Integrated non-CO_2 Greenhouse gas Observing System

integrated carbon observation system

Evaluation of new N_2O analysers

Test campaigns at LSCE

Nov-Dec 2012 and May – Aug 2013

B. Wastine, A. Guemri, B. Lebegue, M. Schmidt

Test campaign at IUP

Sep-Oct 2013

F.Dinger, S. Vadag , M. Schmidt, I.Levin, S.Hammer

W.Kutsch, J. Smith

LSCE

Presentation of the test campaigns

- 5 laser based instruments loaned to LSCE / IUP for evaluation:
  - Ø Picarro G5101-i, loaned by Picarro (N_2O / $\delta^{15}N_2O$ / H_2O)
  - Ø Thermo Iris-4600, loaned by Thermo (N_2O / H_2O)
  - Ø LGR DLT-100, loaned by Andra (N_2O / CO / H_2O)
  - Ø 2 LGR 23r EP loaned by Andra (N_2O / CO / H_2O)
  - Ø Aerodyne loaned by vTI Braunschweig (N_2O/CO/H_2O)

- Compared to the existing instrumentation run at LSCE / IUP for N_2O measurements:
  - Ø GC Agilent 6890 (ECD detector)
  - Ø Ecotech FTIR

- Several tests have been made to assess the performances of the new sensors:
  - Ø Precision, Repeatability, Reproducibility,
  - Ø Drift,
  - Ø Linearity,
  - Ø Temperature dependence,
  - Ø H_2O influence,
  - Ø Parallel measurements of ambient air

Picarro G5101-i

- We tested a prototype of the now commercialized G5101-i unit (thermal regulation was not fully optimized)

- First Picarro CRDS system using a QCL to measure N2O, $\delta^{15}N^{\alpha}$, $\delta 1^{5}N^{\beta}$ and H2O in the mid IR region (4.57 µm).

- System specifications:
  - Cell volume: 48 cc
  - Sample flow: < 50 ml/min
  - Regulated cell pressure: 100 ± 0.001 Torr
  - Regulated cell temperature: 40 ± 0.001 °C

- Approx cost:
  94,000 $ (N2O concentration only)

- Guaranteed Performance specifications:

	Precision 1-σ (100 sec avg)
N2O Concentration	< 0.1 ppb
δ^{15}NAlpha	< 1 per mil
δ^{15}NBeta	<1 per mil

Thermo IRIS 4600

- New mid IR laser based analyzer platform recently launched by Thermo to measure CO, CH4, N2O and CO2 isotopes.
- Employs the Difference Frequency Generation (DFG) laser technology (combination of 2 near-infrared telecom lasers into a single optical fiber to reach the mid IR region).
- Direct Absorbance Spectroscopy in the 4.6 µm region to measure N2O and H2O (no resonant cavity used, path length= 5m only)

- System specifications:
  - Cell length: 40 cm
  - Regulated Sample flow: 300 ml/min
  - Regulated cell pressure: 175 ± 0.002 mbar
  - Regulated cell temperature: 37.5 ± 0.002 °C

- Approx cost: 60,000 $

- Guaranteed performance specifications:

N2O	
Precision 1-σ (10 sec avg)	< 0.6 ppb
Precision 1-σ (3 min avg)	< 0.1 ppb
Variation (24 hour) (peak-to-peak, 60 min avg)	< 2 ppb

LGR N2O/CO-23d and LGR N2O/CO 23r EP

- Instrument purchased by Andra in 2011 and 2013.

  -> 23r EP is the new Enhanced Performance N2O/CO analyzer now commercialized by LGR.

- Approx cost: 90,000 $

- Off-Axis Integrated Cavity Output Spectroscopy with QCL to measure N2O, CO and H2O in the 4.6 µm region

- System specifications:
  - Cell volume: 408 cc
  - Sample flow: ≈ 300 ml/min
  - Regulated cell pressure: 85 ± 0.007 Torr
  - Regulated cell temperature: 27 ± 0.2 °C

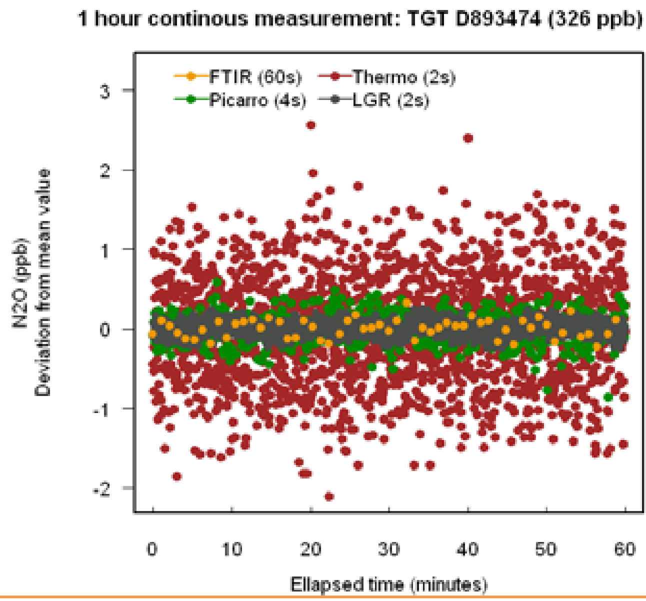
- Guaranteed performance specifications:

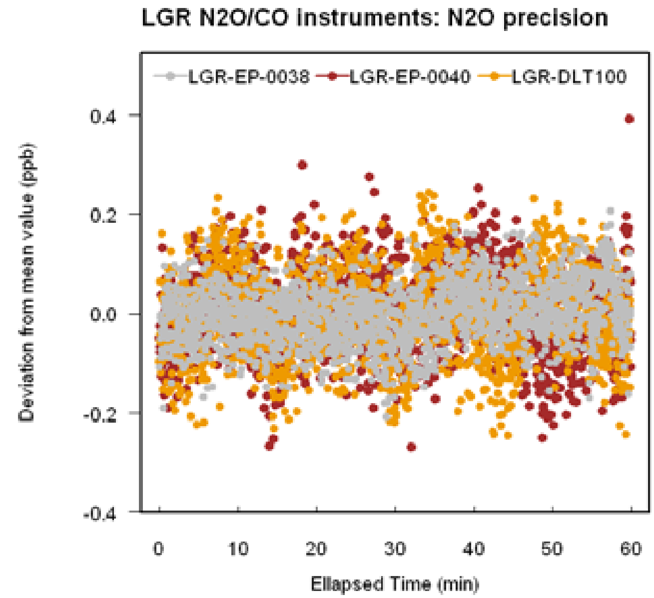
	N2O
Precision 1-σ (3min avr)	0.05 ppb
24h Max Drift (15min avr)	No va

	N2O
Precision 1-σ (3min avr)	0.05 ppb
24h Max Drift (15min avr)	0.1 ppb

Precision and drift

§ Short term analytical noise : -> look at 1 hour period from the tank measurement experiment for the highest possible time resolution





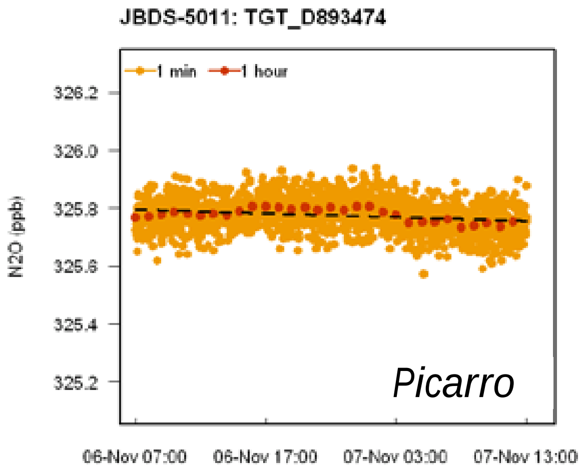
<table>
<tr><th></th><th>Picarro</th><th>LGR</th><th>LGR EP</th><th>Thermo</th><th>FTIR</th></tr>
<tr><td>1σ (raw data)</td><td>0.17 (4s)</td><td>0.09 (2s)</td><td>0.07</td><td>0.67 (2s)</td><td rowspan="2">0.15</td></tr>
<tr><td>1σ (1 min data)</td><td>0.05</td><td>0.04</td><td>0.03</td><td>0.13</td></tr>
</table>

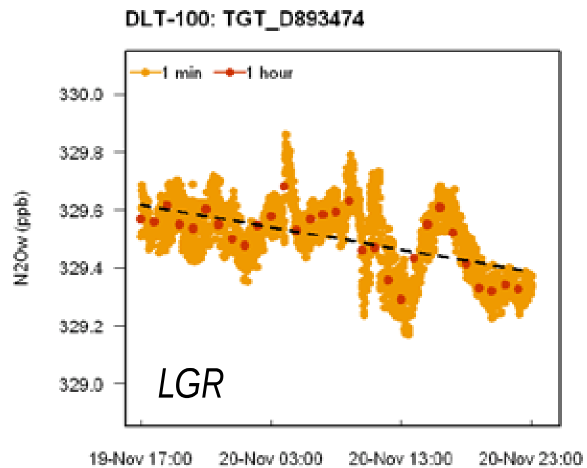
à Highest precision for the LGRs at 0.5 Hz

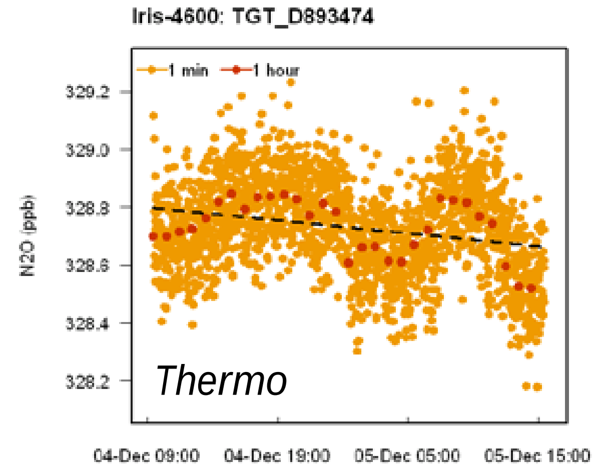
à Thermo and FTIR precision > 0.1 ppb for 1 min avg

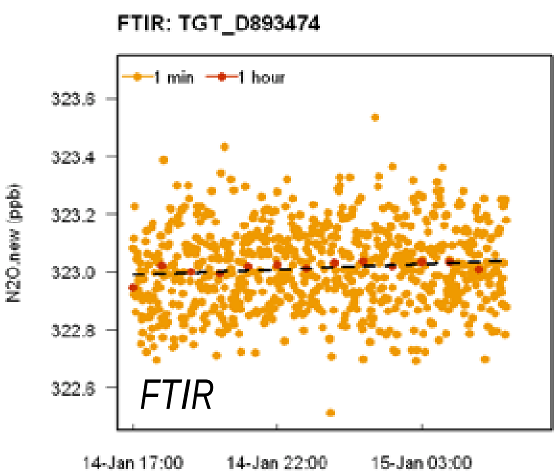
Precision and drift

Methodology: a same TGT tank has been measured for a long period of time (>30 hours, FTIR 13 hours) on each instrument independently. No calibration applied.
> whole distribution of 1 min and 1 hour averaged data









	Picarro	LGR	Thermo	FTIR
1σ (ppb, 1min)	0.05	0.12	0.16	0.14
MaxDrift (ppb,peak to peak)	0.37	0.69	1.05	1.02
Drift (ppb/hr)	-0.001	-0.008	-0.004	0.004

