

The 7th Asia-Pacific GAW Workshop on GHG

WMO/IAEA 6th Round-Robin Comparison & related progress

WMO/IAEA Round Robin Referee: ***Lingxi Zhou**¹
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NOAA Coordinating Team: **Pieter Tans**², **Duane Kitzis**²,
Ken Masarie² (wmorr@noaa.gov)

1. CAMS, CMA, China
2. GMD, ESRL, NOAA, USA,

22-23 Oct. 2015, Jeju



- **The primary goal of the WMO/IAEA RR Comparison Experiment is to assess the level to which participating labs maintain their link to the WMO scales using normal operating procedures.**

- **Maintaining a direct link to the WMO scales and successfully propagating the scales to working laboratory scales are fundamental to the measurement process and to achieving the desired levels of compatibility between laboratories as specified by the GGMT meetings.**

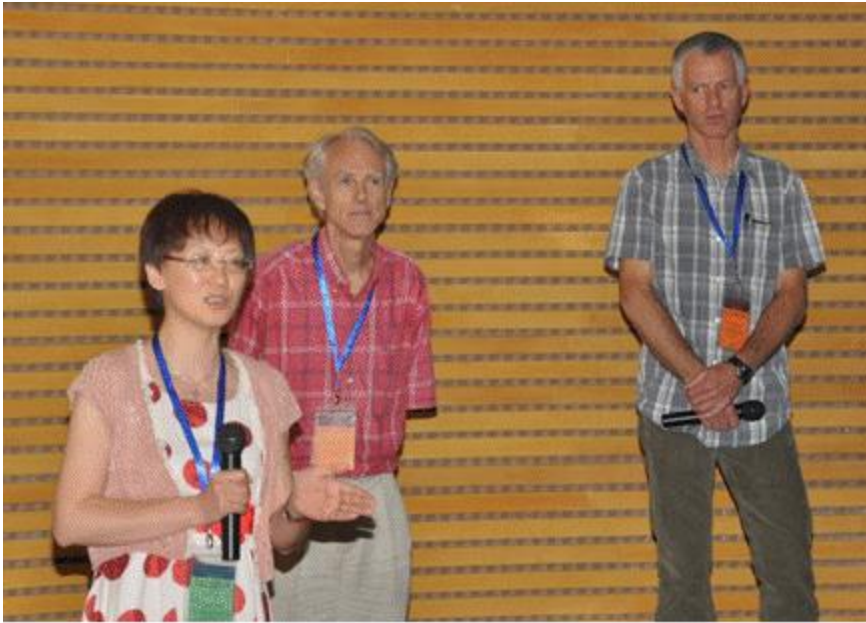


WMO/IAEA Recommended compatibility of

Table 1- Recommended compatibility of measurements within the scope of GGMT

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO ₂	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm	250 – 520 ppm
GAW Report No. 213, July 2014				
CH ₄	± 2 ppb	± 5 ppb	1700 – 2100 ppb	300 – 2600 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	20 -500 ppb
N ₂ O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb	260 – 370 ppb
SF ₆	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt	1.1 – 9.8 ppt
H ₂	± 2 ppb	± 5 ppb	450 – 600 ppb	140 – 1200 ppb
δ ¹³ C-CO ₂	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB	
δ ¹⁸ O-CO ₂	± 0.05‰	± 0.1‰	-2 to +2‰ vs. VPDB	
Δ ¹⁴ C-CO ₂	± 0.5‰	± 3‰	0-70‰	
Δ ¹⁴ C-CH ₄	± 0.5‰		50-350‰	
Δ ¹⁴ C-CO	± 2 molecules cm ⁻³		0-25 molecules cm ⁻³	
δ ¹³ C-CH ₄	± 0.02‰	± 0.2‰		
δD-CH ₄	± 1‰	± 5‰		
O ₂ /N ₂	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

- **A dedicated website**
(<http://www.esrl.noaa.gov/gmd/ccgg/wmorr>)
was developed and works well which covers
General Info (Docs & Guidelines), **Products** (Archived Results & WMO Reports), **Current RR** (Instructions, Participants, Calibration Scales, Cylinders, Time-Table, Status, and Reporting function such as Account Information, Cylinder Arrival, Cylinder Shipping and Measurement Results), **Contact & Feedback**
- **[Participants will no longer report results directly to the WMO/IAEA RR referee.](#)**



- **A dedicated RR website**

Ken Masarie



- **Duane Kitzis, doorway at NWR**



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NOAA Coordinating Team

Pieter Tans (Carbon Cycle Group Chief)
Duane Kitzis (Logistics)
Ken Masarie (Web and Data Management)

WMO/IAEA Round Robin Referee

Lingxi Zhou (Referee)
E-mail: zhoulx@cams.cma.gov.cn

- The 6th RR started in **Jan. 2014** and officially close on **7 Sept. 2015**
- Labs in each of the 5 circuits (**Circuit 1: 13 labs, Circuit 2: 8 labs, Circuit 3: 10 labs, Circuit 4: 11 labs, Circuit 5: 6 labs**) received a set of two RR cylinders.



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WMO/IAEA Round Robin Comparison Experiment - Current Status

Round Robin #6 is currently underway [started: January 2014]

State of the current Round Robin experiment. The initial TimeTable, set by the NOAA Team, may be adjusted based on actual cylinder arrival and shipping dates reported by participants.

Please Note: The current Round Robin experiment will close on **2015-09-07**.

X - awaiting input information from lab.

The actual departure date as reported by the participant is displayed as

- **yyyy-mm-dd** if it is on or before the actual arrival date plus the scheduled number of weeks
- **yyyy-mm-dd** if it is within 2 weeks of the actual arrival date plus the scheduled number of weeks
- **yyyy-mm-dd** if it is beyond 2 weeks of the actual arrival date plus the scheduled number of weeks.

[All Circuits](#)
[Circuit 1](#)
[Circuit 2](#)
[Circuit 3](#)
[Circuit 4](#)
[Circuit 5](#)

Round Robin #6: 48 labs total

Circuit 1: 13 labs

Cylinders: CB10006, CB09974



Circuit 1: 13 labs

Cylinders: CB10006, CB09974

Lab	Scheduled Arrival	Scheduled Departure	Scheduled Weeks	Actual Arrival	Actual Departure	Measurements Completed	Results Reported
1. NCAR (United States)	2014-02-27	2014-03-20	3	2014-02-25	2014-03-26	✓	✓
2. NOAA-CSD (United States)	2014-04-10	2014-04-24	2	2014-04-11	2014-05-02	✓	✓
3. NEON (United States)	2014-05-08	2014-05-22	2	2014-05-08	2014-05-28	✓	✓
4. NIST (United States)	2014-05-29	2014-06-19	3	2014-06-03	2014-07-11	✓	✓
5. HU (United States)	2014-07-03	2014-07-24	3	2014-07-15	2014-08-05	✓	✓
6. PSU (United States)	2014-07-31	2014-08-14	2	2014-08-07	2014-08-22	✓	✓
7. CALTECH (United States)	2014-08-21	2014-09-18	4	2014-09-09	2014-10-06	✓	✓
8. BLG (United States)	2014-09-25	2014-10-23	4	2014-10-09	2014-11-05	✓	✓
9. AMERIFLUX (United States)	2014-10-30	2014-11-13	2	2014-11-12	2014-11-24	✓	✓
10. EC (Canada)	2014-11-20	2014-12-18	4	2014-12-04	2014-12-22	✓	✓
11. NOAA (United States)	2015-01-05	2015-02-16	6	2015-01-05	2015-06-15	✓	N/A
12. HMS (Hungary)	2015-06-30	2015-07-14	2	2015-06-15	2015-07-10	✓	✓
13. AEMET (Spain)	2015-08-04	2015-09-01	4	2015-07-20	2015-08-17	✓	✓



Circuit 2: 8 labs

Cylinders: CB10295, CB10296

Lab	Scheduled Arrival	Scheduled Departure	Scheduled Weeks	Actual Arrival	Actual Departure	Measurements Completed	Results Reported
1. NCAR (United States)	2014-02-27	2014-03-20	3	2014-02-25	2014-03-26	✓	✓
2. CSIRO (Australia)	2014-04-20	2014-05-18	4	2014-04-21	2014-05-29	✓	✓
3. NIWA (New Zealand)	2014-05-25	2014-06-22	4	2014-06-10	2014-07-08	✓	✓
4. SAWS (South Africa)	2014-06-29	2014-07-27	4	2014-07-29	2014-10-10	✓	✓
5. CMA (Peoples Republic of China)	2014-08-03	2014-08-31	4	2014-10-21	2014-11-21	✓	✓
6. KMA/KGAWC (Republic of Korea)	2014-12-09	2015-01-06	4	2014-12-09	2015-02-03	✓	✓
7. NOAA (United States)	2015-02-06	2015-03-06	4	2015-02-09	2015-07-07	✓	N/A
8. MGO (Russia)	2015-07-19	2015-08-02	2	2015-07-27	2015-08-14	✓	✓

Circuit 3: 10 labs

Cylinders: CB09968, CB10288

Lab	Scheduled Arrival	Scheduled Departure	Scheduled Weeks	Actual Arrival	Actual Departure	Measurements Completed	Results Reported
1. NCAR (United States)	2014-02-27	2014-03-20	3	2014-02-25	2014-03-26	✓	✓
2. LSCE (France)	2014-04-30	2014-05-28	4	2014-05-07	2014-06-16	✓	✓
3. WCC-EMPA (Switzerland)	2014-06-04	2014-07-02	4	2014-06-19	2014-07-11	✓	✓
4. EMPA (Switzerland)	2014-07-09	2014-08-06	4	2014-07-21	2014-08-26	✓	✓
5. FMI (Finland)	2014-08-13	2014-09-10	4	2014-09-01	2014-10-01	✓	✓
6. IMAU (Netherlands)	2014-09-17	2014-10-15	4	2014-10-02	2014-11-13	✓	✗
7. RUG (Netherlands)	2014-11-25	2014-12-23	4	2014-11-14	2015-01-15	✓	✓
8. ECN (The Netherlands)	2015-01-15	2015-02-12	4	2015-01-16	2015-02-02	✓	✓
9. UEA (United Kingdom)	2015-02-19	2015-03-19	4	2015-02-15	2015-04-01	✓	✓
10. RHUL (United Kingdom)	2015-03-26	2015-04-23	4	2015-04-01	2015-05-05	✓	✓

Circuit 4: 11 labs

Cylinders: CB10259, CB10281

Lab	Scheduled Arrival	Scheduled Departure	Scheduled Weeks	Actual Arrival	Actual Departure	Measurements Completed	Results Reported
1. NCAR (United States)	2014-02-27	2014-03-20	3	2014-02-25	2014-03-26	✓	✓
2. UHEI-IUP (Germany)	2014-05-20	2014-06-17	4	2014-05-30	2014-07-10	✓	✓
3. UBA/SCH (Germany)	2014-07-29	2014-08-26	4	2014-07-14	2014-07-30	✓	✓
4. KIT/IMK-IFU (Germany)	2014-09-02	2014-09-16	2	2014-08-01	2014-09-24	✓	✓
5. UBA/ZUG (Germany)	2014-09-23	2014-10-21	4	2014-09-25	2014-10-20	✓	✓
6. MPI-BGC (Germany)	2014-10-28	2014-11-25	4	2014-10-27	2014-12-18	✓	✓
7. RSE (Italy)	2015-02-17	2015-03-03	2	2014-12-30	2015-01-27	✓	✓
8. IAFMS (Italy)	2015-03-10	2015-03-24	2	2015-01-27	2015-02-03	✓	✓
9. UNIURB (Italy)	2015-03-31	2015-04-28	4	2015-02-03	2015-04-15	✓	✓
10. ENEA (Italy)	2015-05-05	2015-05-19	2	2015-04-30	2015-06-12	✓	✓
11. ICOS (European Union)	2015-06-17	2015-07-15	4	2015-06-29	2015-07-29	✓	✓



Circuit 5: 6 labs

Cylinders: CB10067, CB09973

Lab	Scheduled Arrival	Scheduled Departure	Scheduled Weeks	Actual Arrival	Actual Departure	Measurements Completed	Results Reported
1. JMA (Japan)	2013-12-12	2014-01-09	4	2013-09-24	2013-11-13	✓	✓
2. MRI (Japan)	2014-01-16	2014-02-06	3	2013-11-14	2013-12-13	✓	✓
3. AIST (Japan)	2014-04-03	2014-05-01	4	2013-12-13	2014-01-24	✓	✓
4. NIES (Japan)	2014-02-27	2014-03-27	4	2014-01-24	2014-02-14	✓	✓
5. TU (Japan)	2014-04-03	2014-05-01	4	2014-02-18	2014-04-14	✓	✓
6. NCAR (United States)	2014-07-01	2014-07-22	3	2014-07-01	2015-06-10	✓	✓

- As in previous RR, air in each cylinder is near ambient range of CO_2 , CH_4 , CO , H_2 , N_2O , SF_6 , O_2/N_2 , $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ of CO_2
- The preliminary results reported by the participants posted to the dedicated RR website on 8 Sept. (the week before GGMT-2015)
- It is not terribly useful to send results once the RR results are made available to all participants because the experiment is no longer a blind.



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WMO/IAEA Round Robin Comparison Experiment - Archived Results

Round Robin 6 (2014-2015) ▾

Parameter: CH4 ▾

- CH4
- CO2
- CO2C13
- CO2O18
- CO
- N2O
- SF6
- H2
- O2N2

Results

All Circuits

Scales

Cylinders

1

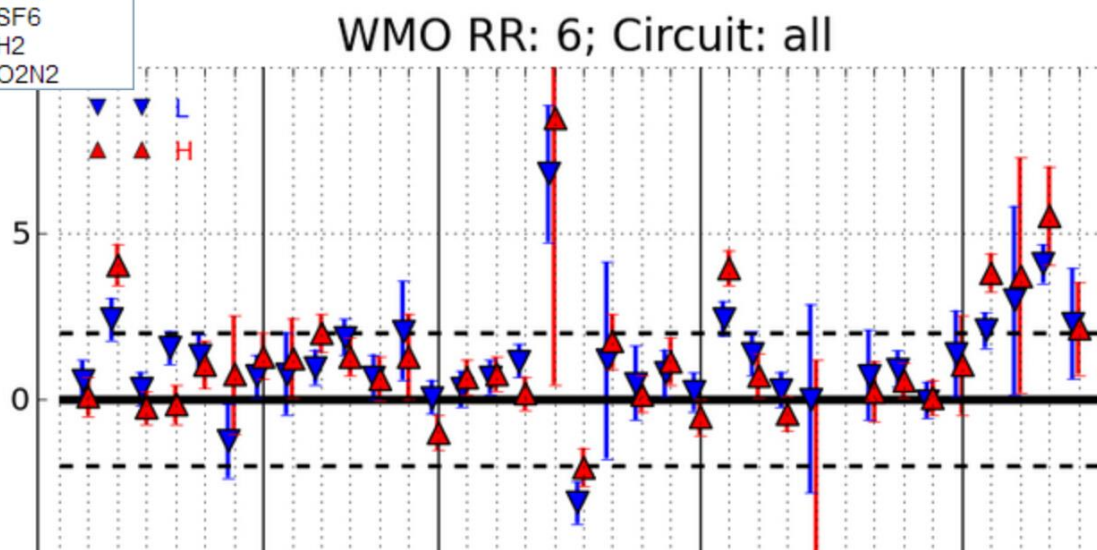
Circuit 2

Circuit 3

Circuit 4

Circuit 5

inus NOAA (Δ CH₄, ppb)



- **6th RR** 40 labs reported for CO₂, 36 for CH₄, 28 for N₂O, 18 for SF₆, 27 for CO, 10 for H₂, 15 for CO₂ stable isotopes, and 6 for O₂/N₂
- **5th RR** 39 labs reported for CO₂, 26 for CH₄, 21 for N₂O, 17 for SF₆, 23 for CO, 10 for H₂, 10 for CO₂ stable isotopes.
- **4th RR** 26 labs reported for CO₂, 12 for CH₄, 6 for N₂O, 6 for SF₆, 8 for CO, 2 for H₂, and 7 for CO₂ stable isotopes.



