Evaluation of the use of PICARRO analysers for CO2/CH4 continuous measurements by CRDS

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15th WMO IAEA expert meeting, Jena

Context: CRDS instrumentation more and more used…

- 2007, 14th WMO expert meeting, Helsinky :

  ”It is recommended that new robust analytical technologies (e.g laser-based optical analysers) are tested […] A forum should be established to distribute the results and generate discussion […] Specific areas that need to be investigated are calibration frequency and ability to correct for water vapour dilution”

- 2008: ICOS report published on the evaluation of the Picarro EnviroSense analyser

- 17-18 Nov 2008: “ICOS Atmospheric stations instrumentation” workshop in Gif sur Yvette, France

  → 10 presentations (6 institutes represented) focused on new CRDS instrumentation for CO2/CH4

Objective: share experience gained with Picarro EnviroSense / G1301 instruments

1. Link to a CO_2/CH_4 reference scale

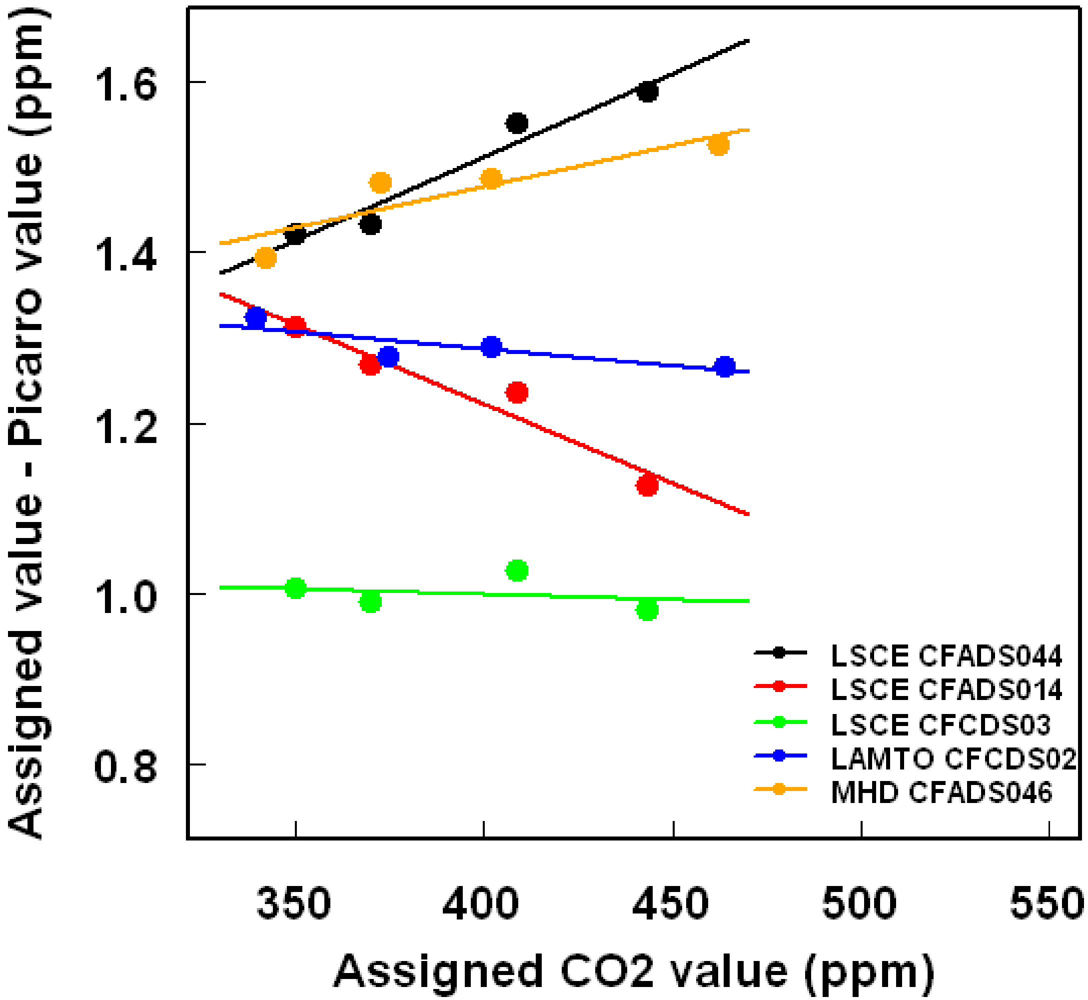
2. Drift, stability check

3. Water vapour correction

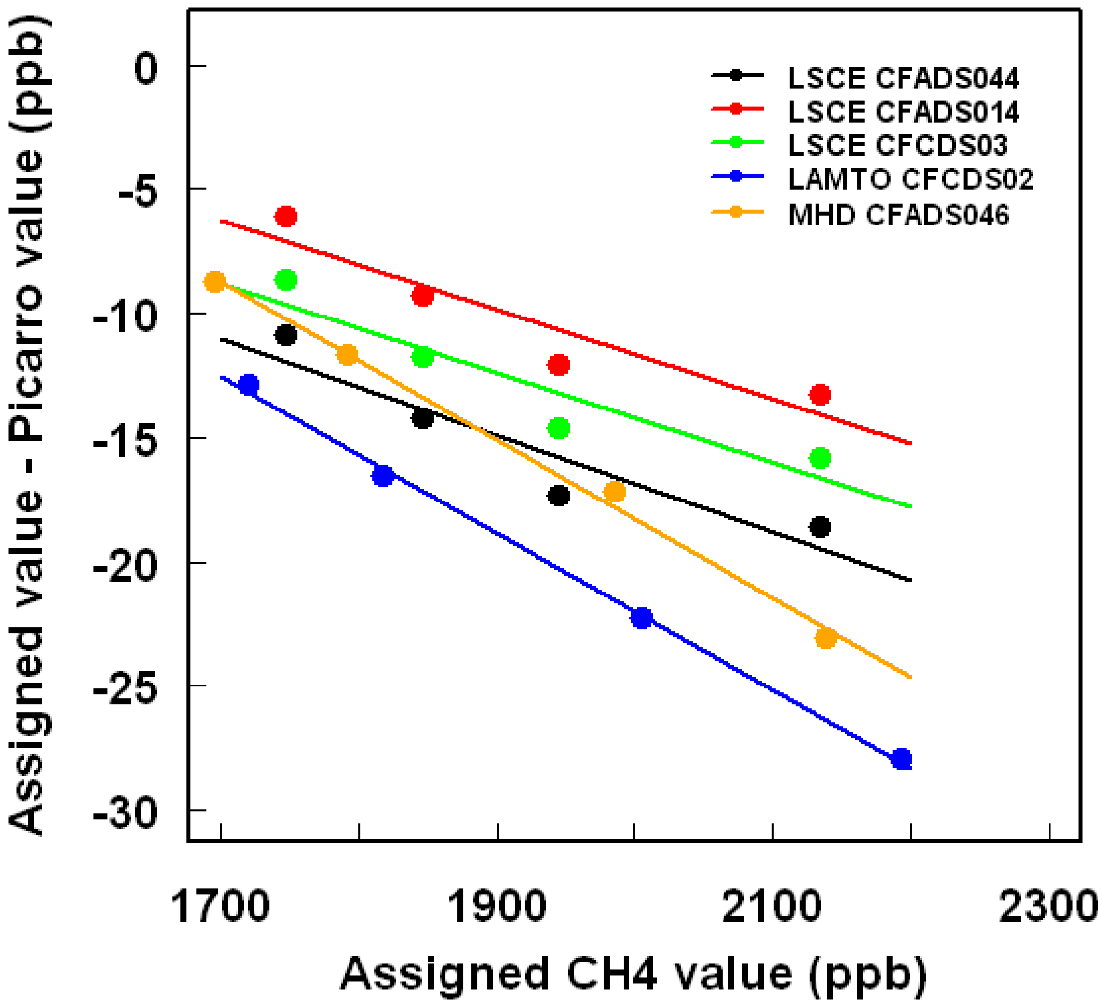
Picarro instruments in use

ID	Purchase date	Calibration frequency	Calibration range	Calibration cylinders
LAMTO-CFCDS02	March 08	1 / 14 days	CO_2:340 – 465 ppm CH_4:1720-2190 ppb	4 filled with synthetic air
LSCE-CFCDS03	March 08	≈ 1 / month	CO_2:340 – 465 ppm CH_4:1720-2190 ppb	4 filled with natural air
LSCE-CFADS014	July 08	≈ 1 / month		
LSCE-CFADS044	April 09	≈ 1 / month		
LSCE-CFADS045	April 09	≈ 1 / month		
RHUL#1	Sept 08	≈ 1 / month	CO_2:380 – 420 ppm CH_4:1830-2030 ppb	5 filled with natural air
RHUL#2	Sept 08	≈ 1 / month		
RHUL#3	Sept 08	≈ 1 / month		
MHD-CFADS046	May 09	1 / 10 days	CO_2:340 – 460 ppm CH_4:1700-2140 ppb	4 filled with synthetic air

