integrated carbon observation system

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Water Vapor Issue Update

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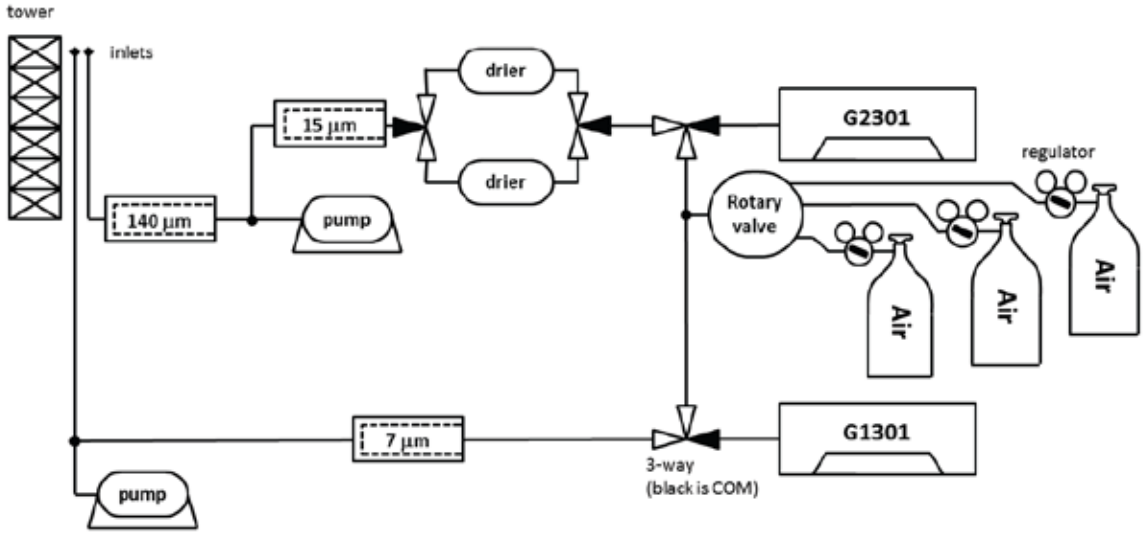
Field Observation

In-situ comparison between 2 Picarro CO2/CH4/H2O (G2301 and G1301) analyzers at Mace Head:

- One instrument measures wet ambient air.
- One instrument measures dry ambient air downstream a cryogenic water trap.

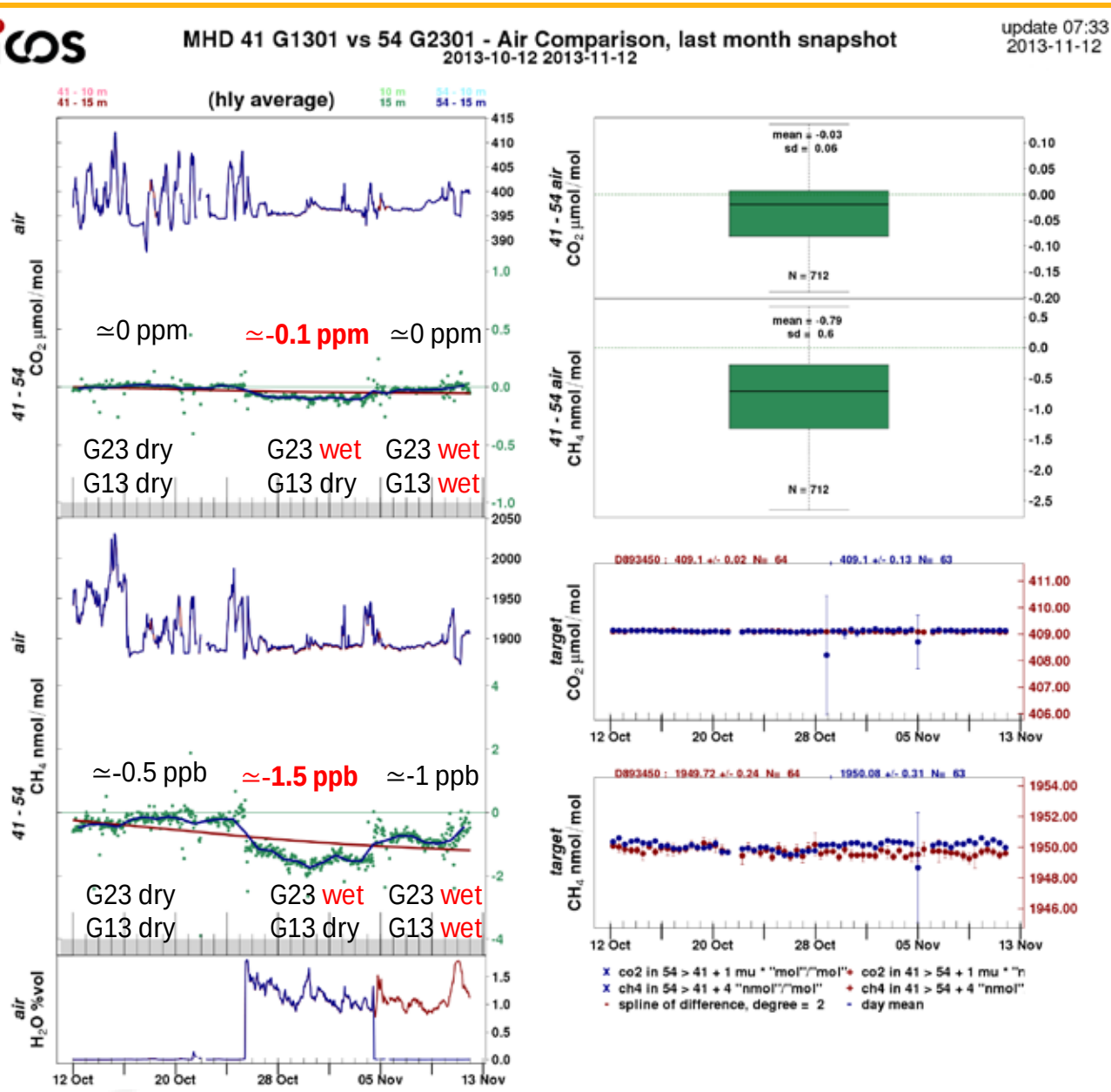
Both instrument are calibrated at the same time using the same set of calibration gases. Both instruments use the same water vapor correction coefficient (Chen et al. 2010).

