

Document reference: ATC-ML-IT-RP-93-1.0_IT_590

**ICOS ATC Metrology Laboratory
Evaluation report
for the ICOS instrument 590**

Tests by C. Philippon
Approved by O. Laurent
Date: 2017-09-18

Document history

Version	Date	Actions
1.0	2017-09-18	Creation

Diffusion

- ATC internal
- ICOS community
- Public

Repository

- Alfresco in Library/Documents/Common/ICOS-RI/ATC/MetrologyLab/Reports
- ICOS ATC website: <https://icos-atc.lsce.ipsl.fr/docs>

Disclaimer

The contents of this document (including any attachments) may be privileged, confidential or copyrighted under applicable law and are intended solely for use by the intended recipient. The status is discussed only using the indicated version of the ICOS atmospheric station specifications.

Contents

1 Instrument references	4
2 Outlet valve characterization	4
3 Continuous Measurement Repeatability (CMR) assessment	5
4 Short term stability and drift assessment	7
5 Short Term Repeatability (STR) assessment	9
6 Long Term Repeatability (LTR) assessment	11
7 Atmospheric pressure sensitivity	13
8 Inlet pressure sensitivity	15
9 Temperature sensitivity	17
10 Water vapor correction assessment	19
10.1 Factory correction	19
10.2 Determination of H ₂ O correction coefficients by the MLab	21
10.3 MLab correction	23
11 Calibration	24
12 Linearity	27
13 Laboratory inter-comparison	28
13.1 Without drying system	28
13.1.1 Factory water vapor correction	28
13.1.2 Water vapor correction coefficients determined by ATC	30
13.2 With drying system	32
14 Summary	34
15 Screenshots	36
Certificate of Compliance	

1 Instrument references

Owner	Reception Date	Departure date
CNR-ISAC	2017-08-09	2017-09-11

ICOS ID	Brand	Model	S/N	Software release version
590	PICARRO	G2401	2871-CFKADS-2269	G2000-1.6.0.14

ID	Associated documents	Reference	Date
AD1	Procedure of initial tests	ATC-ML-IT-PR-02-2.0	2016-10-14
AD2	ICOS atmospheric station specifications	ATC-GN-GN-SP-1.2	2016-08
AD2	Incoming control sheet	ATC-ML-IT-IC-52	2017-08-09
AD3	Follow-up sheet	ATC-ML-IT-FS-77	2017-08-09

In the following pages, we present the results of the tests performed at the ATC MLab. For more details about these tests, please refer to the procedure of initial tests [AD1]. For each test, we either show the results not corrected for the water vapor (w, e.g. CO_2w) or corrected for the water vapor using the factory correction or the ATC correction (d, e.g. CO_2d). Except for the temperature test, the laboratory temperature is regulated at $22^\circ\text{C} \pm 2$.

2 Outlet valve characterization

Methodology: Three tests are performed. The first test consists in determining the effective opening value of the outlet proportional valve (without unit, from 0:closed to 65000 fully open).

In the second test, the cavity is first evacuated and then closed for 5 minutes and the pressure is monitored to evaluate the leakage rate.

Finally, the nominal value of the outlet valve (when nothing is connected to the instrument inlet) is measured.

After performing these tests, the results are the following:

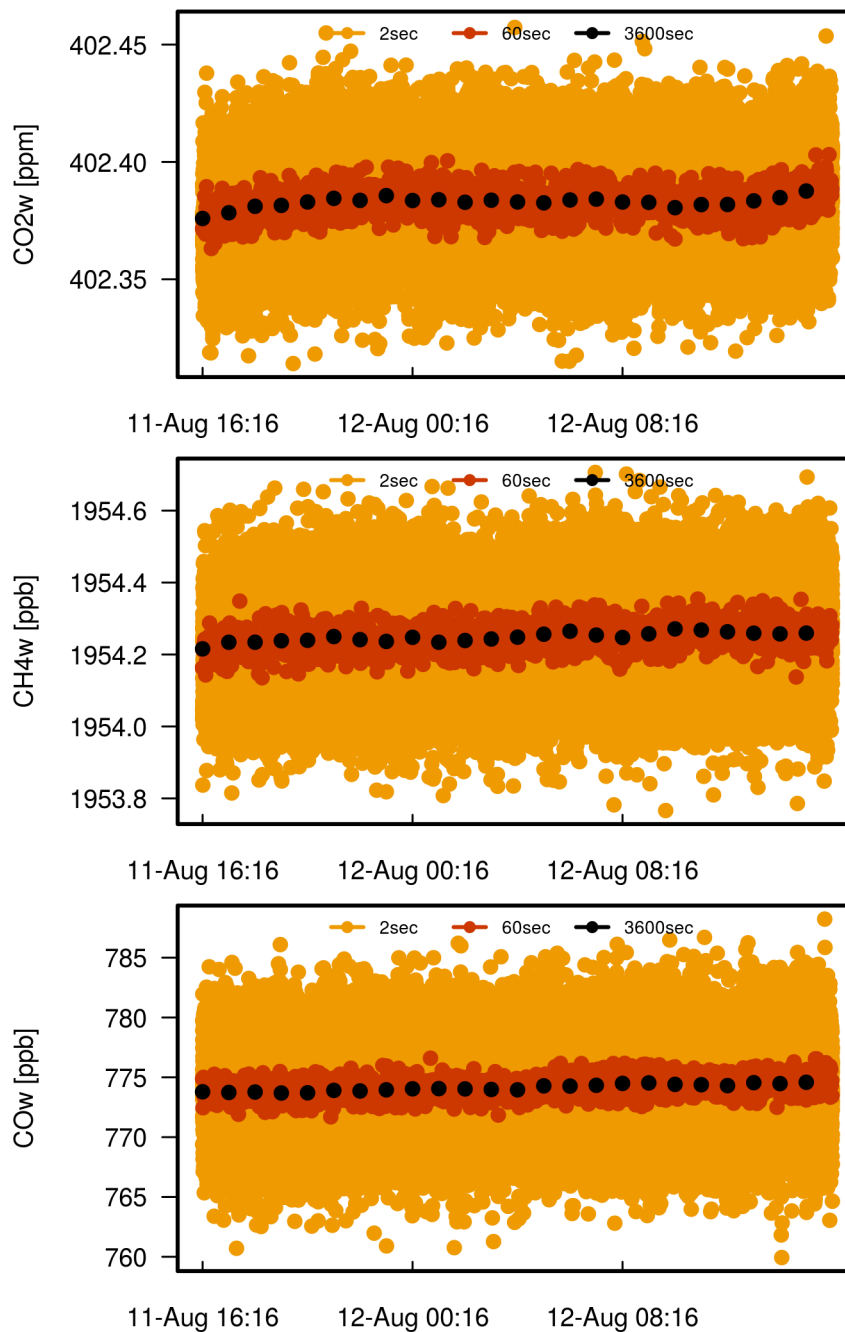
The outlet valve first opens at 18000.