N2O (ppb)	LGR-EP-38	LGR-EP-40	LGR-DLT100
MaxDrift (p. to peak)	0.19	0.50	0.49

24 h

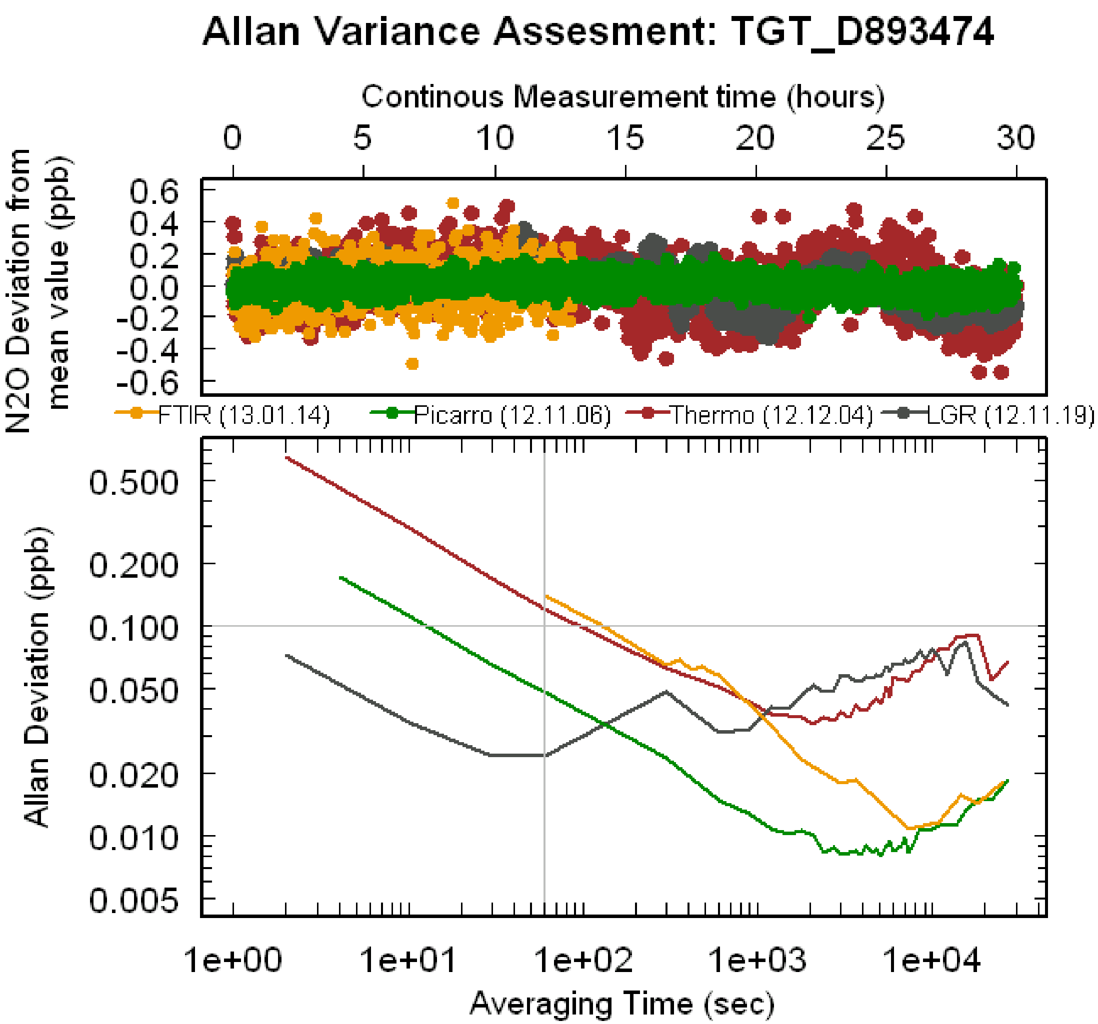
à Picarro analyzer extremely stable (0.024 in 24h)

à Highest drift seen on the LGR.

à both “EP” instruments exceed the guaranteed 0.1 ppb 24h

Precision and drift

§ Allan Deviation: -> optimal averaging times



§ LGR : high precision at high temporal resolution with optimal averaging time of 1 min ; afterwards drift is dominant.

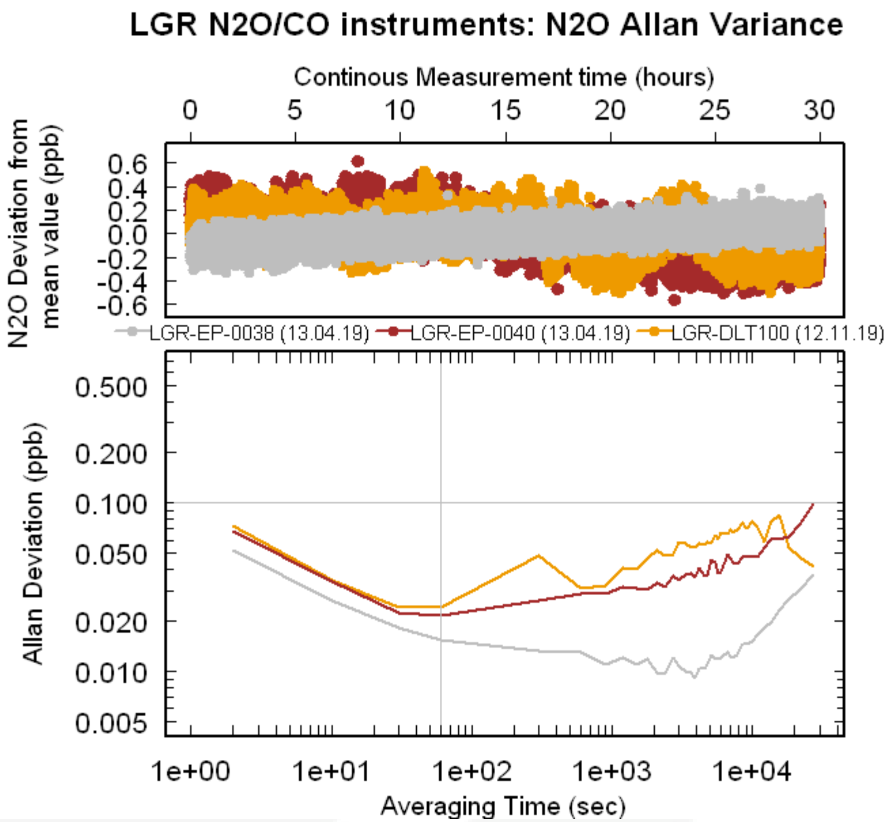
§ Picarro: longer integration times leads to better precision. Drift only appears beyond 1 hour averaging time.

§ Thermo: Allan deviation goes down 0.1 ppb from 1’30” averaging time. No drift observed within a 1 hour period.

§ FTIR: Allan deviation goes down 0.1 ppb from 2’ averaging time. Precision significantly improved for longer integration times.

LGR

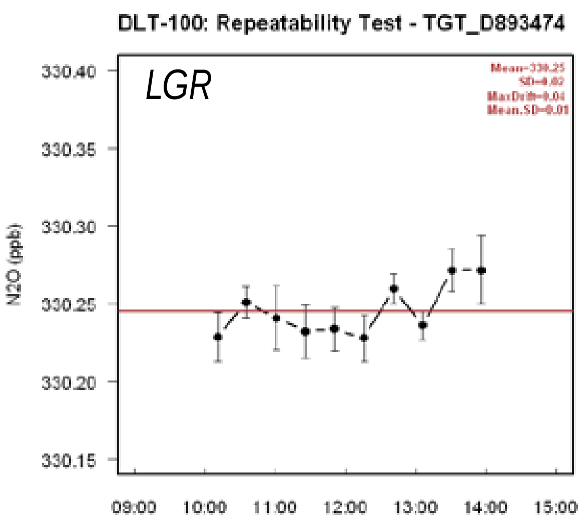
§ Methodology: Measure continuously a tank filled with dry natural air for a long period of time (30 hours). Calculate Allan deviations. No calibration applied.

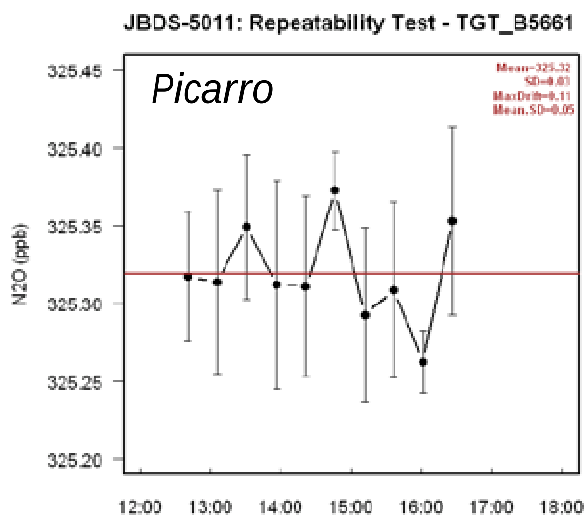


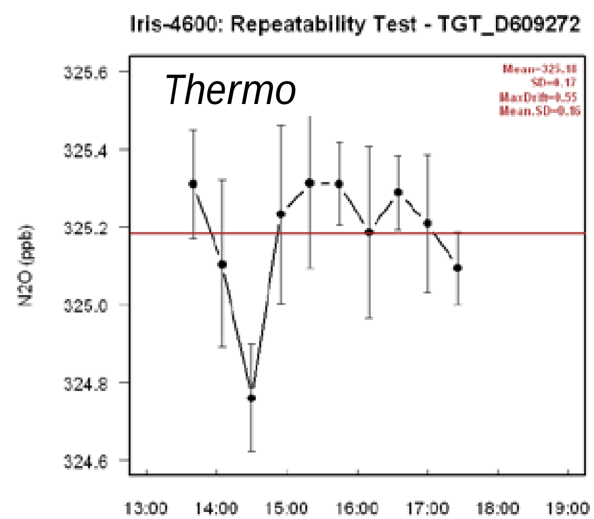
- No significant improvement in N2O stability with "EP" instruments
- Both "EP" analyzers show different pattern: the LGR-0038 unit is significantly more precise and stable for N2O

Repeatability Assesment

§ Methodology: Measure 10 times a TGT tank for 20 minutes alternatively with ambient air (5'). Calculate a N2O mean value (last 5 minutes) for each TGT measurement periods and look at dispersion (1 σ). No calibration applied



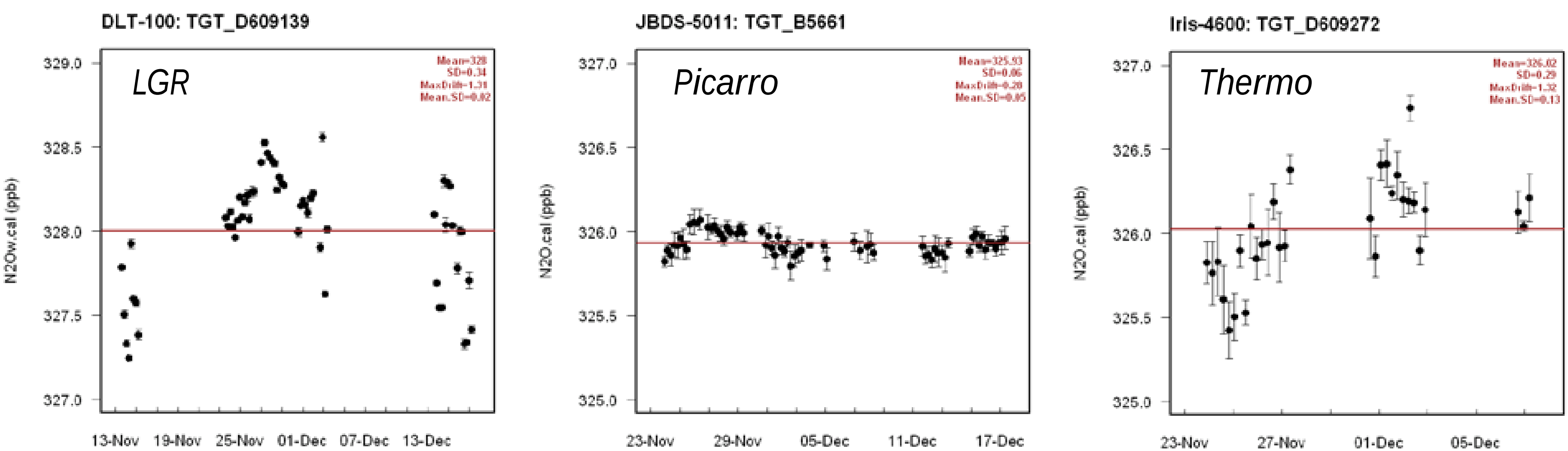




N=10	LGR	Picarro	Thermo
1σ	0.02	0.03	0.17
Max Drift (peak to peak)	0.04	0.11	0.55
Mean 1σ (over 5min avg)	0.01	0.05	0.16

Reproducibilty Assesment

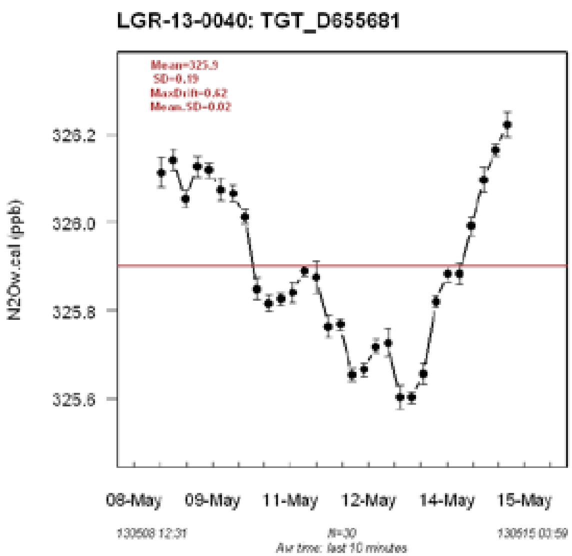
§ Methodology: For each instrument, a TGT tank was regularly measured (for 20 minutes every 5 hours) alternatively with ambient air. For each TGT measurement period, a mean value was calculated over the last 5 minutes. Look at dispersion (1σ) over the whole time series (calibration corrections applied)