<u>Station Setup:</u>



The water vapor correction of the Picarro G2301 introduces **0.1 ppm bias on CO2** measurement for a **1 -1.5%v H2O**.
Same statement for CH4.

This significant bias is not detectable without a such comparison or a suitable water vapor correction check.



According to Rella et al. (2013):

- Using the Chen et al. (2010) correction on all the instruments would introduce an uncertainty of **0.1 ppm for CO2** up to 2%v of H2O and **1 ppb for CH4** up to 0.9% of H2O (based on a Monte Carlo simulation).
- Due to instrument-to-instrument variability, there is no single set of coefficient that could be applied equally well to all instruments.
- It is highly recommended that the correction functions be determined for each individual instrument independently, especially for humidity above 2% H2O.
- The uncertainty in determination of the water correction factors is mainly dominated by the experimental bias inherent to the methodologies.

2 methods tested :

- Water droplet test : can be easily performed on field. Suitable for assessment?
- Humidifier controlled bench: for the determination of the water vapor correction coefficients at the start of life of the instruments?

Method 1: Water Droplet test

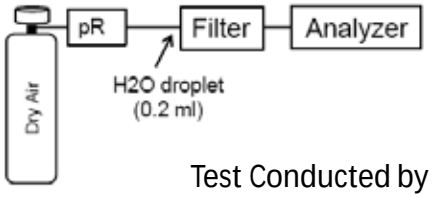
- Between 29.01.2013 and 15.03.2013, **57 water droplet tests** have been performed on the Picarro CFADS045 (model G1301).
- These experiments have been conducted using **3 different experimental conditions**:
  1/ injection of 0.2 ml water droplet upstream an inline hygroscopic filter from **M&C** (**model LB-1SS, stainless steel**)
  2/ injection of 0.2 ml water droplet upstream an inline hygroscopic filter from **M&C** (**model LB-1PV, pvdf polymer**)
  3/ injection of 0.2 ml water droplet **directly through the instrument inlet** (using the hygroscopic properties of the internal filter)
- To assess the **reproducibility** and the **repeatability** of the different methods, the experiments, for each condition, were conducted once a week over the test period. Each experiment consisted in the repeated (3 times) injections of the water droplet.

Date	Droplet injection	Repeated tries	H2O range covered (%v)
2013-01-31	M&C PVDF filter	3	2.0
2013-02-01	M&C SS filter	3	2.8
2013-02-08	M&C PVDF filter	3	2.3
2013-02-07	M&C SS filter	3	2.7
2013-02-14	No additional filter	3	6.2
2013-02-15	M&C PVDF filter	2	2.2
2013-02-15	M&C SS filter	3	2.5
2013-02-20	No additional filter	4	6.3
2013-02-21	M&C PVDF filter	3	2.1
2013-02-22	M&C SS filter	3	2.5
2013-02-27	No additional filter	3	5.7
2013-02-28	M&C PVDF filter	3	2.1
2013-03-01	M&C SS filter	3	2.5
2013-03-06	No additional filter	3	6.2
2013-03-07	M&C PVDF filter	3	2.2
2013-03-08	M&C SS filter	3	2.7
2013-03-13	No additional filter	3	6.2
2013-03-14	M&C PVDF filter	3	2.2
2013-03-15	M&C SS filter	3	2.5

- Picarro Water correction for CO2 and CH4:

$$\frac{Cwet}{Cdry} = 1 + I1.H2O + I2.H2O^2 \quad (1)$$

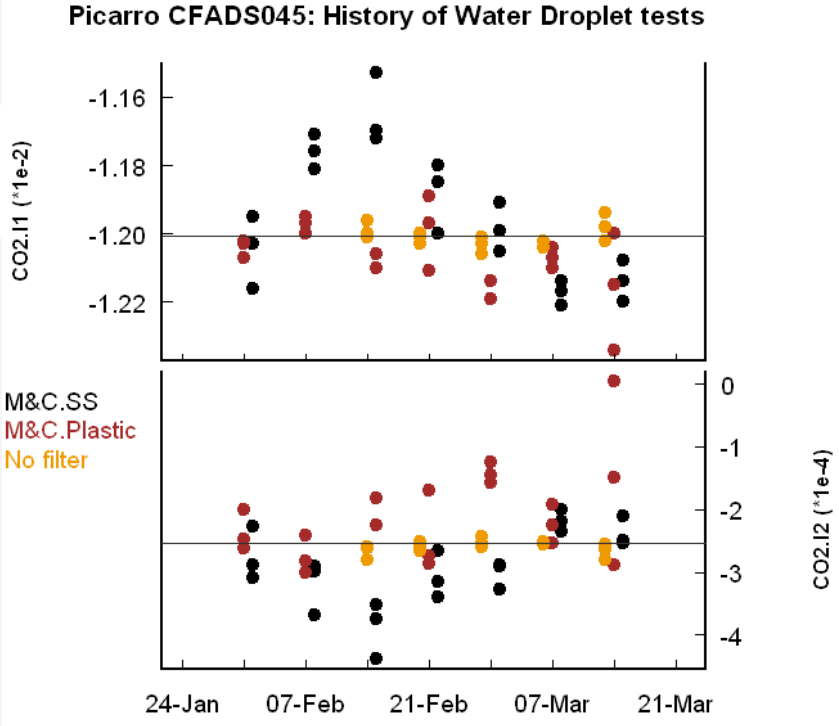
	CO2		CH4	
	I1	I2	I1	I2
Chen et al.	-0.012	-2.67E-04	-0.00982	-2.39E-04



Test Conducted by Benoit Wastine

Method 1: Water Droplet test

Distribution of the correction coefficients obtained for each individual droplet injection