The leakage rate is 0.040 Torr in 1 minute. The median is around 0.056 Torr for the instruments tested up to now at the MLab.

Its nominal outlet valve value is 34000. Above this value, the instrument inlet is in overpressure. Under it, it is in underpressure.

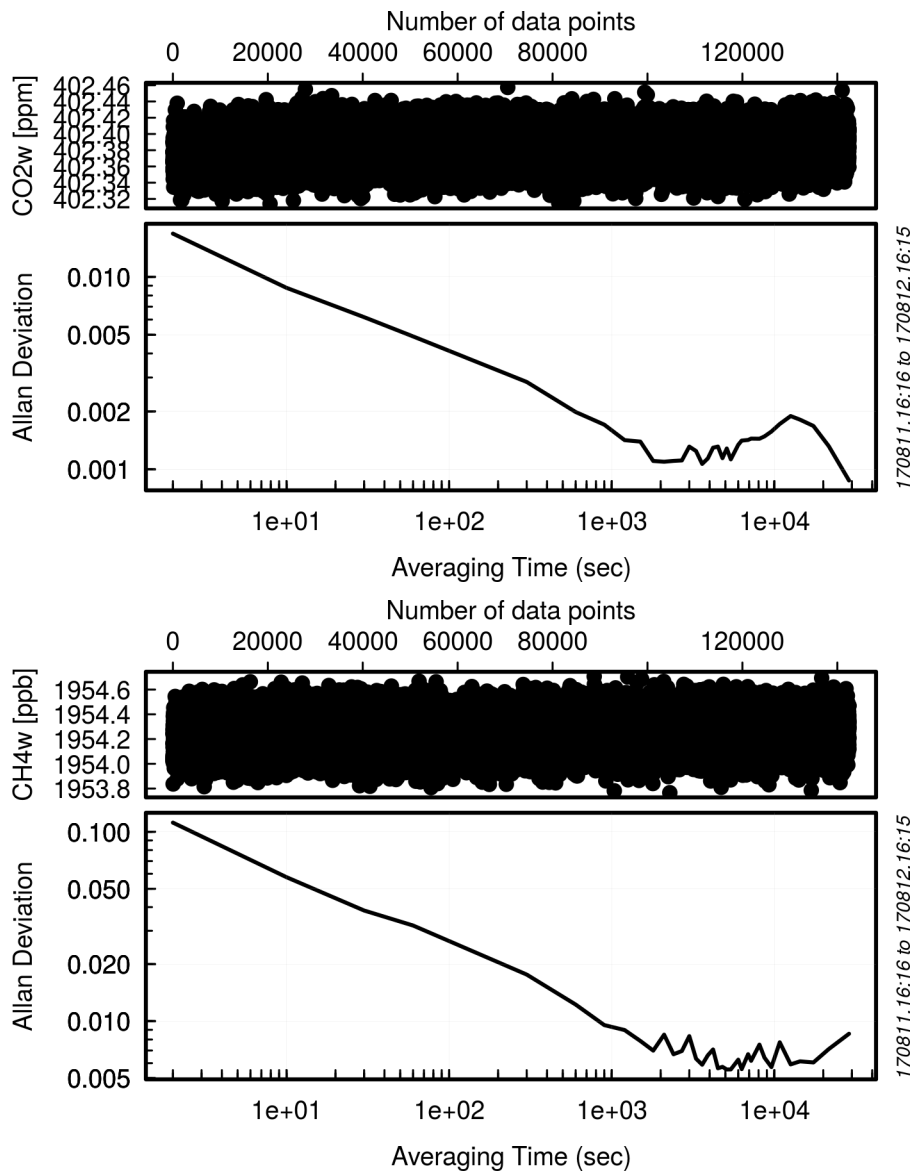
3 Continuous Measurement Repeatability (CMR) assessment

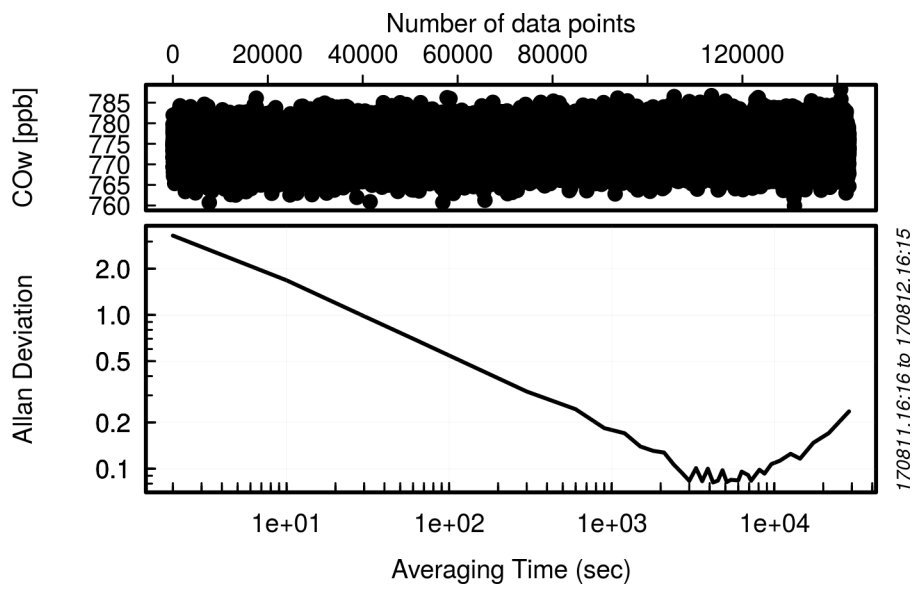
Methodology: Measure continuously a tank filled with dry natural air during at least 25 hours. Look at data distribution for different integration times. First hour not taken into account (stabilization time). No calibration applied.



4 Short term stability and drift assessment

Methodology: Measure continuously a tank filled with dry natural air during at least 25 hours. Calculate Allan deviations. First hour not taken into account (stabilization time). No calibration applied.