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WMO/IAEA Round Robin Comparison Experiment - Current Calibration Scales

Round Robin #6 is currently underway [started: January 2014]

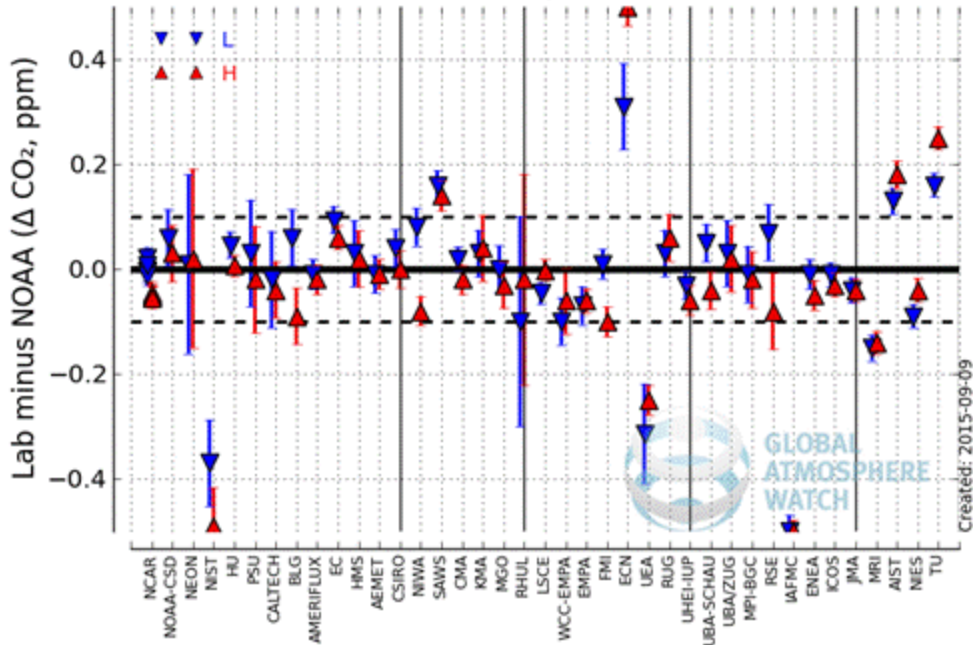
Calibration scales of the current WMO/IAEA Round Robin Experiment.

A World Meteorological Organization (WMO) Central Calibration Laboratory (CCL) is responsible for maintaining and distributing the WMO Mole Fraction scale for a specified gas in air. NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) is the WMO CCL for CO₂, CH₄, N₂O, SF₆, and CO. Max Planck Institute for Biogeochemistry (MPI-BGC) laboratory in Jena, Germany is the CCL for H₂ and for the stable isotopes of CO₂ ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$).

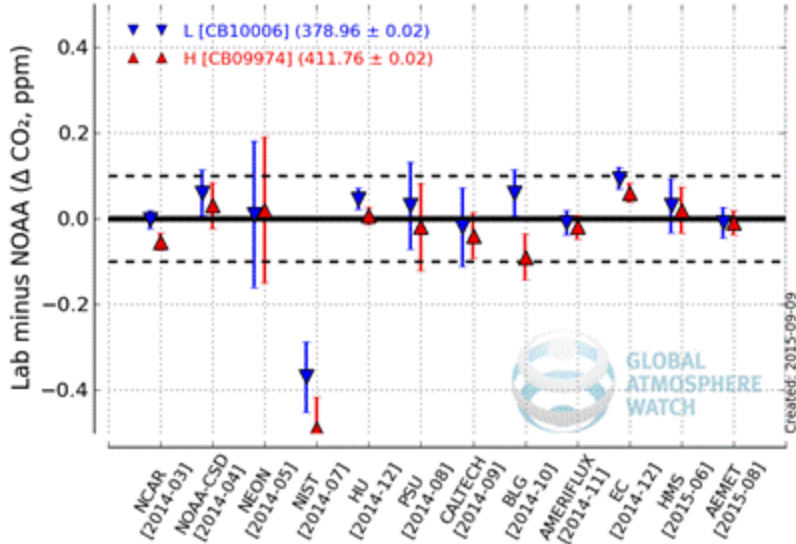
The following table summarizes the calibration scales used to assign values to the current WMO Round Robin cylinders. **Please Note:** For these experiments, H₂ values have been assigned to the WMO Round Robin cylinders by NOAA and the stable isotopes of CO₂ values have been assigned by the University of Colorado (CU), Institute of Arctic and Alpine Research (INSTAAR), Stable Isotope Laboratory (SIL).

Parameter(s)	Calibration Scale*	Primary Contact	Lab
CO ₂	WMO-CO2-X2007	Pieter Tans	NOAA
CH ₄	WMO-CH4-X2004A	Ed Dlugokencky	NOAA
CO	WMO-CO-X2014	Paul Novelli	NOAA
N ₂ O	WMO-N2O-X2006A	Brad Hall	NOAA
SF ₆	WMO-SF6-X2014	Brad Hall	NOAA
H ₂	NOAA-H2-X1996	Paul Novelli	NOAA
$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (CO ₂)	SIL Lab Scale	Bruce Vaughn	SIL

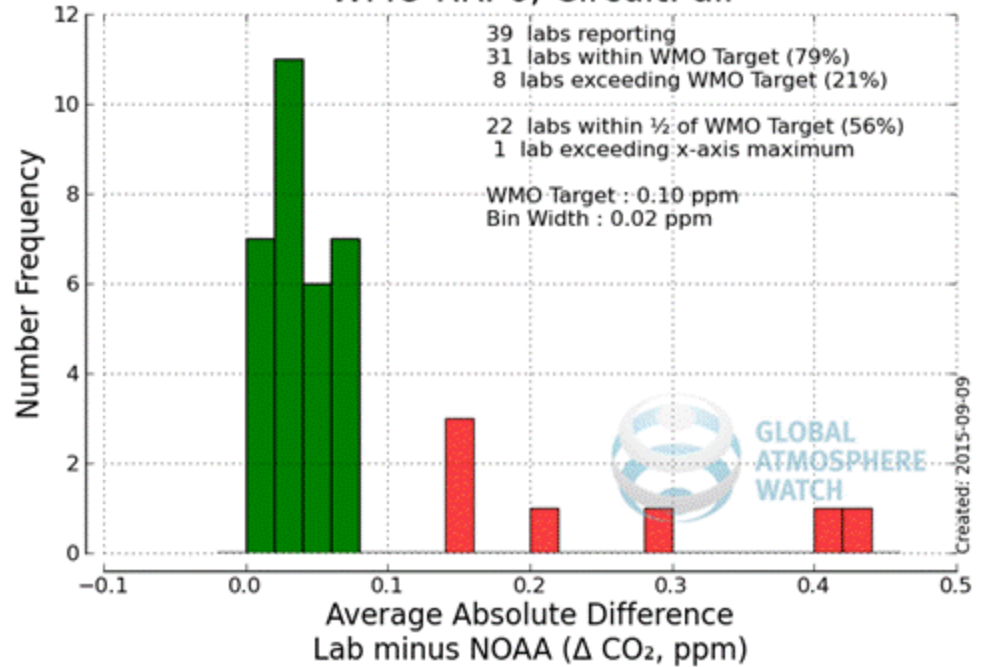
WMO RR: 6; Circuit: all

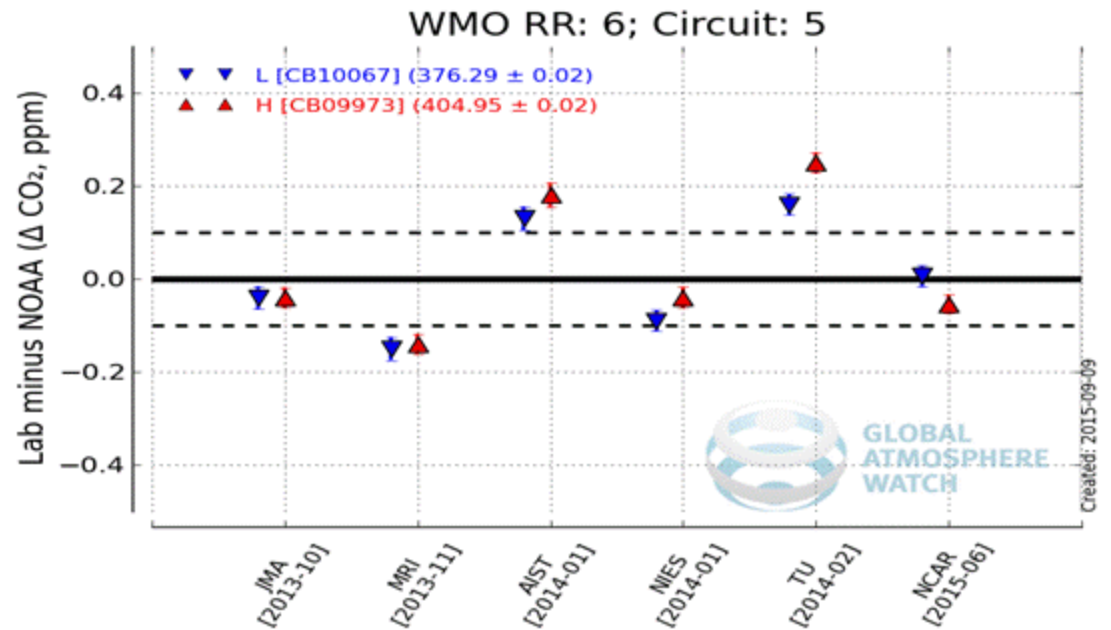
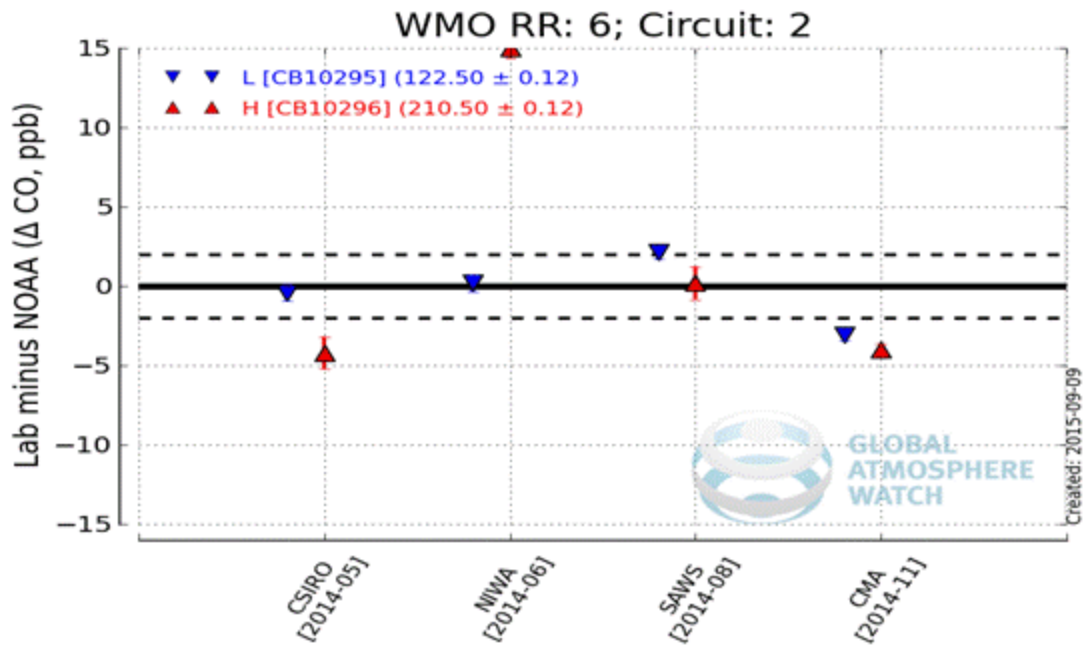


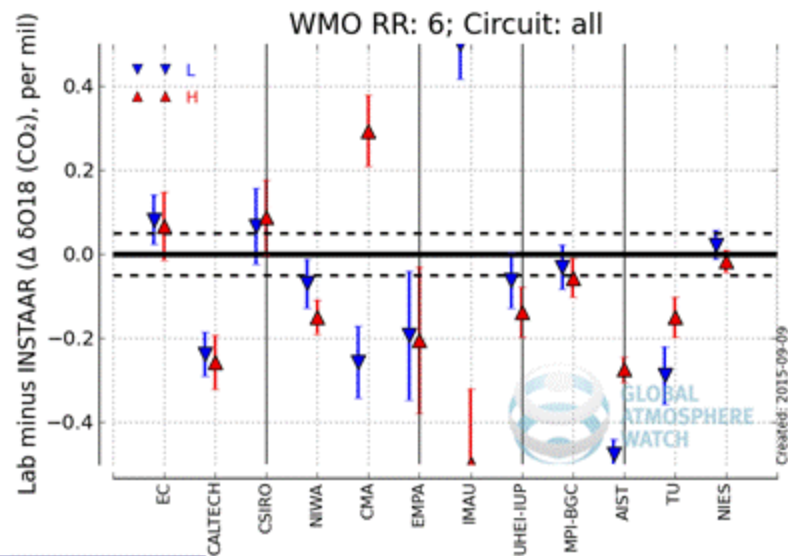
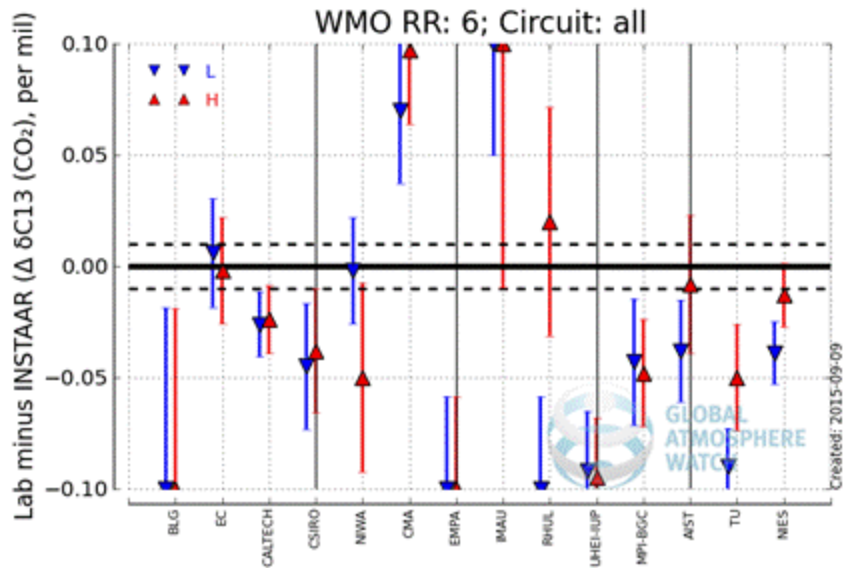
WMO RR: 6; Circuit: 1