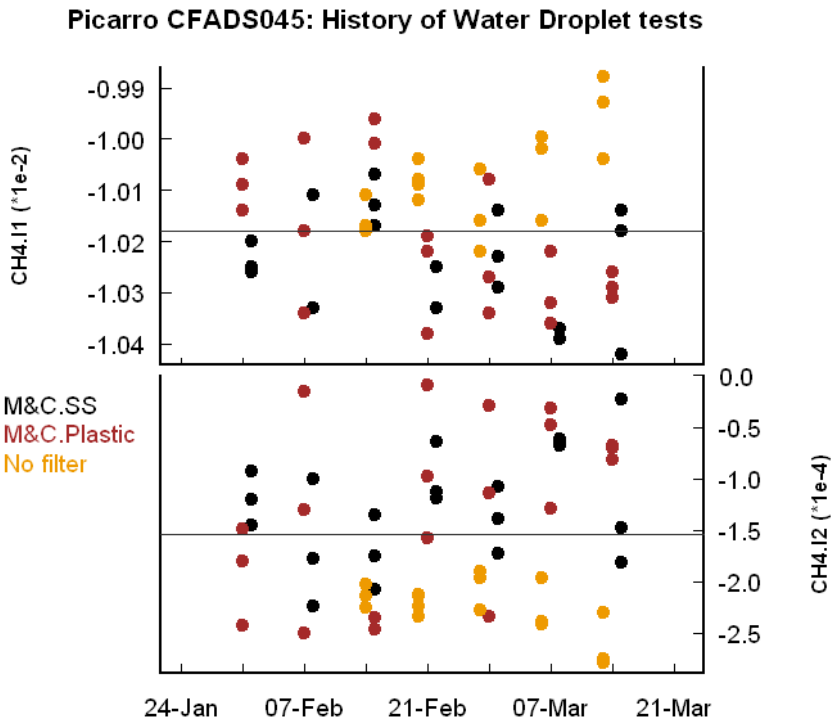


Fig.2a,b: time series of the water correction coefficients determined for CO2 (a) and CH4 (b) using the 3 different methods

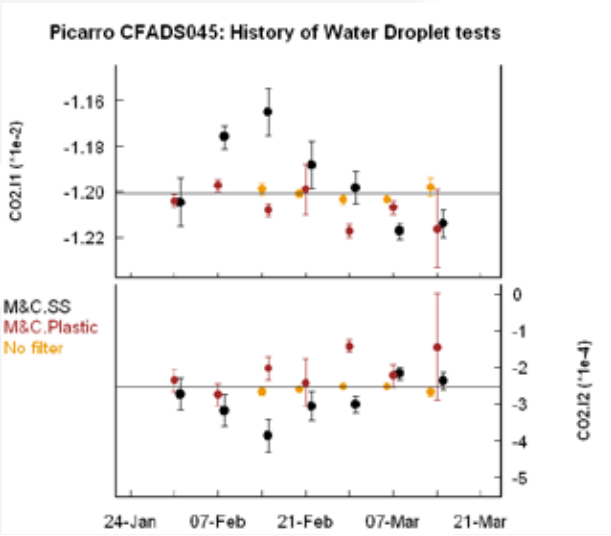
Ø High variability intra and inter experiment when using the external hygroscopic filter

Ø Better repeatability and reproducibility (especially for CO2) when no extra filter is used

Østrong anti-correlation between the 2 correction coefficients, indicative of a compensating effect where a more negative slope is counterbalanced by a more positive quadractic term.

Method 1: Water Droplet test

Distribution of the correction coefficients obtained for each day of experiment



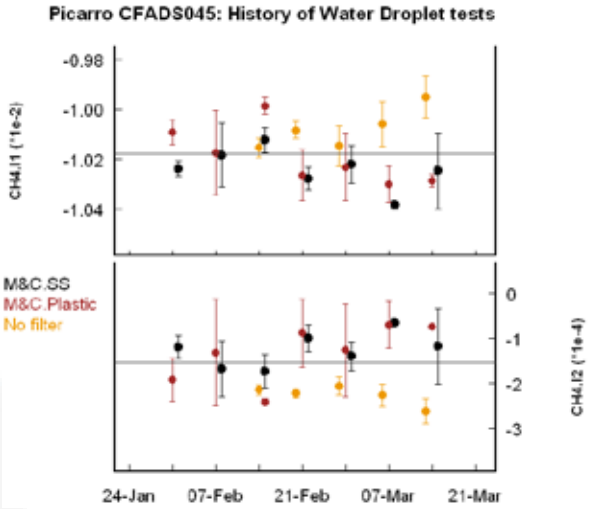
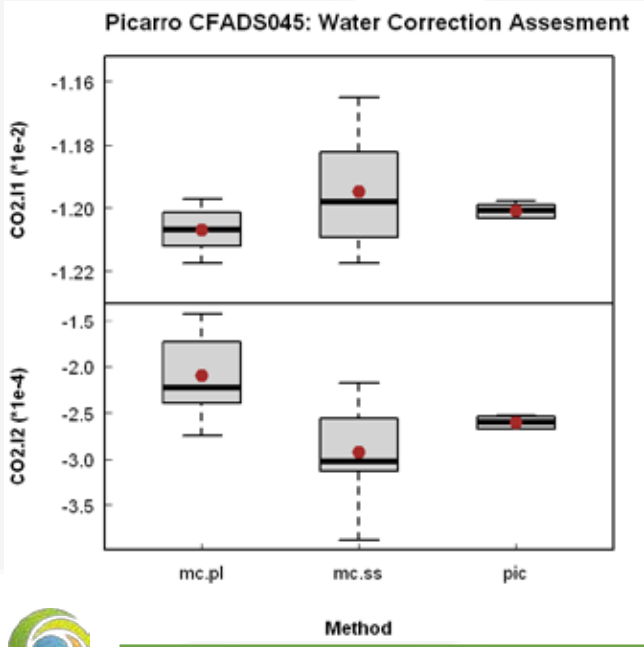


Fig.5a,b: CO2 (a) and CH4 (b) mean correction coefficients calculated for each day of experiment considering all droplet injections.