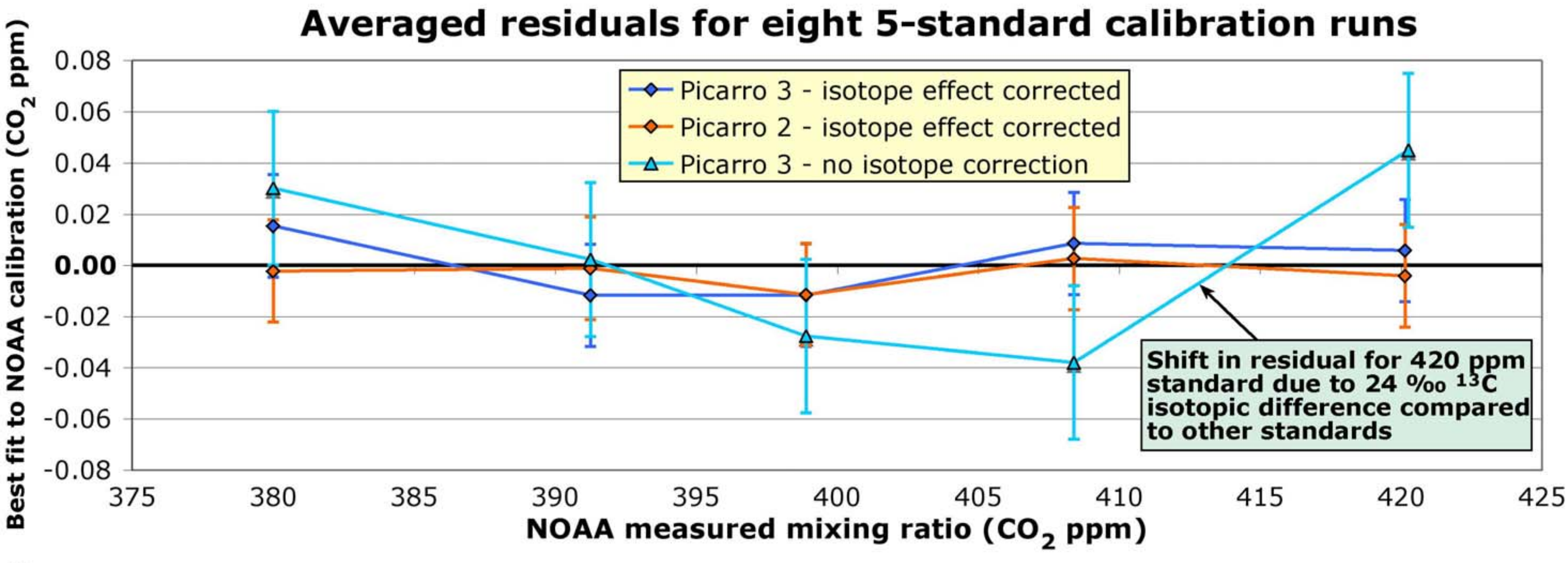
1. Initial calibration: CO_2



1. Initial calibration: CH4



1. Initial calibration: isotopic effect



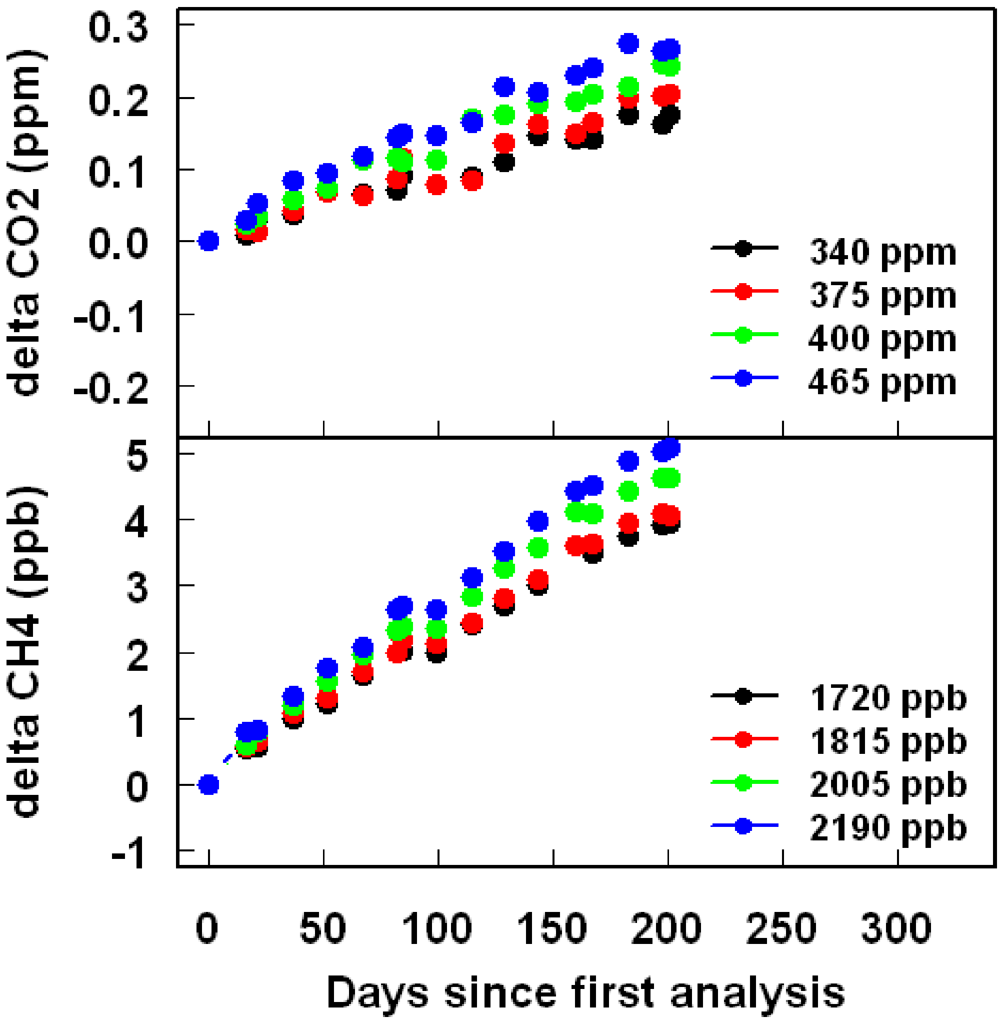
RHUL Name	Cylinder Identifier	CO_2 (ppm)	$\delta^{13}CO_2$ (‰, PDB)	$\delta^{18}CO_2$ (PDB-CO_2)	CRDS ^{13}C Correction (ppm)
NOAA 2 (2000-)	CA 04038	**420.25**	**-11.69**	**-6.72**	**0.015**