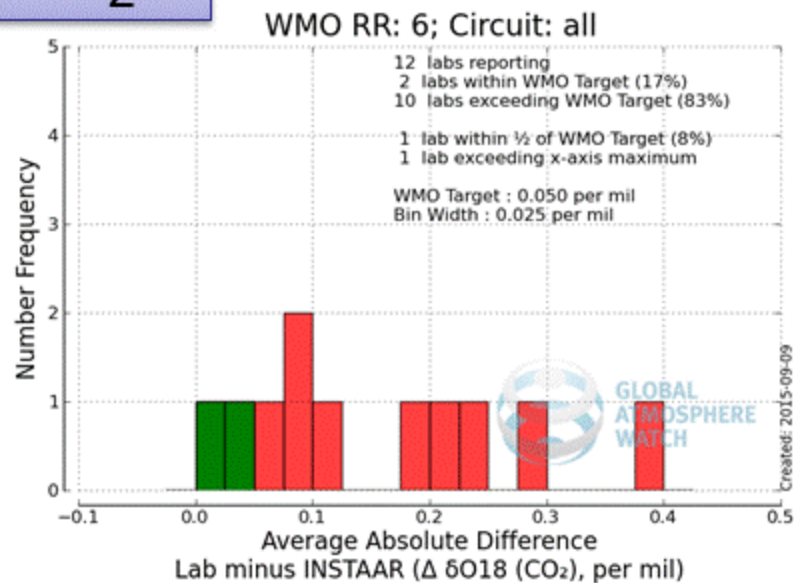
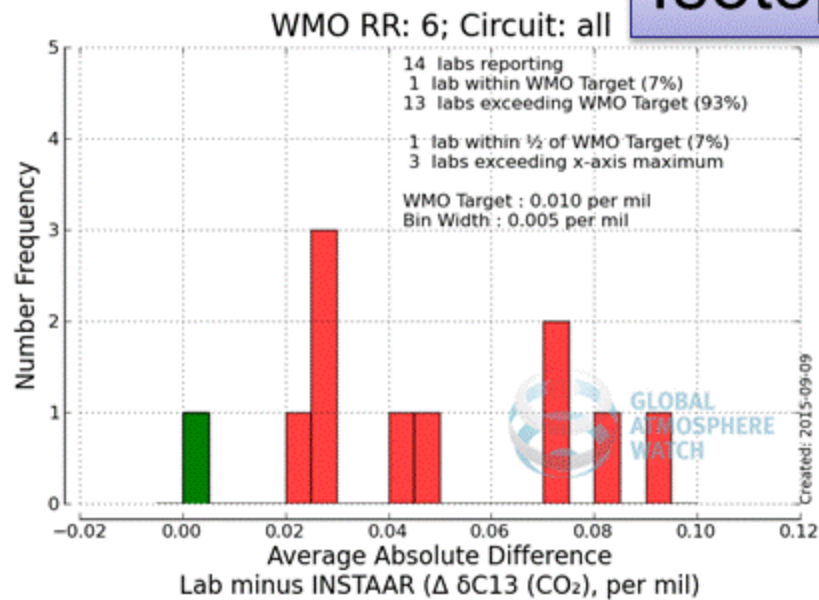
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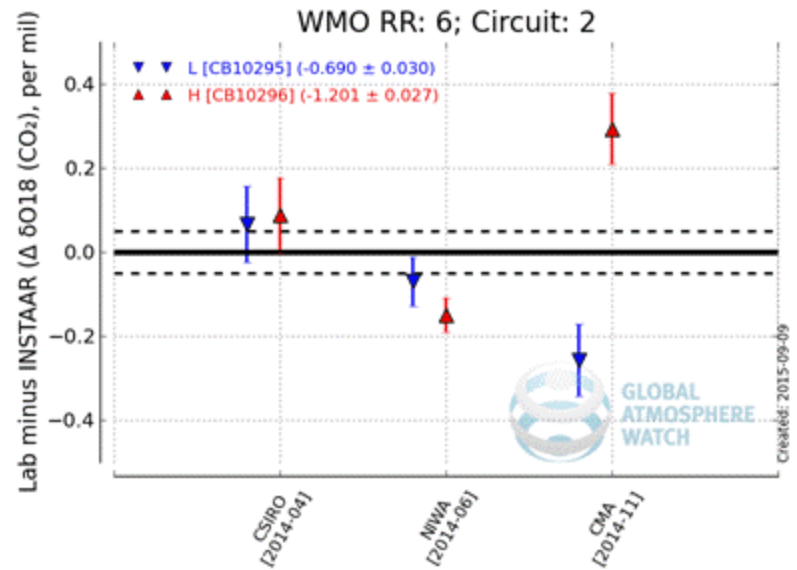
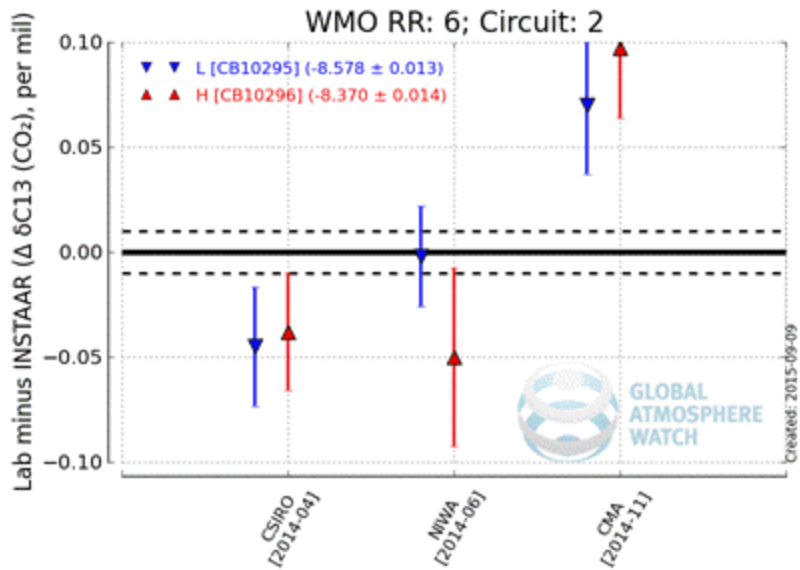




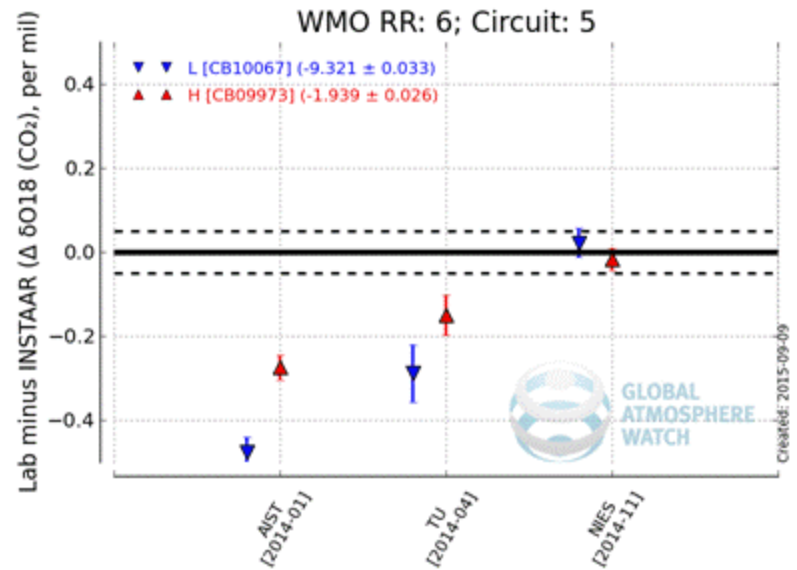
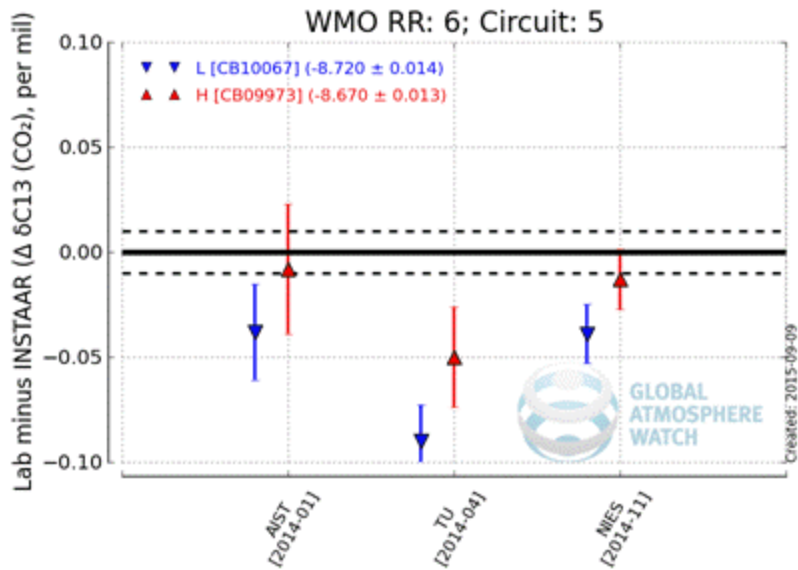


Isotope CO_2

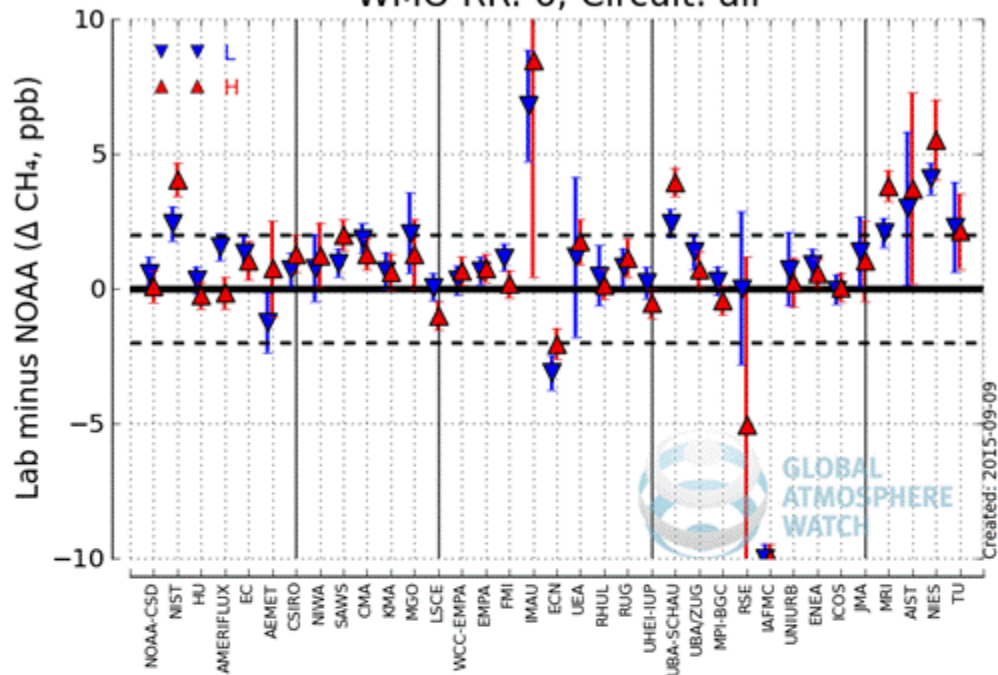




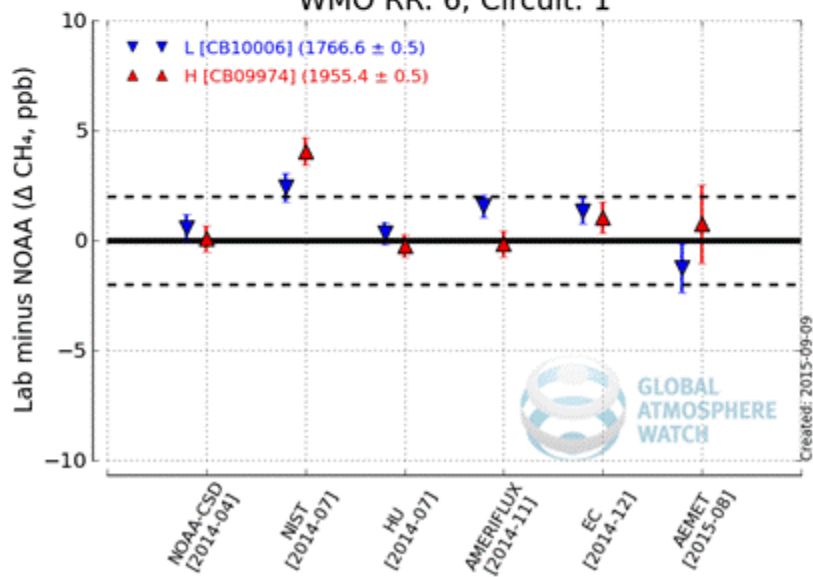
Isotope CO₂



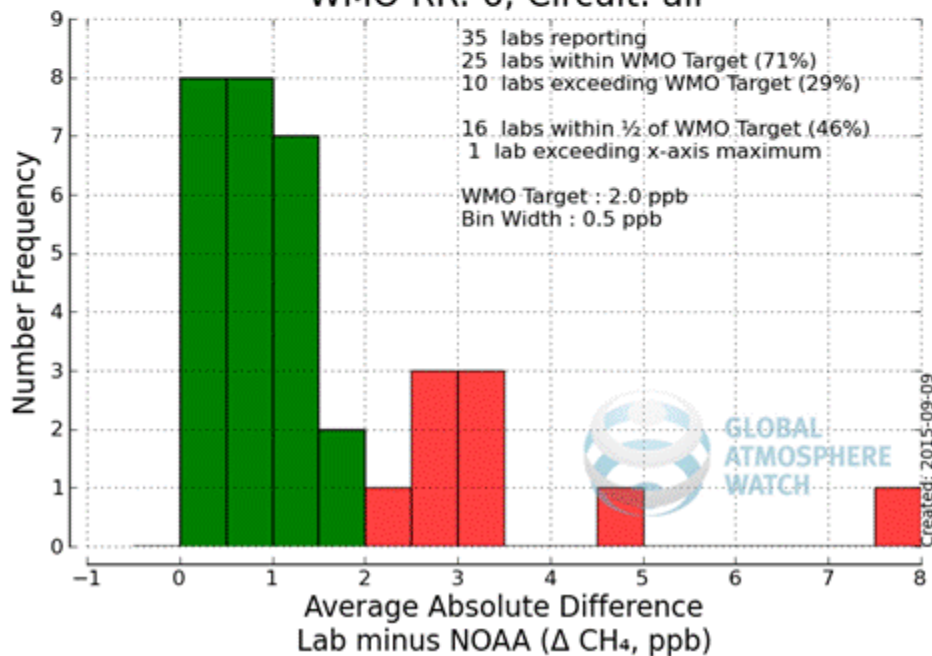
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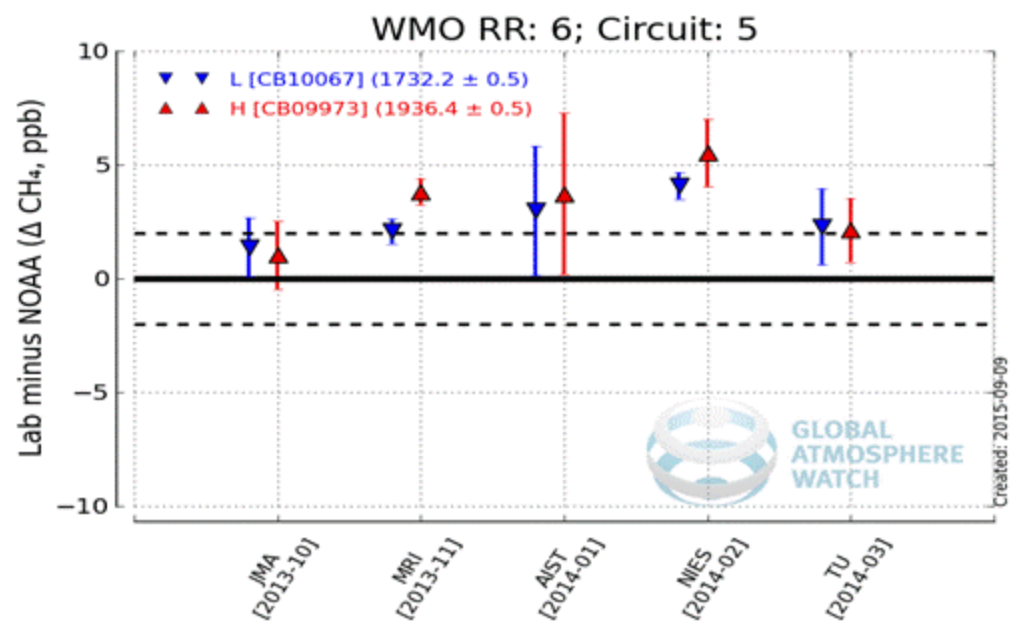
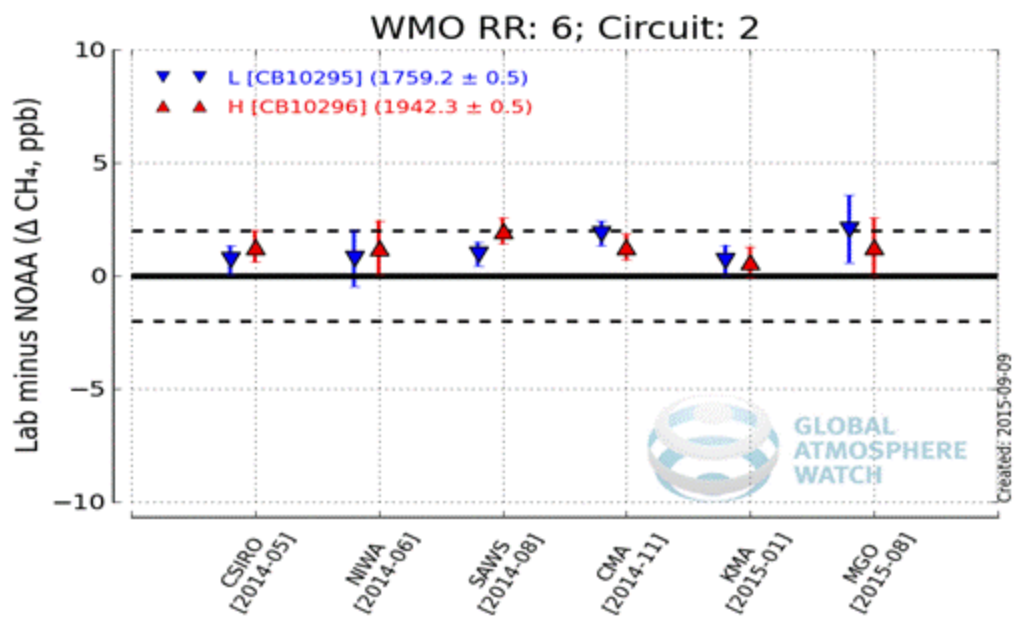