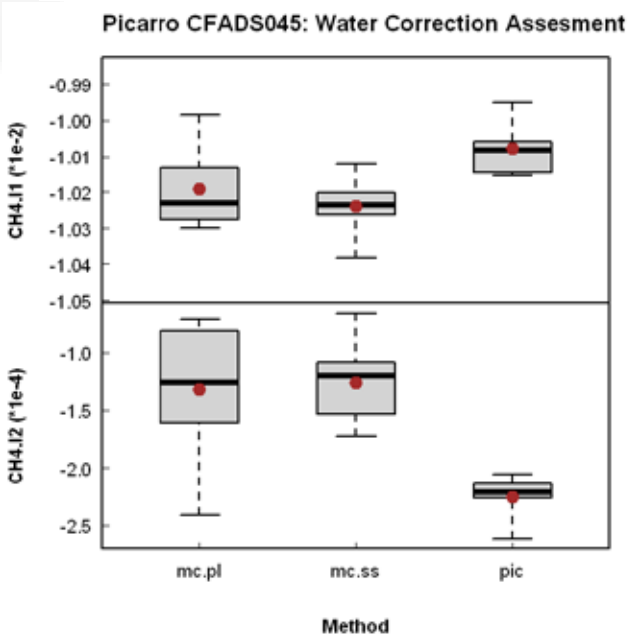


Fig.6a,b: boxplots summarizing the distribution of the results obtained with the different methods. These boxplots have been drawn using the correction coefficients calculated for each day of experiment as the average of the results obtained for each water droplet injection.

Method 1: Water Droplet test

Summary

§ **Repeatability**: agreement between the repeated determination of the correction coefficients.

Method	CO2.I1 (*10^{-2})	CO2.I2 (*10^{-4})	CH4.I1 (*10^{-2})	CH4.I2 (*10^{-4})
M&C SS filter	0.0076	0.3286	0.0071	0.3936
M&C PVDF filter	0.0060	0.5019	0.0084	0.5836
No additional filter	0.0023	0.0816	0.0065	0.1861

§ **Reproducibility**: agreement between the multiple determination of the correction coefficients over the test period.

Method	CO2.I1 (*10^{-2})	CO2.I2 (*10^{-4})	CH4.I1 (*10^{-2})	CH4.I2 (*10^{-4})
M&C SS filter	0.0195	0.5619	0.0081	0.3776
M&C PVDF filter	0.0077	0.5011	0.0116	0.6394
No additional filter	0.0024	0.0700	0.0083	0.2139

§ **Uncertainty** assessment of the correction coefficients:

Method	CO2.I1 (*10^{-2})	CO2.I2 (*10^{-4})	CH4.I1 (*10^{-2})	CH4.I2 (*10^{-4})
M&C SS filter	0.021	0.651	0.011	0.545
M&C PVDF filter	0.010	0.709	0.014	0.866
No additional filter	0.003	0.108	0.011	0.283

Method 1: Water Droplet test

Effect on the CO2/CH4 corrected values

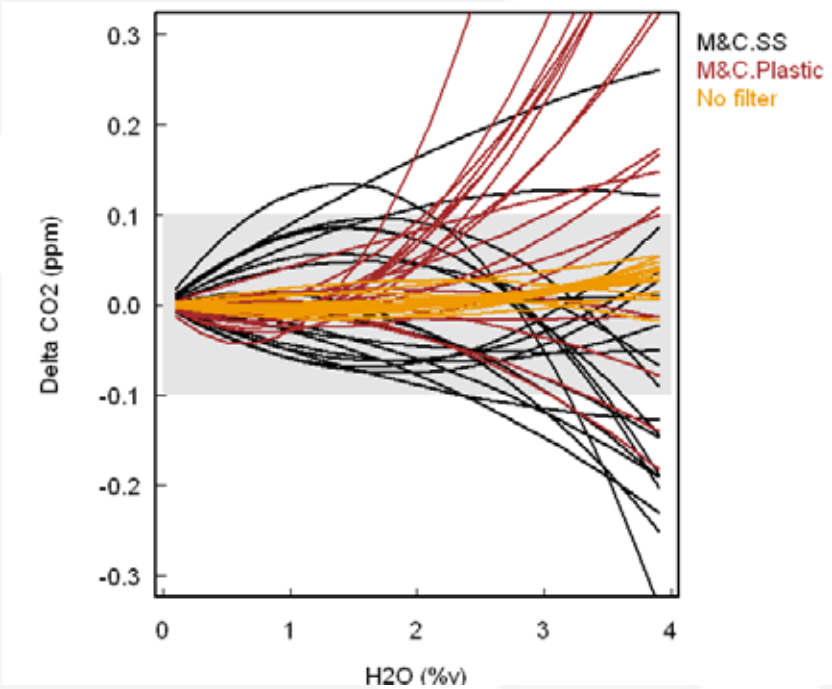


Fig.7: differences in the corrected CO2 values when using the Chen et al correction coefficients or the individual correction coefficients determined experimentally over the test period.