NOAA 5 (2008-)	CA 07811	**408.39**	**-34.92**	**-32.83**	**0.125**
NOAA 6 (2009-)	CA 08325	**398.89**	**-36.03**	**-32.95**	**0.122**
NOAA 7 (2009-)	CA 08329	**391.25**	**-36.05**	**-32.96**	**0.120**
NOAA 8 (2009-)	CA 08347	**380.00**	**-36.03**	**-32.99**	**0.117**

Source: R. Fisher, D. Lowry (RHUL)

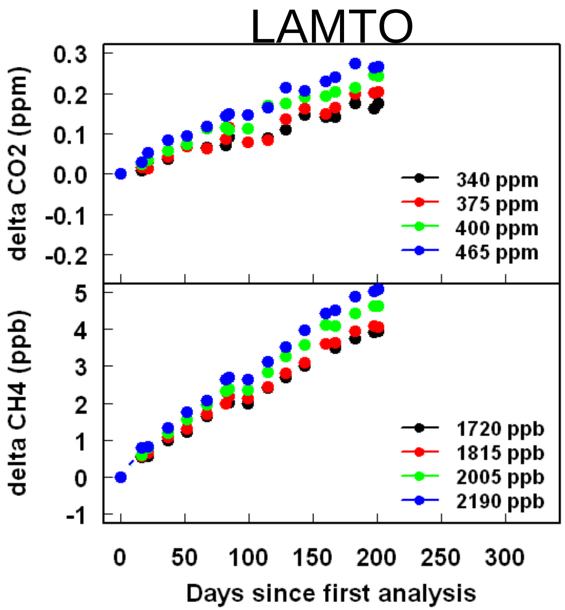
2. Stability check

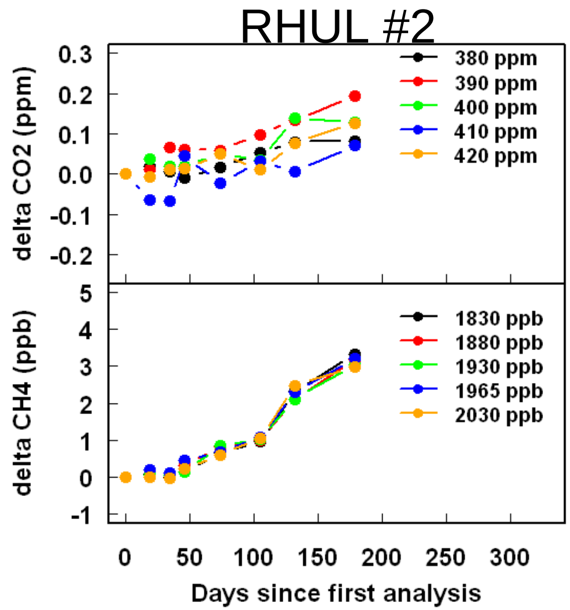
LAMTO, CFCDS02:

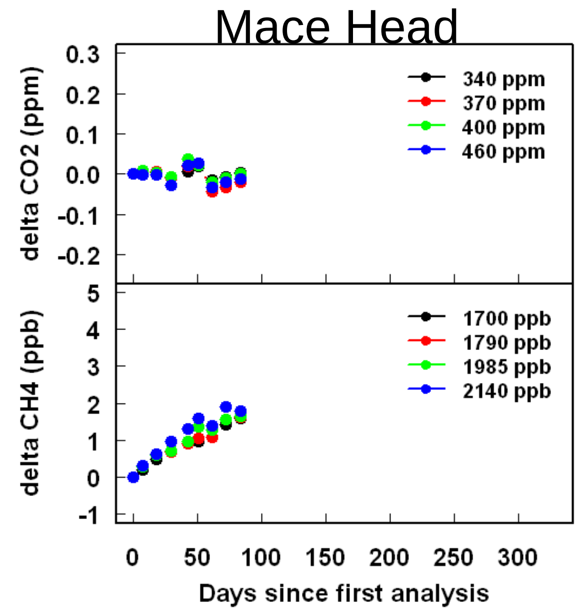
- 4 calibration cylinders measured every 2 weeks
- Drift in concentration if correction remained unchanged since first analysis

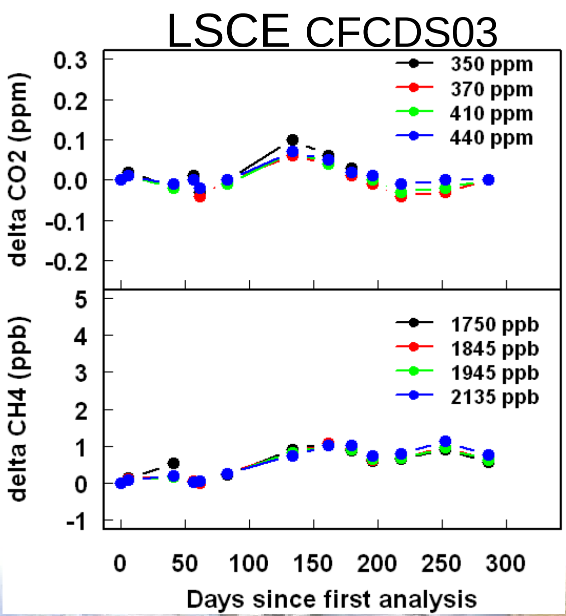