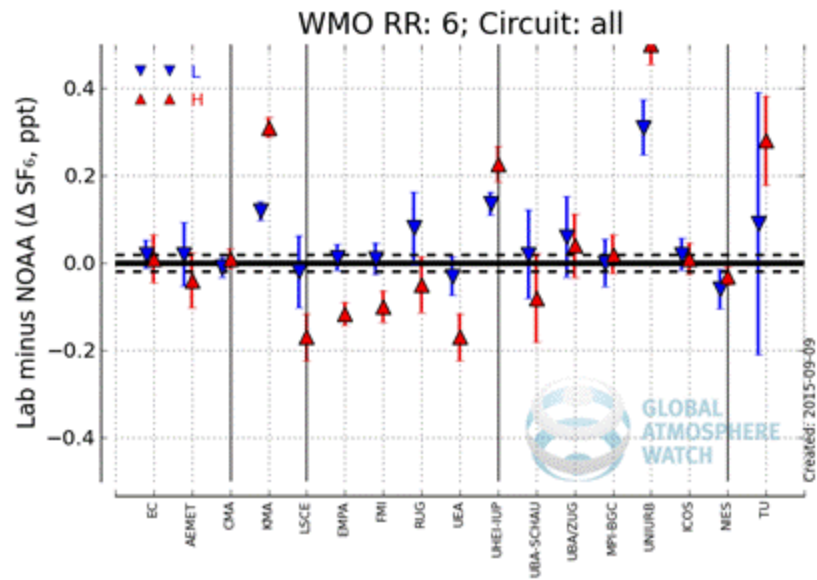
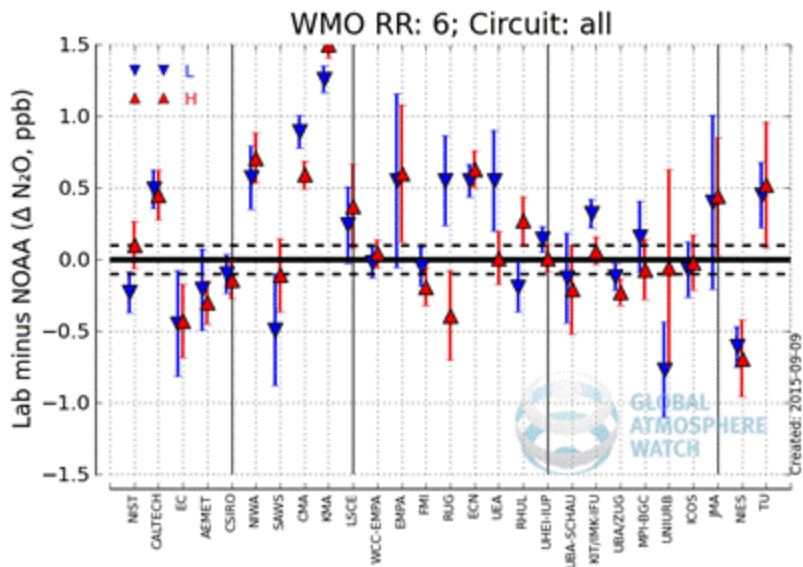
WMO RR: 6; Circuit: 1



WMO RR: 6; Circuit: all

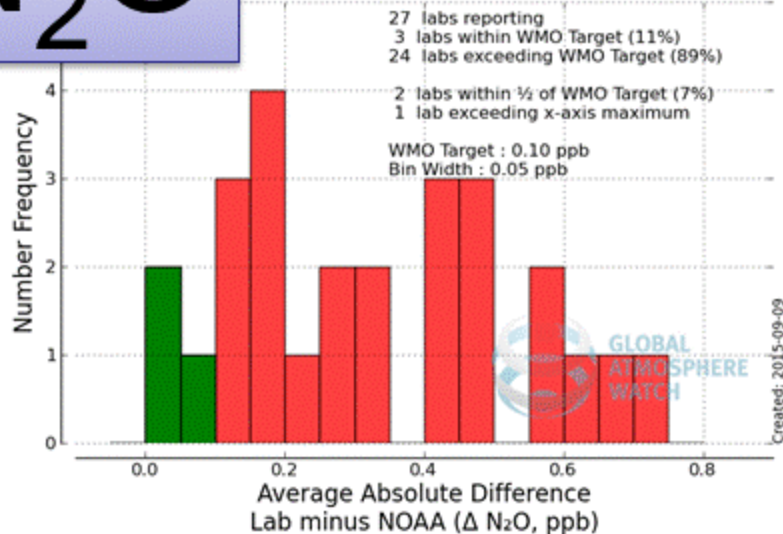






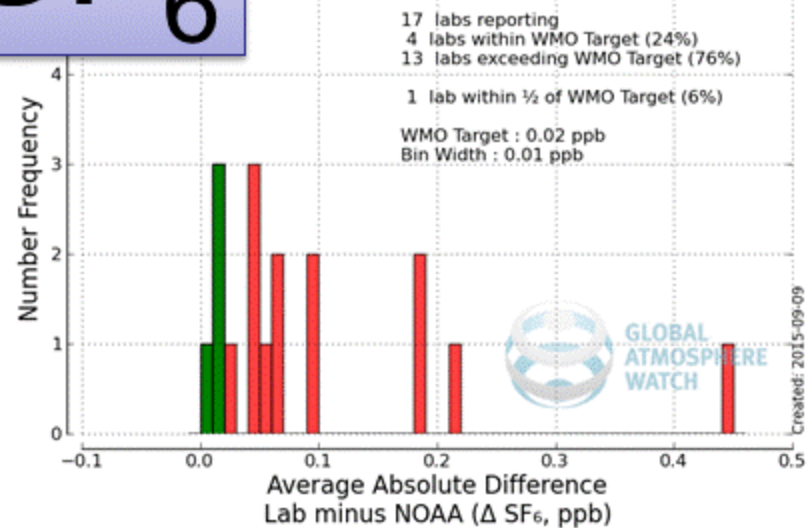
N₂O

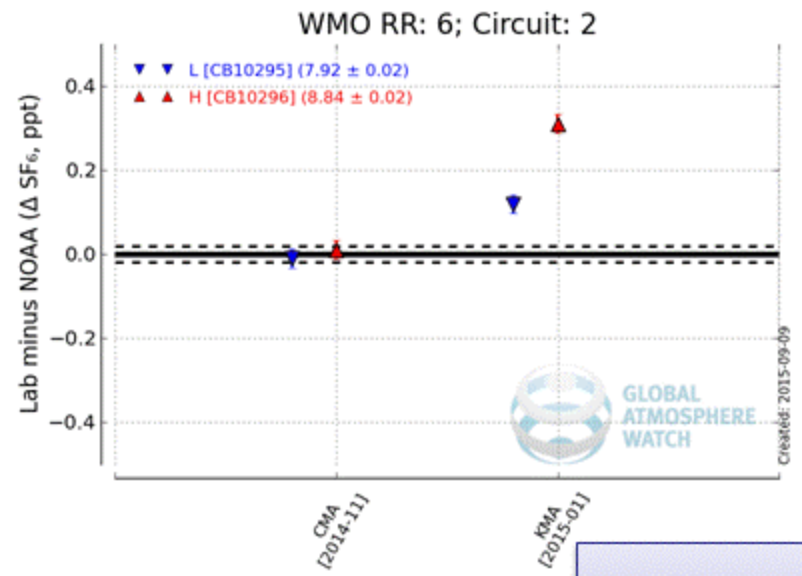
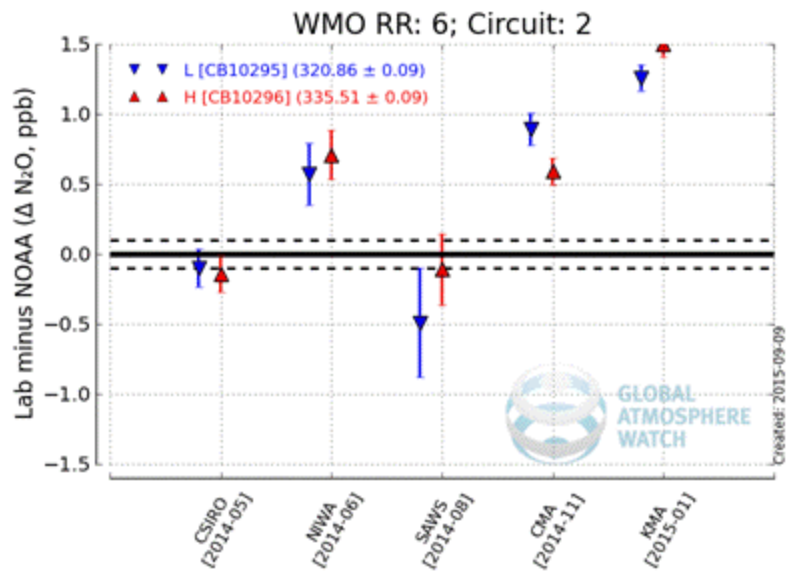
WMO RR: 6; Circuit: all



SF₆

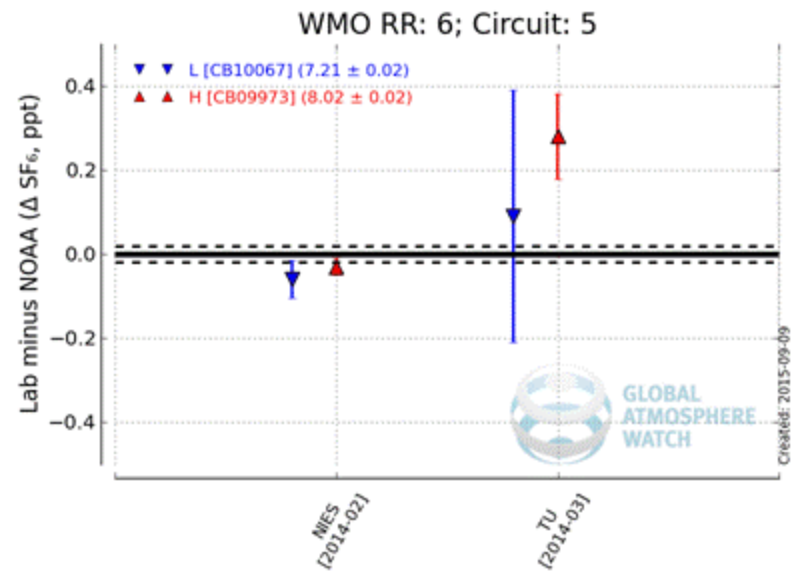
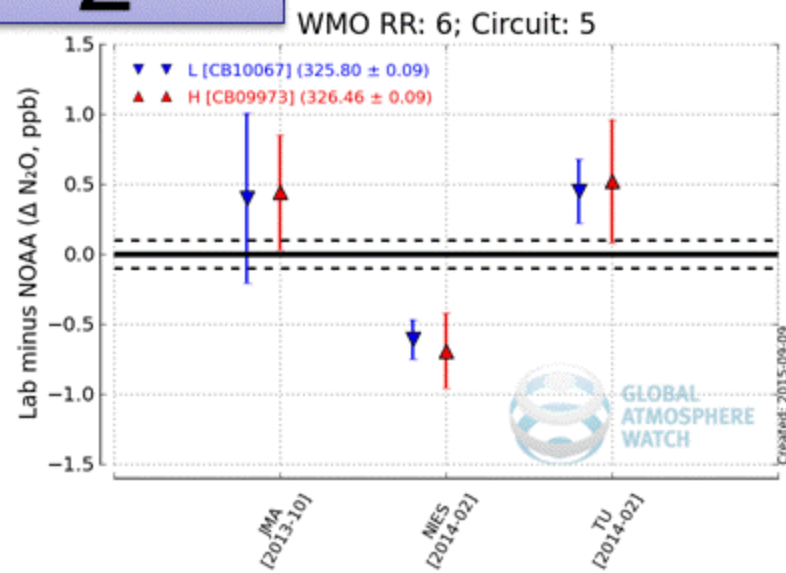
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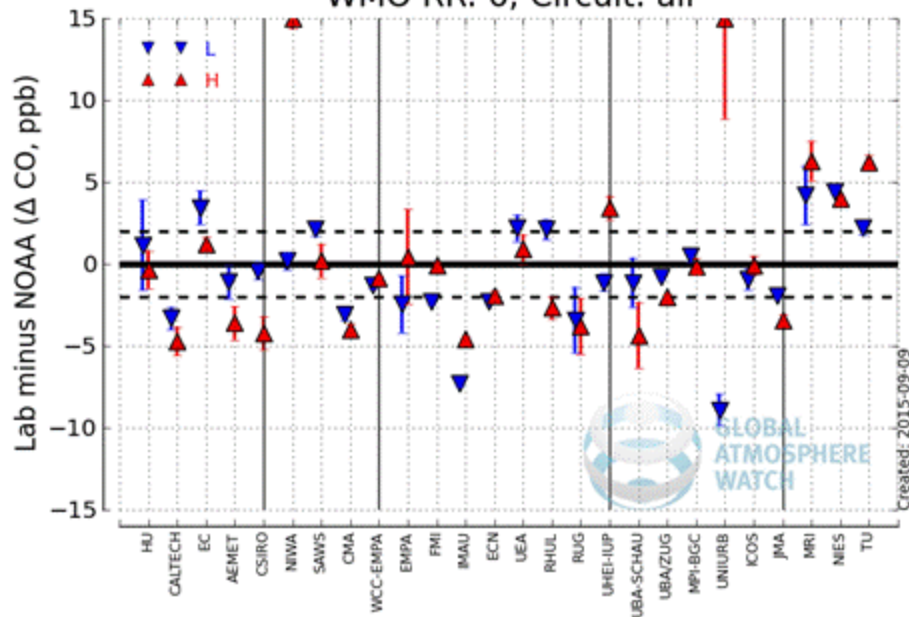