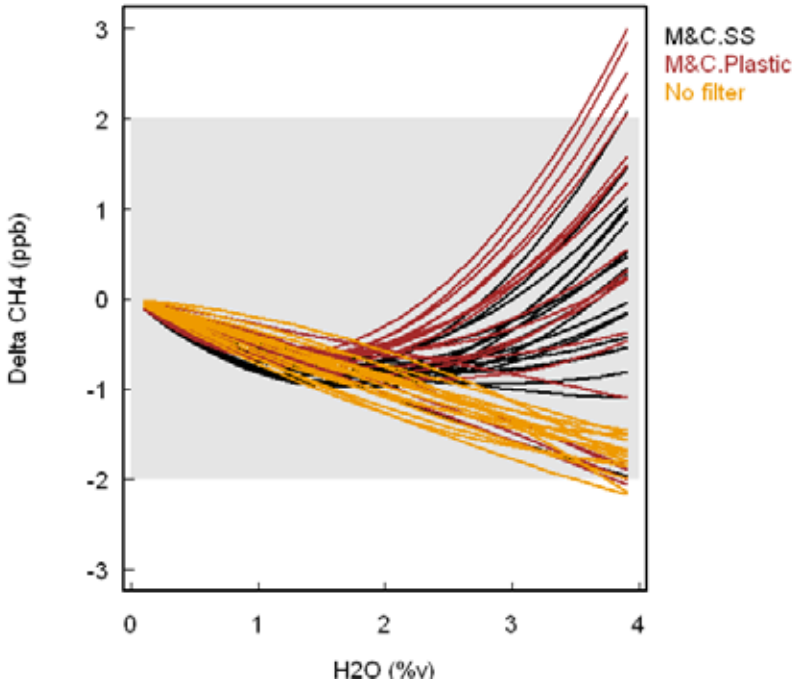
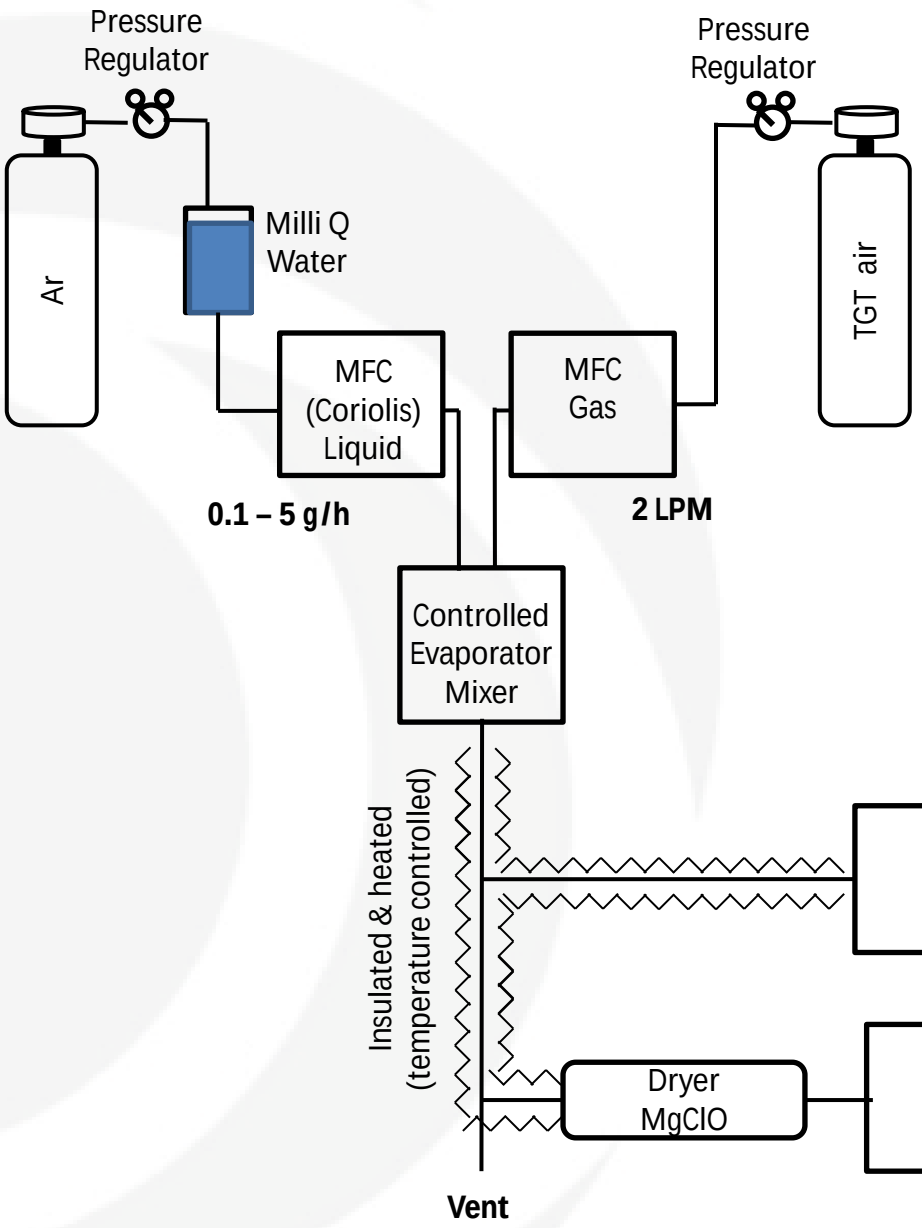
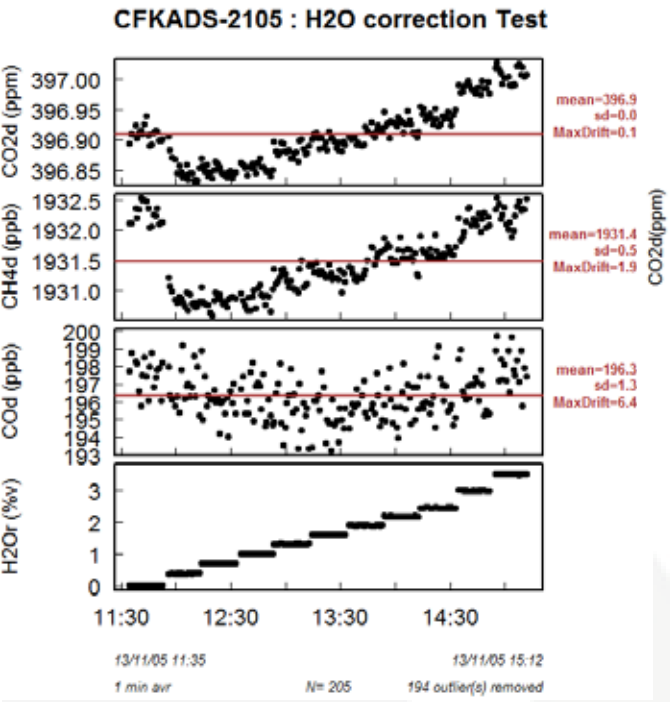


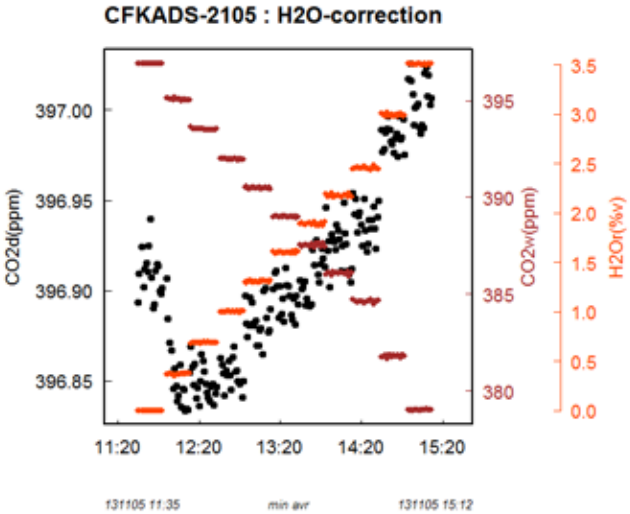
Fig.8: differences in the corrected CH4 values when using the Chen et al correction coefficients or the individual correction coefficients determined experimentally over the test period.