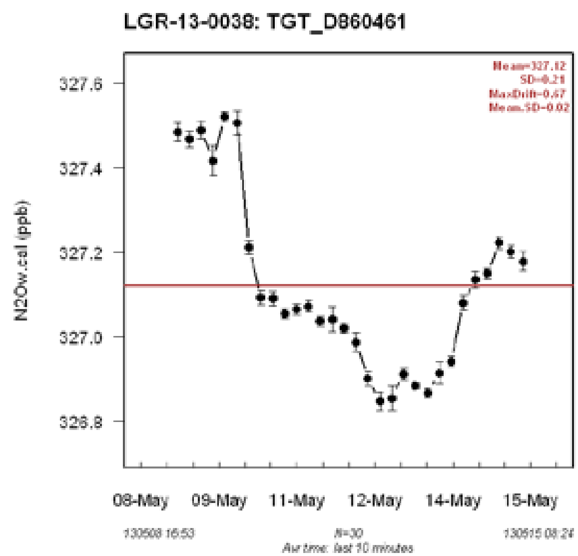


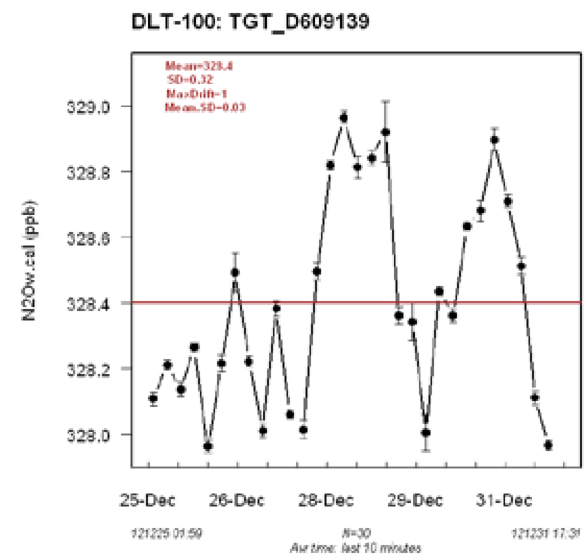
	LGR	Picarro	Thermo	FTIR	GC Gif
N	58 (32 days)	65 (24 d)	31 (14 d)	95 (38d)	1 year
1σ	0.34	0.06	0.29	0.09	0.29
Max Drift (peak to peak)	1.31	0.28	1.32	0.55	

Reproducibility assessment: N2O

§ Methodology: Measure a tank filled with dry natural air for 30 minutes alternatively with 5 hours of ambient air measurement. For each period of tank measurement, calculate a mean value (last 10 minutes) and look at dispersion (1 σ). Calibration applied.







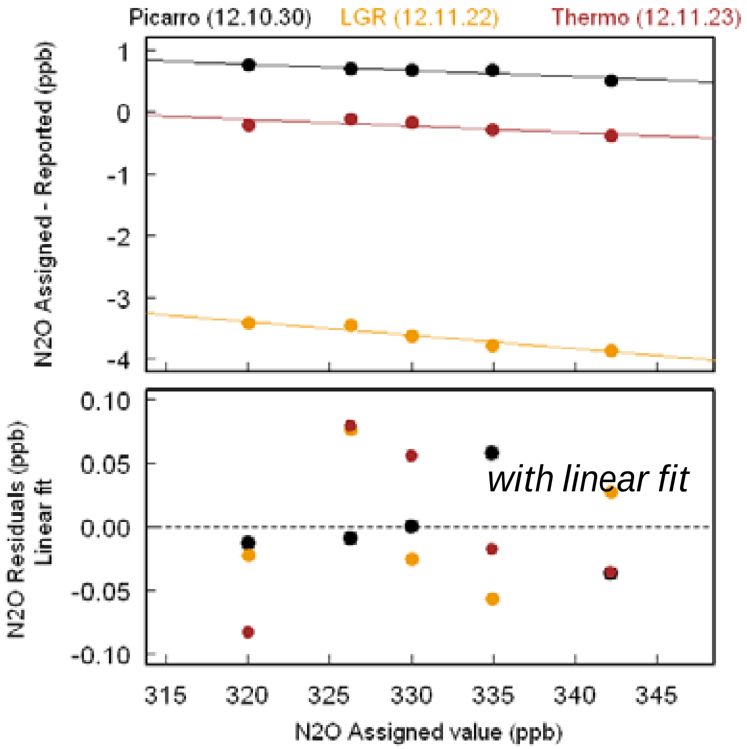
N2O (ppb)	LGR-EP-40	LGR-EP-38	LGR-DLT100
N	30	30	30
Reproducibility	0.2	0.2	0.3
MaxDrift (p.to peak)	0.6	0.7	1.0

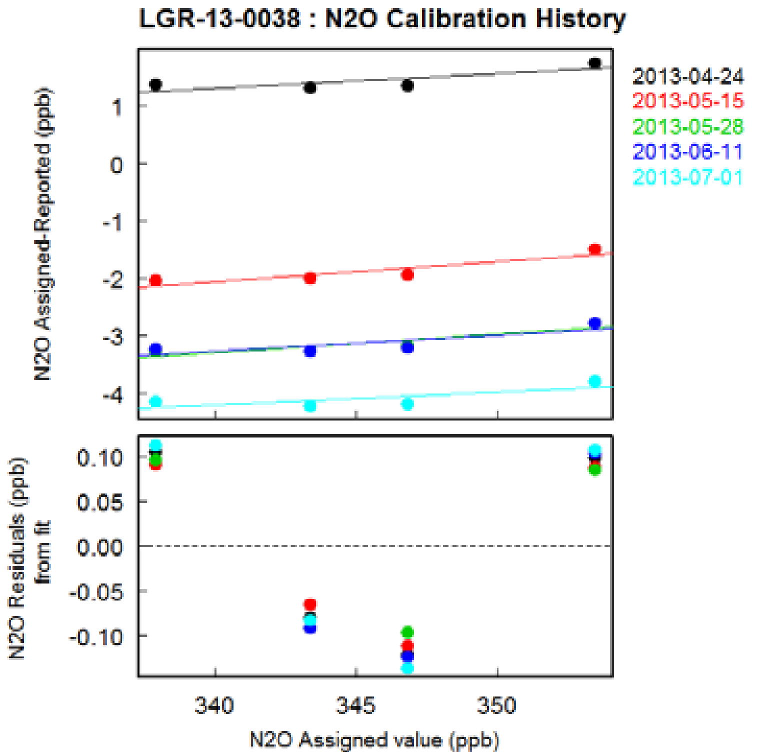
→

- "EP" LGR-40 and LGR-38 compare well with slightly enhanced stability compared to the "classic" LGR DLT100 unit.
- An appropriate calibration strategy has to be defined to bring the reproducibility for N2O below 0.1 ppb

Linearity Assesment

§ Methodology: Measure 5 N2O standards filled and calibrated by MPI Jena and compare the reported vs assigned N2O values.





à All instrument responses well characterized by a linear fit

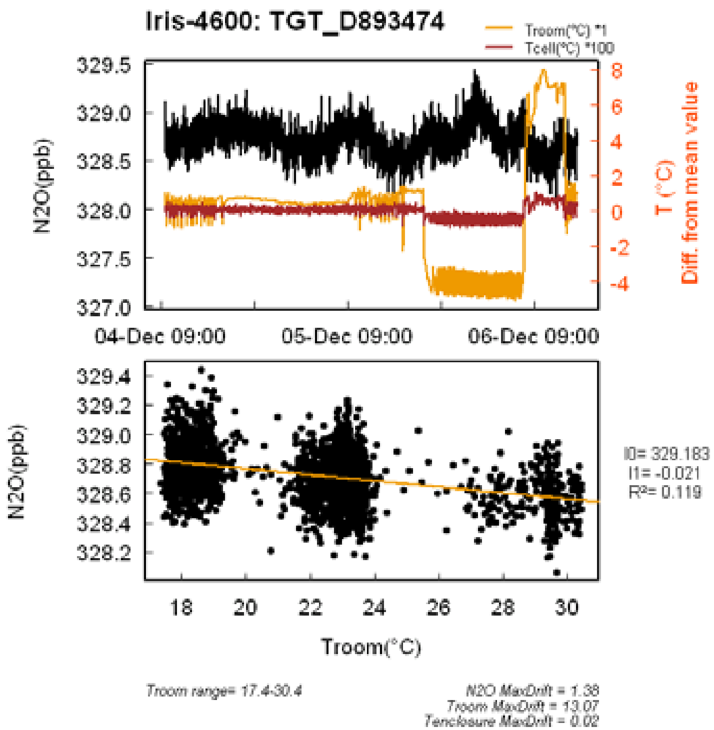
à No major gain to apply a quadratic function

à LGR 0038 show large Large drift in the N2O values of about 5 ppb in 2 months while the drift didn't exceed 1.5 ppb for the LGR-048 instrument over the same period.

Temperature dependence

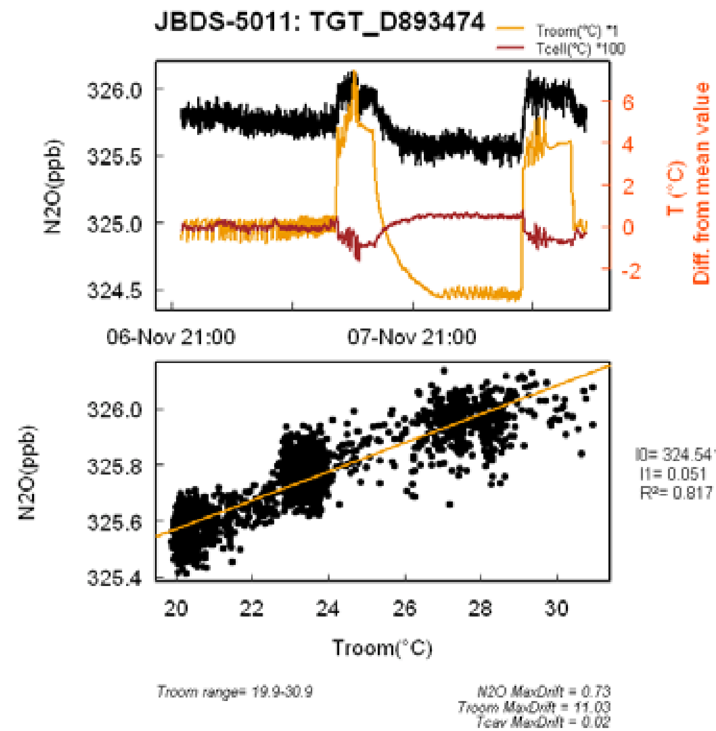
§ Methodology: Vary lab temperature while the instrument is measuring continuously a TGT tank.

§Thermo: 17 <Troom (°C)< 30



No significant temperature dependence

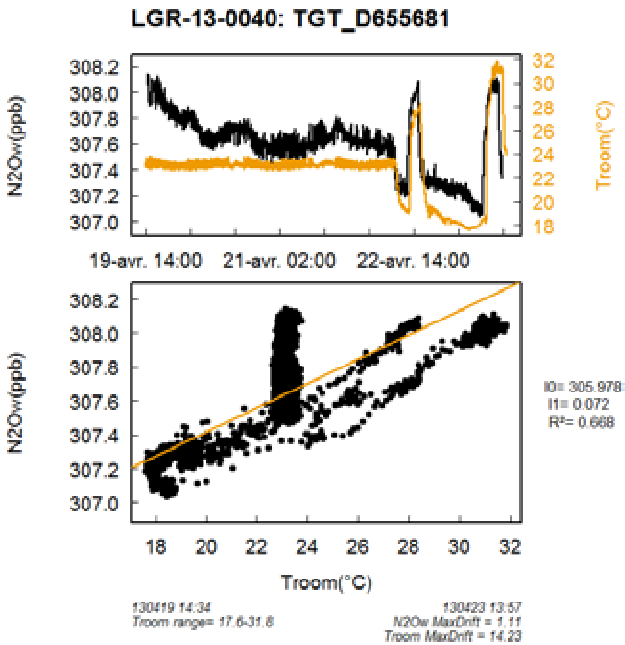
§ Picarro: 20 <Troom (°C)< 31

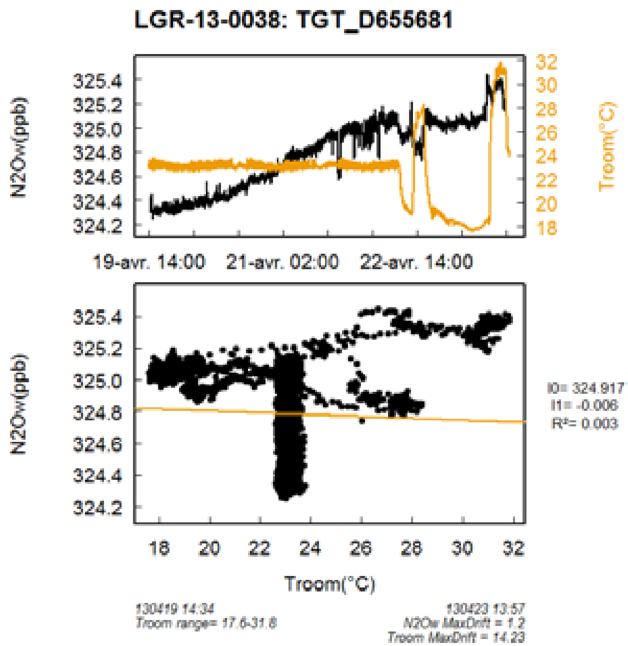


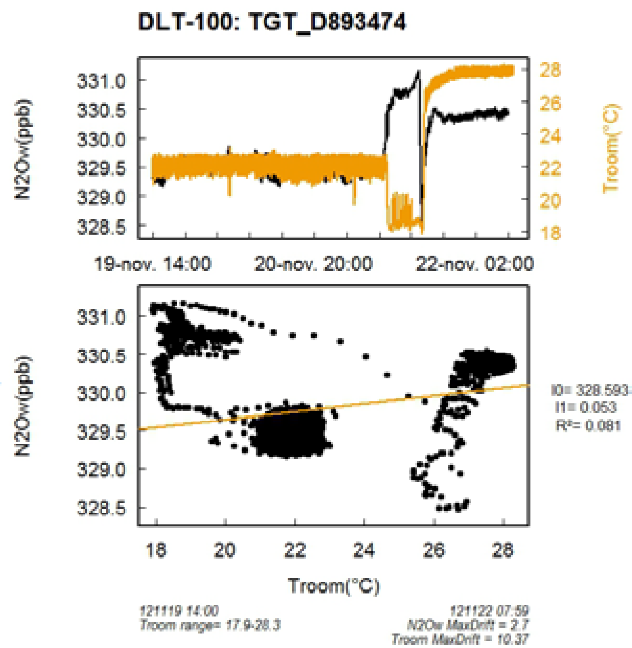
Temperature dependence of about +0.05 ppb/°C know by Picarro. Must have been corrected now.