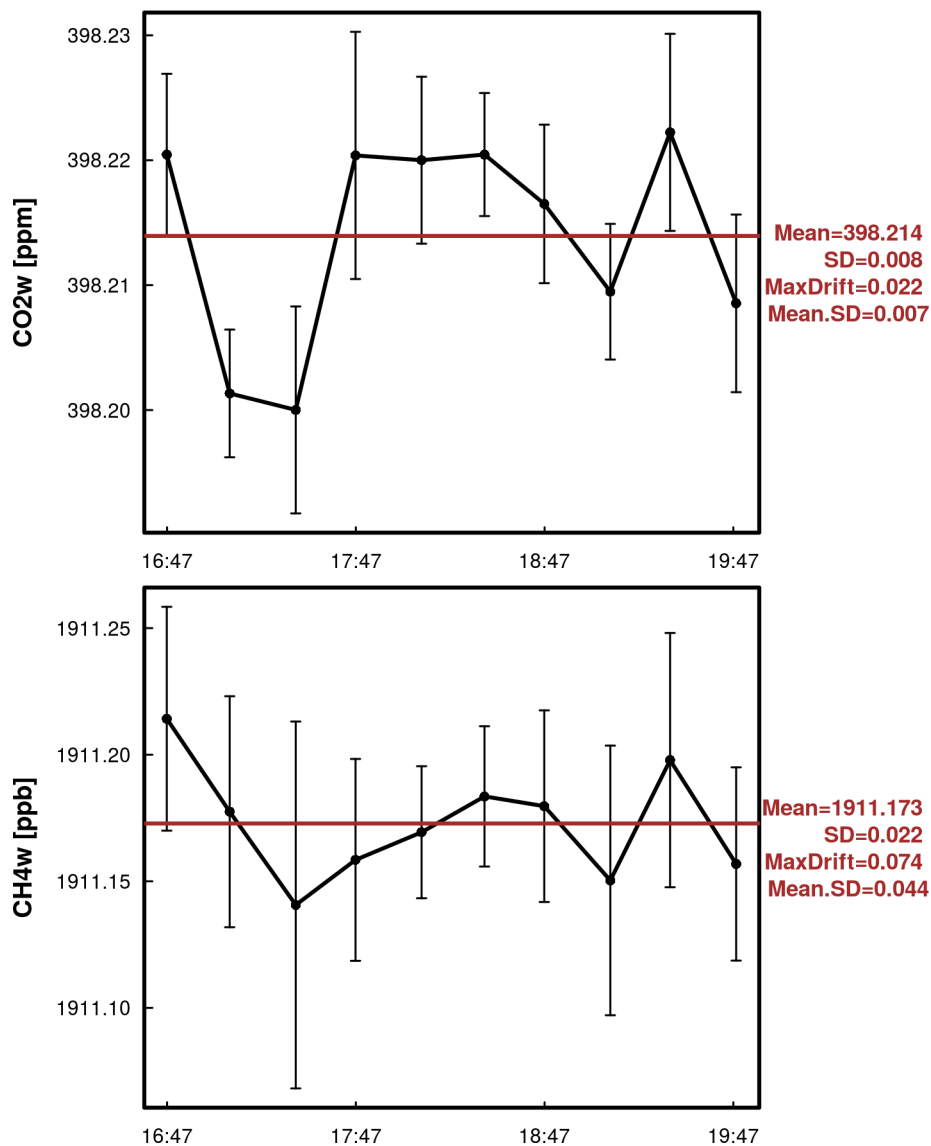


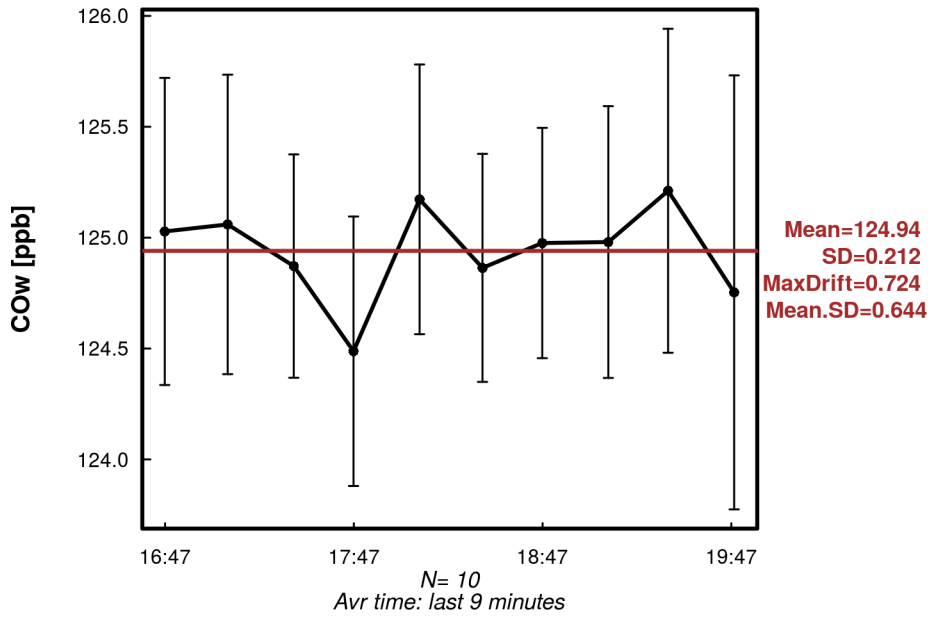
	CO ₂	CH ₄	CO
Optimum Averaging time (s)*	3600	3600	3600
Optimum Allan deviation [ppb]*	1	0.01	0.08
Allan deviation at 1 min [ppb]	5	0.03	0.70
Allan deviation at 5 min [ppb]	3	0.02	0.32
Allan deviation at 10 min [ppb]	2	0.01	0.24
Allan deviation at 15 min [ppb]	2	0.01	0.18
Allan Deviation at 1 hr [ppb]	1	0.01	0.08

* The optimum is searched in the first one hour window.

5 Short Term Repeatability (STR) assessment

Methodology: Measure a tank filled with dry natural air for 15 min and wet ambient air for 5 minutes alternatively 10 times. For each period of tank measurement, calculate a mean value (discard the first minutes for stabilization). Look at the dispersion (1σ) of the mean values (10 points). No calibration applied.