N₂O

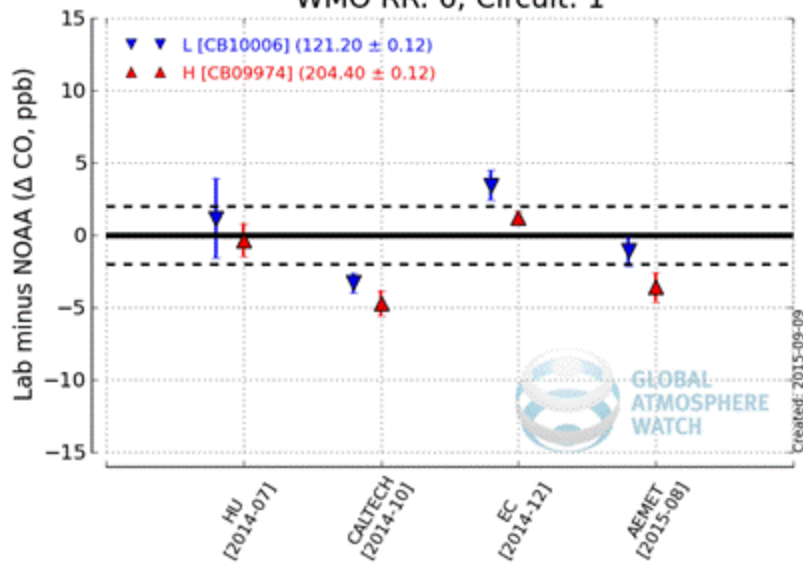
SF₆



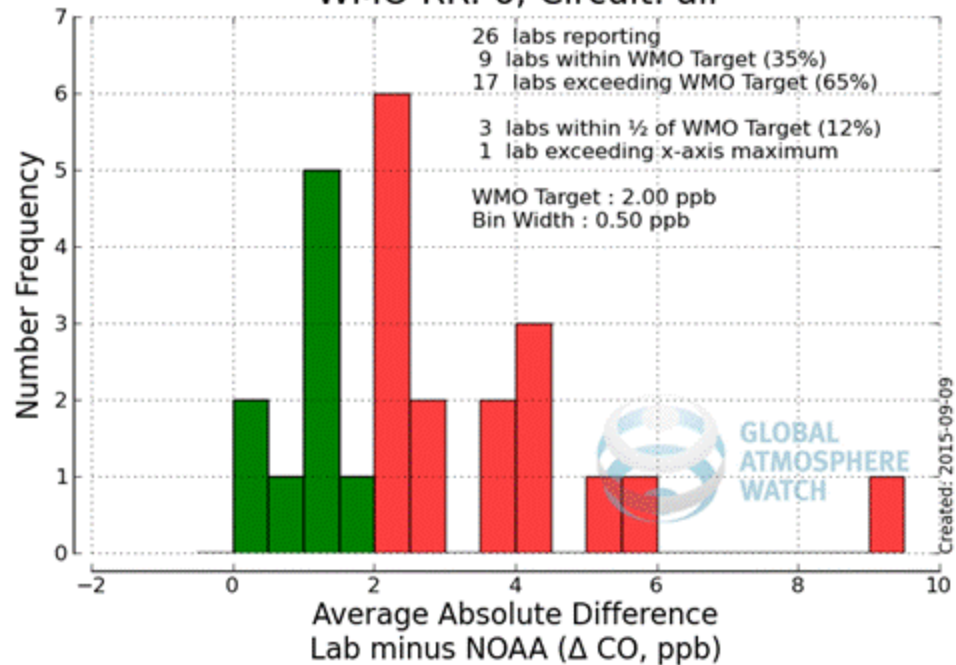
WMO RR: 6; Circuit: all

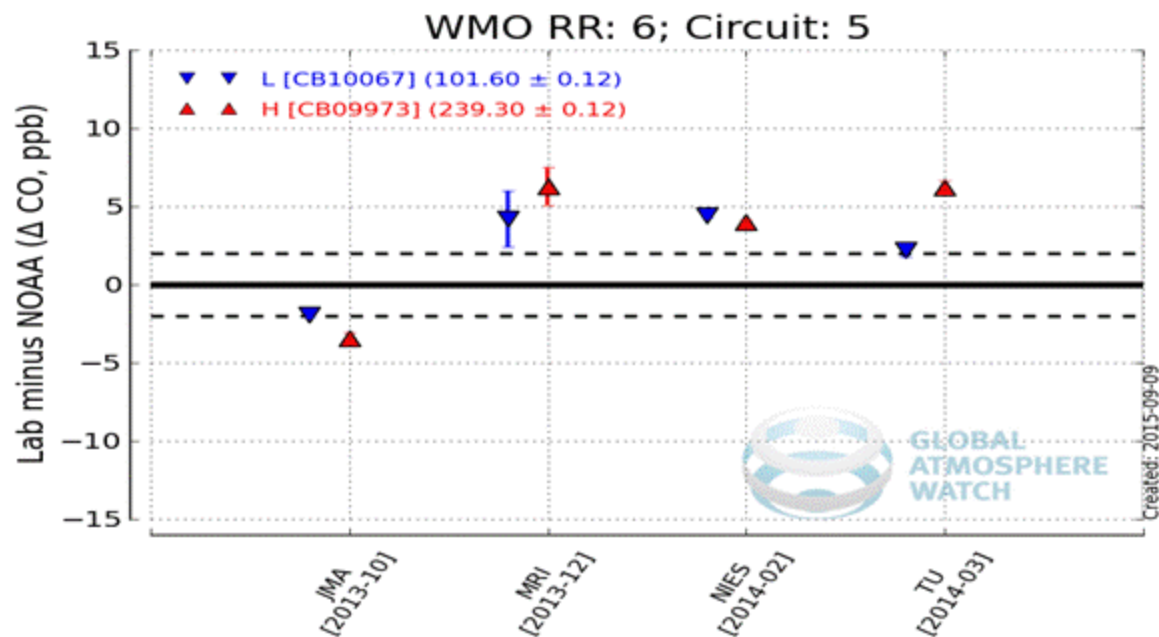
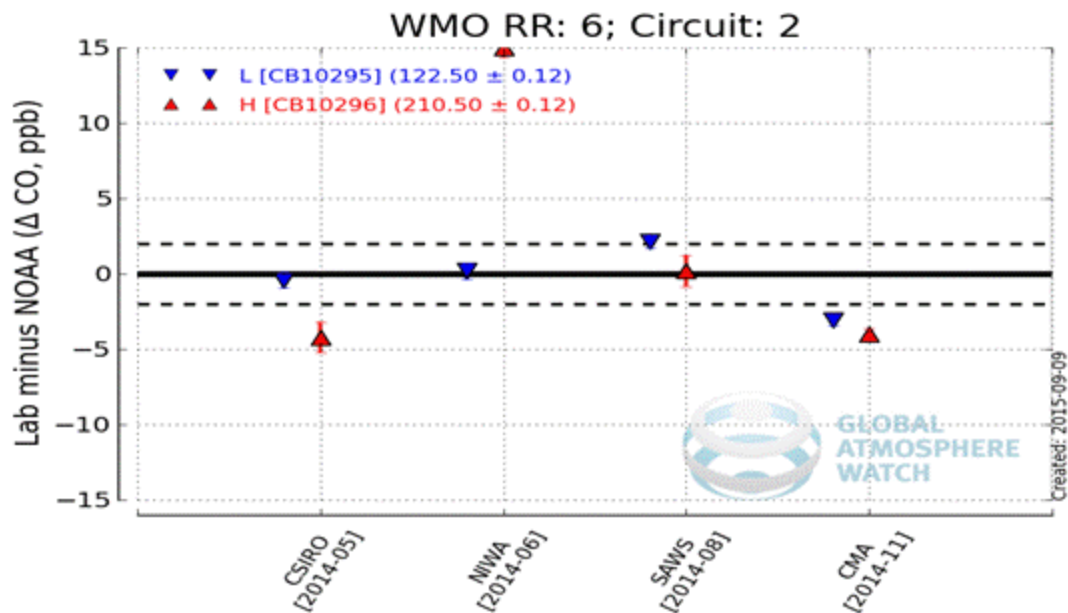


WMO RR: 6; Circuit: 1



WMO RR: 6; Circuit: all

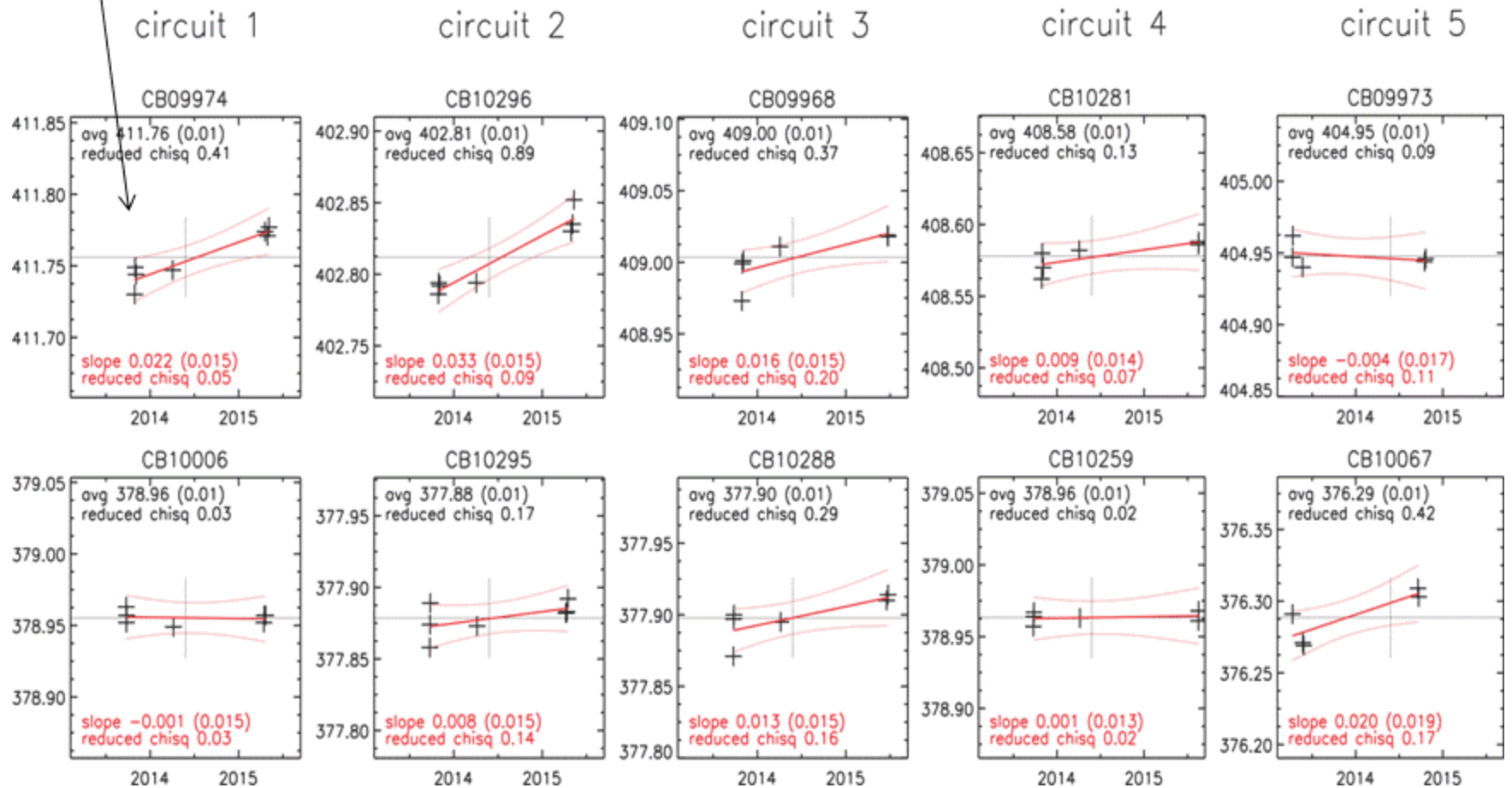




- **Stability of cylinders in the period of 6th RR for CO₂, CH₄, N₂O, SF₆ and CO**
- **Most participants reported uncertainty as one std about the mean of N measurements, the reference labs (e.g., NOAA, INSTAAR, NCAR) report the one std estimate of the reproducibility.**
- **This is an easy way to ensure that uncertainties are reported in a consistent and meaningful way across all parameters.**

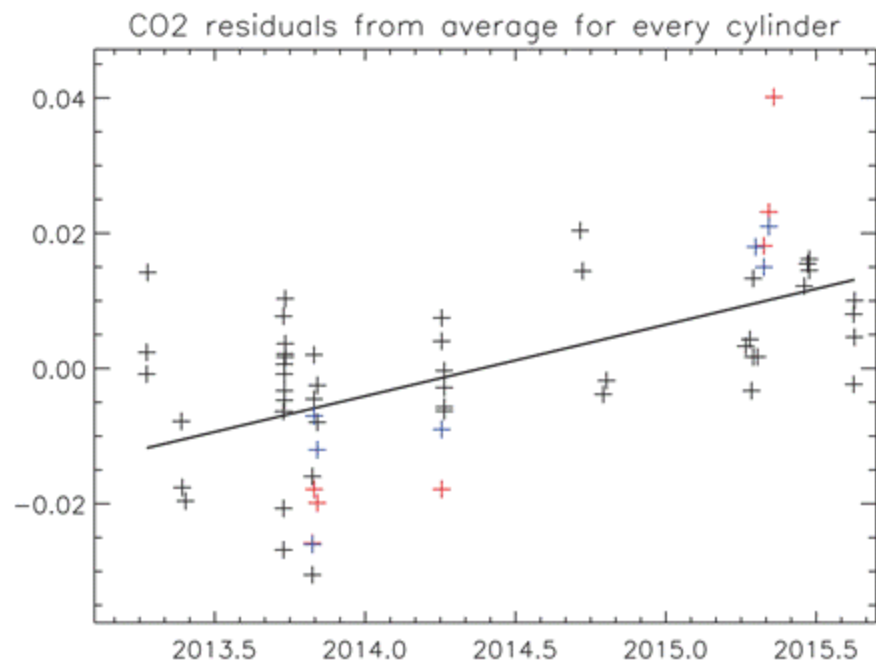
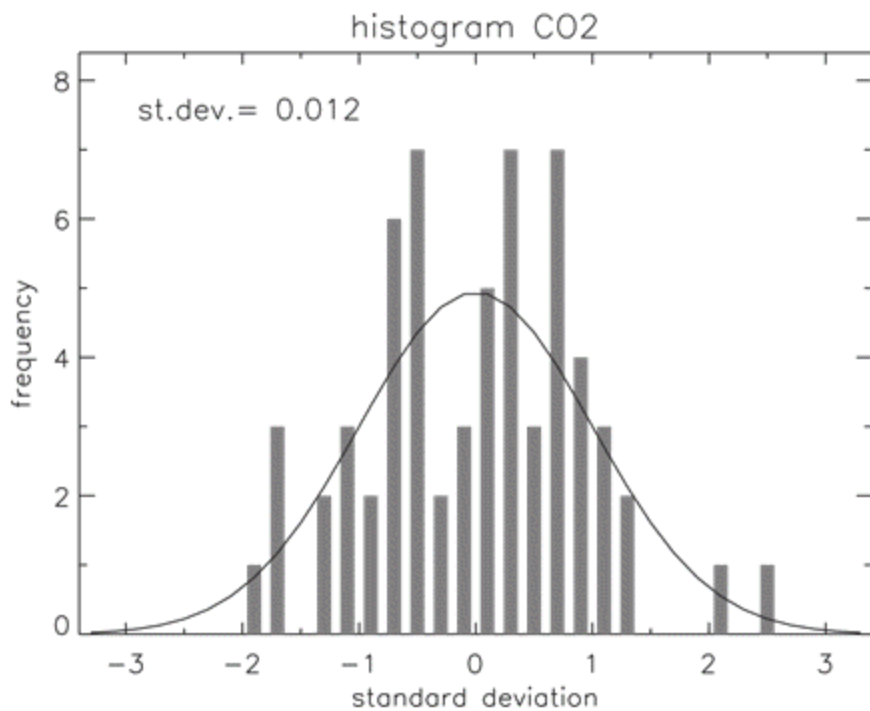
Long-term
reproducibility
0.028 ppm (1- σ)