Temperature Influence: N2O

§ Methodology: Measure continuously a tank filled with dry natural air and vary the room temperature. No calibration applied.



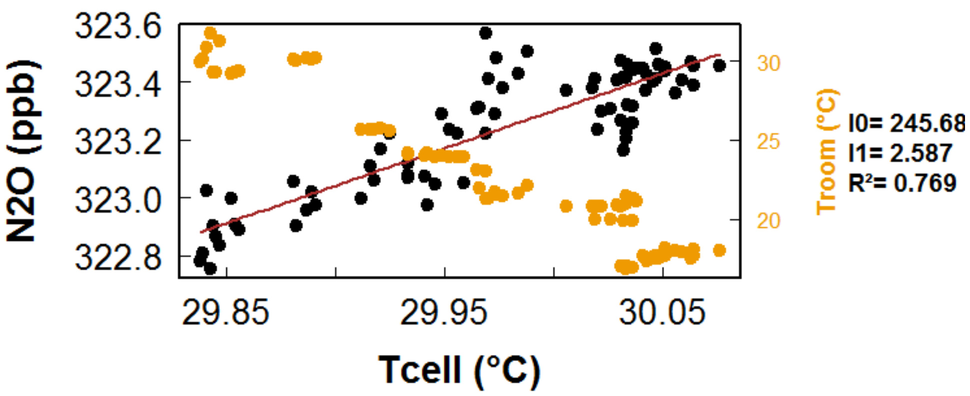




- "EP" LGR-0040: an apparent temperature dependence is seen (≈ +0.07 ppb /°C) beside a non negligible "natural" variability observed for N2O during the experiment (about 0.5 ppb peak to peak difference over a 3 day period at constant lab temperature)
- "EP" LGR-0038: no significant temperature influence observed, but large "natural" variability of the N2O signal, about 0.7 ppb peak to peak difference over a 3 day period at constant lab temperature.
- "Classic" DLT-100: an apparent and high temperature dependence is seen, but no linear relationship !

Temperature dependence

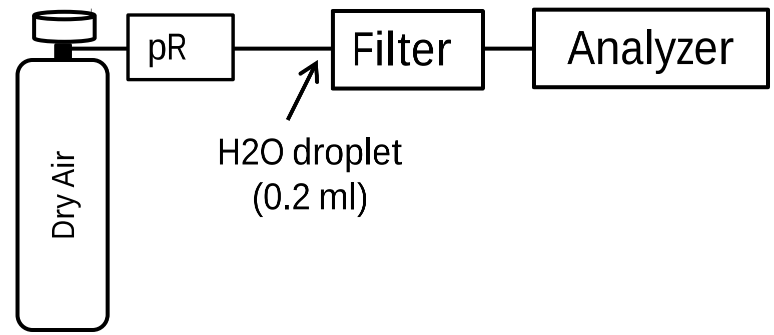
§ FTIR: 17 <Troom (°C)< 31



Temperature dependence = major issue

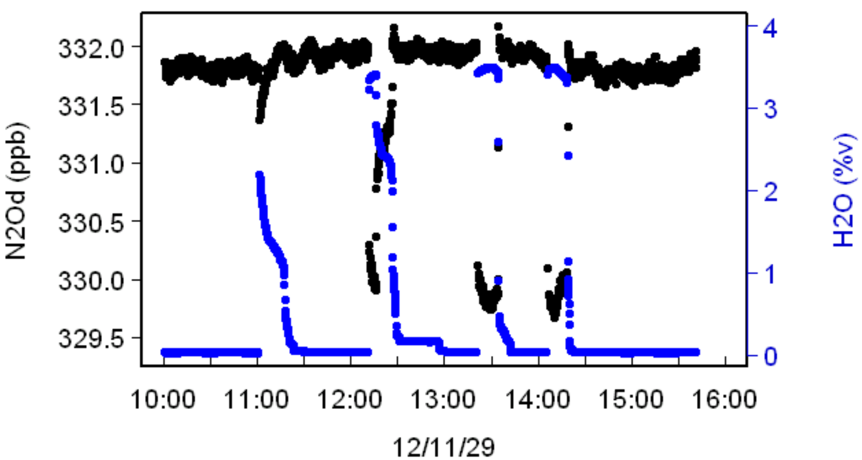
Water vapour correction

§ Methodology: Perform the water droplet test using an hygroscopic filter to assess the water vapour influence and evaluate the efficiency of the water correction if provided.



§ LGR: water vapour correction provided by LGR.

N2O corrected and H2O

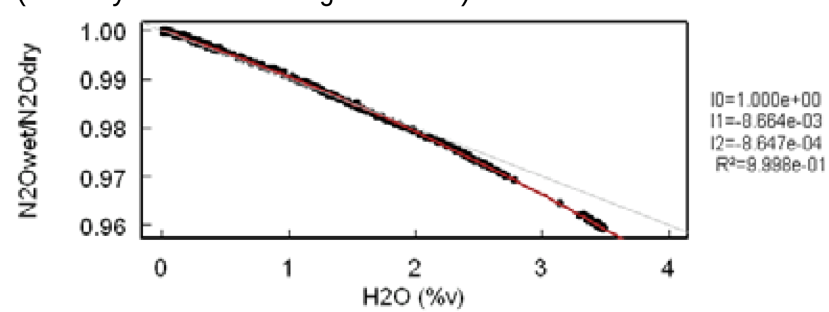


-> LGR correction based on dilution only (pressure broadening effect not taking into account)

-> Do not correct efficiently when H2O > 2%v.

->For the “EP” units, the water correction for N2O is clearly not applicable

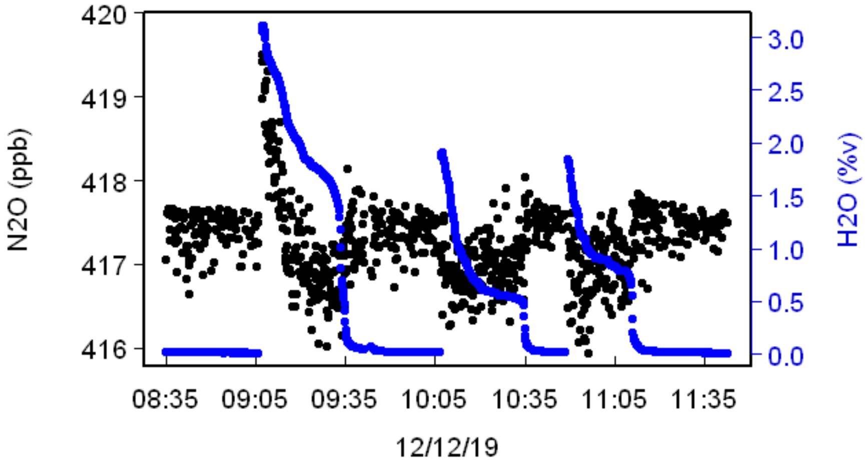
Water correction derived from the experiment :
(N2Odry= TGT tank assigned value)



Water vapour correction

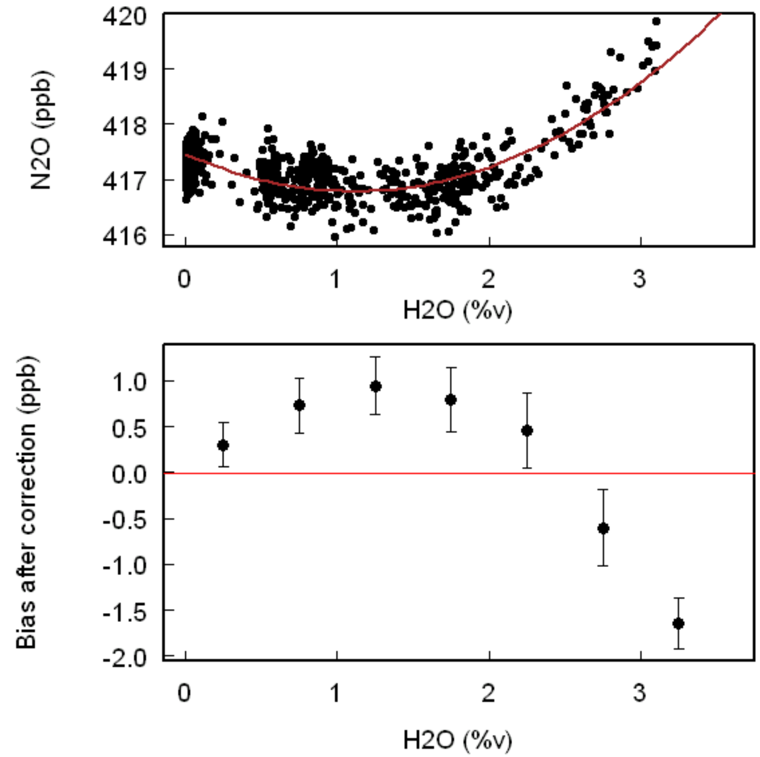
§ Thermo: water vapour correction provided.

N2O corrected and H2O



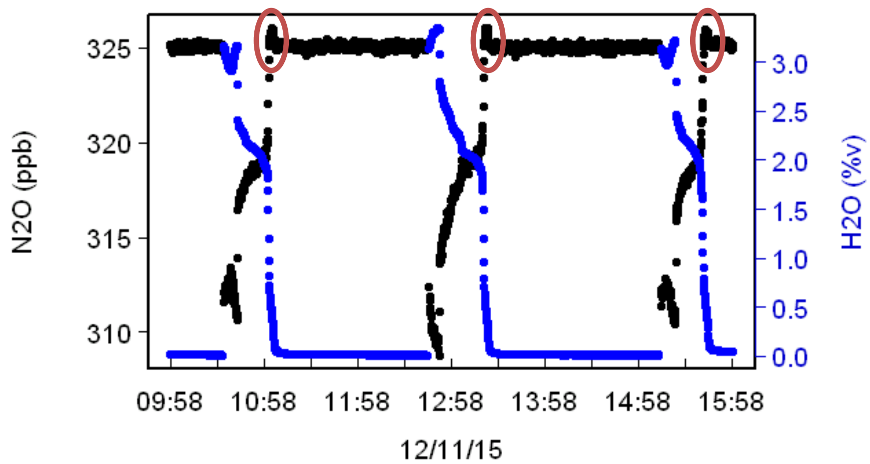
-> Thermo correction not suitable for accurate measurements.