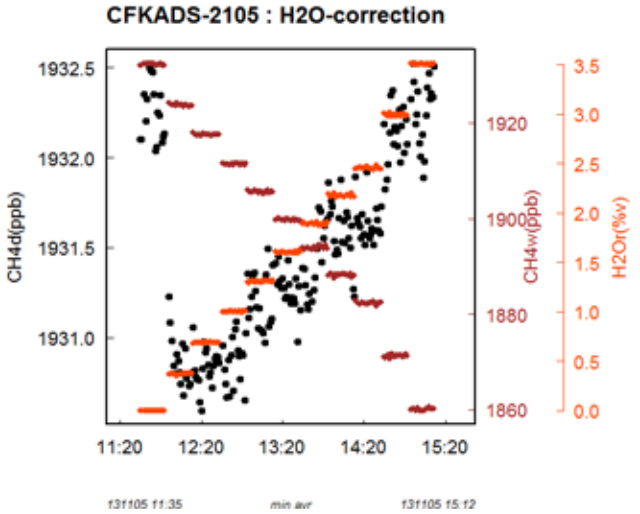
Method 2: Humidifier Controlled Bench

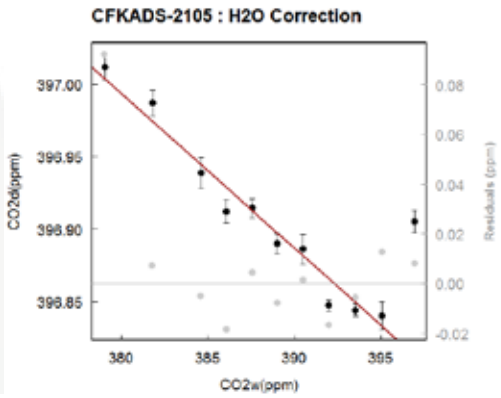


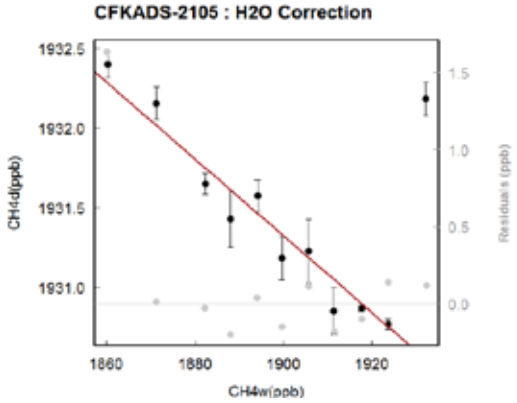
Method 2: Humidifier Controlled Bench

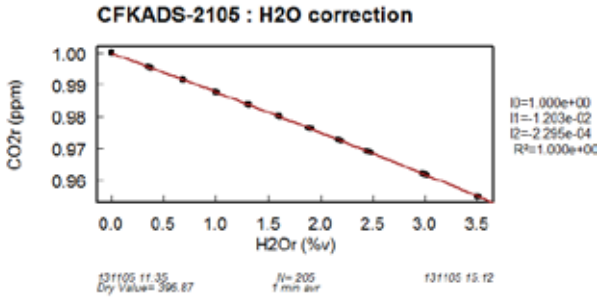


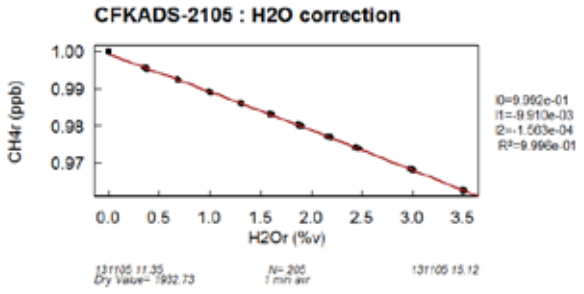