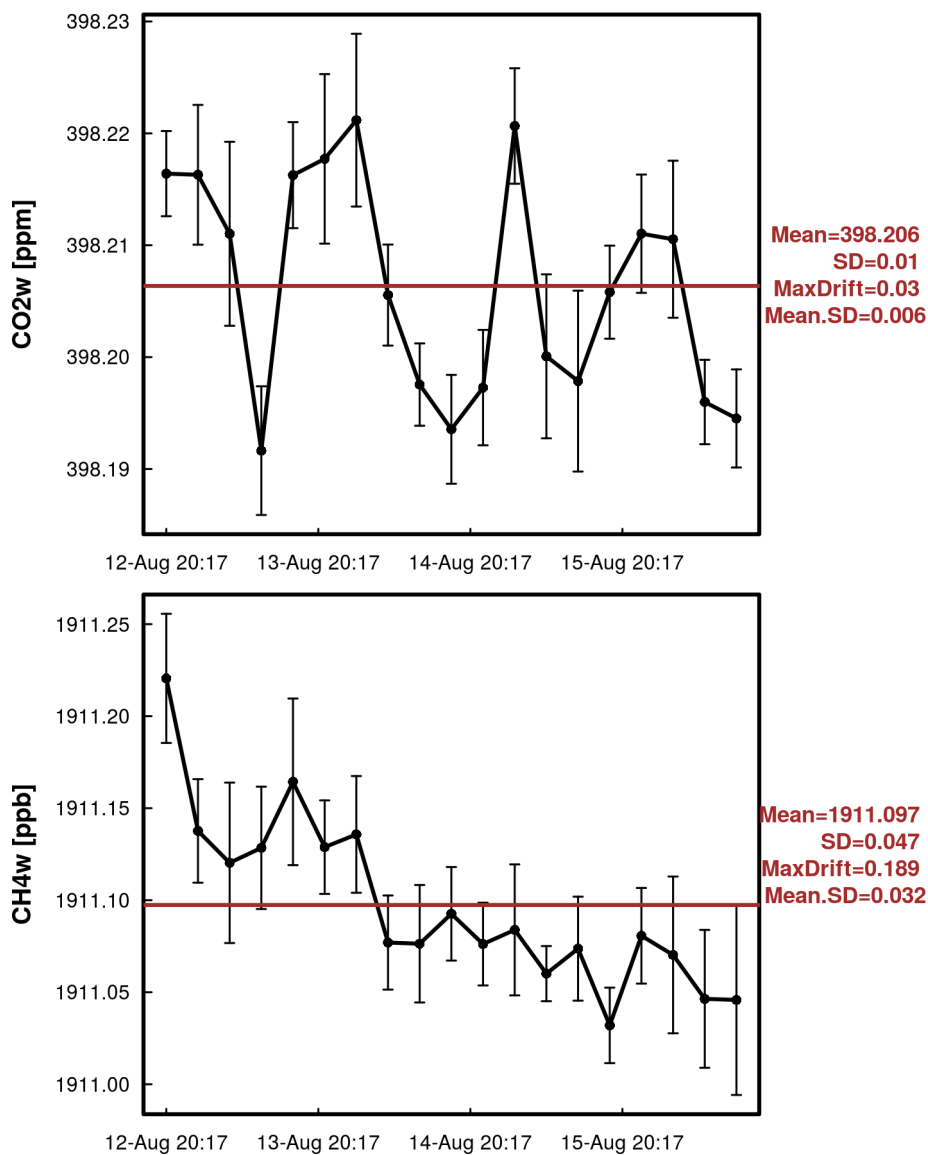


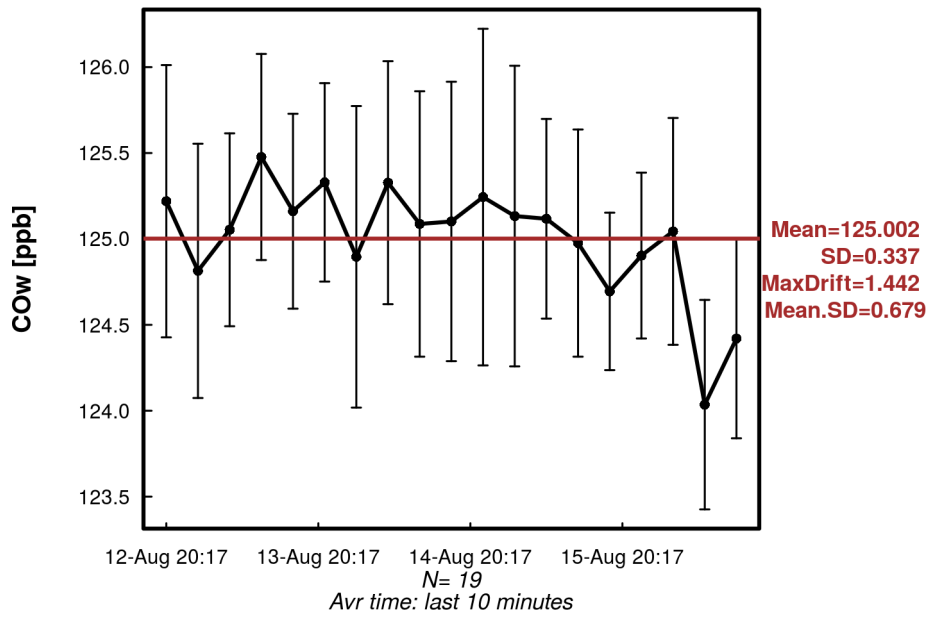


	CO ₂ [ppb]	CH ₄ [ppb]	CO [ppb]
Short term repeatability (1σ , 9 minute average raw data)	8	0.02	0.21
MaxDrift (peak to peak, 9 minute average raw data)	22	0.07	0.72

6 Long Term Repeatability (LTR) assessment

Methodology: Measure alternatively over 72 hours a tank filled with dry natural air for 30 minutes and 270 minutes of wet ambient air. For each period of tank measurement, calculate a mean value (discard the first minutes for stabilization). Look at the dispersion (1σ) of the mean values. No calibration applied.

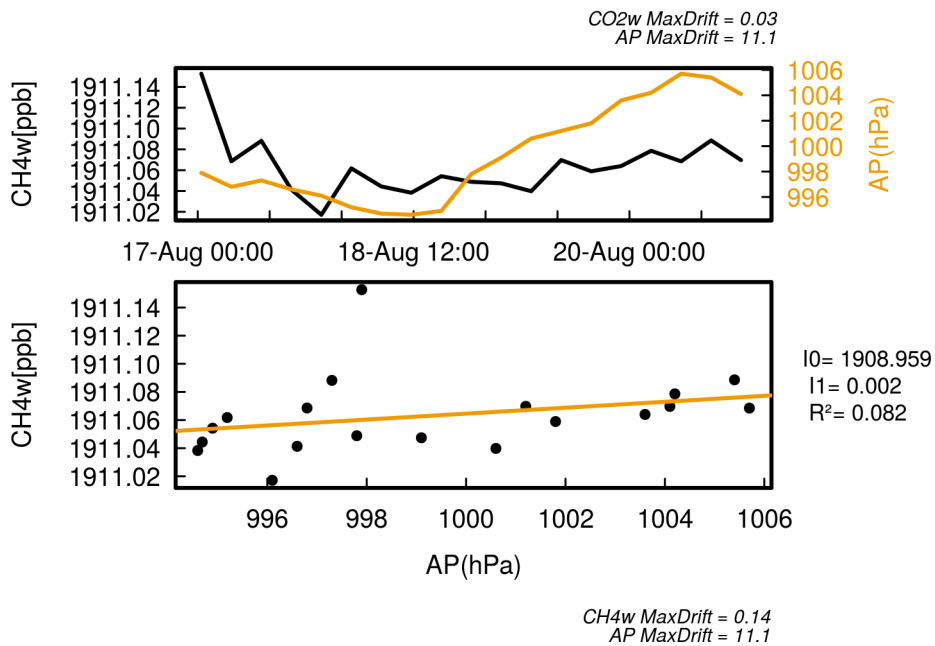
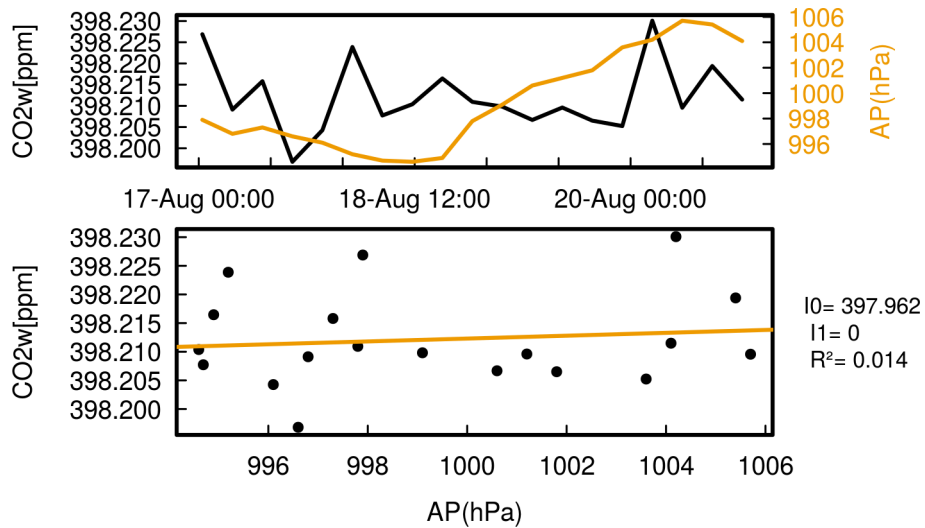