N2Ocorrected=f(H2O)

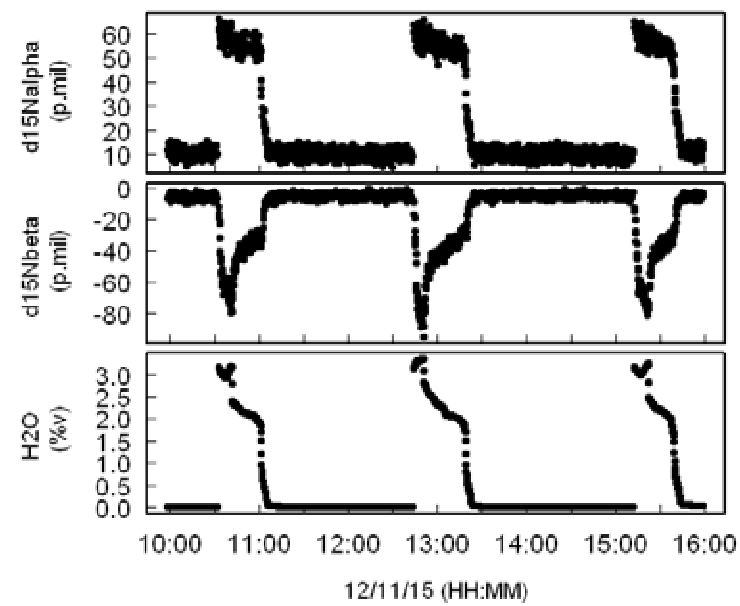


Water vapour correction

N2O reported and H2O



$\delta^{15}N^{\alpha}$, $\delta 1^{5}N^{\beta}$ and H2O



Water correction derived from the experiment :
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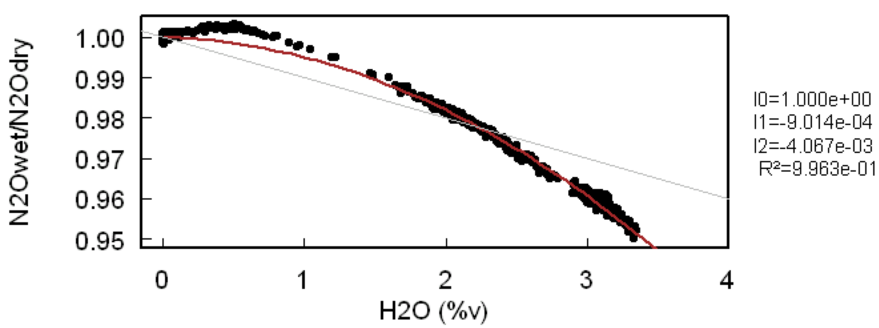
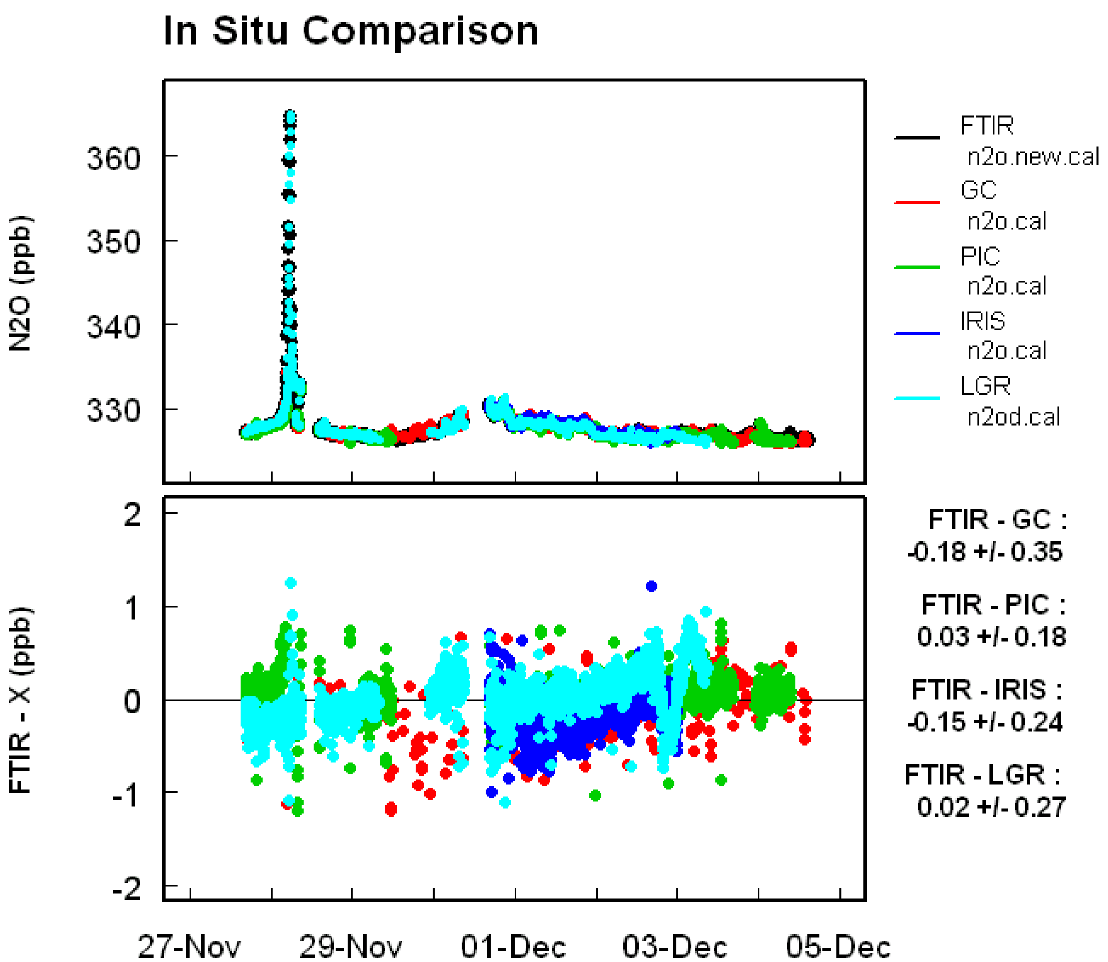


-> A priori water correction not easy to derive. Wet/Dry ratio does not vary in usual way (cf. sudden N2O enhancements when H2O goes down to zero)

-> Cross talk issues with other species ?

Ambient Air Comparison



§ All instruments equipped with a dedicated sample line to measure ambient air above lab roof (7 m a.g.l).

§ GC, Picarro, LGR and Thermo instruments measured dry ambient air using a cryogenic trap.

§ FTIR instrument measured dry ambient air using Nafion + magnesium perchlorate.

§ All instruments compared to FTIR (minute averages)

Aerodyne QCL analyzer for N_2O, CO and H_2O: Tests and comparisons in Heidelberg

Florian Dinger[1], Jeremy Smith[2], Werner Kutsch[2], Sanam Vardag[1], Martina Schmidt[1], Ingeborg Levin[1] and Samuel Hammer[1]

[1]*Institut für Umweltphysik, Uni Heidelberg*

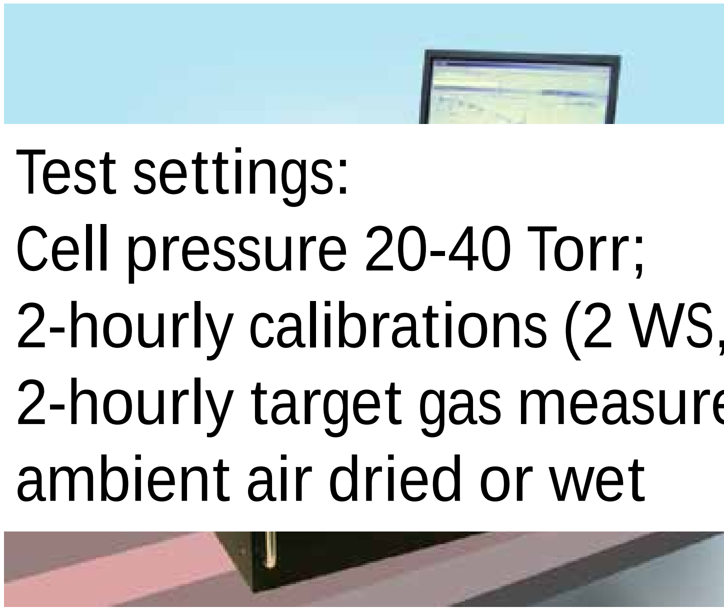
[2] *Thünen Institut, Braunschweig*

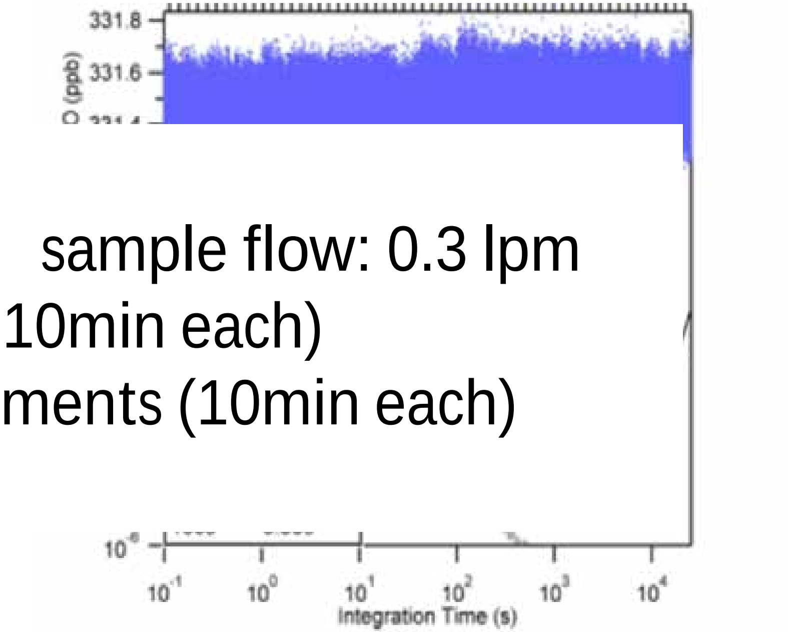
ICOS Atmosphere Monitoring Station Assembly (MSA)

13.-14.November 2013, Paris

Nitrous Oxide Monitors

WORLD'S MOST PRECISE NITROUS OXIDE (N_2O) MONITORS





Test settings:

Cell pressure 20-40 Torr;   sample flow: 0.3 lpm

2-hourly calibrations (2 WS, 10min each)

2-hourly target gas measurements (10min each)

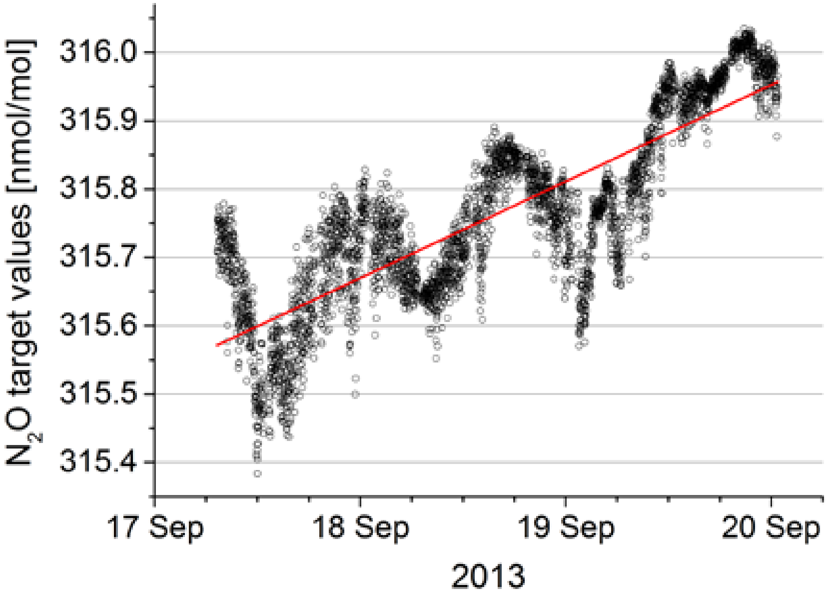
ambient air dried or wet

- Øcell volume: 500 ml
- Øcell pressure: 5-50 Torr
- Øoptical pass: 76m

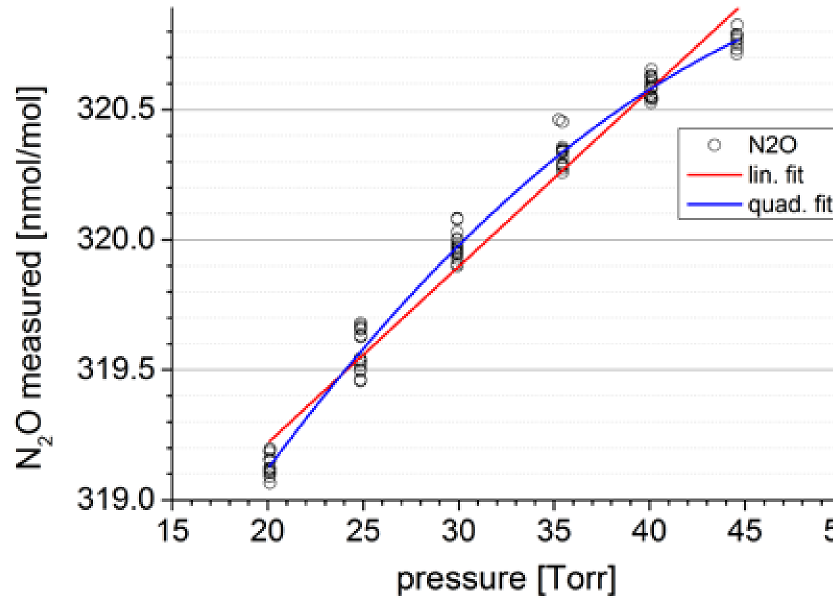
Øsample flow: 30-500 lpm (build for Eddy covariance)