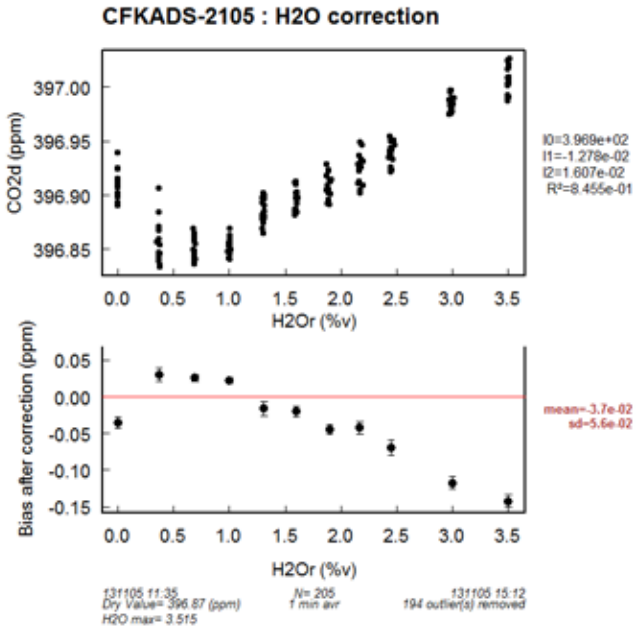


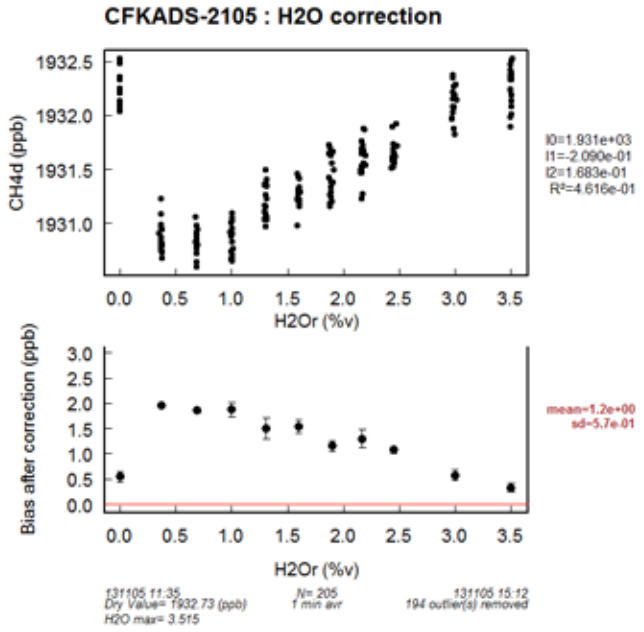


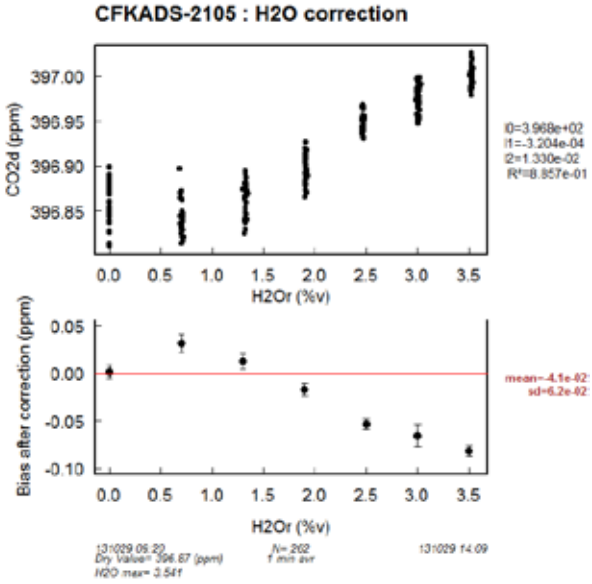
Humidifier well controlled (stable) :
SD H20: <150 ppm

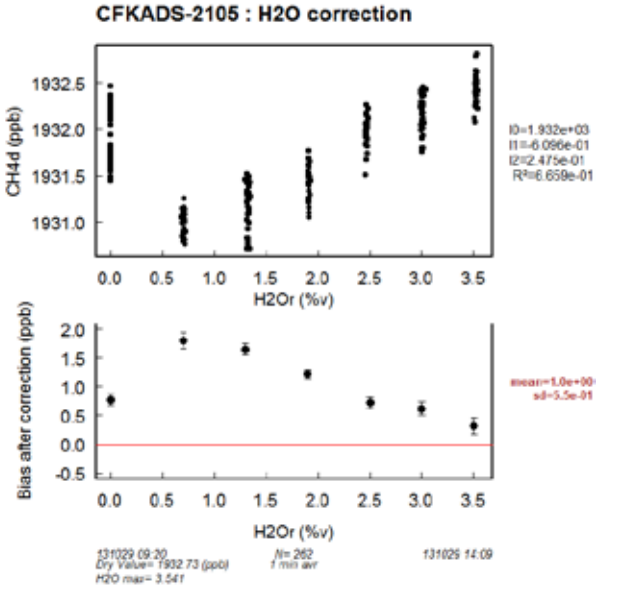
Water correction used here the Chen et al. Coefficients.