Stability of cylinders in 6th RR - CO₂



Stability of cylinders in 6th RR - CO₂

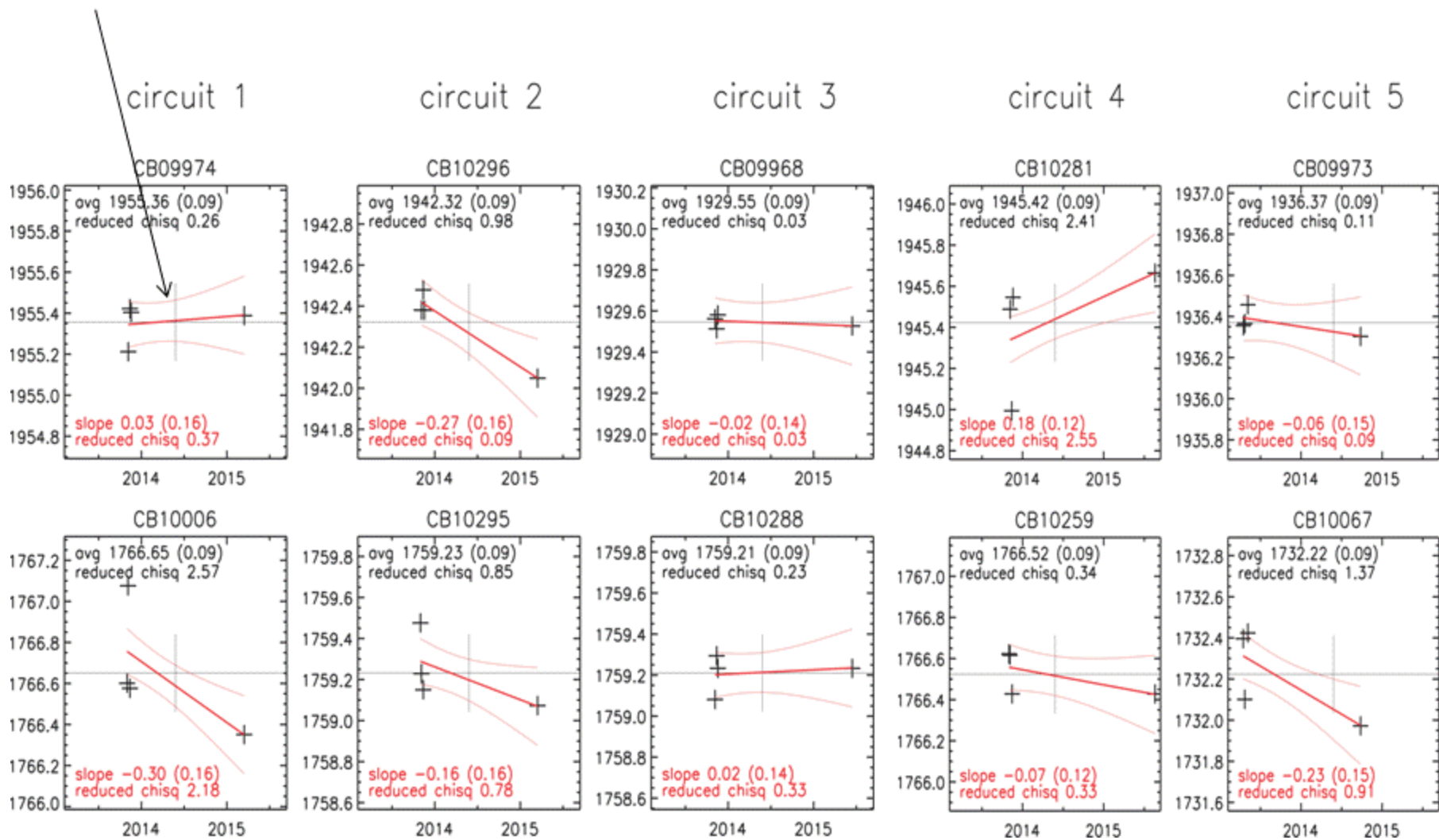
red "+" corresponds to
CB10296 0.033 ppm/yr
blue "+" to CB09974
0.024 ppm/yr



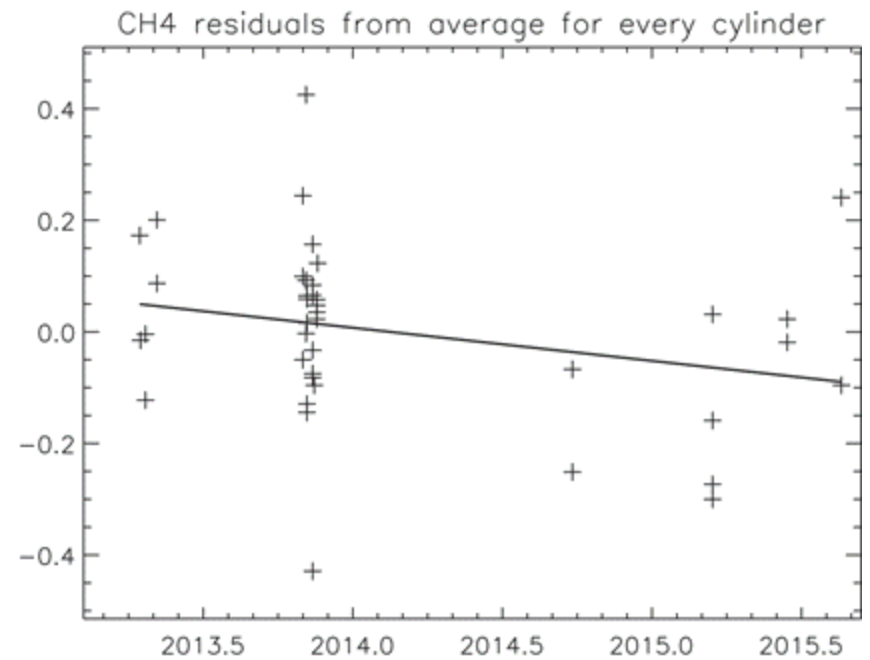
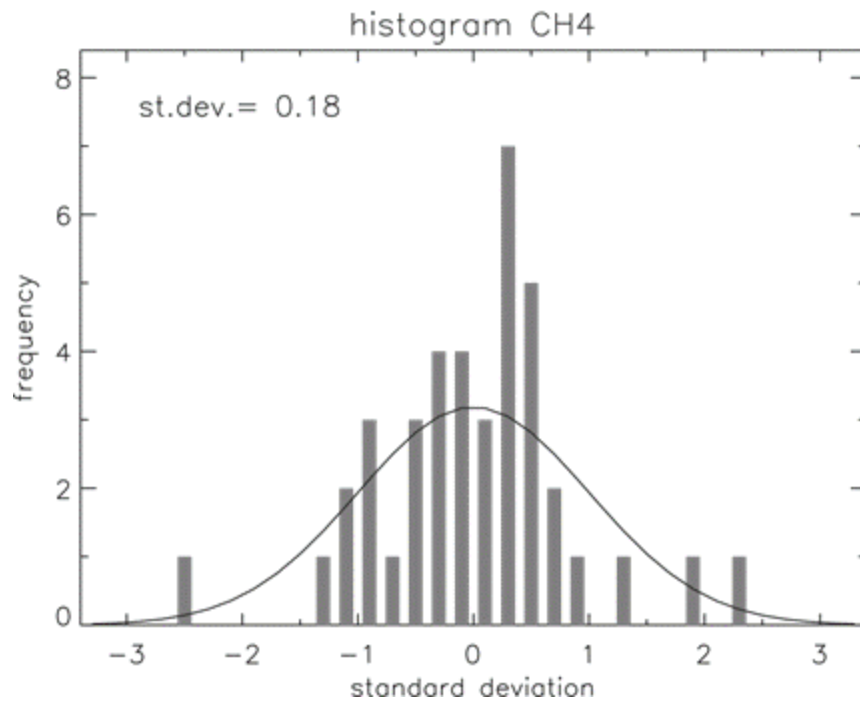
(st. dev. is smaller than long-term reproducibility) (Average slope for all cylinders 0.011 ppm/yr)

Long-term
reproducibility
0.19 ppb ($1-\sigma$)

Stability of cylinders in 6th RR – CH₄

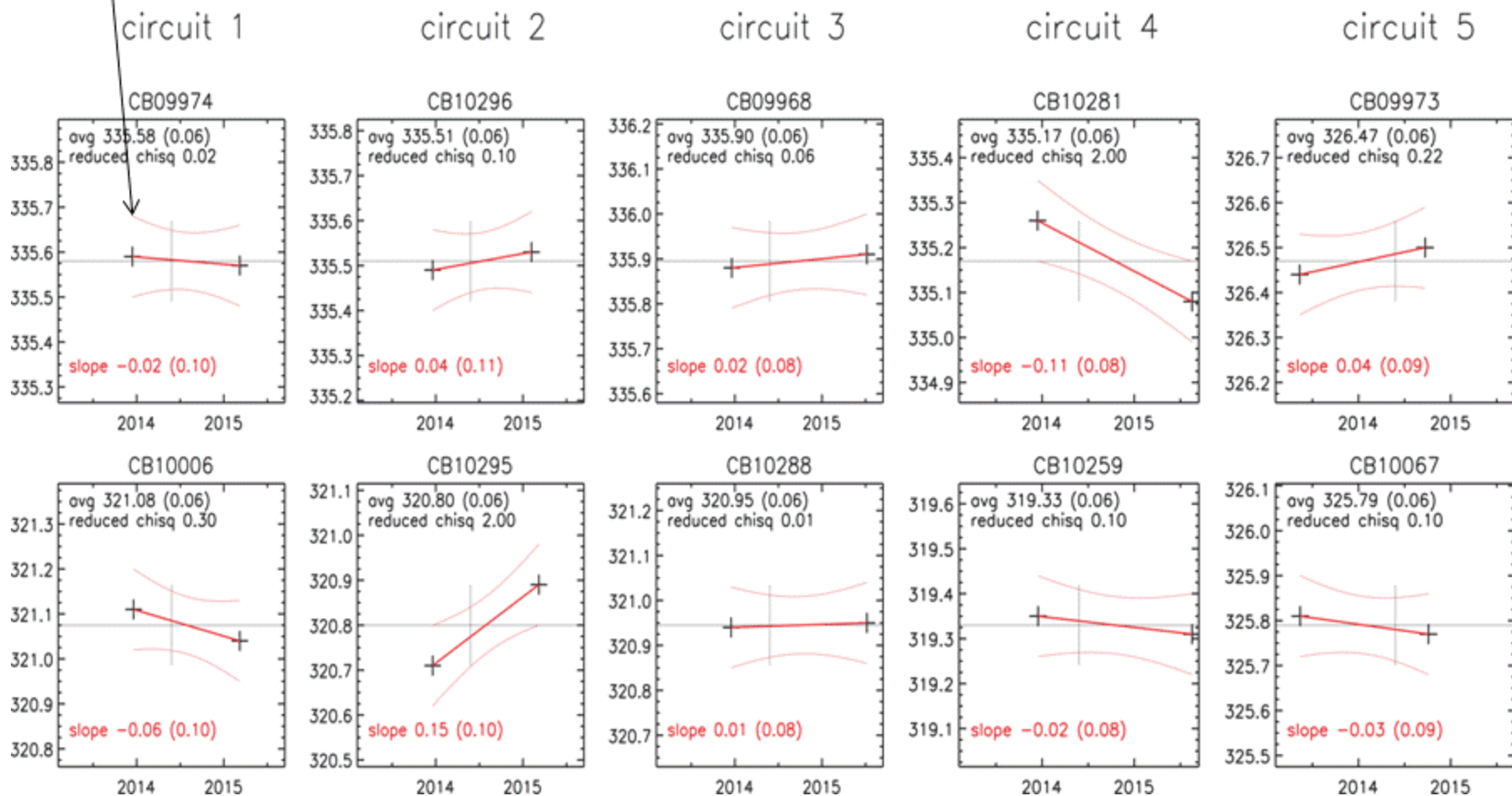


Stability of cylinders in 6th RR – CH₄

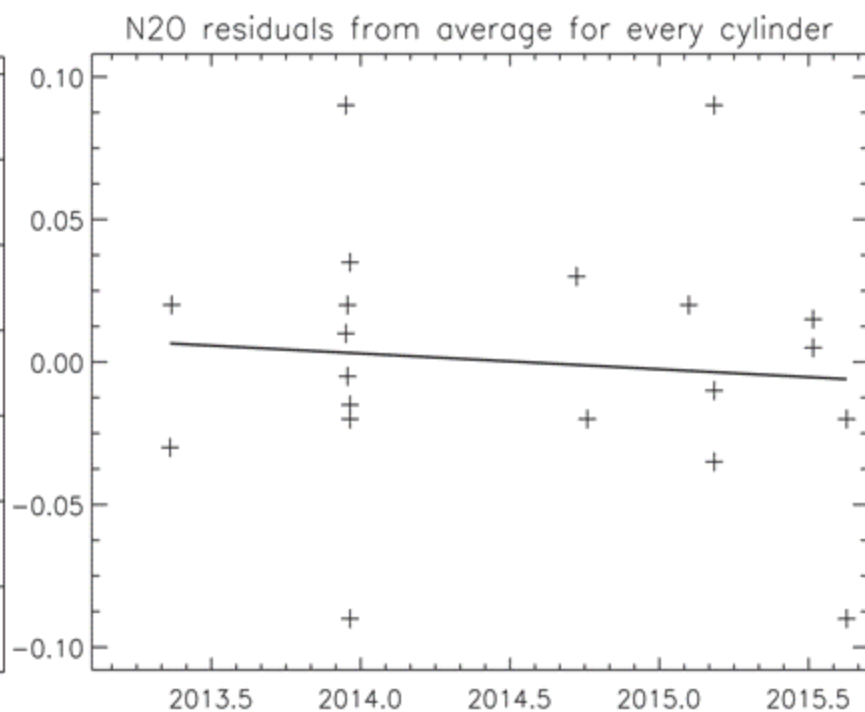
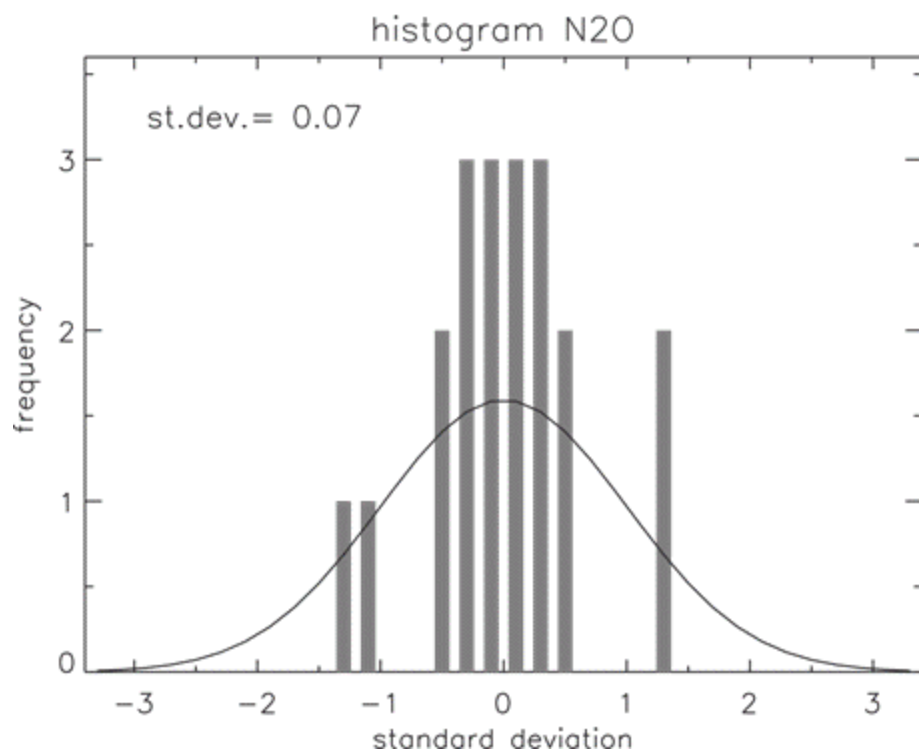


Long-term
reproducibility
0.09 ppb (1- σ)

