | 23/09/2009 | -242.93 | -398.44 | -413.90 | basic entry from csv, no info available |
| $O_2/N_2$ precision (per meg) | | 3.89 | 1.75 | 3.31 | |
| $CO_2$ mole fraction (ppm) | 23/09/2009 | 359.430 | 383.610 | 358.360 | basic entry from csv, no info available |
| $CO_2$ precision (ppm) | | 0.005 | 0.004 | 0.013 | |
| $Ar/N_2$ ratio (per meg) | dd/mm/yyyy | | | | basic entry from csv, no info available |
| $Ar/N_2$ precision (per meg) | | | | | |
| Make and model of regulators used: | | ... | | | |
| If you have given numbers in the 'precision' rows, please describe here how you calculate these: | | ... | | | |
| Are these final or provisional values? Please describe: | | ... | | | |
| Describe the on-site callibration you performed before analysing these cylinders: | | ... | | | |

# Submitting data (iii)

- **I strongly recommend submitting data via an automated ASCII text file**
  - Much faster after initial setup; reduces human errors



# Submitting data (iv)

- Example ASCII text file from Britt Stephens (NCAR)
  - Generated automatically in Britt's lab by his data processing code

GOLLUM_Logsheet_NCAR_Bilbo06

File Edit View

```
NB: all text after // on each line is not processed. 22 total rows in file mandatory. ';' delimiter mandat
Loop;                   B
Participant ID;         NCAR
Revised data;           Y
Revision number;        7
Averaged data?;         Y
O2 scale info;          SIO2017 O2 Scale (w/CO2-dilution corrected to WMO scale), -43 to -940 per meg, Jul
CO2 scale info;         WMO X2019 CO2 Scale (see SIO scale in separate file), 333 to 504 ppm, May 2021
Ar scale info;
Regulator info;         Air Liquide, Model-14
Precision details;      1 standard deviation of the average results from 3 separate days
Calibration details;    Annually, 6 primaries that have had numbers assigned at Scripps (O2 and CO2) and a
Damage noted;
Other comments;         Revision for changes to WMO CO2 and SIO O2 scales.
O2 analysis date;       20060723
CO2 analysis date;      20060723
Ar analysis date;       NaN
Results for all 3 cylinders below. If a cylinder is not analysed, please enter date and ID with all other
cyl ID   Pi  Pf  O2conc O2prec CO2conc CO2prec Arconc Arprec
CC177811 101 104 -398.88 1.02 383.572 0.006 NaN NaN
CC178269 127 127 -239.77 1.11 359.823 0.006 NaN NaN
CC180655 130 125 -412.18 1.19 358.7 0.029 NaN NaN
```

# Viewing data

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## Results 2004–14

Frodo and Bilbo cylinder intercomparisons:

| | | |
|---|---|---|
| $O_2/N_2$ | plots | Download O2N2 2004-14 summary CSV file |
| $CO_2$ | plots | Download CO2 2004-14 summary CSV file |
| $Ar/N_2$ | plots | Download ArN2 2004-14 summary CSV file |
| Cylinder Pressures | plot | |

## Results 2021 – present

Frodo and Bilbo cylinder intercomparisons:

| | |
|---|---|
| $O_2/N_2$ | plots |
| $CO_2$ | plots |
| $Ar/N_2$ | plots |
| Cylinder Pressures | plot |

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UEA Software and Website Design and Development — envSoft — envSoft@uea.ac.uk

# Viewing data: Live website demonstration

https://gollum.uea.ac.uk/results/index.php

- Note: unusual error bars (for summary average plots)
- "Zero" refers to SIO measurements in Oct/Nov2020
  - Or Sep2004, for the older period
- Stations with calibration scale offsets are indicated in legend
- Diamonds = Frodo; Circles = Bilbo
- Dashed horizontal lines = WMO compatibility goals

# Very preliminary and provisional results

- **VERY IMPORTANT:**
  - GOLLUM data are currently a mess, sorry!
  - Many different calibration scales; sometimes not even known
  - Much data not updated to latest scales
  - Some data not yet received
  - Some obvious errors, which labs need more time to investigate

- **Please do not draw any negative conclusions from the following slides!**
  - These slides are only to demonstrate some of the analyses that are possible with GOLLUM data

# Smorgasbord of calibration scales

| Organisation | $O_2/N_2$ | $CO_2$ | $Ar/N_2$ |
|---|---|---|---|
| AIST | AIST | AIST | ? |
| CIO-RUG | SIO2017 | ? | – |
| ICOS | Pre-SIO2017 | WMO X2019 | ? |
| MPI-BGC | Pre-SIO2017 | ? | ? |
| NCAR | SIO2017 | SIO $CO_2$[1] + WMO X2019 | – |
| NIES | NIES original | NIES 09 | – |
| NIWA | Pre-SIO2017 | ? | – |
| PU | PU | WMO X2007 | ? |
| SIO | SIO2017 | SIO $CO_2$[1] | SIO $Ar/N_2$ |
| TU | TU | TU | – |
| UBERN | ? | ? | ? |
| UEA | Pre-SIO2017 | SIO $CO_2$[1] + WMO X2007 | – |