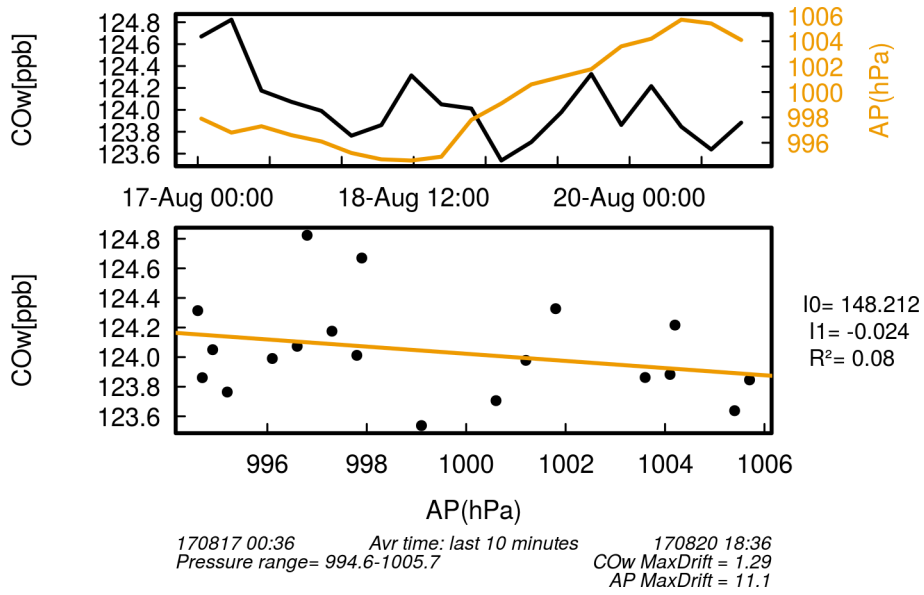


	CO ₂ [ppb]	CH ₄ [ppb]	CO [ppb]
Long term repeatability (1 σ , 10 minute average raw data)	10	0.05	0.34
MaxDrift (peak to peak, 10 minute average raw data)	30	0.19	1.44

7 Atmospheric pressure sensitivity

Methodology: Measure alternatively over 72 hours a tank filled with dry natural air for 30 minutes and 270 minutes of wet ambient air. For each period of tank measurement, calculate a mean value (last 10 minutes) and look at the correlation of the tank measurement with atmospheric pressure (AP) variation.