Source: http://www.aerodyne.com/products/nitrous-oxide-monitors

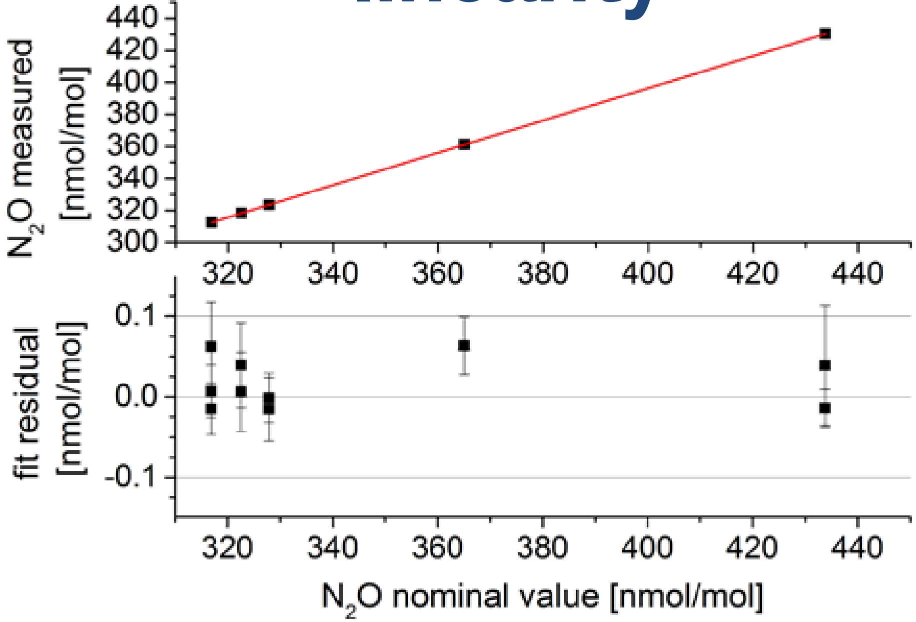
drifts



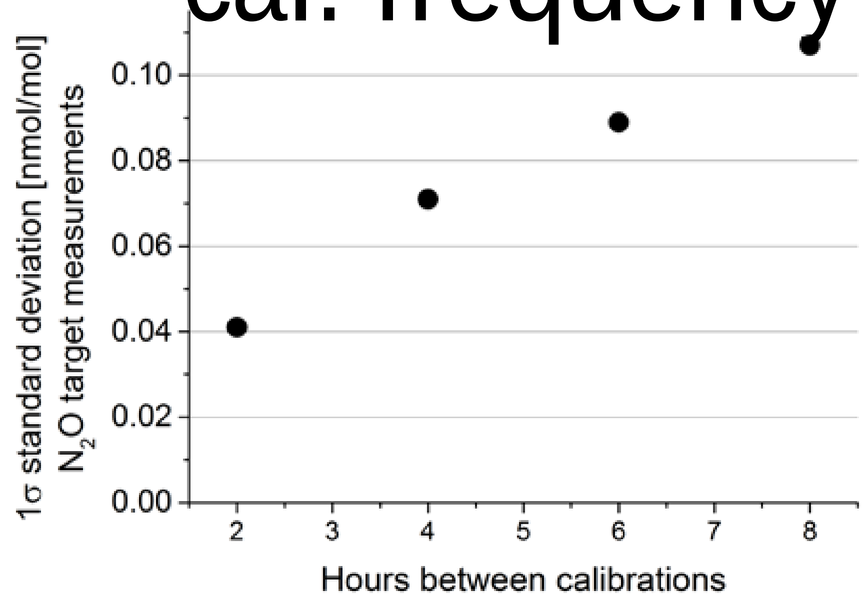
cross-sensitivity



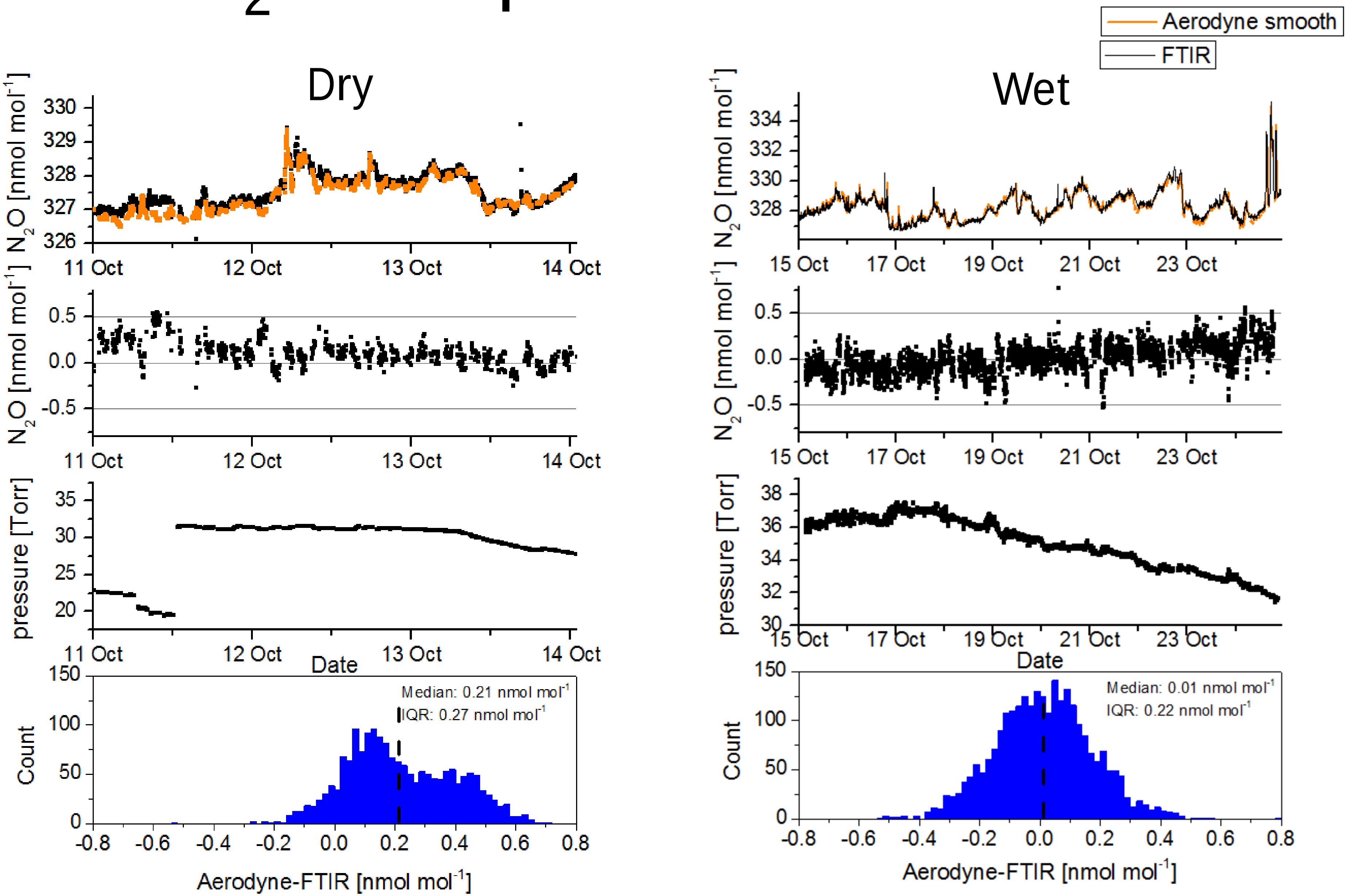
linearity



cal. frequency



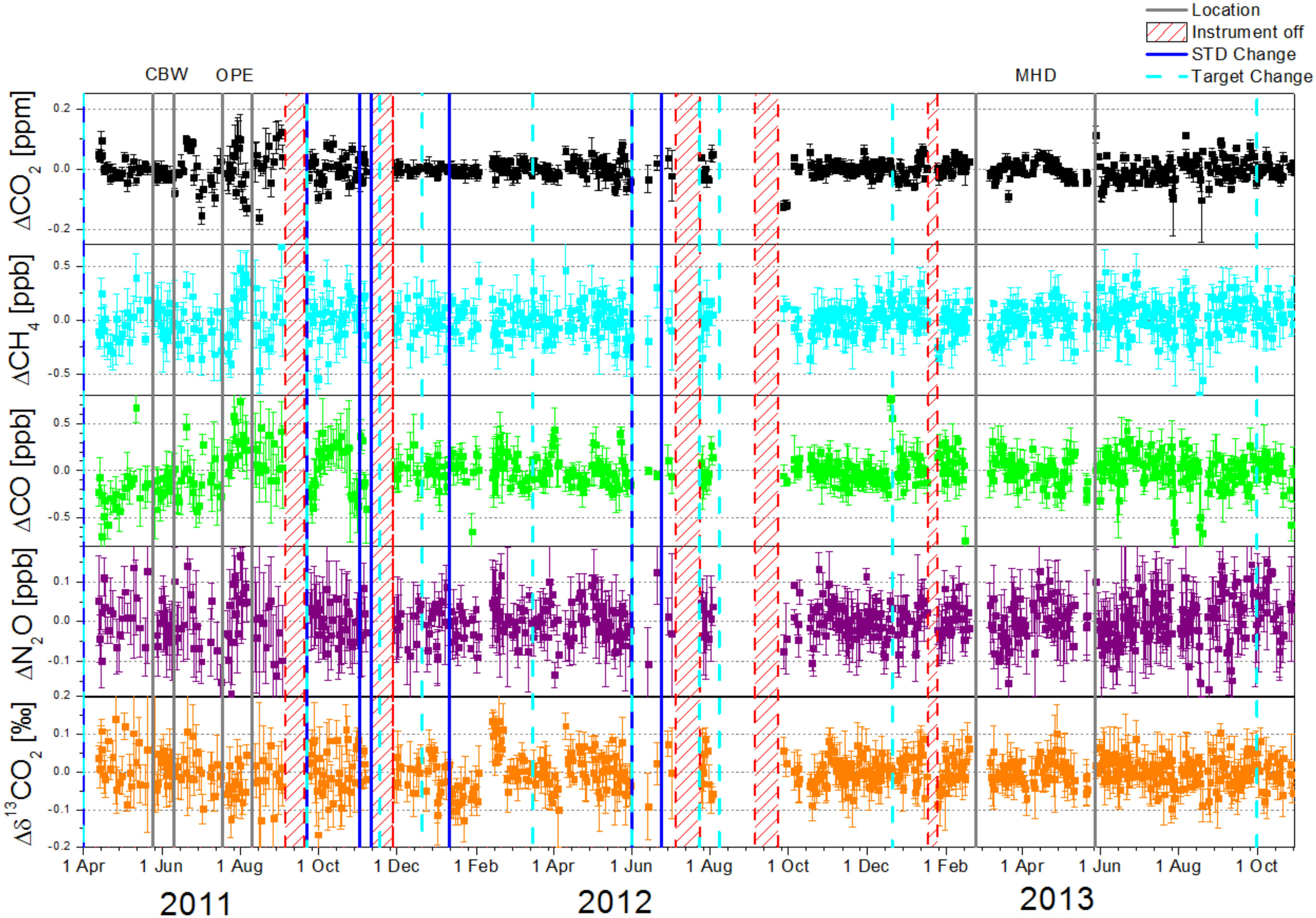
N_2O comparison to the FTIR



Summery and remaining issues

- High precision, however frequent calibration is necessary to gain high accuracy
- No active pressure and flow control, sample handling should be revisited for atmospheric monitoring
- Pressure cross-sensitivity depends on instrument settings
- Lowest sampling frequency at 1Hz, unnecessary fast for atmospheric monitoring
- No drying necessary

FTIR target record



1σ

0.05ppm

0.26ppb

0.40ppb

0.09ppb

0.06‰

4. Summary

	LGR	LGR EP	Picarro	Thermo	Aerodyne	FTIR
Precision -sec (ppb)	0.09	0.07	0.17	0.67	**0.02**	
Precision 1-min (ppb)	0.04	0.03	0.05	0.13	**0.01**	0.15
30 hour Drift (ppb/hr)	-0.008	0.004 (?)	**-0.001**	-0.004	0.006	0.004
Repeatability (ppb)	**0.02**	**0.02**	0.03	0.17		
Reproducibility (ppb)	0.34	0.2	**0.06**	0.29	0.04*	0.09
Temperature dependence	--	--	-	+	NA	-
H_2O correction	-	--	NA	--	++	NA

-- to ++: poor to good (qualitative)
NA: not applicable
* Two hourly calibrated

4. Conclusion

§ From the results gained so far :

- Ø LGR instrument is the most precise (high temporal resolution), but drift compromises measurements (1 day time scale) -> need to adjust proper calibration strategy.
  The new Enhanced Performance does not correct this drift issue
- Ø Picarro instrument is the most stable, with low drift and good precision.
- Ø Thermo instrument with lowest performances
- Ø FTIR instrument compares well, with low drift and good precision.
- Ø Aerodyne needs also a more frequent calibration strategy

§ Water corrections appear to be not efficient enough for the LGR and Thermo instruments, while not existing for the Picarro.