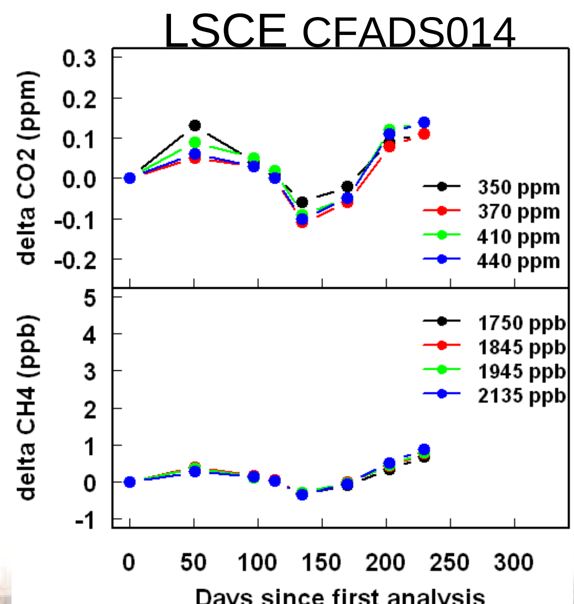
2. Stability check

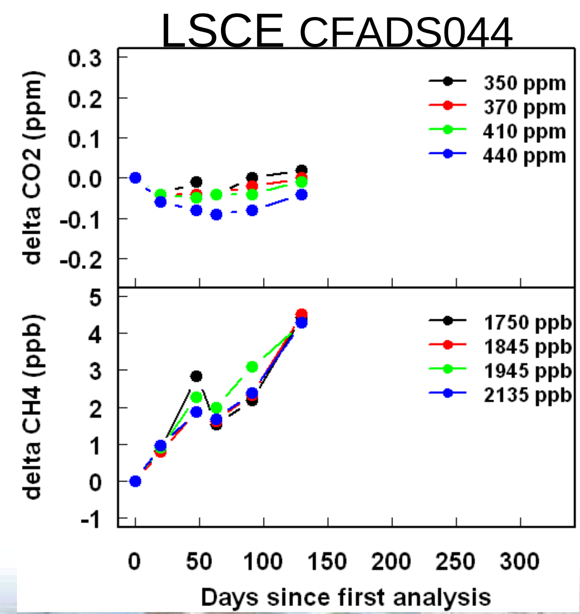




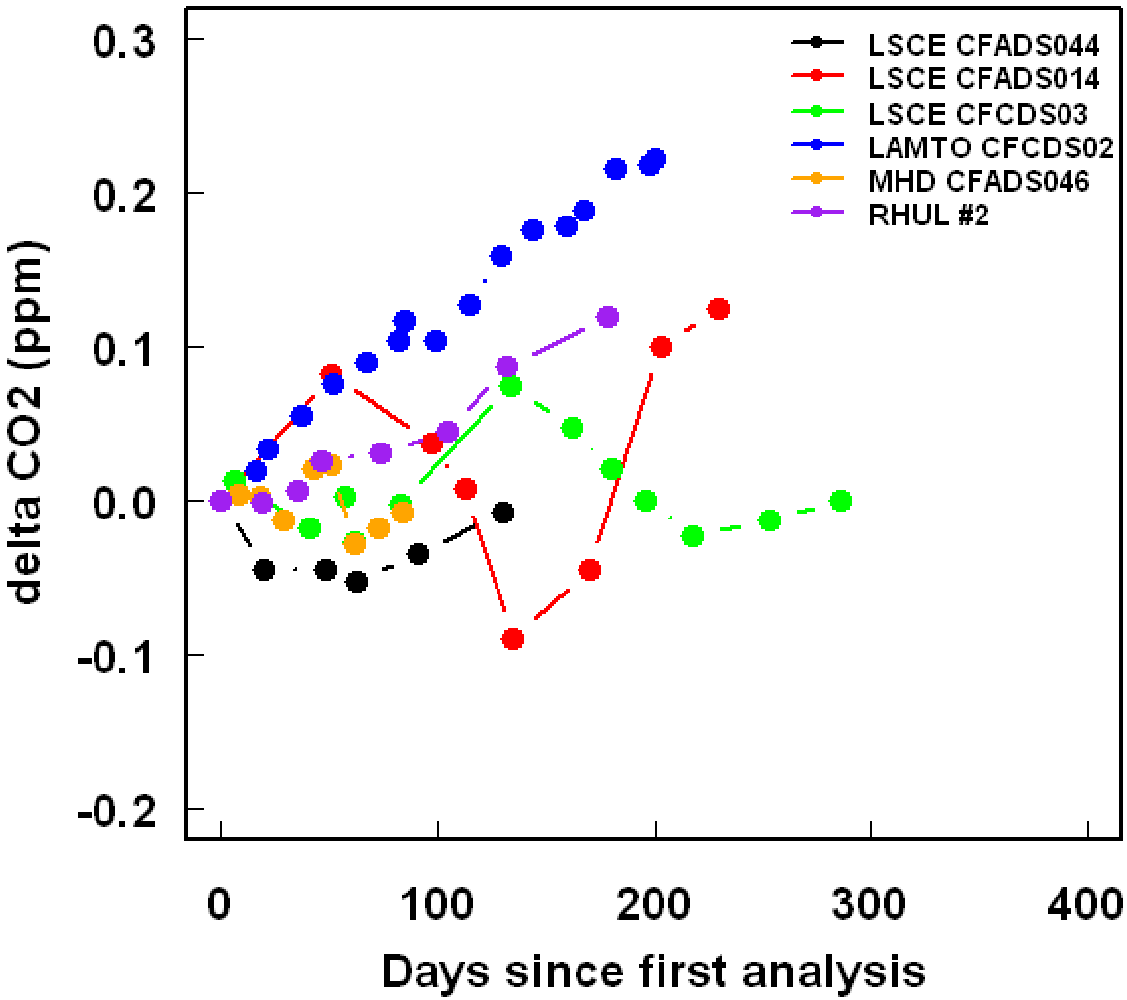




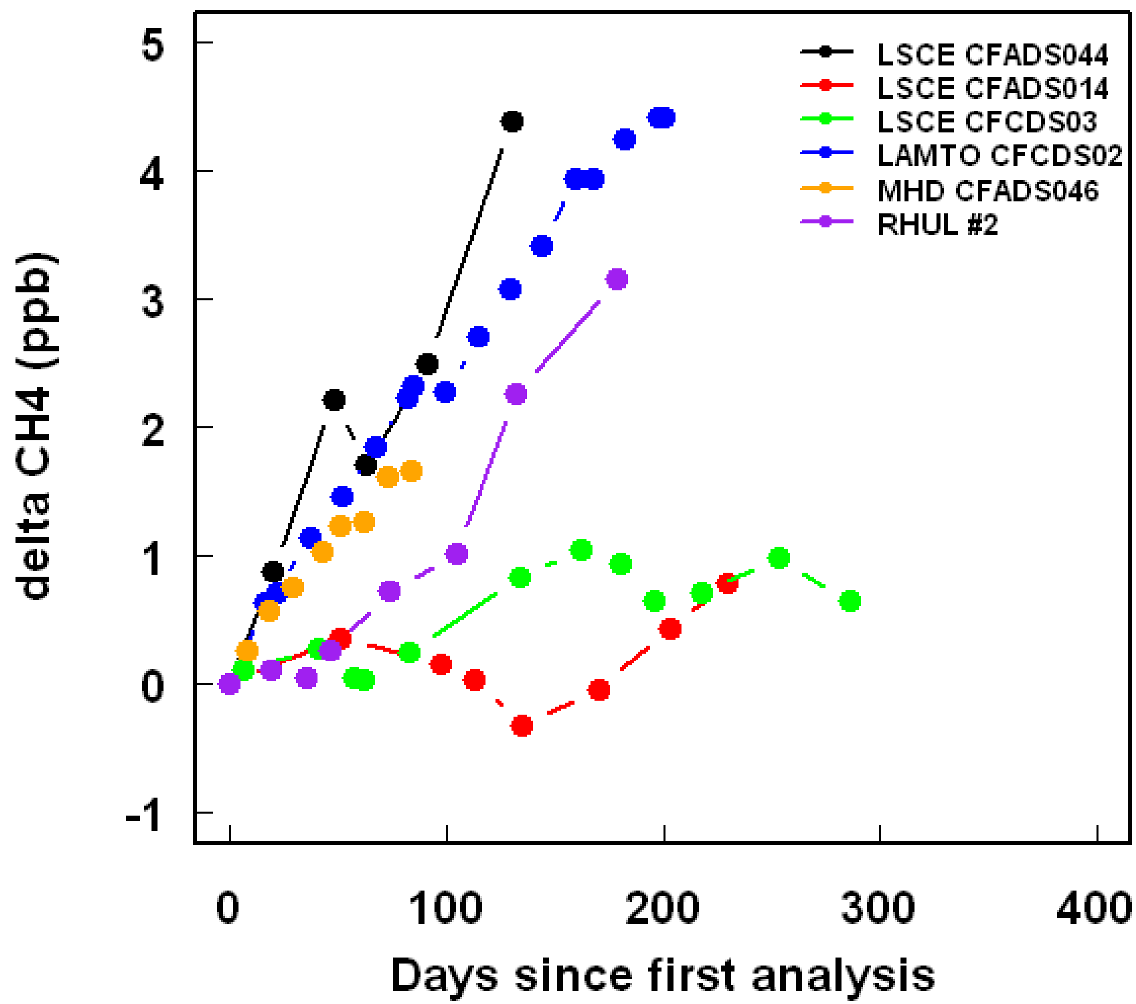