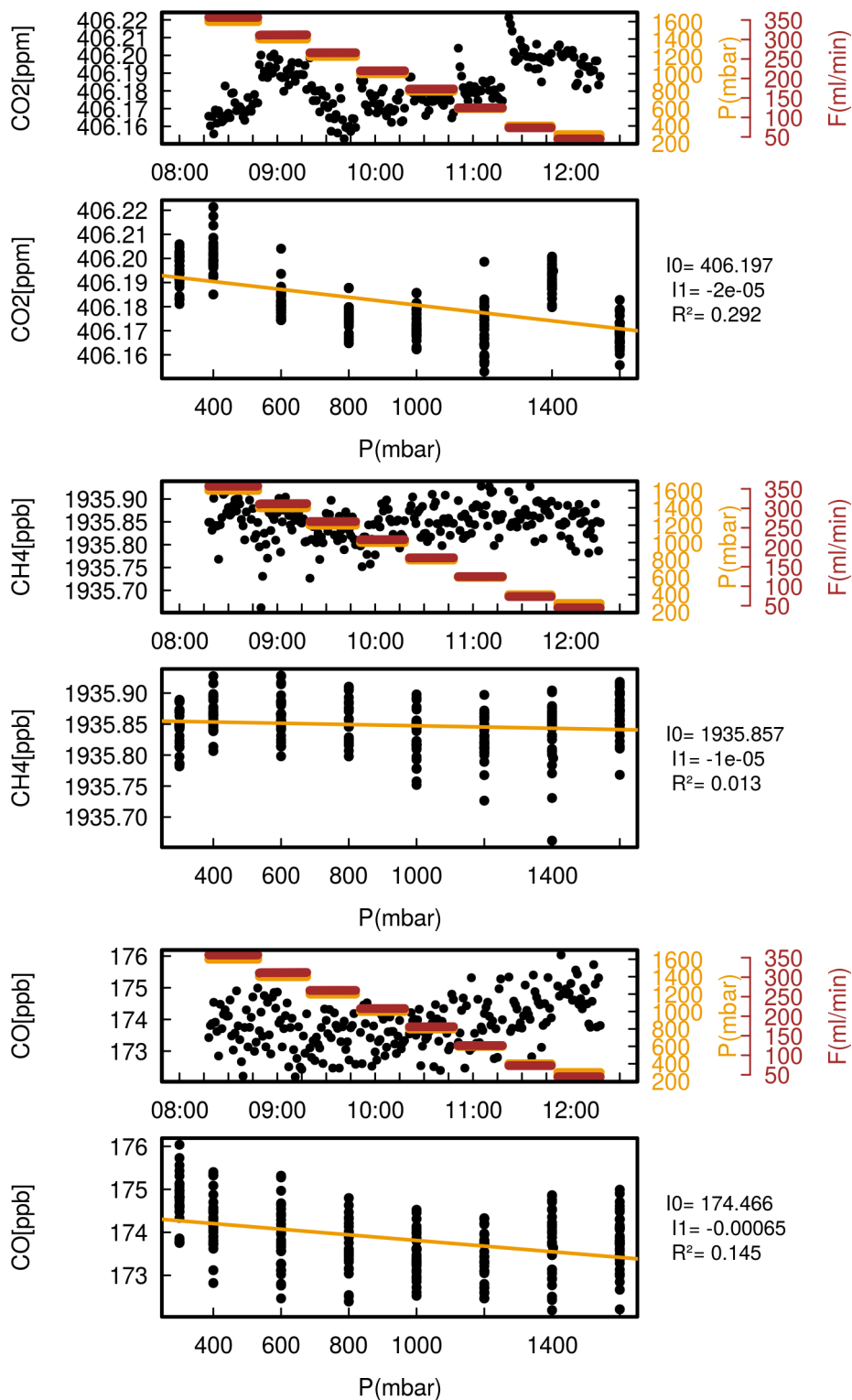


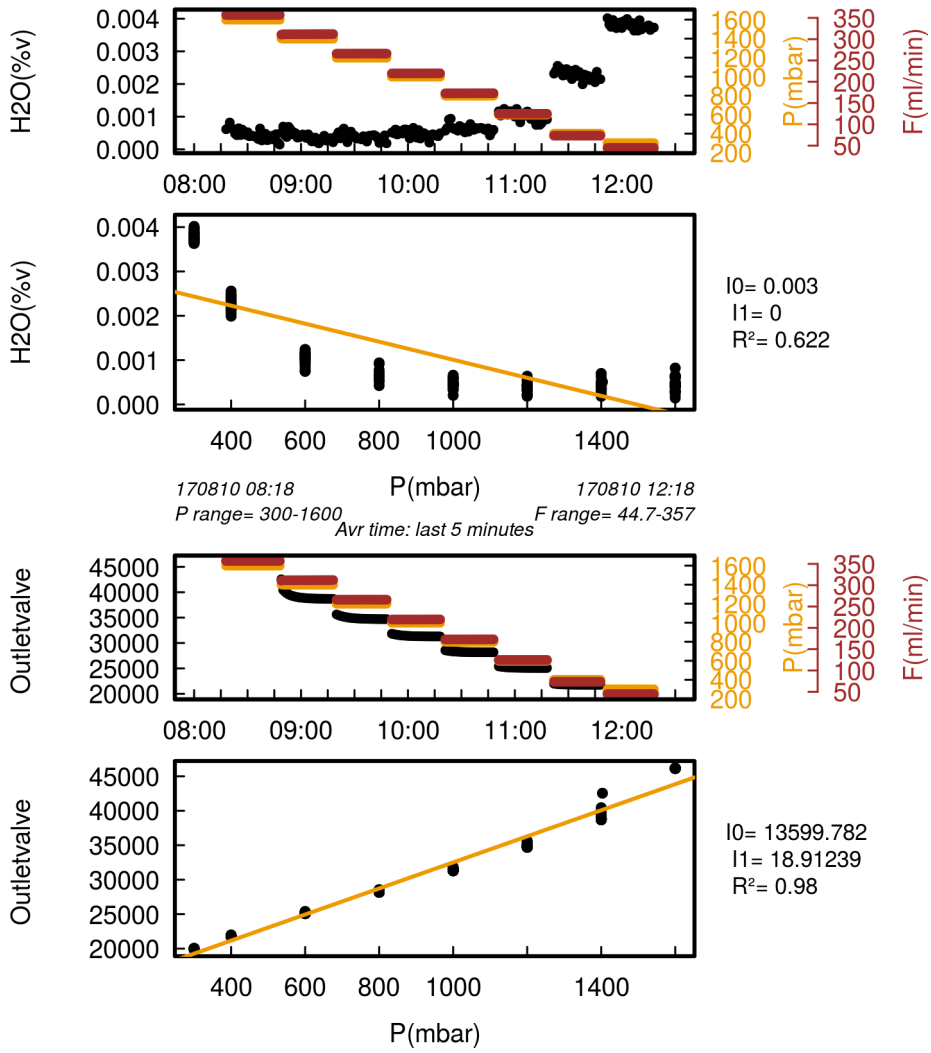
	CO ₂	CH ₄	CO
Atmospheric pressure sensitivity (ppb/hPa)	NS	NS	NS

Not significant (NS) if $R^2 < 0.5$ or the absolute value of the slope lower than 1, 0.02 and 0.03 ppb/hPa for CO₂, CH₄ and CO respectively

8 Inlet pressure sensitivity

Methodology: Measure continuously a tank filled with dry natural air through an electronic pressure controller at the instrument inlet. Change sequentially (step of 30 minutes) the instrument inlet pressure (maximum range from 1600 mbar absolute to 300 mbar absolute) thanks to the pressure controller. The valid range is evaluated as the range where CO₂ mixing ratios are ± 0.02 ppm from the mixing ratio at atmospheric pressure.