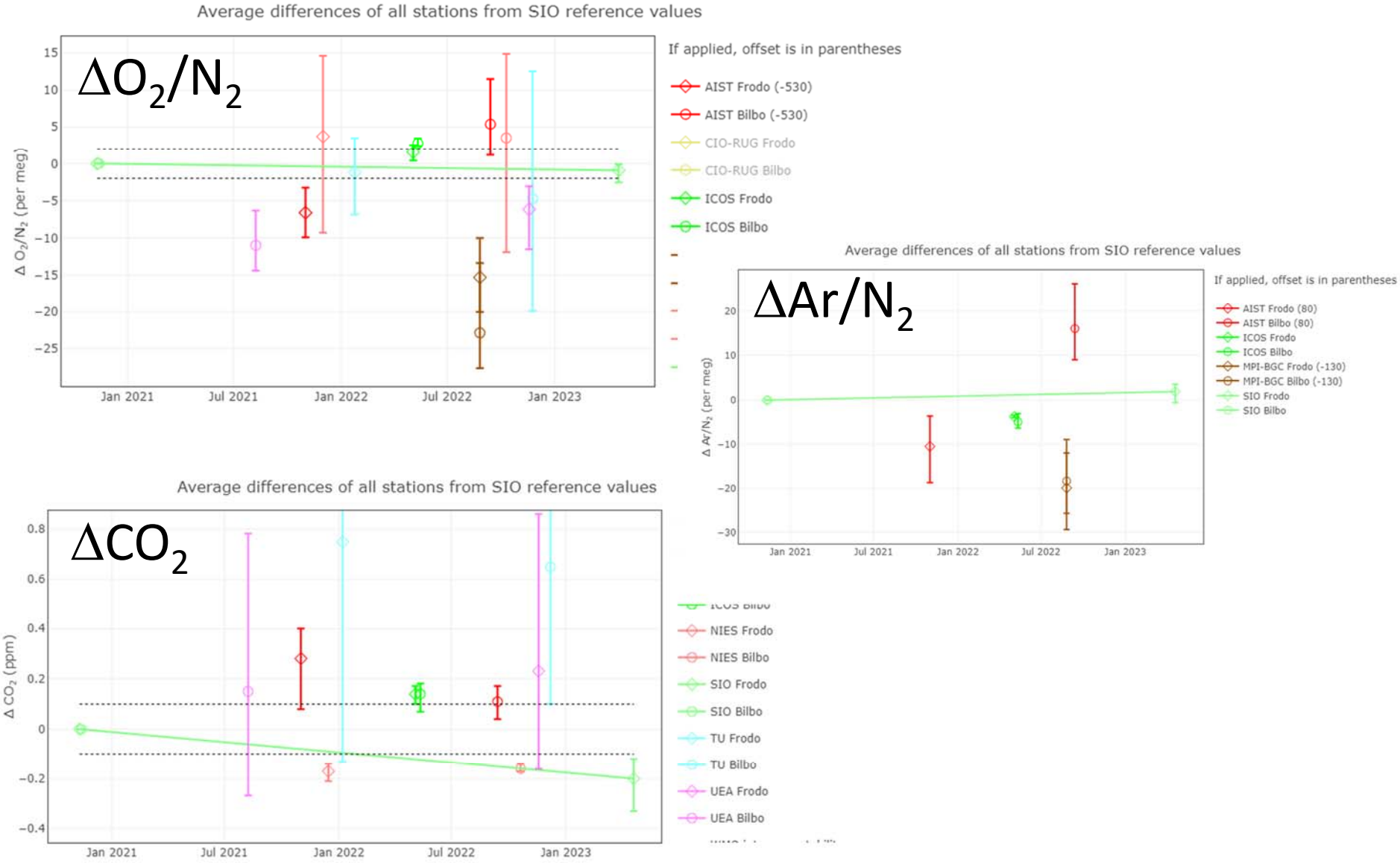
[1] But what does "SIO $CO_2$" mean?

# Smorgasbord of calibration scales

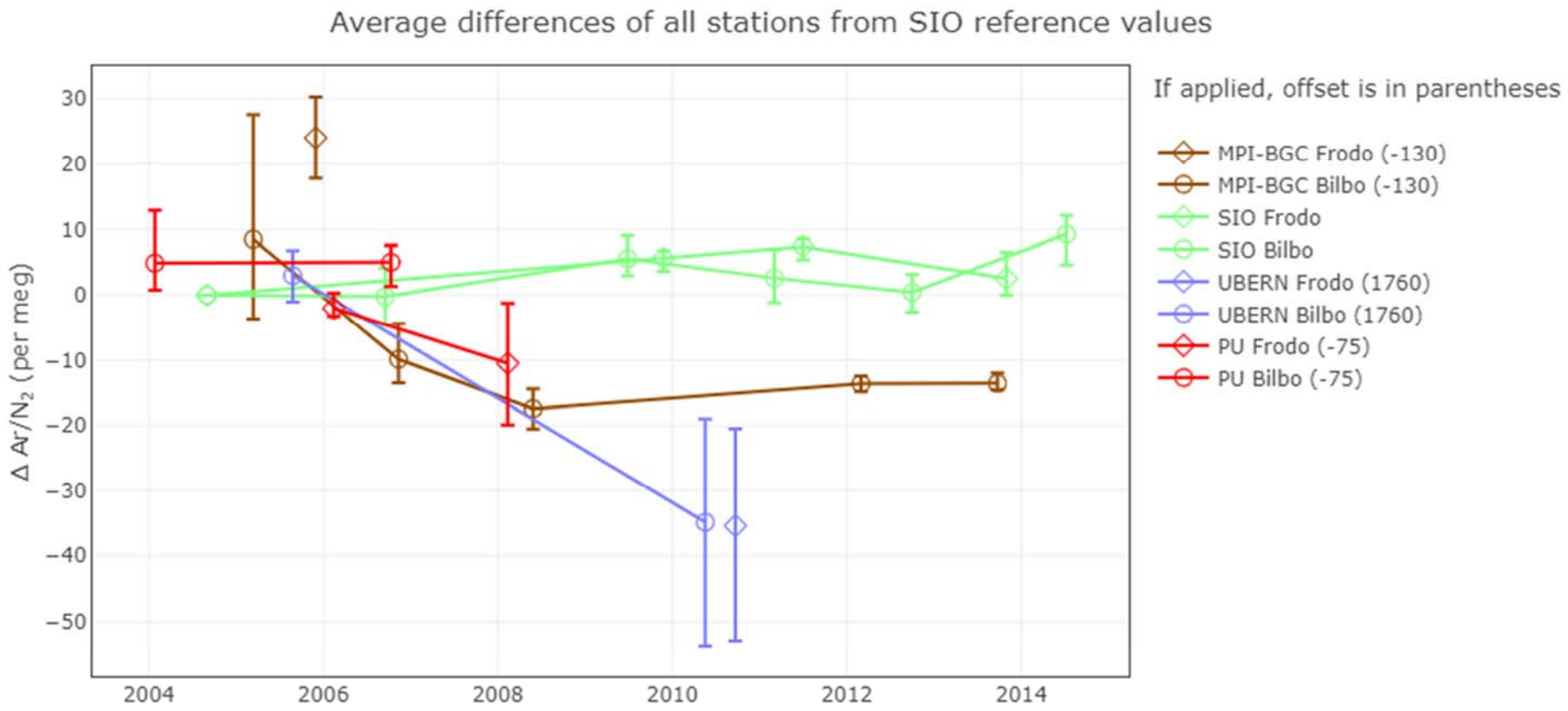
| Organisation | $O_2/N_2$ | $CO_2$ | $Ar/N_2$ |
|---|---|---|---|
| AIST | AIST | AIST | ? |
| CIO-RUG | SIO2017 | ? | – |
| ICOS | Pre-SIO2017 | WMO X2019 | ? |
| MPI-BGC | Pre-SIO2017 | ? | ? |
| NCAR | SIO2017 | SIO $CO_2$[1] + WMO X2019 | – |
| NIES | NIES original | NIES 09 | – |
| NIWA | Pre-SIO2017 | ? | – |
| PU | PU | WMO X2007 | ? |
| SIO | SIO2017 | SIO $CO_2$[1] | SIO $Ar/N_2$ |
| TU | TU | TU | – |
| UBERN | ? | ? | ? |
| UEA | Pre-SIO2017 | SIO $CO_2$[1] + WMO X2007 | – |

[1] But what does "SIO $CO_2$" mean?