2. Stability check: mean CO2 drift



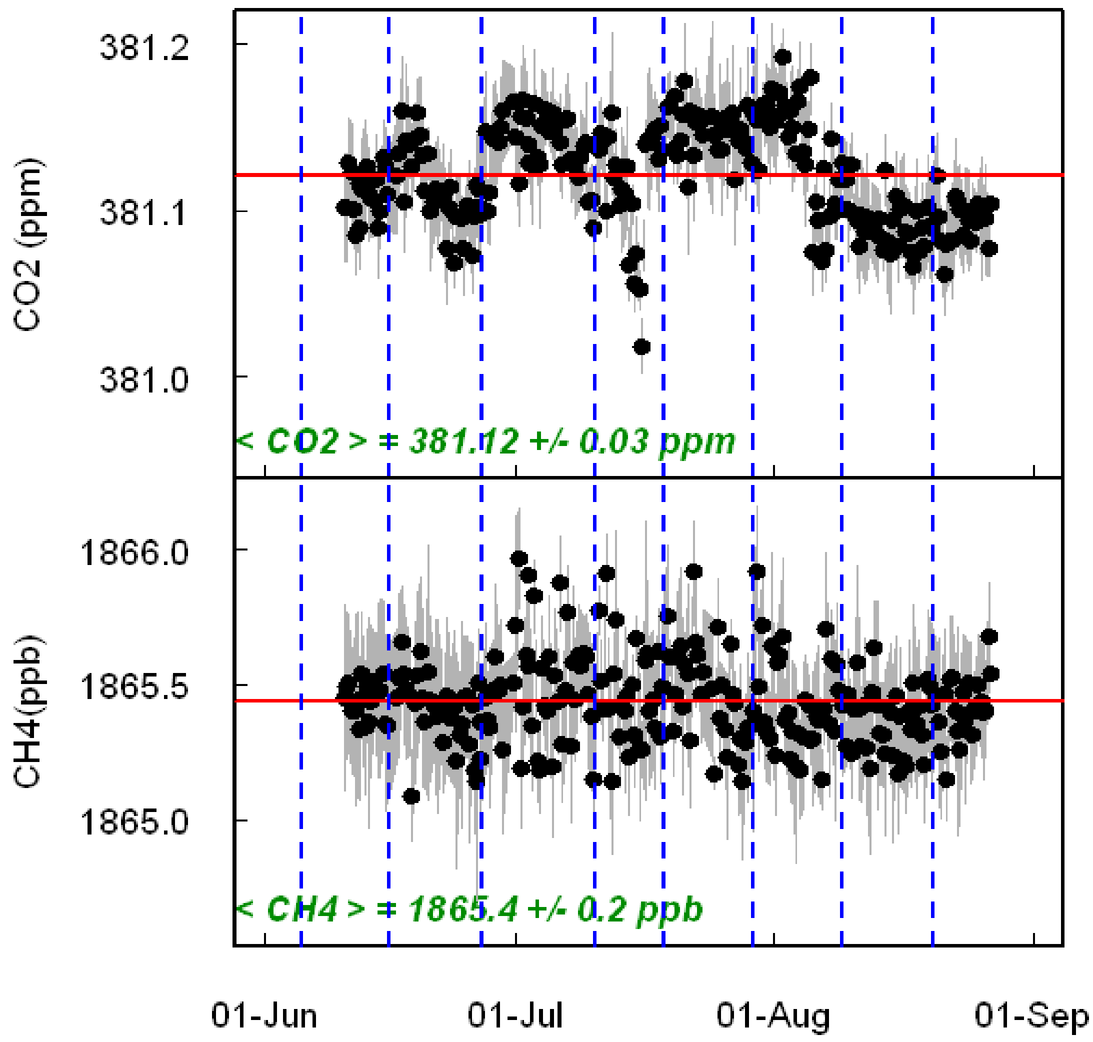
2. Stability check: mean CH4 drift



2. Stability check: TARGET cylinder

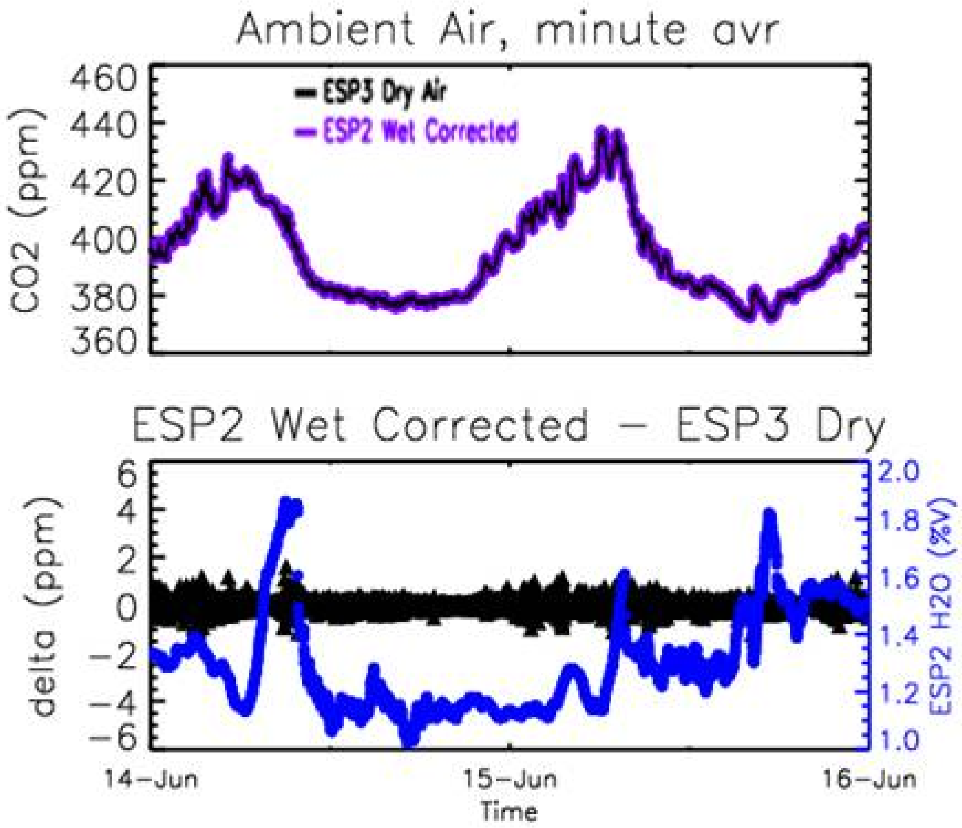
CFADS-046 at Mace Head:

- 1 Calibration / 10 days
- Target cylinder measured every 7 hours for 30 mn
- Concentrations corrected via interpolation between 2 calibration episodes



3. Water vapour correction

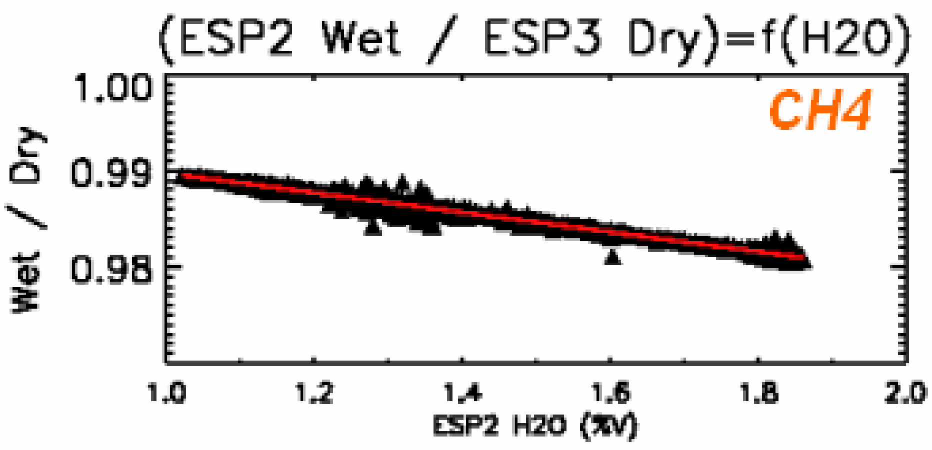
- Tests at LSCE in 2008: check validity of Picarro water correction for CO_2



Mean diff = 0.04 ± 0.23 ppm

3. Water vapour correction

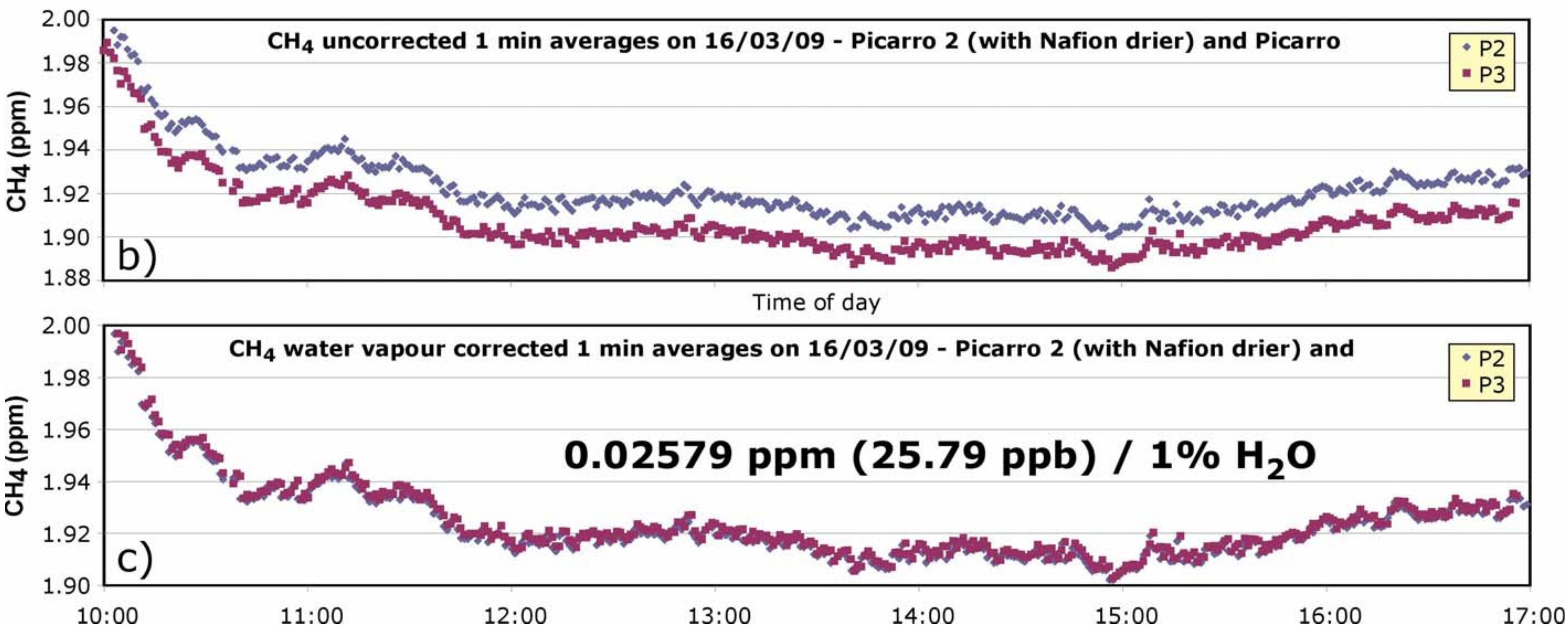
- Tests at LSCE in 2008: try to establish a correction for CH4