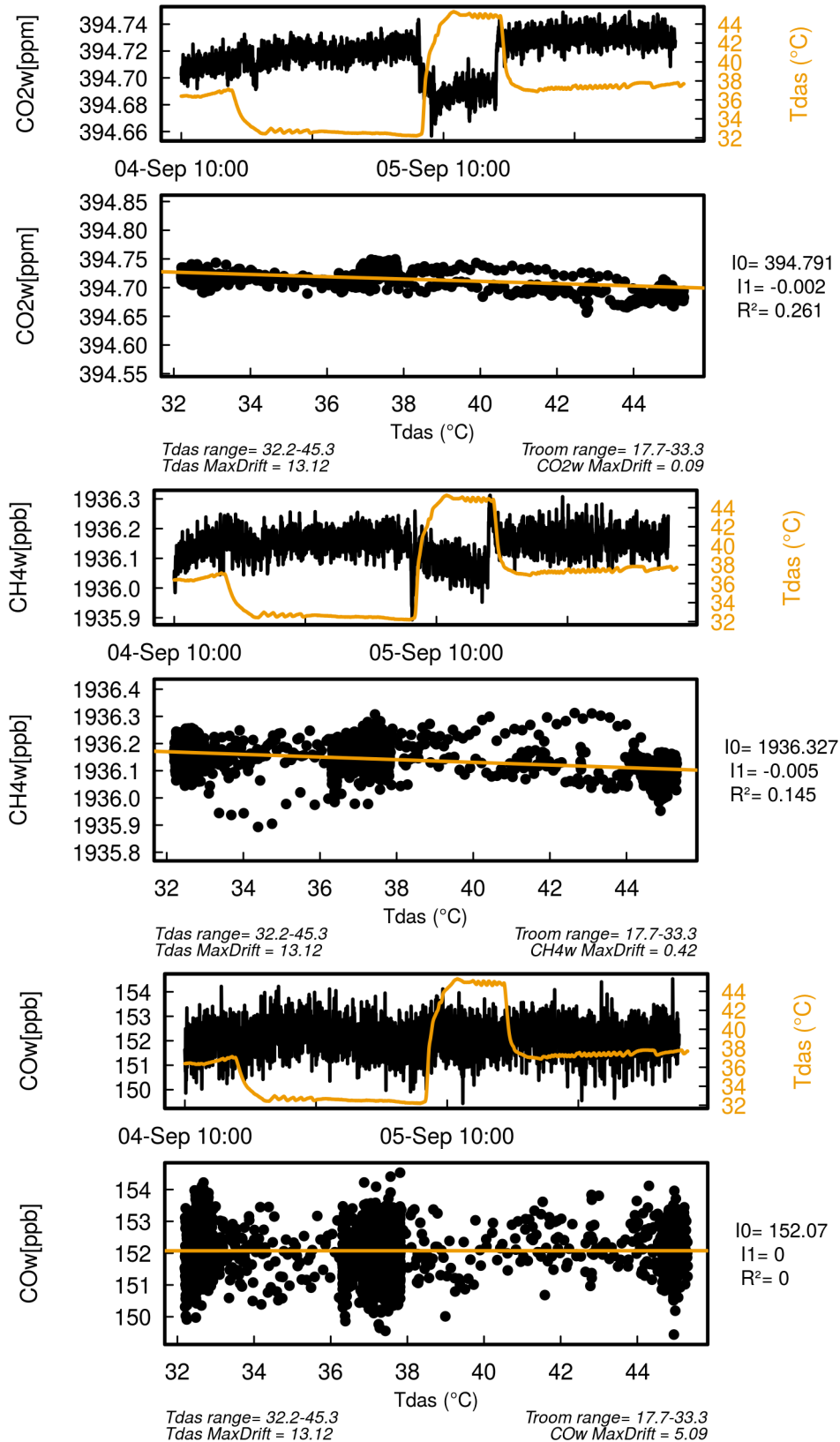


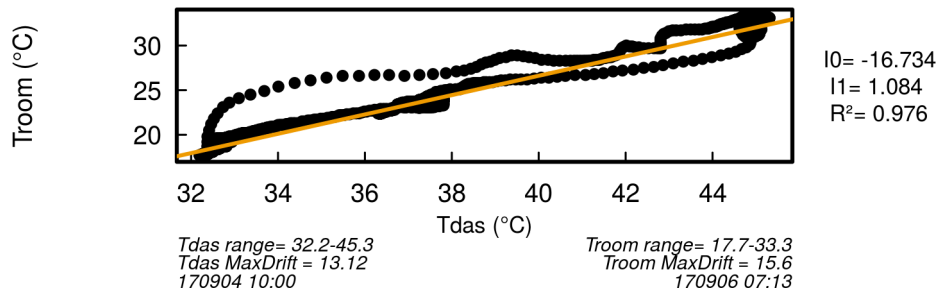


	Min	Max
Valid Outletvalve range	25100	46100
Valid inlet pressure range (mbar absolute)	600	1600

9 Temperature sensitivity

Methodology: Measure a tank filled with dry natural air while changing the room temperature (T_{room}). Look at the correlation of the measurement stability with the instrument internal temperature (T_{das}).





	CO ₂	CH ₄	CO
Ambient temperature sensitivity (ppb/°C)	NS	NS	NS

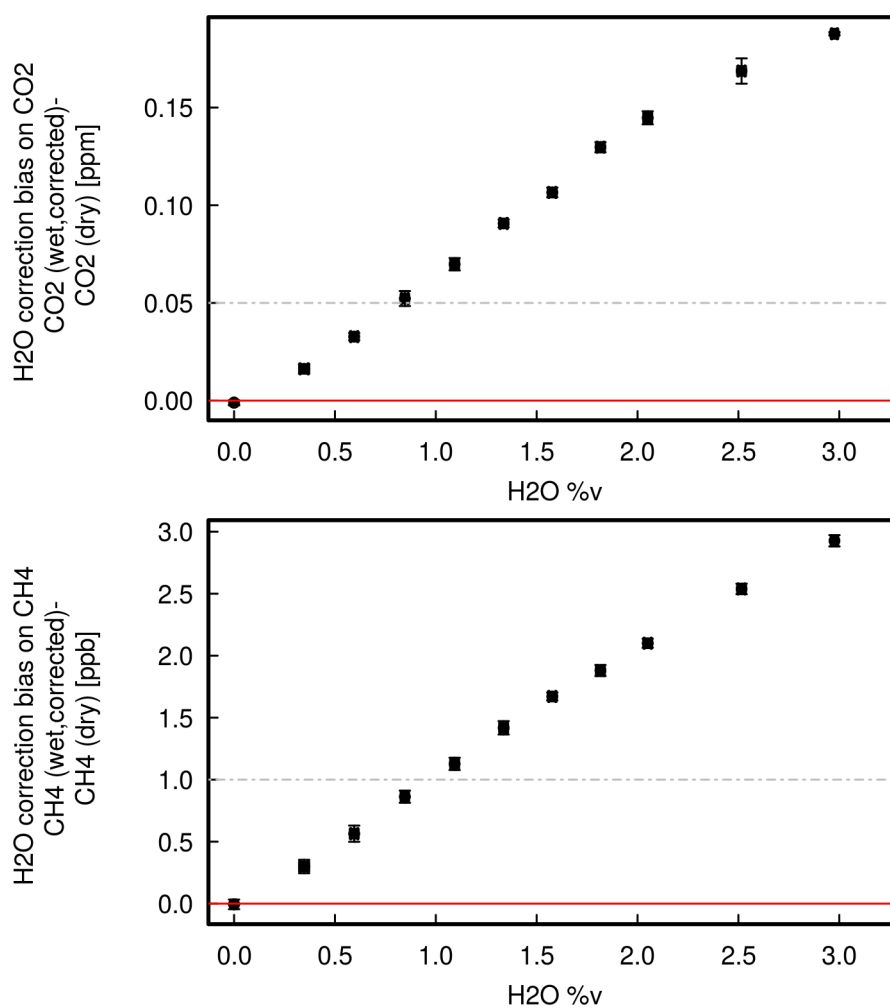
Not significant (NS) if $R^2 < 0.45$ or the absolute value of the slope lower than 5, 0.1 and 0.2 ppb/°C for CO₂, CH₄ and CO respectively

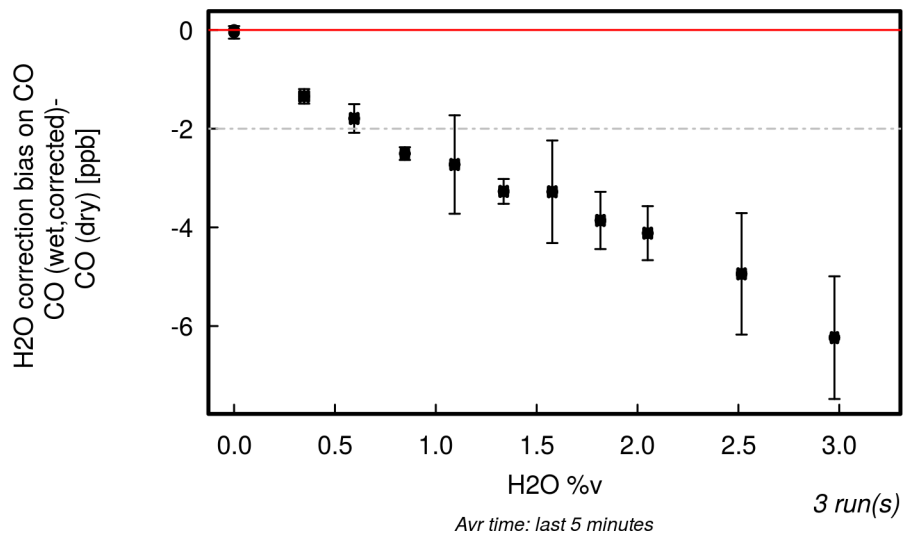
10 Water vapor correction assessment

Methodology: Measure a tank filled with dry natural air during at least 1h. Then humidify by 20 minute steps the tank gas at 0.25/0.5/0.75/1/1.25/1.5/1.75/2/2.5/3 %v of water vapor. Finally, stop humidifying and measure the tank filled with dry natural air during more than 1 hour. Repeat the experiment at least twice, usually three times. Check the water vapor correction bias depending on the H₂O level. Determine an optimized water vapor correction bias.