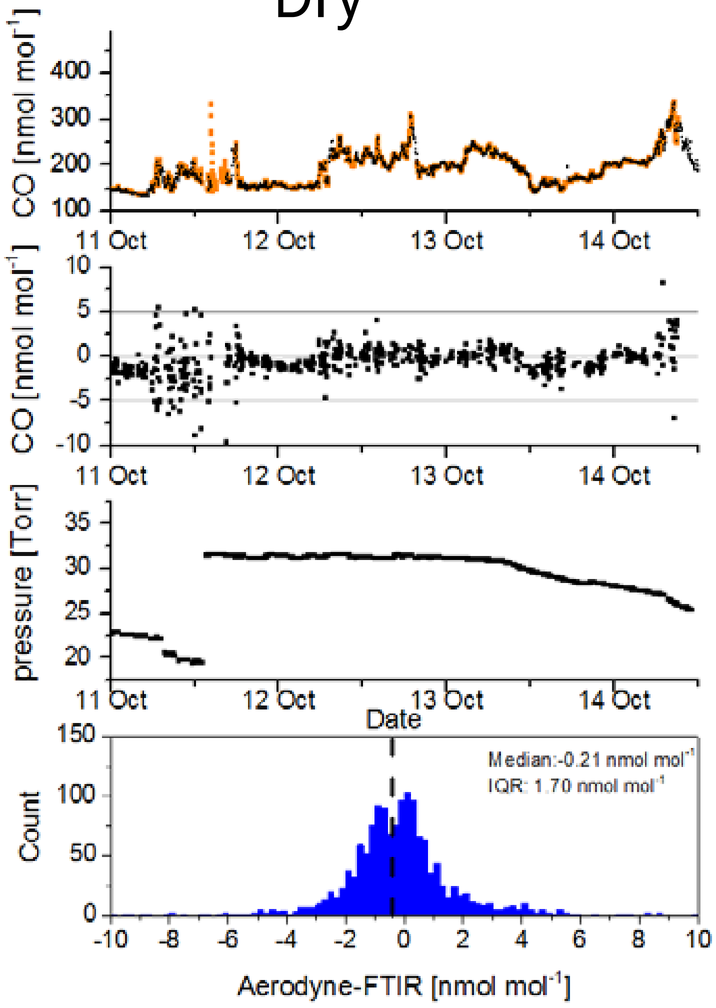
§Water correction works well for Aerodyne

§ Ongoing work: Aerodyne is at the moment under standard test at LSCE

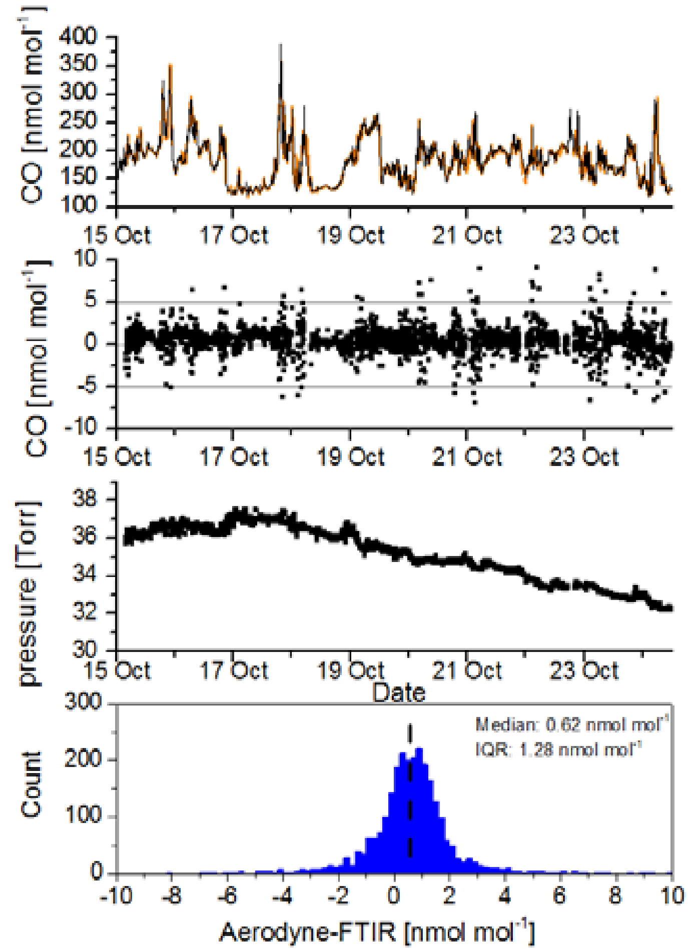
§ Still some data to be explored to understand/present some issues (water vapour corrections, potential cross talks).