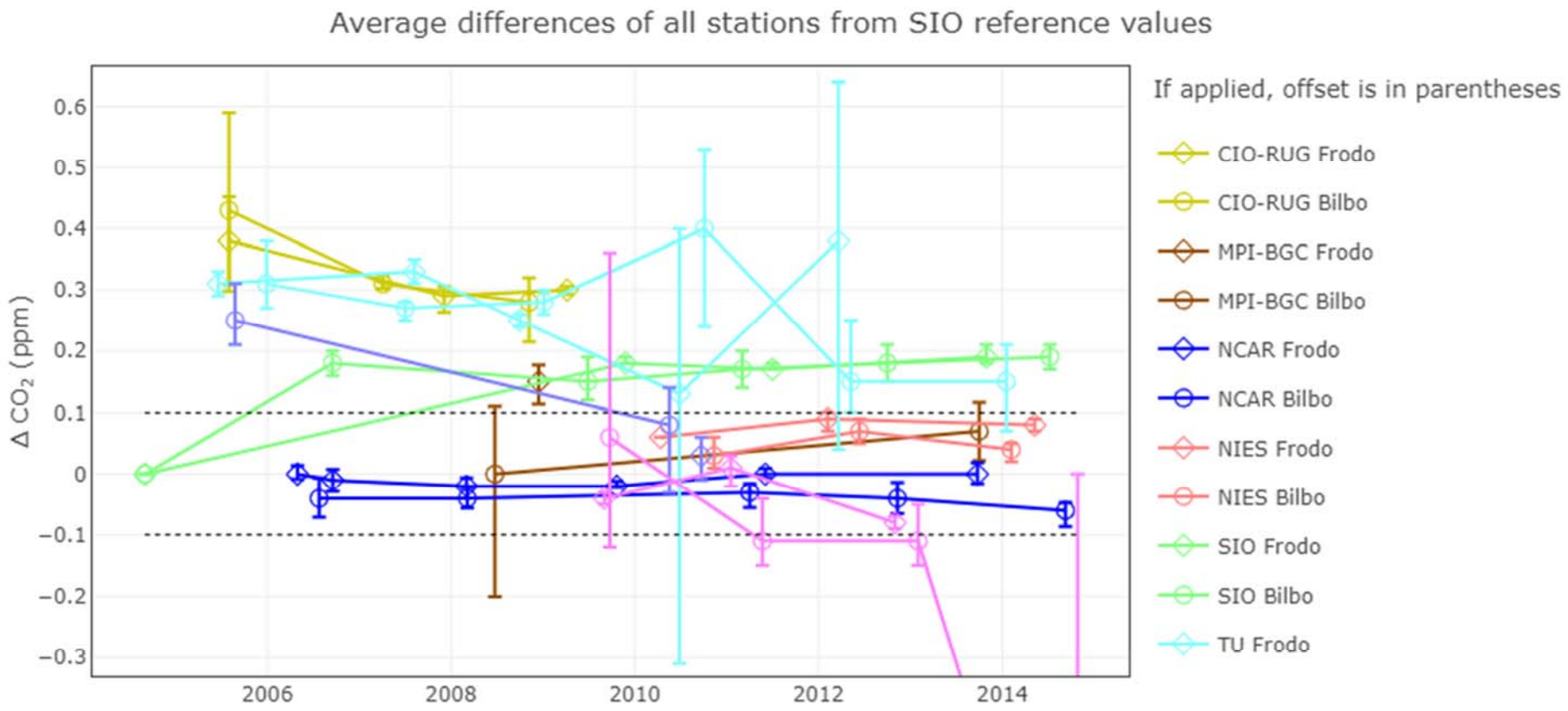
# 2021-2023 summary results: $O_2/N_2$, $CO_2$, $Ar/N_2$