Stability of cylinders in 6th round-robin – N₂O

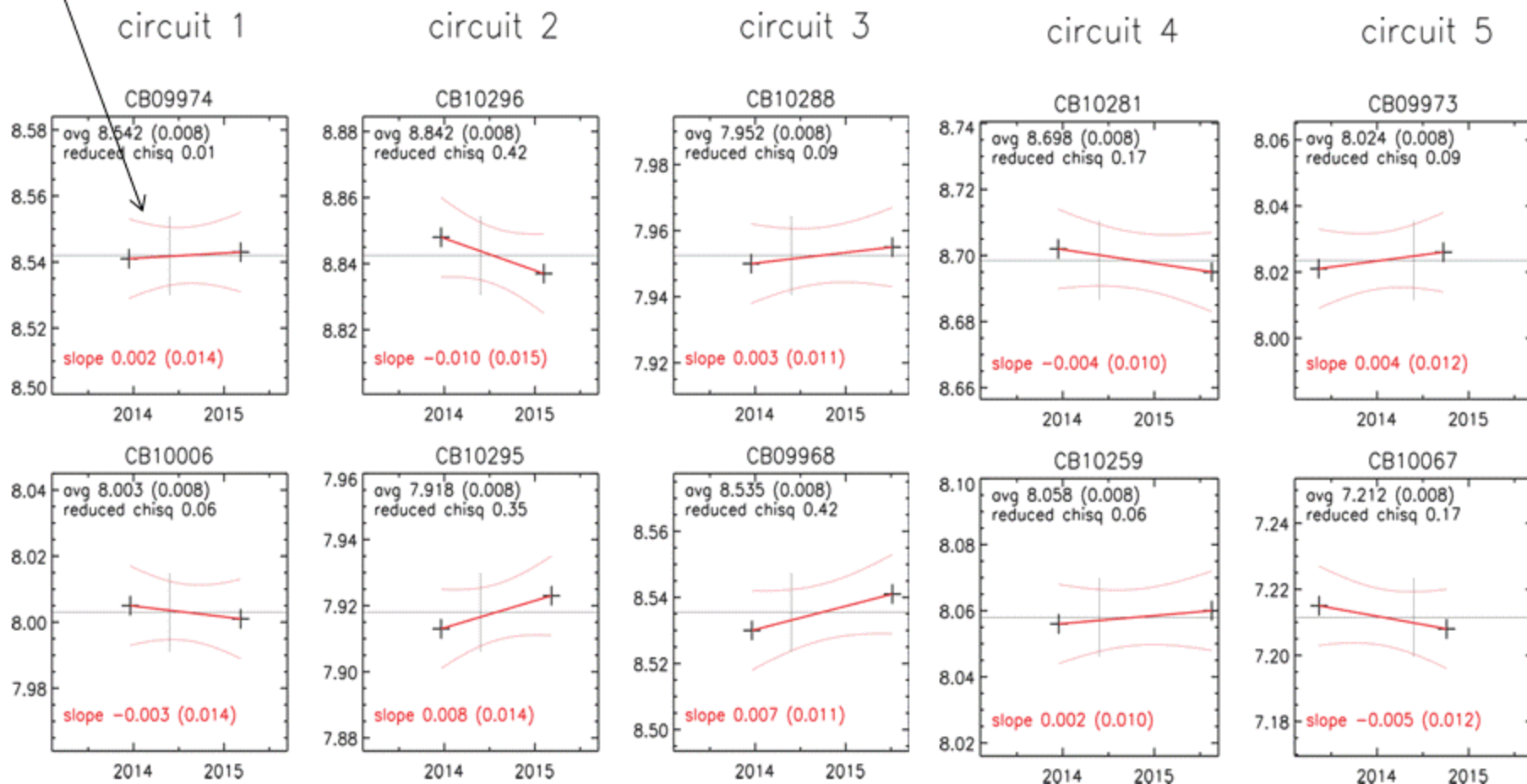


Stability of cylinders in 6th RR – N₂O



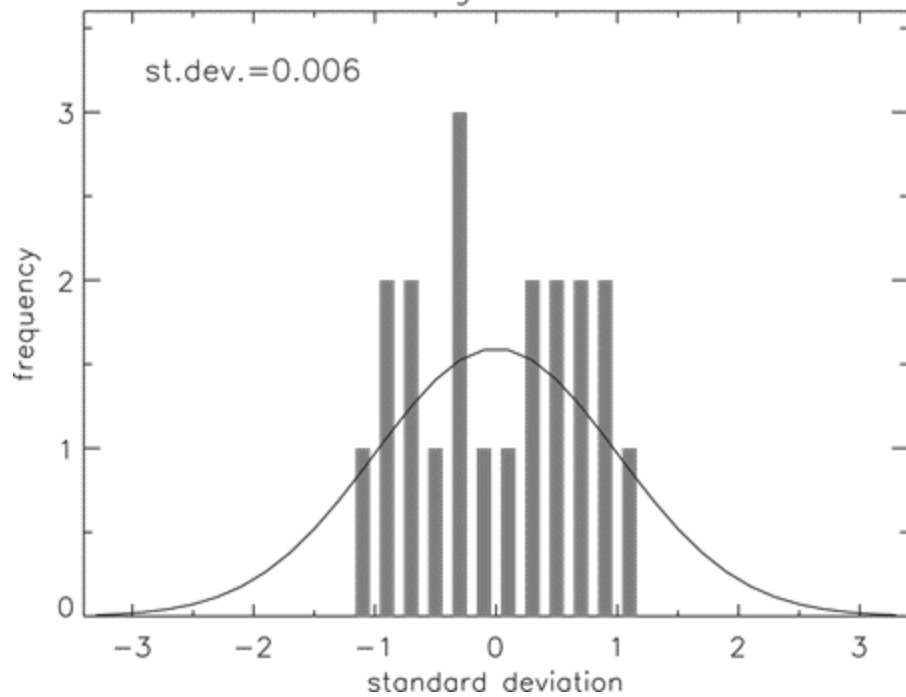
Long-term
reproducibility
0.012 ppt (1- σ)

Stability of cylinders in 6th RR – SF₆

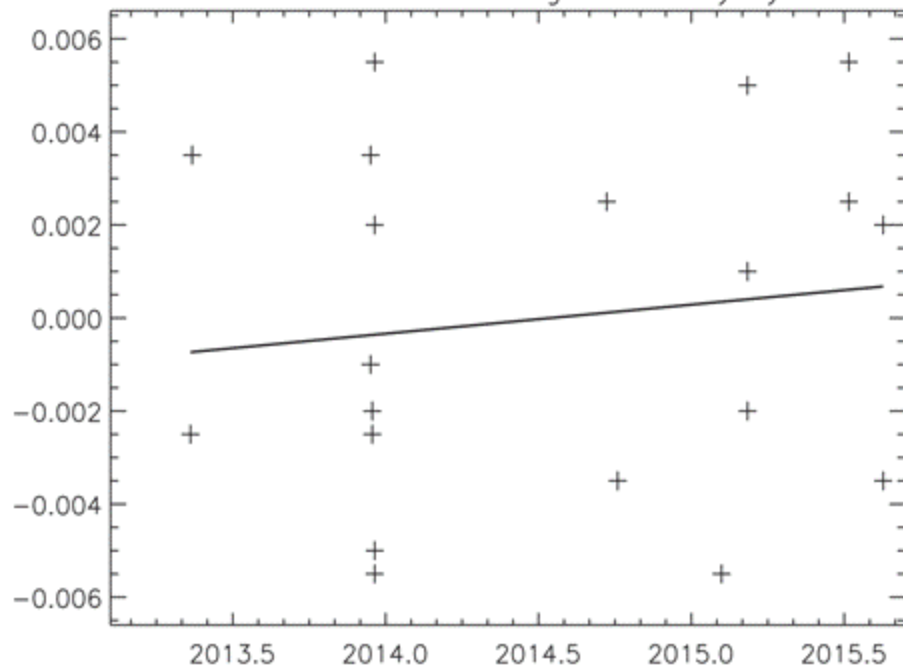


Stability of cylinders in 6th RR – SF₆

histogram SF6



SF6 residuals from average for every cylinder



Long-term
reproducibility
0.32 ppb (1- σ)

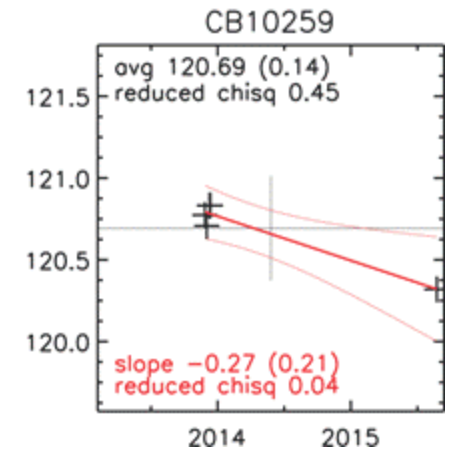
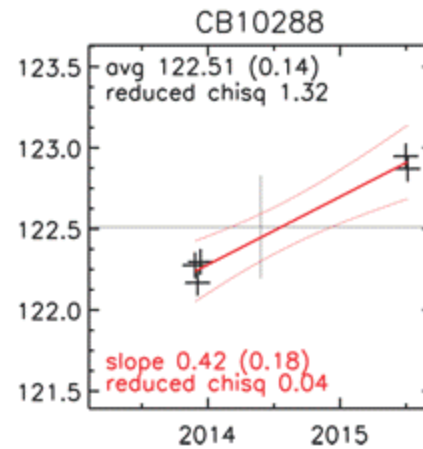
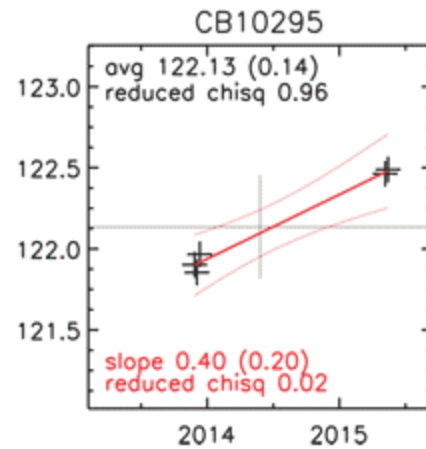
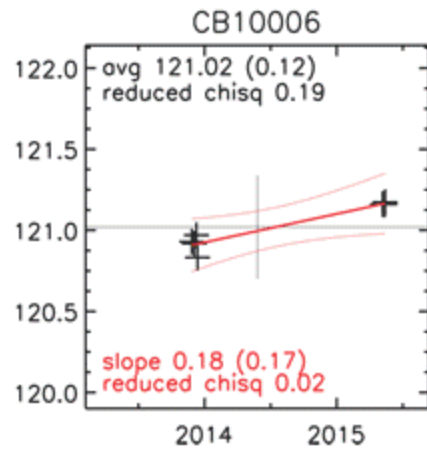
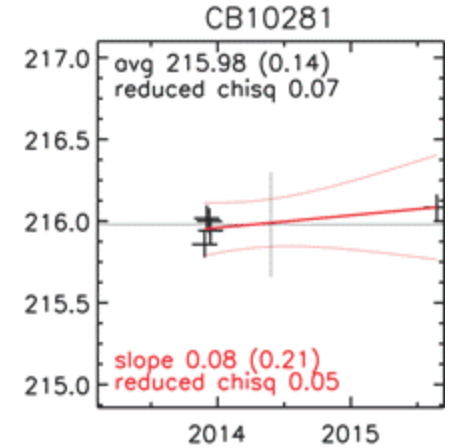
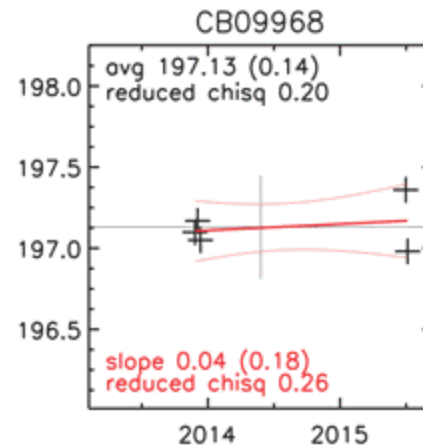
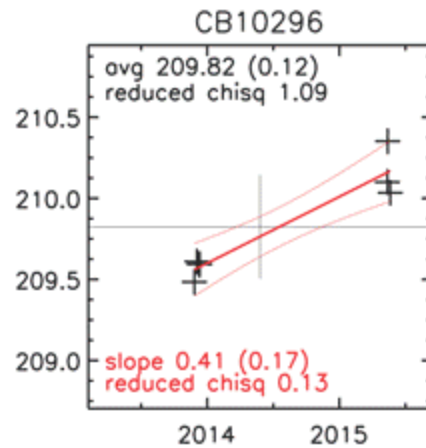
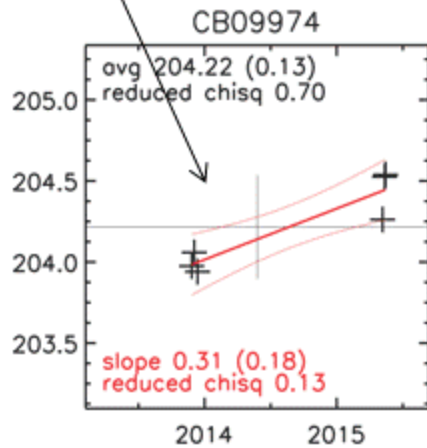
Stability of cylinders in 6th RR - CO