CO comparison to the FTIR

Dry



Wet



Instrument top view, outer and inner covers removed

IR Detector

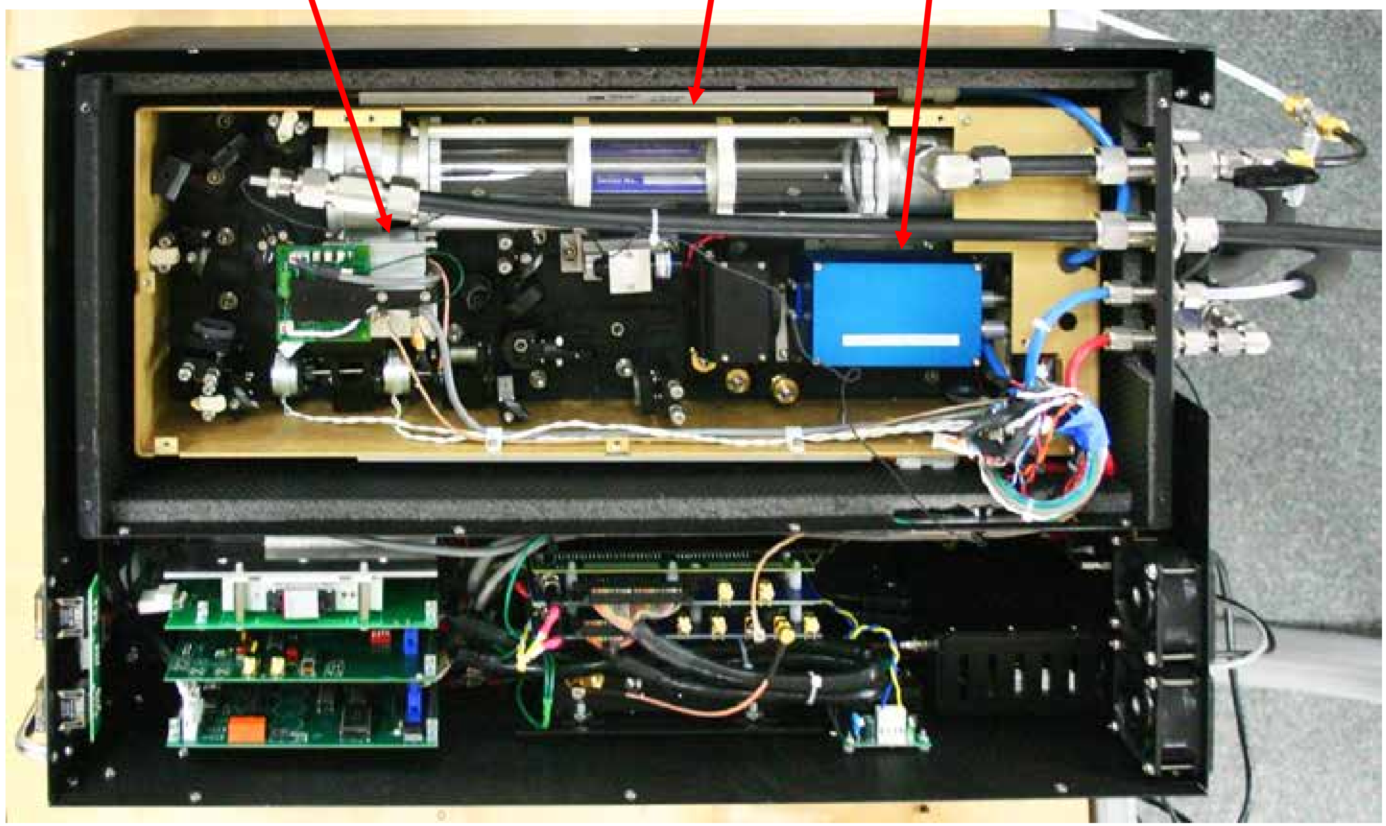
76 m multi-pass cell

QC Laser

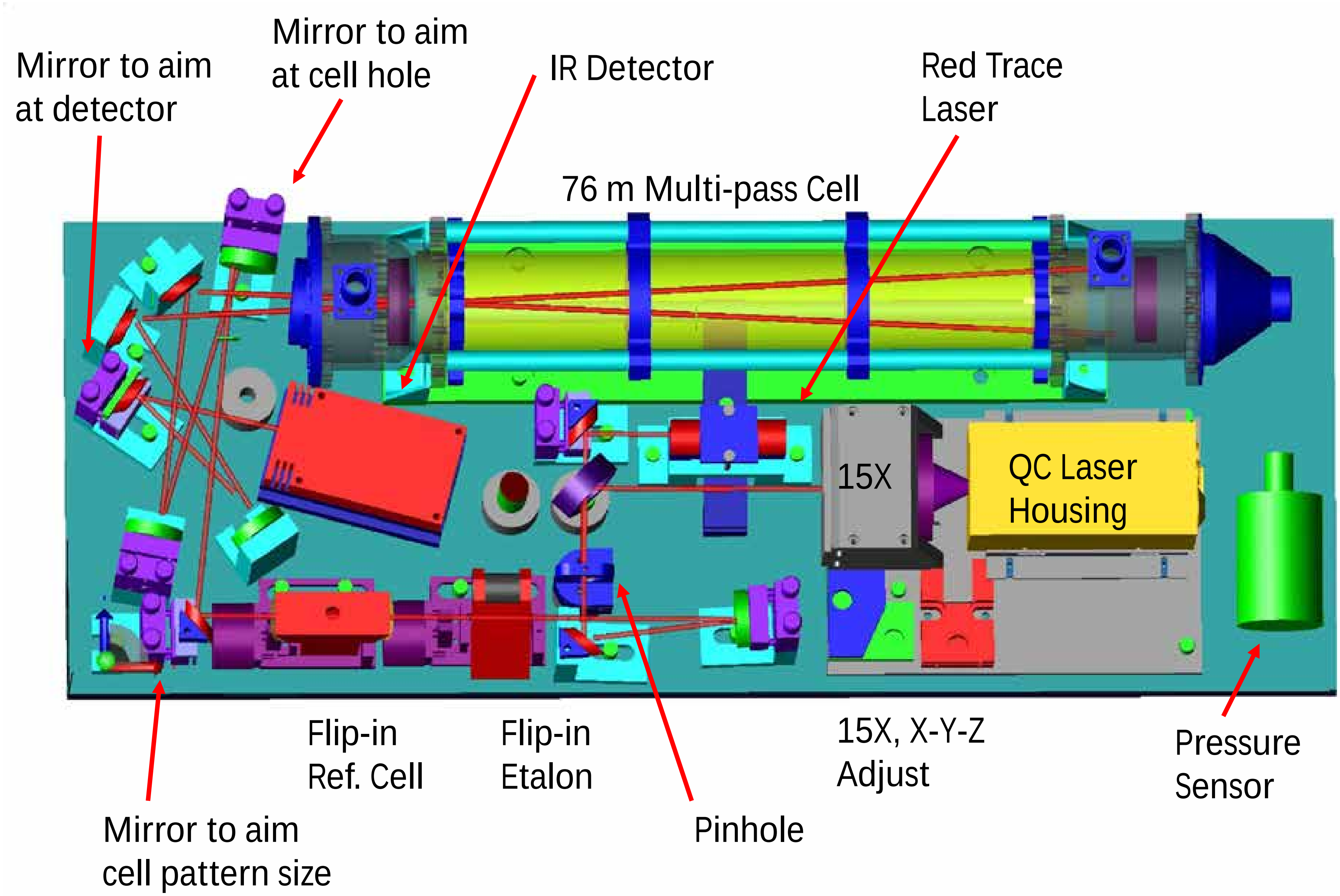
Gas, water connections

Optics Section

Electronics Section

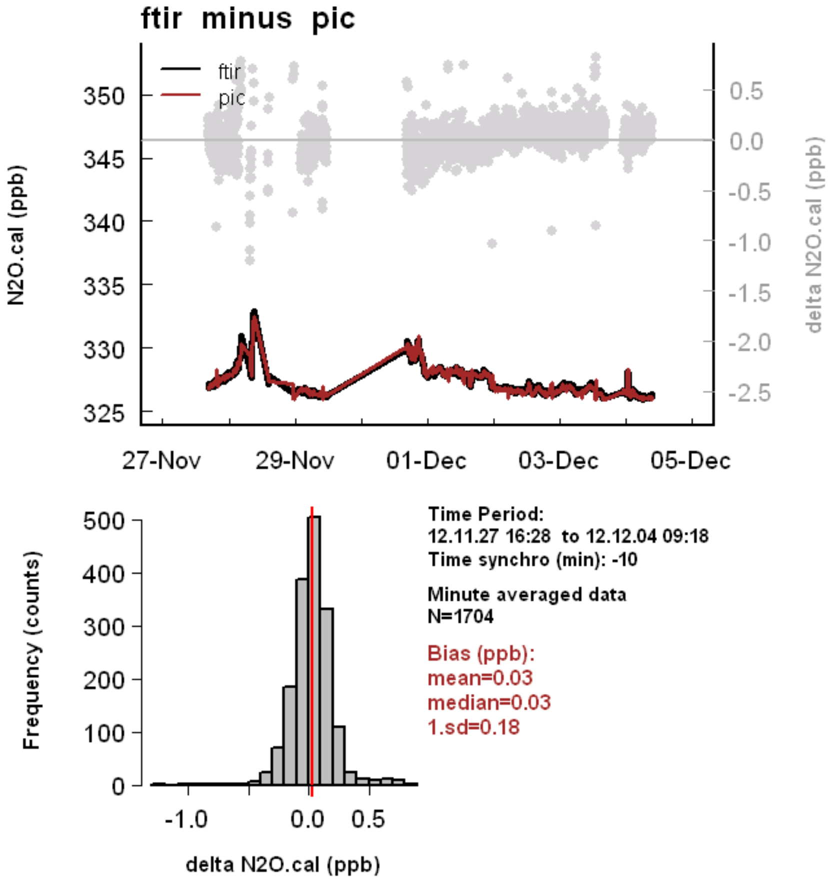


Optical Module Diagram

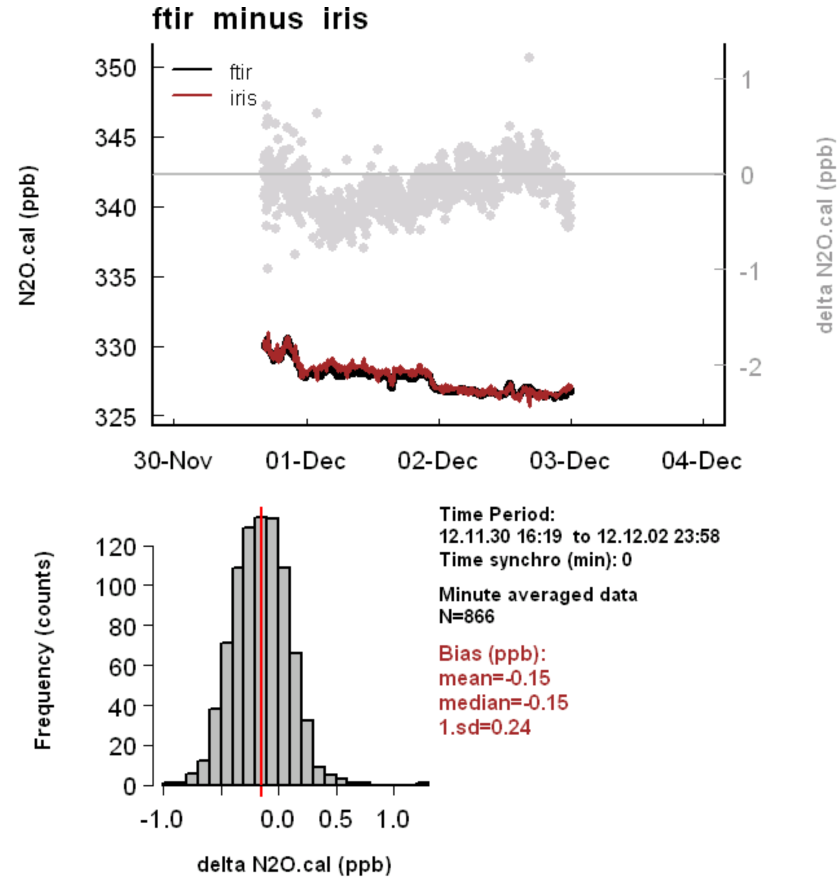


Ambient Air Comparison

§ FTIR – Picarro:



§ FTIR – Thermo:

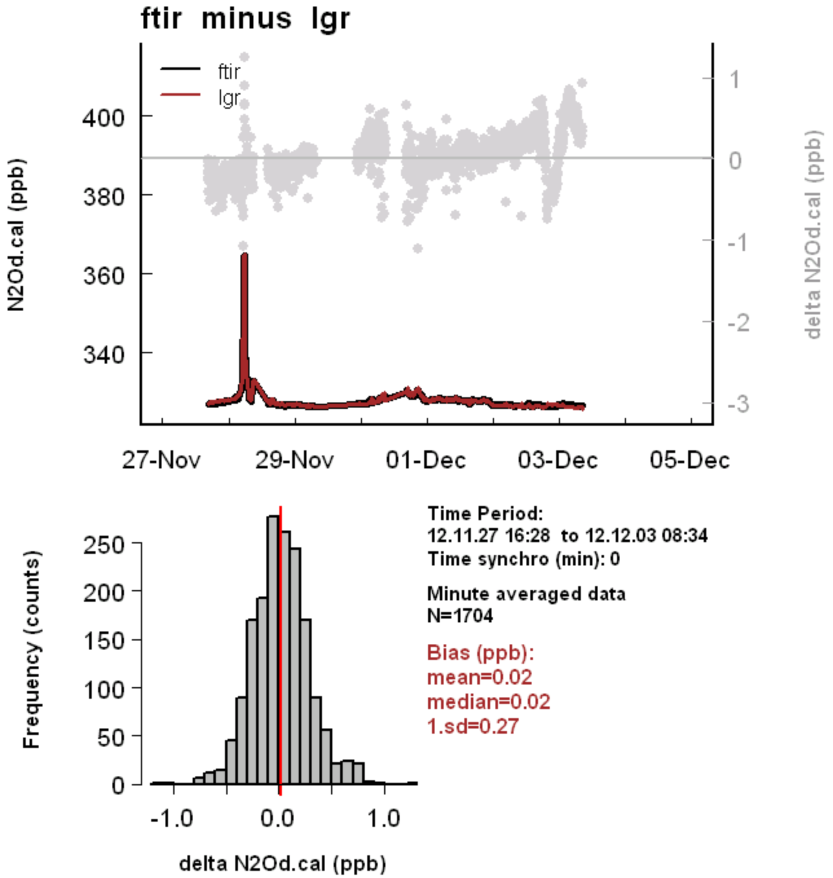


Ø Good overall agreement between the 2 instruments

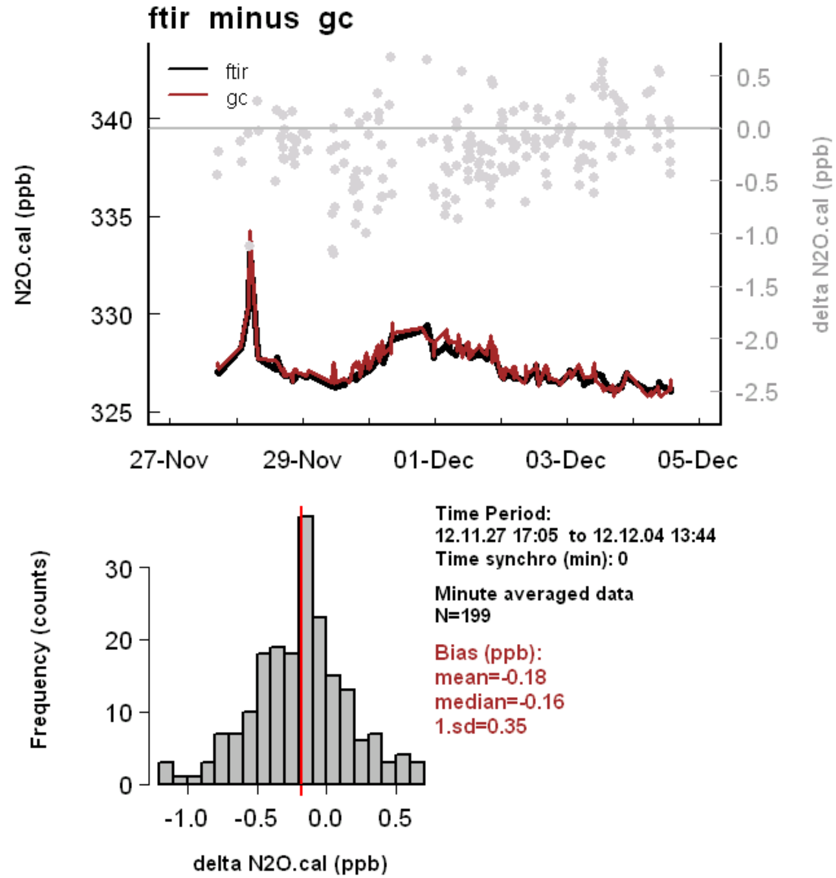
Ø significant bias
Ø scatter in the difference (Thermo drift ?)

Ambient Air Comparison

§ FTIR – LGR:



§ FTIR – GC:

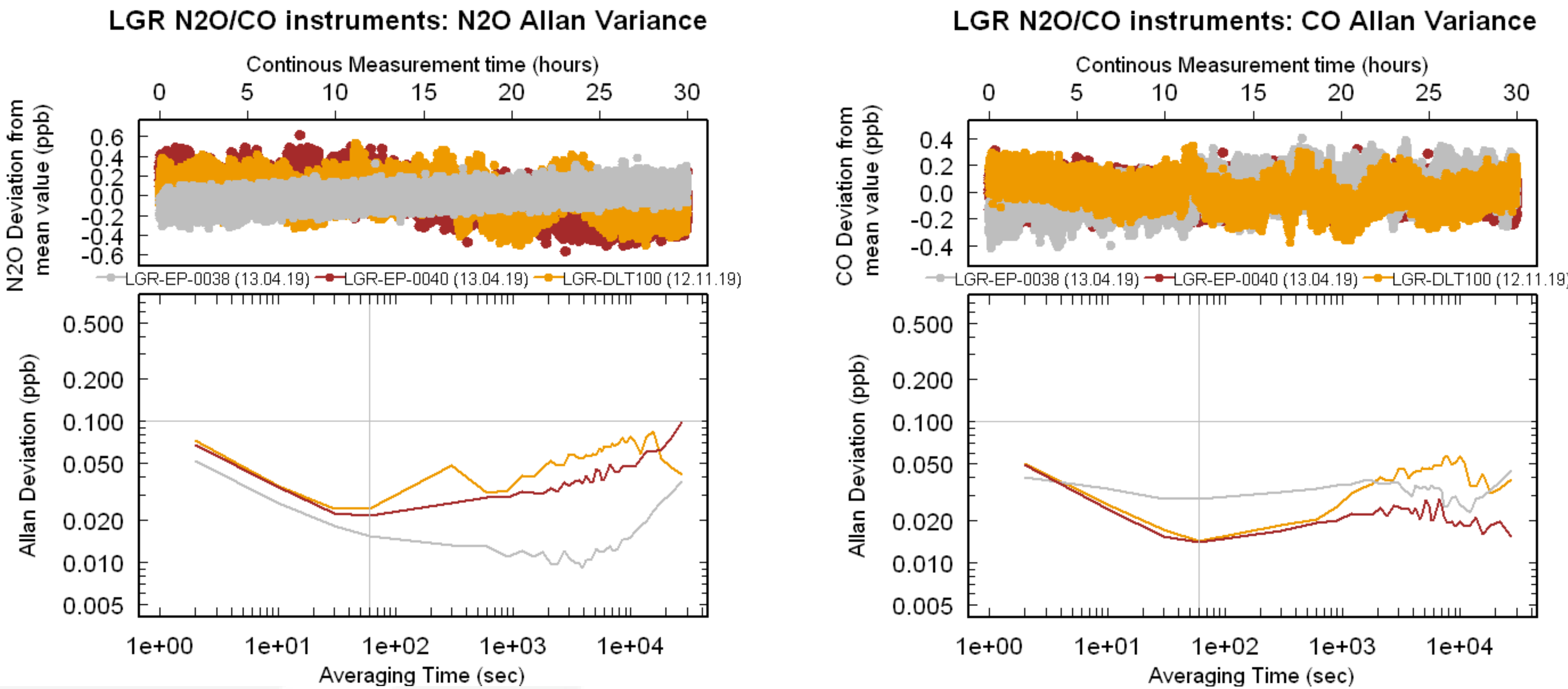


- Ø No significant bias,
- Ø But difference increases over the time

- Ø Significant bias observed
- Ø High variability due to different sampling rate

3. Allan Variance Calculation

§ Methodology: Measure continuously a tank filled with dry natural air for a long period of time (30 hours). Calculate Allan deviations. No calibration applied.



- No significant improvement in N2O and CO stability with “EP” instruments
- Both “EP” analyzers show different pattern: the LGR-0038 unit is significantly more precise and stable for N2O but not for CO