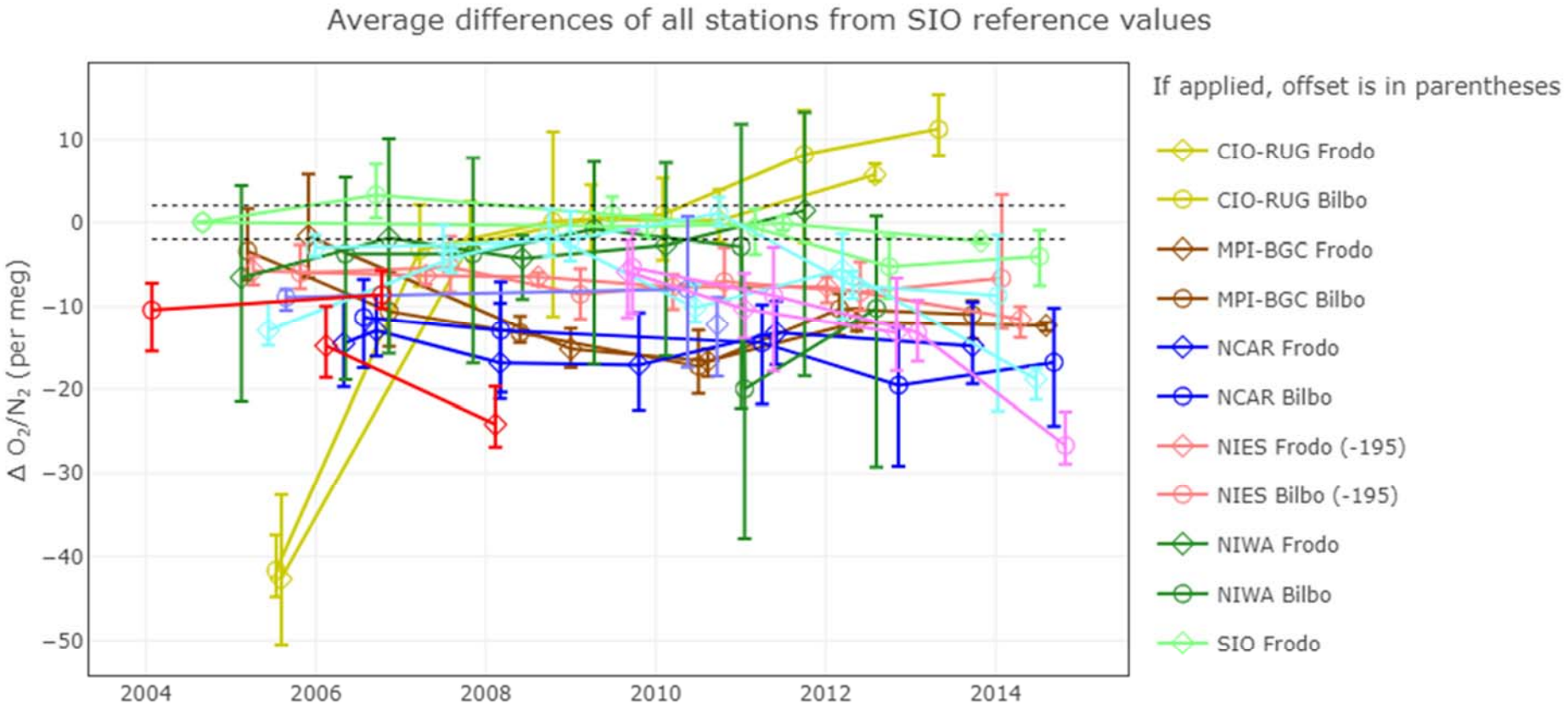
# 2004-2014 summary results: $Ar/N_2$



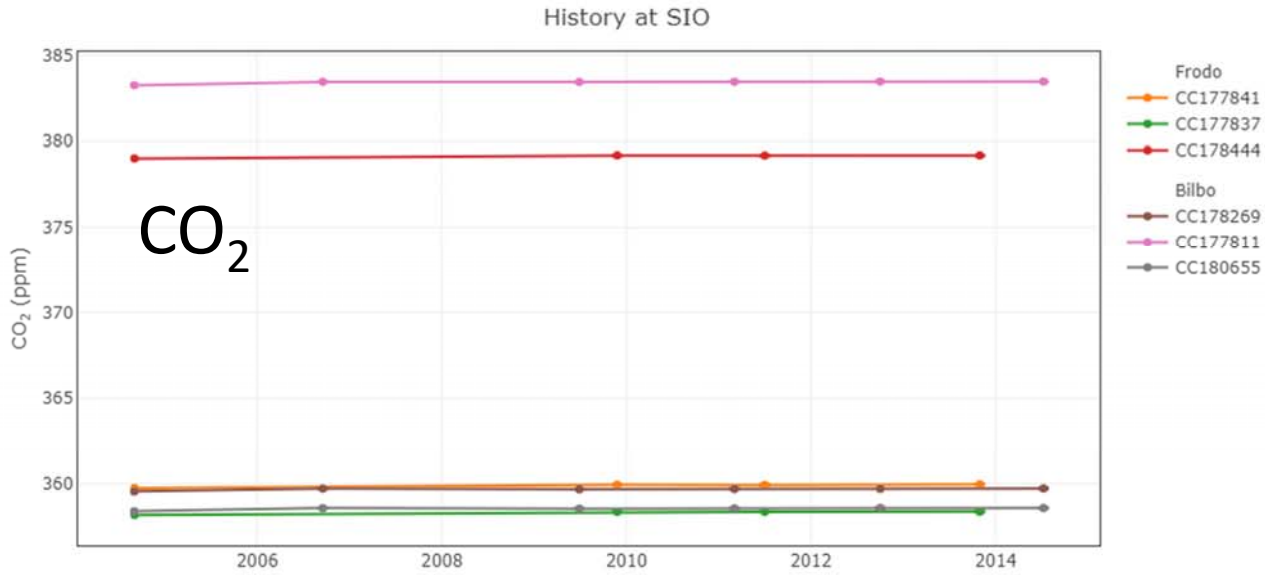
# 2004-2014 summary results: $CO_2$



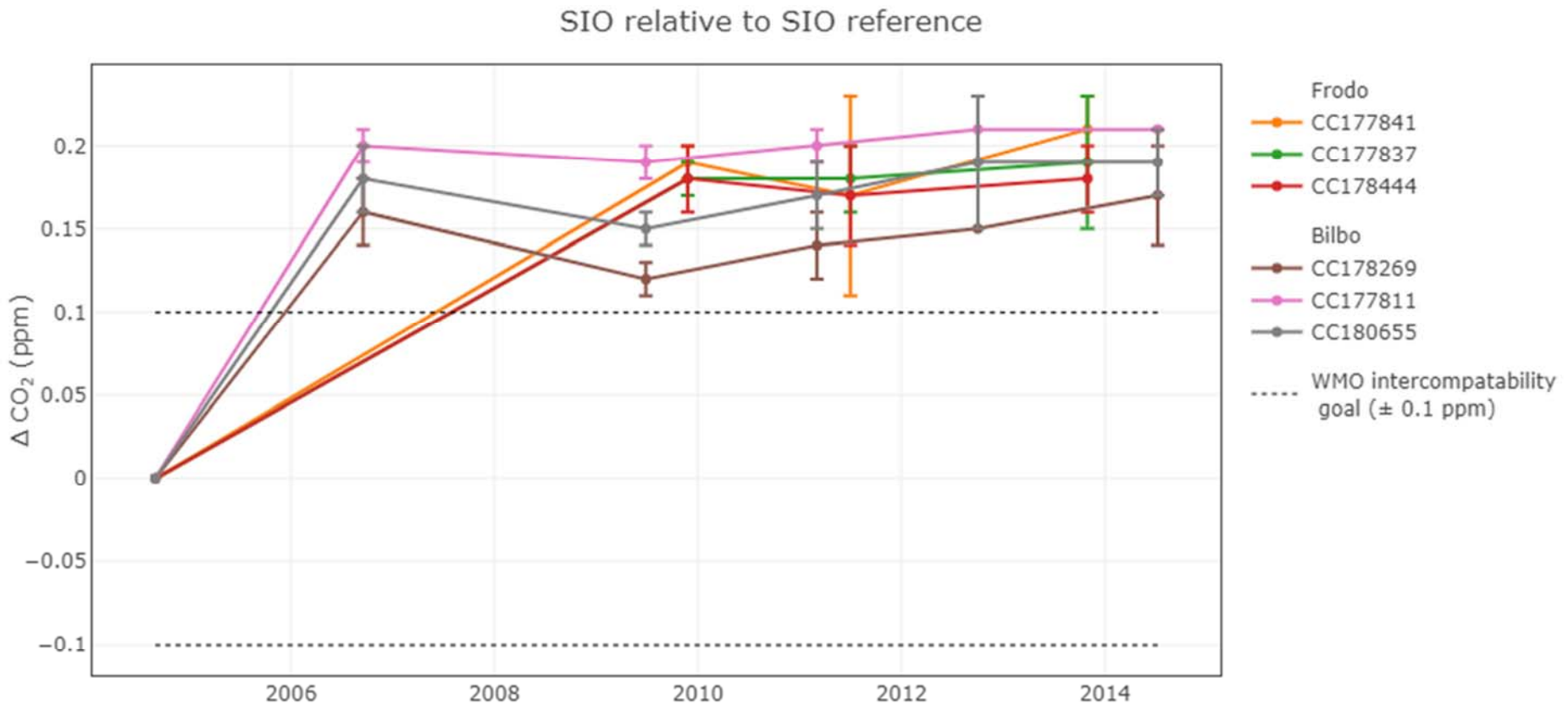
# 2004-2014 summary results: $O_2/N_2$