Method 2: Humidifier Controlled Bench









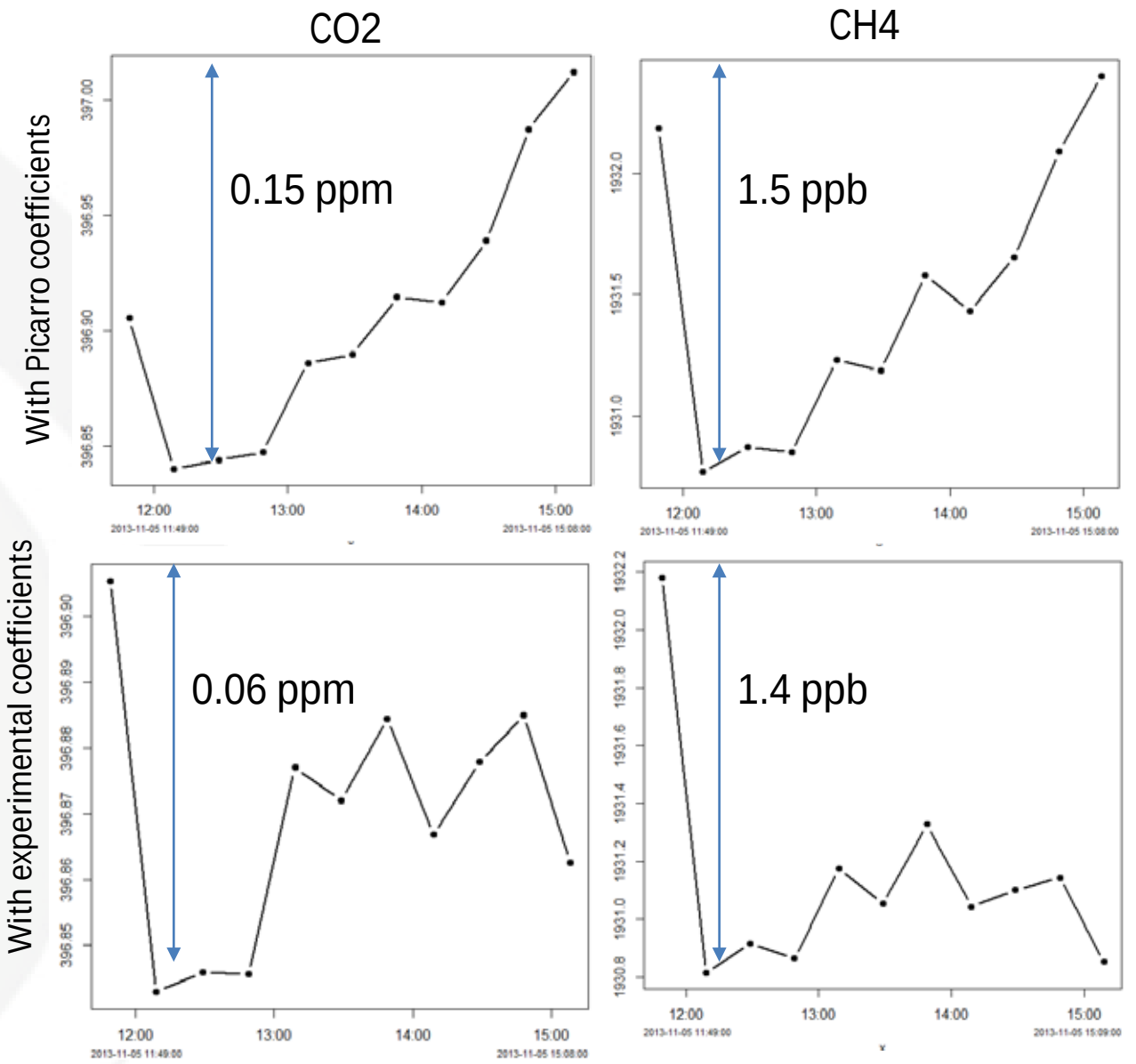
Method 2: Humidifier Controlled Bench

Variability of the correction coefficients:

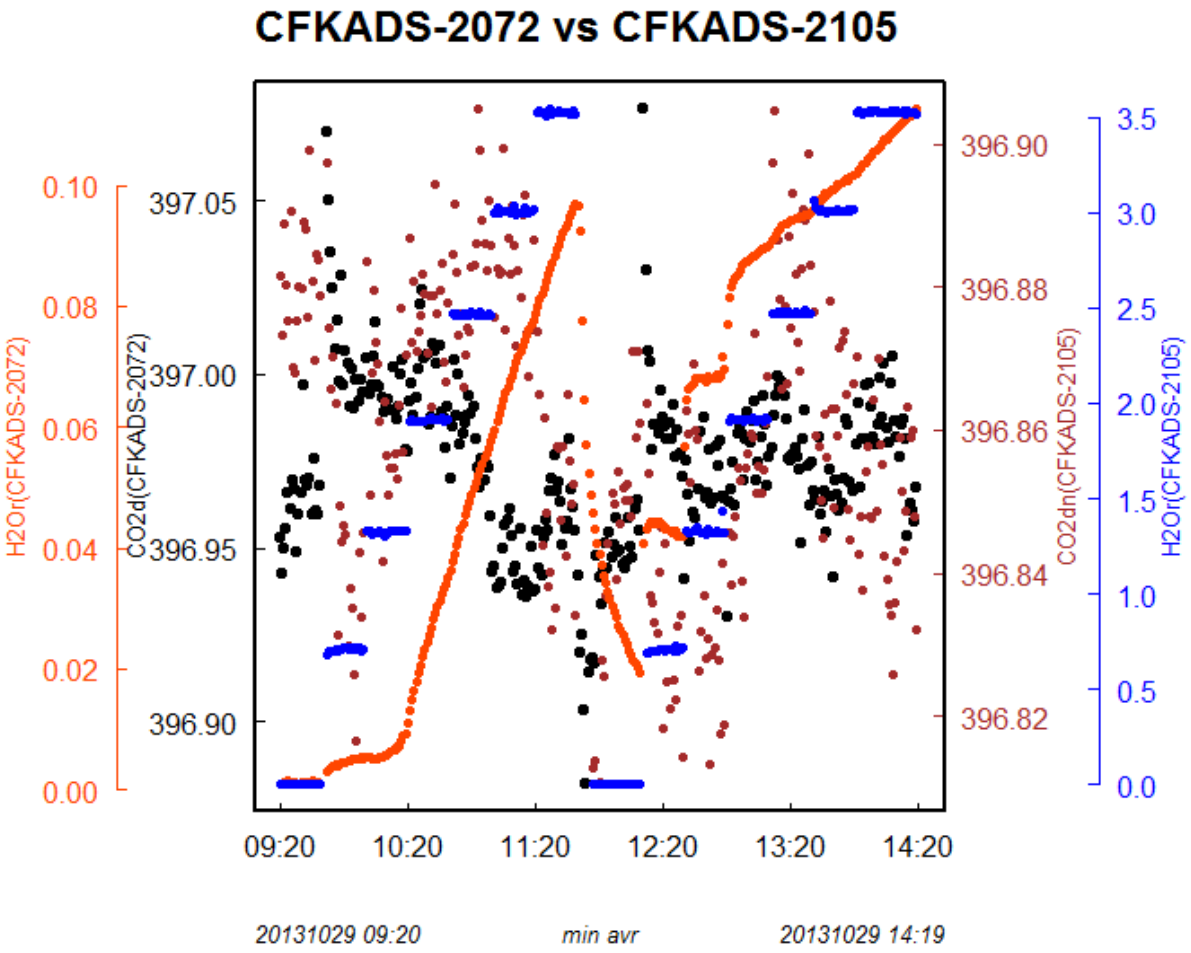
	Nb steps	CO2.I1 (E-2)	CO2.I2 (E-4)	CH4.I1 (E-2)	CH4.I2 (E-4)
24/10/2013	7	-1.198	-2.426	-1.018	-1.077
25/10/2013	7	-1.199	-2.397	-1.016	-1.090
29/10/2013	7	-1.200	-2.361	-1.012	-1.141
05/11/2013	11	-1.203	-2.295	-0.991	-1.563
Chen et al.		-1.2	-2.674	-0.982	-2.393
Reproductibility (1σ) with Droplet test		0.0024	0.0700	0.0083	0.2139

Method 2: Humidifier Controlled Bench

Using the experimentally determined correction coefficients reduce the Bias for H20 > 2%



Method 2: Humidifier Controlled Bench



Work in progress...