$$(CH_4)_{cor} = \frac{(CH_4)_{raw}}{1 - 0.0102018 \times H_2O}$$

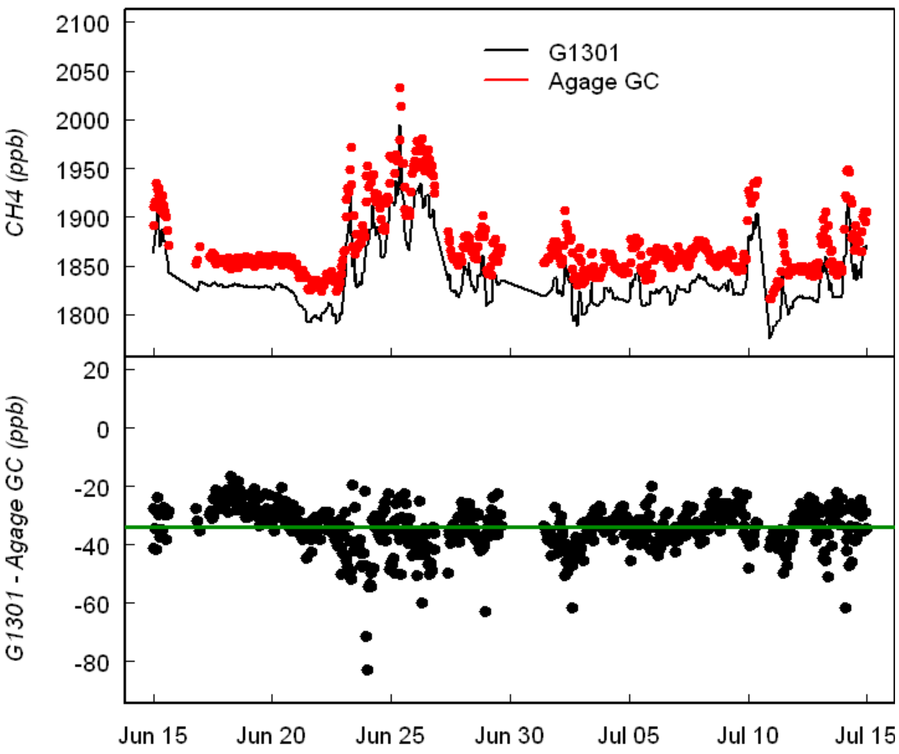
3. Water vapour correction

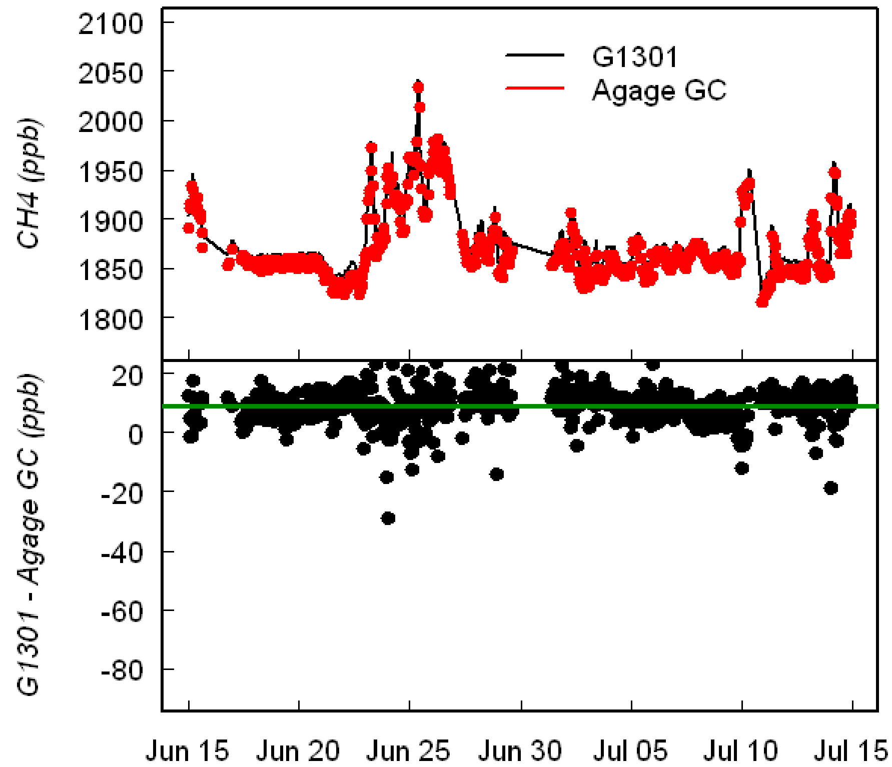
- Similar work done by RHUL group (source D. Lowry):



3. Water vapour correction

- Validity of the correction established for CH4:
  comparison at Mace Head between the AGAGE GC (data from S.O'Doherty) and the Picarro (non-dried air)

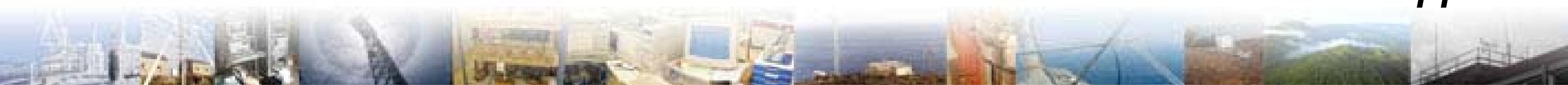




Mean diff = -34 ± 7 ppb

With LSCE correction: -2 ± 6 ppb

With RHUL correction: 9 ± 6 ppb



Conclusions

- Need to calibrate the Picarro analysers and to know precisely the isotopic composition of the calibration cylinders.
- Calibration frequency: inconsistencies between instruments → need to establish an individual strategy with an initial phase of frequent calibrations.
- Water vapour correction: reliable for CO2, possible for CH4, but probably better to dry the air to eliminate any potential errors.
- Experience gained from the field: robust instrumentation.

Thank you