# 2004-2014: Scripps in more detail: Ranges

# 2004-2014: Scripps in more detail: $CO_2$ trends



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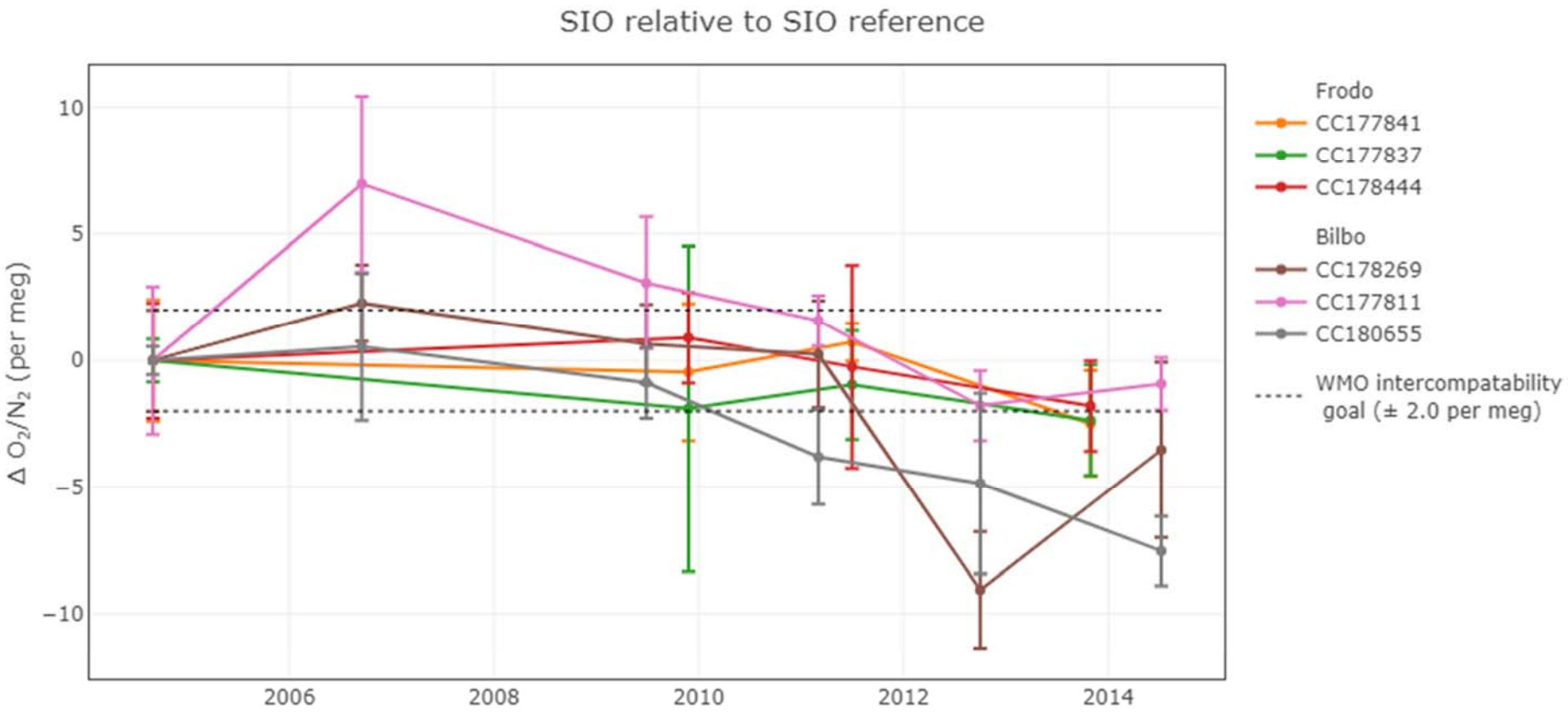
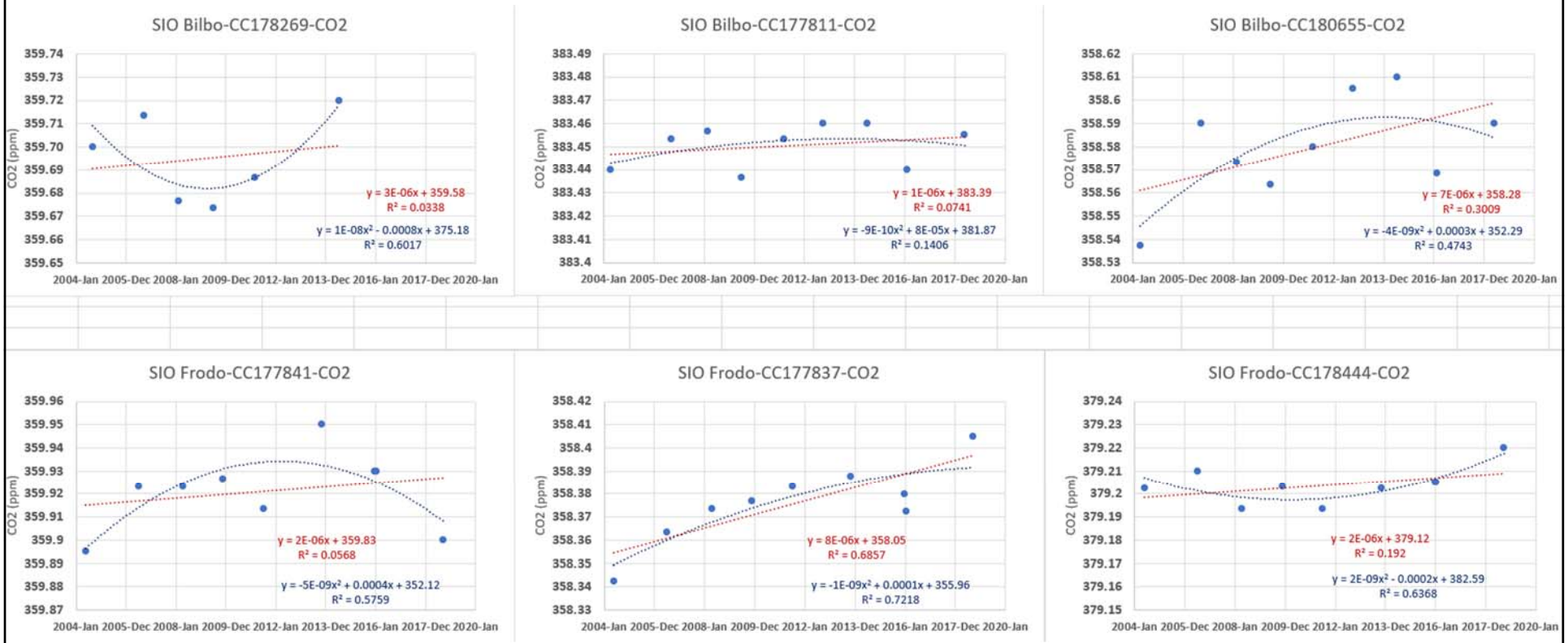