circuit 1

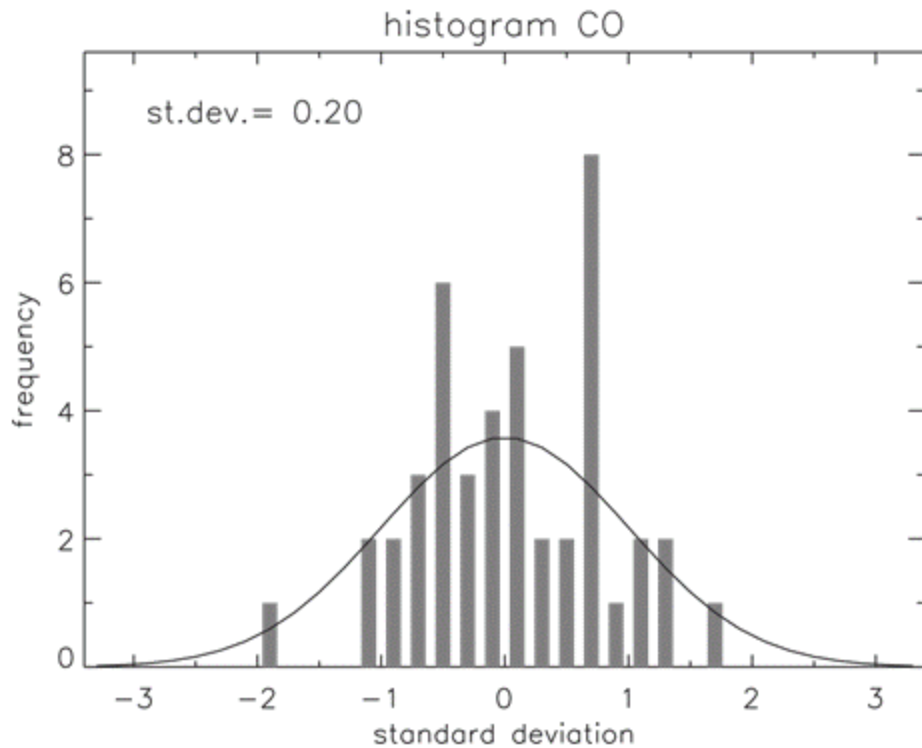
circuit 2

circuit 3

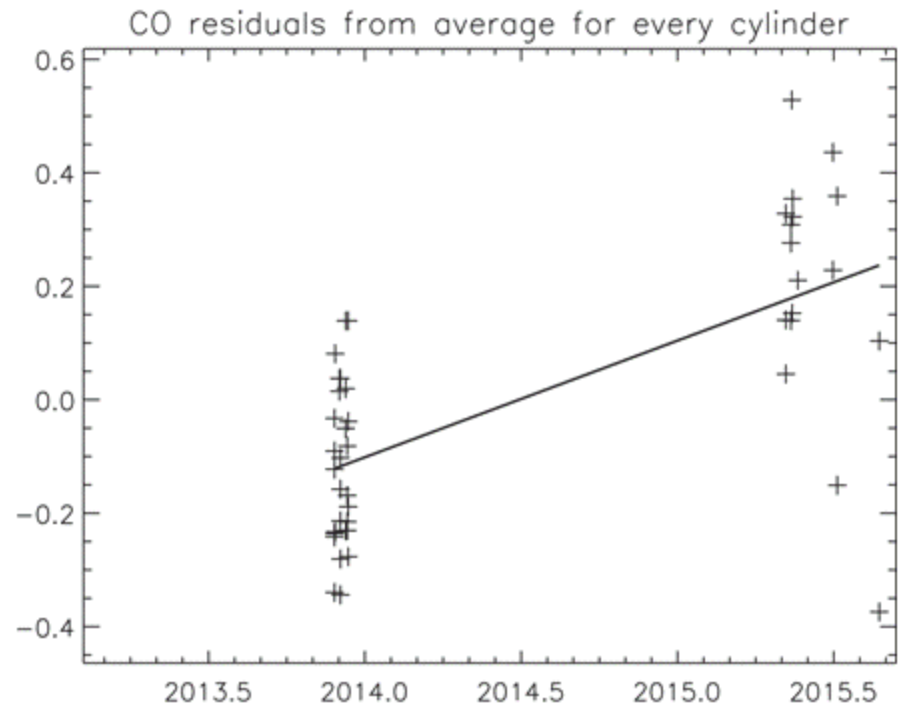
circuit 4



Stability of cylinders in 6th RR - CO



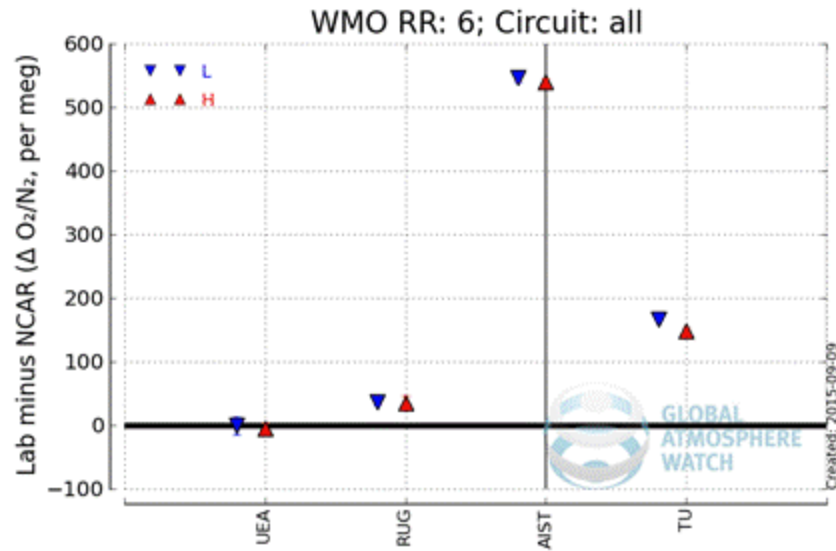
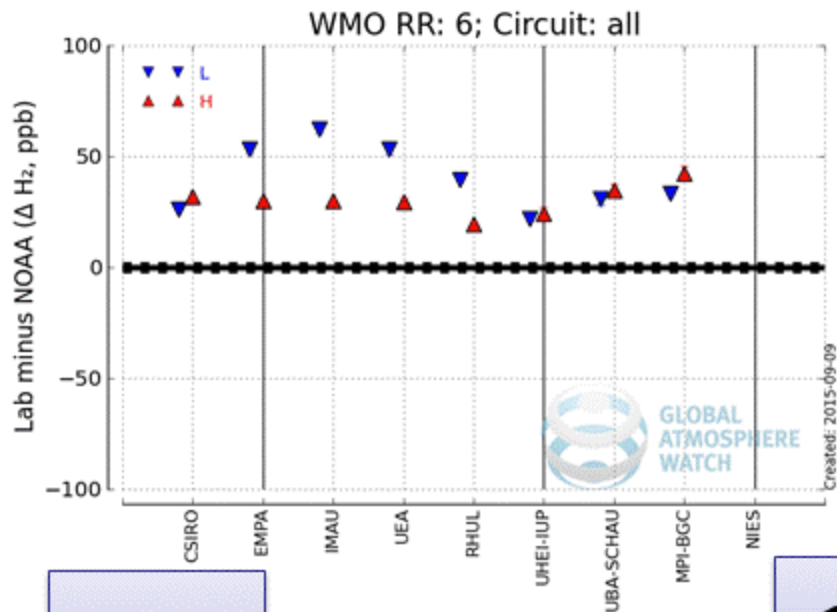
(st. dev. is smaller than long-term reproducibility)



(Average slope for all cylinders 0.21 ppb/yr)

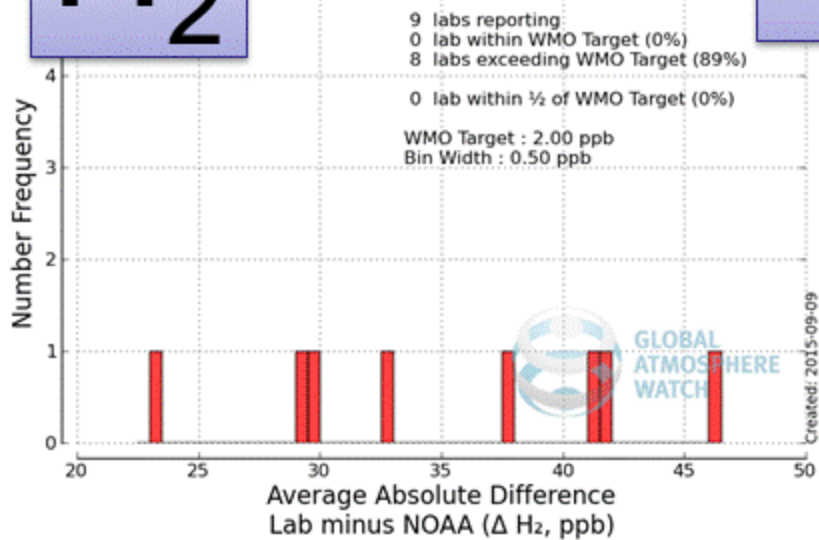
A long way to go
Feedback are expected
and appreciated.....

Thanks



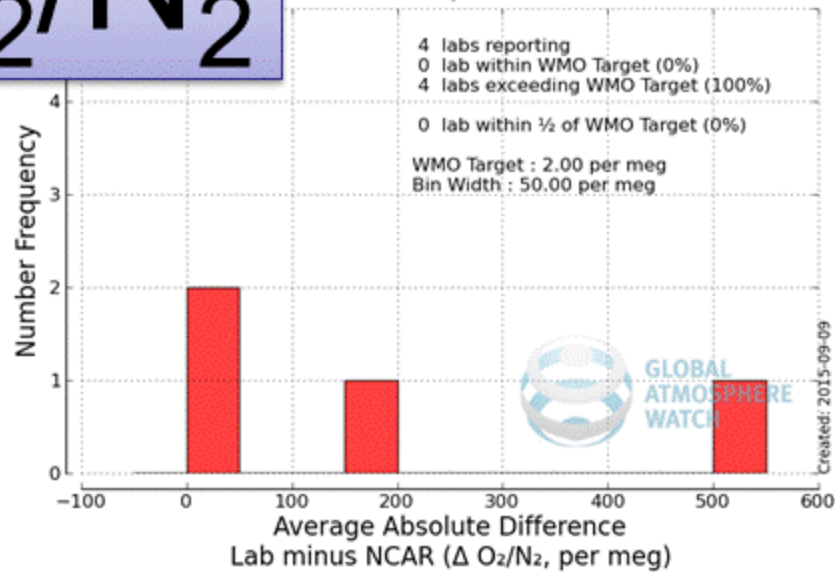
H₂

WMO RR: 6; Circuit: all

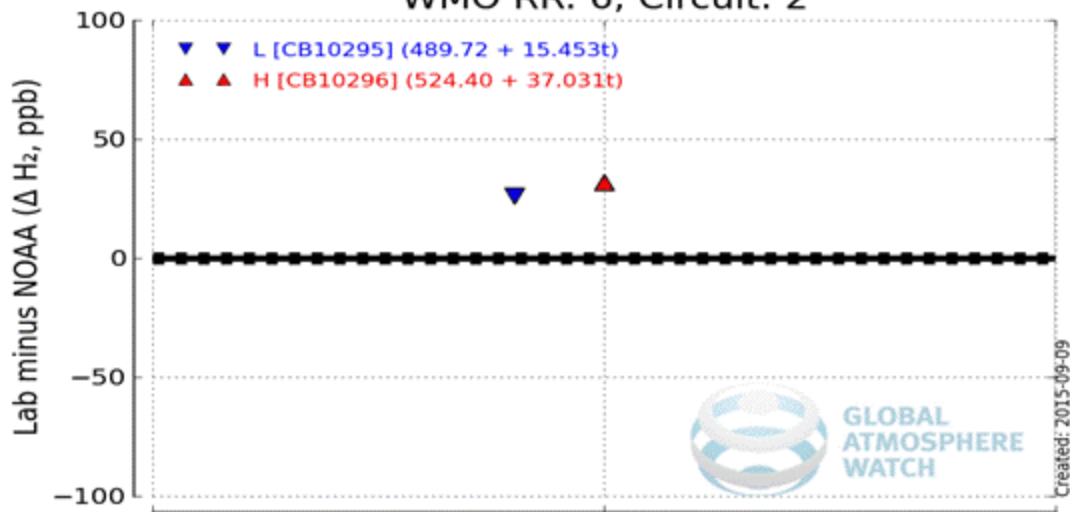


O₂/N₂

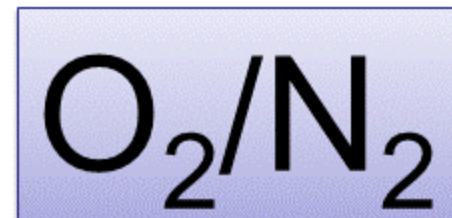
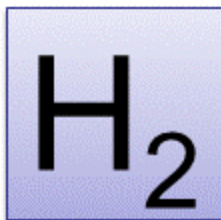
WMO RR: 6; Circuit: all



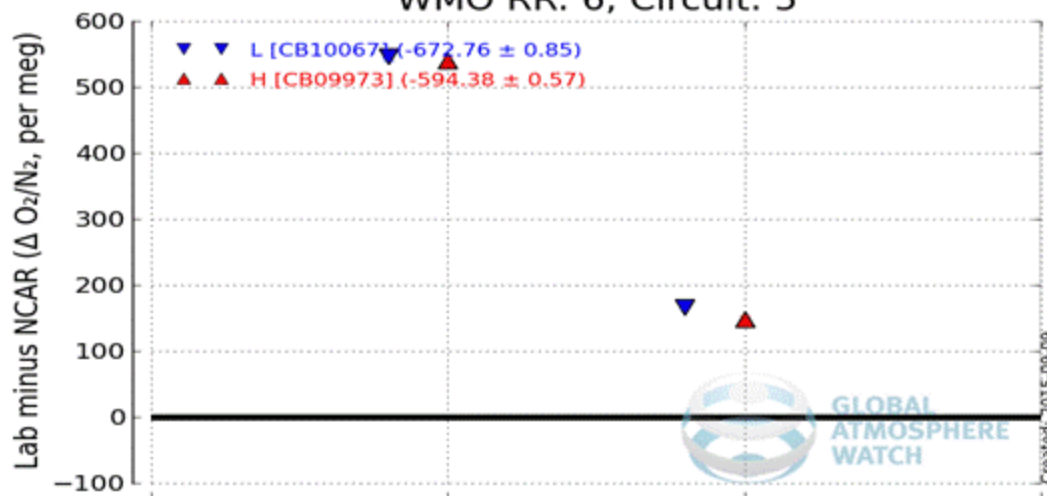
WMO RR: 6; Circuit: 2



CSIRO
[2014-05]



WMO RR: 6; Circuit: 5

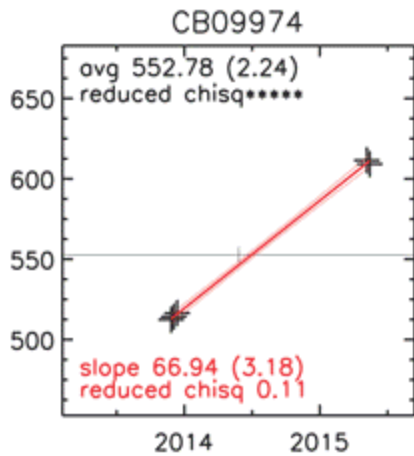


ANST
[2014-01]

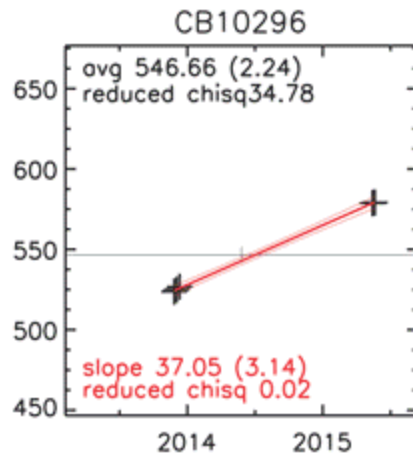
TU
[2014-03]

Stability of cylinders in 6th RR – H₂

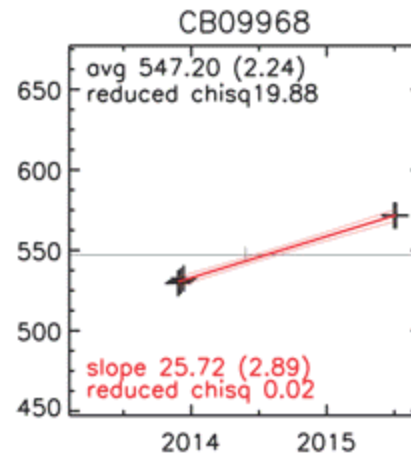
circuit 1



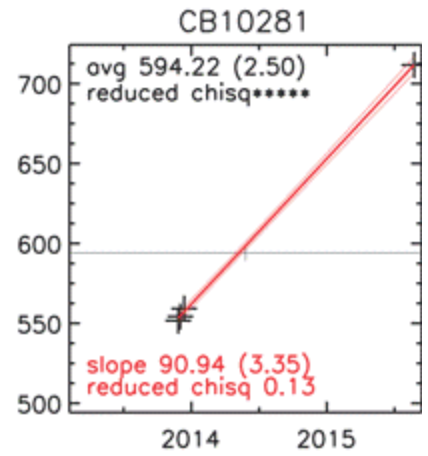
circuit 2



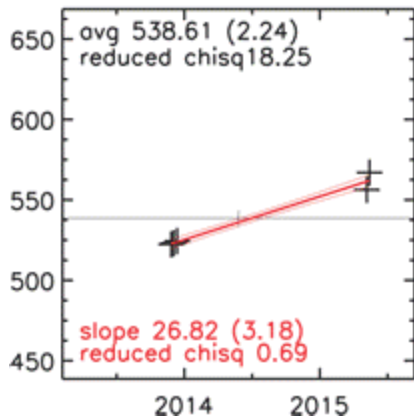
circuit 3



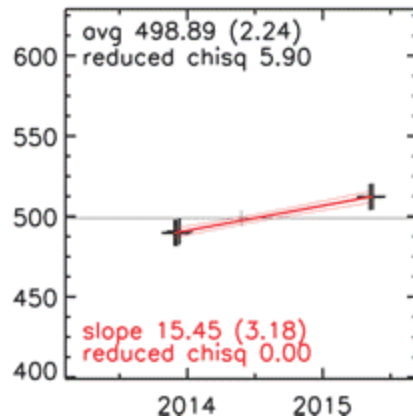
circuit 4



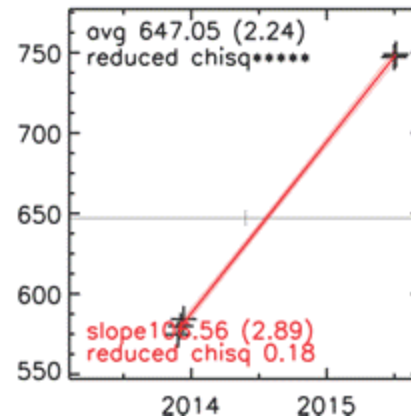
CB10006



CB10295



CB10288



CB10259