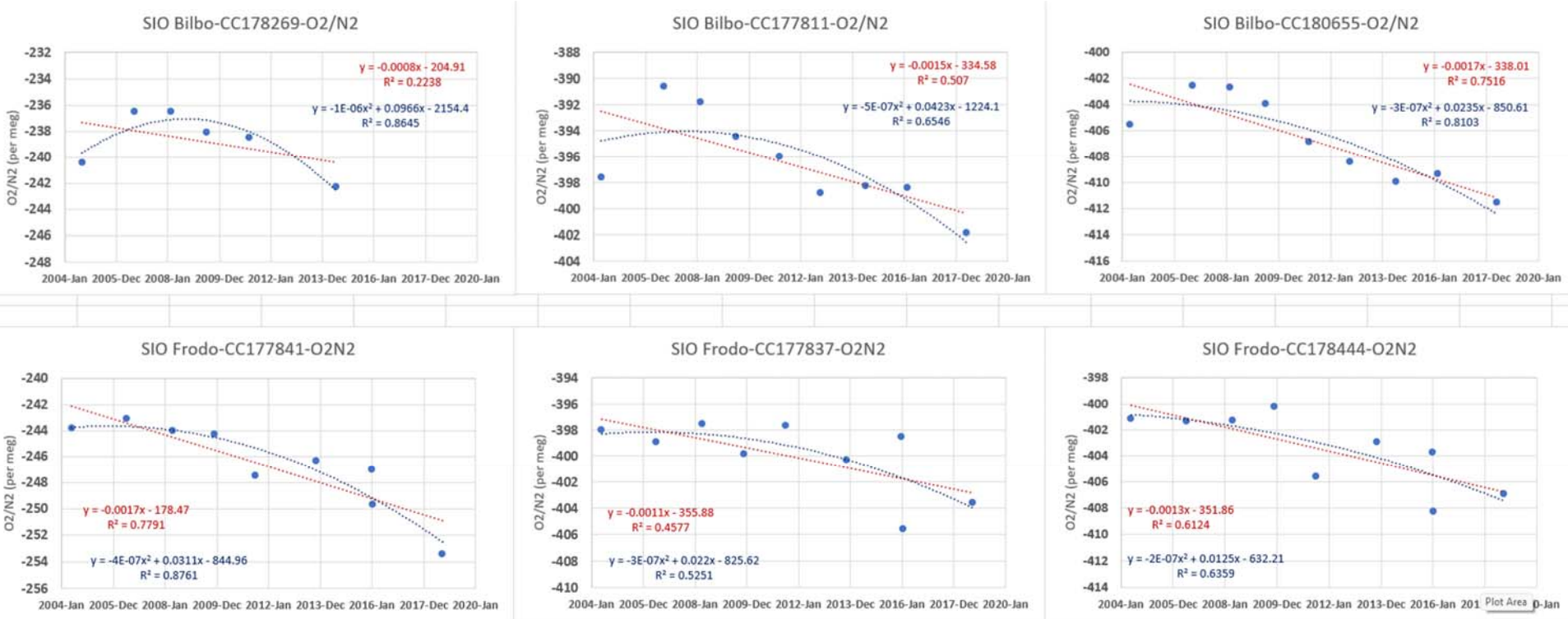
# Linear + quadratic fits to Scripps $CO_2$

- Additional Scripps measurements in 2016 and 2018, allows more robust trend lines
- Linear fits in red; quadratic fits in blue



# Linear + quadratic fits to Scripps $O_2/N_2$

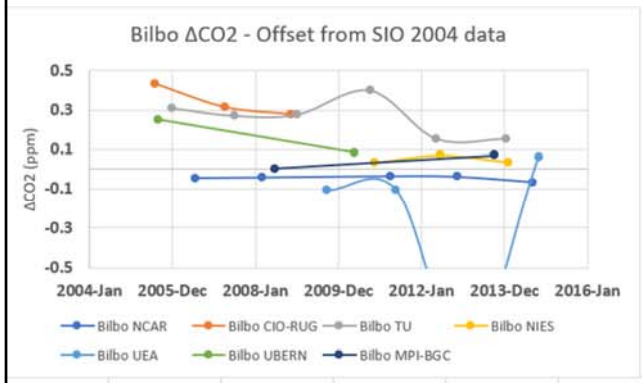
- Additional Scripps measurements in 2016 and 2018, allows more robust trend lines
- Linear fits in red; quadratic fits in blue

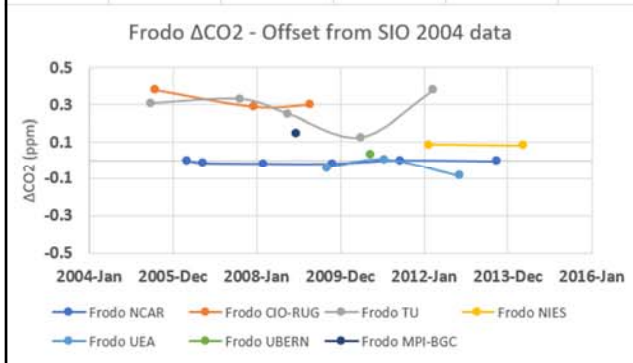


# Recalculate all results with Scripps fits: $CO_2$

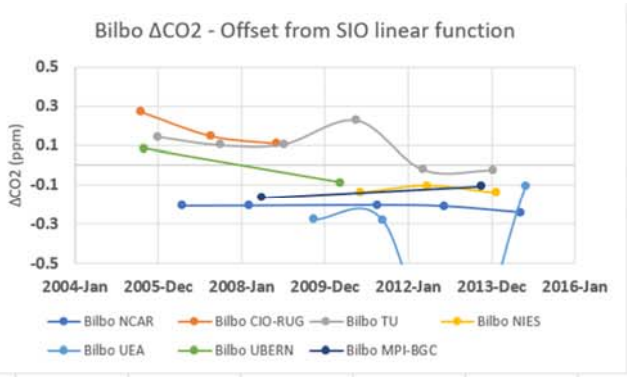
- Do we get better agreement with linear or quadratic fits, compared to SIO 2004 offset?
  - No point trying to answer this until better quality control + scale updates

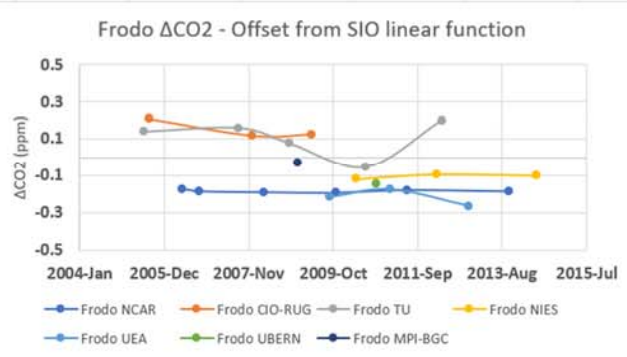
SIO 2004 offset



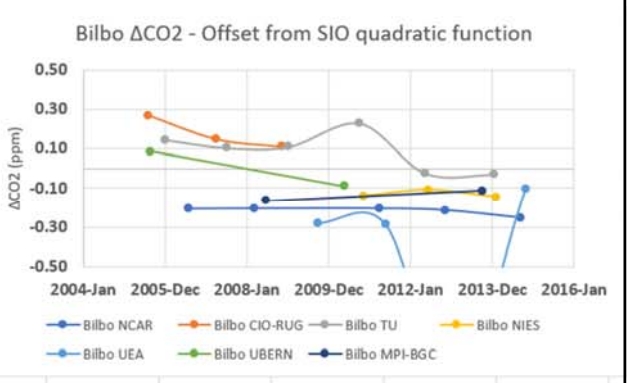



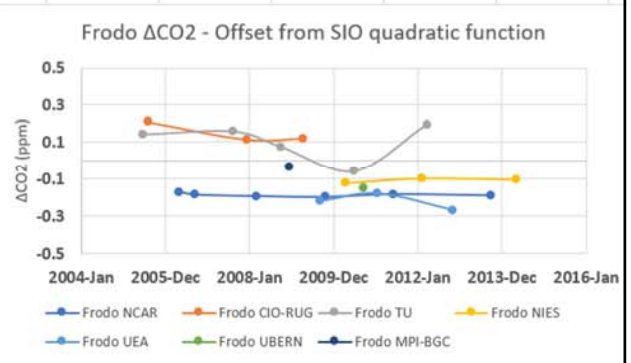

Linear offset




Quadratic offset

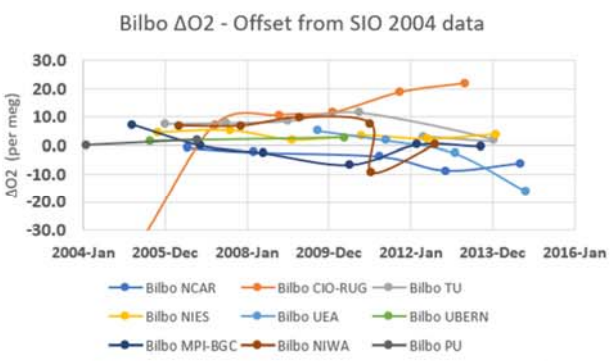


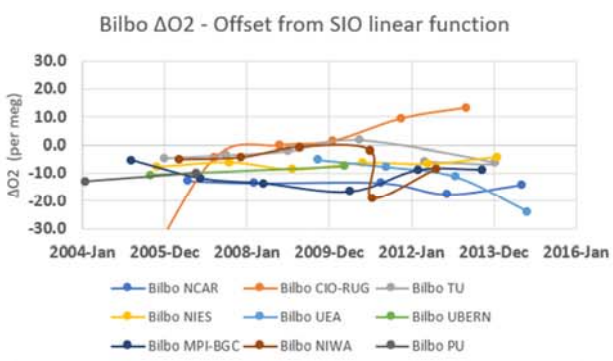
# Recalculate all results with Scripps fits: $O_2/N_2$

- Do we get better agreement with linear or quadratic fits, compared to SIO 2004 offset?
  - No point trying to answer this until better quality control + scale updates

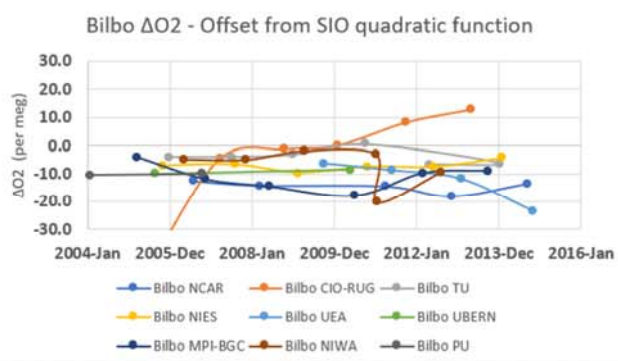
SIO 2004 offset

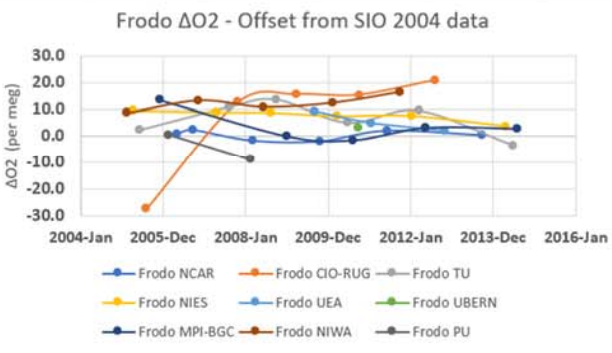


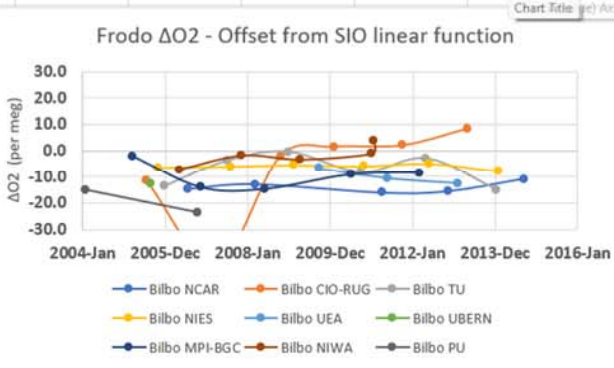

Linear offset

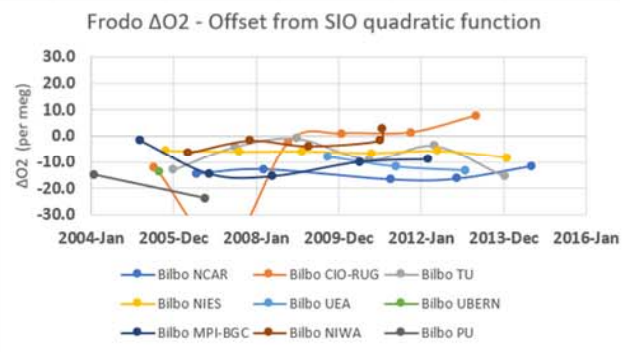



Quadratic offset



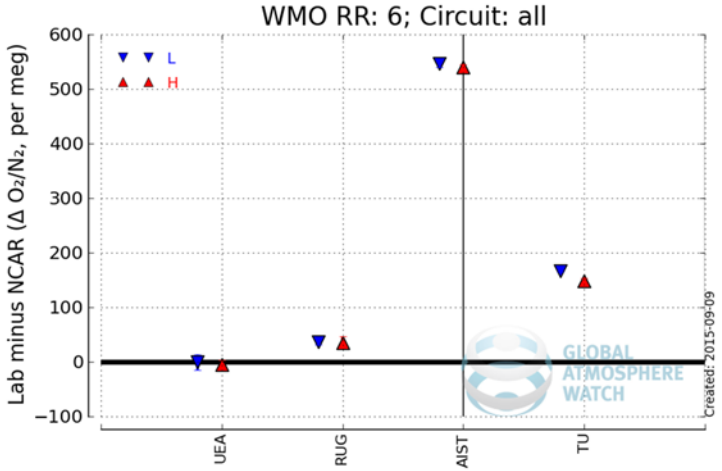



# Other $O_2$ intercomparison programmes

- "Sausage" flask intercomparison
  - GOLLUM ran such a programme for a few years in the 2000's
  - Any interest in restarting this?
- Co-located "supersite" measurements
  - Flasks from two organisations: e.g. ALT (SIO + MPI-BGC)
  - Continuous and flasks: e.g. LJO
  - Do we want more of these?
- WMO Round Robins
  - Britt (NCAR) measures these for $O_2/N_2$, so these act like a GOLLUM snapshot
    - You need to tell NOAA (Duane) that you want to do $O_2/N_2$ analyses
    - Figure shows 2014/15 WMO RR:

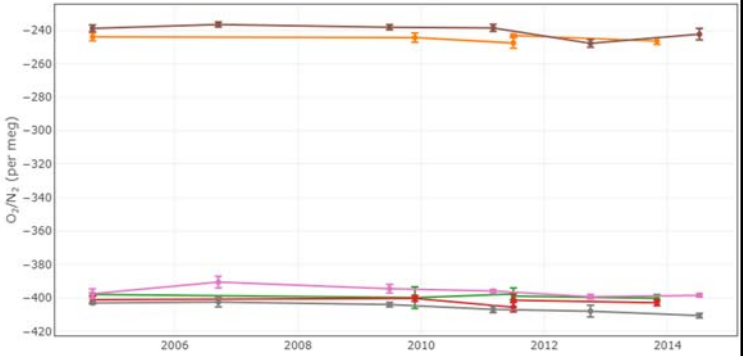


# Future outlook: Suggestions and plans (i)

- Establish recommendations for best practice to maintain links to SIO $O_2$ scale
  - A) For those who have Scripps Primary cylinders
  - B) For those who maintain their own in-house scales
- GOLLUM cylinders **must** rotate faster
  - 5 weeks in each laboratory (+ shipping time)
  - Average so far = ~8 weeks
- GOLLUM data **must** be submitted timely
  - 5 weeks after analyses
- Many labs **must** update to SIO 2017 $O_2$ scale
  - And any successor SIO $O_2$ scale
  - Suggested goal to do so: 1 year after scale is released
  - My lab is also very guilty here!!
- New scale releases from SIO should be announced on GOLLUM mailing list
  - (To add/remove people to GOLLUM (or APO) mailing lists – email Andrew)
- **I welcome feedback and criticism** – website, protocols, data analyses…

# Future outlook: Suggestions and plans (ii)

- Next steps – my request:
  - Everyone to quality control their GOLLUM data, including checking how it looks on the website
  - Where relevant, everyone to update to SIO 2017 $O_2$ scale
    - And apply next SIO scale update promptly
  - Then we will look again at linear + quadratic offsets
    - Any suggestions for alternative offset analyses?
- What should we do about $CO_2$, given the scale differences?
- Have not looked at mole fraction dependencies, but this will be limited by the mole fractions of the cylinders:
  - 2021-onwards will be better…
- Cylinders with dip tubes?




- Finally, how to use GOLLUM results to merge datasets for the data users???
  - In “Cucumbers” ICP, we quantified average lab offsets over 5-year timeframes