$$H_2O \text{ correction bias} = C_{\text{humidified gas, water vapor corrected}} - C_{\text{not humidified gas}} \quad (1)$$

10.1 Factory correction





10.2 Determination of H₂O correction coefficients by the MLab

$$C_r = \frac{C_{wet}}{C_{dry}} = 1 + I_1 * H_2O_r + I_2 * H_2O_r^2 \quad (2)$$

with H_2O_r : Instrument reported value (not calibrated). The “calibrated” H₂O value is:

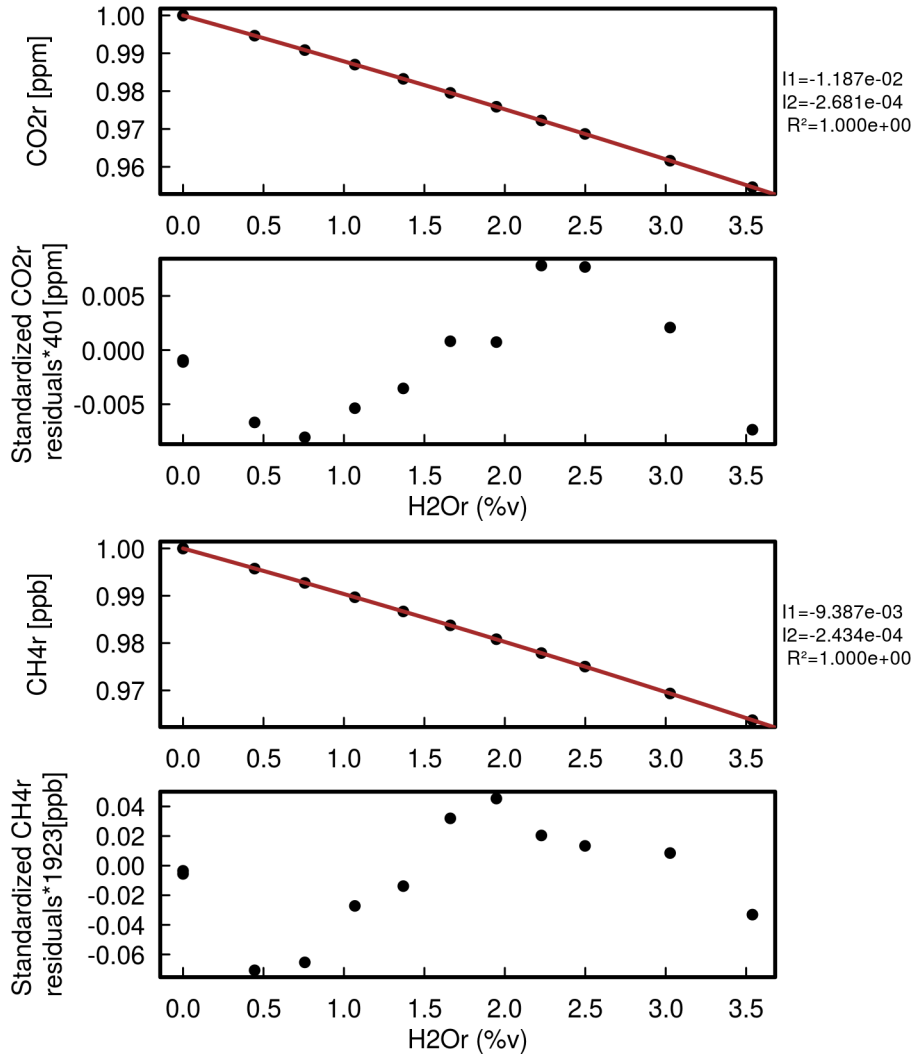
$$H_2O = 0.772 * H_2O_r + 0.019493 * H_2O_r^2 \quad (3)$$

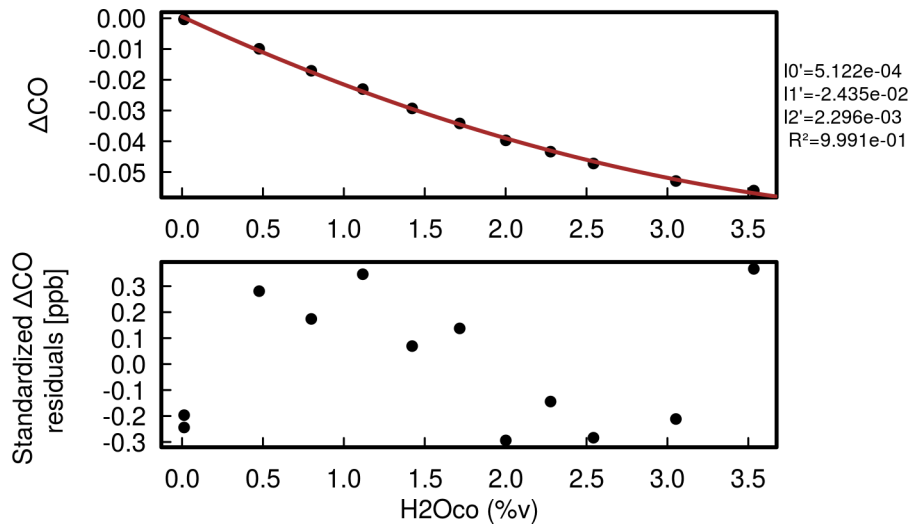
For CO, we define CO_{wet} as the sum of two terms:

$$CO_{wet,not\ calibrated} = CO_{wet\ no\ H_2O\ line\ interference\ corr} + \Delta CO \quad (4)$$

The first term is calculated using the CO, CO₂ and H₂O peaks that are interfering with each other but does not take into account the line interference of the H₂O peak on the CO peak which is represented by ΔCO . We estimate the H₂O correction by plotting the second term versus the H₂O using the H₂O peak close to the CO line (H_2O_{co}).

$$\Delta CO = I_0' + I_1' * H_2O_{co} + I_2' * H_2O_{co}^2 \quad (5)$$



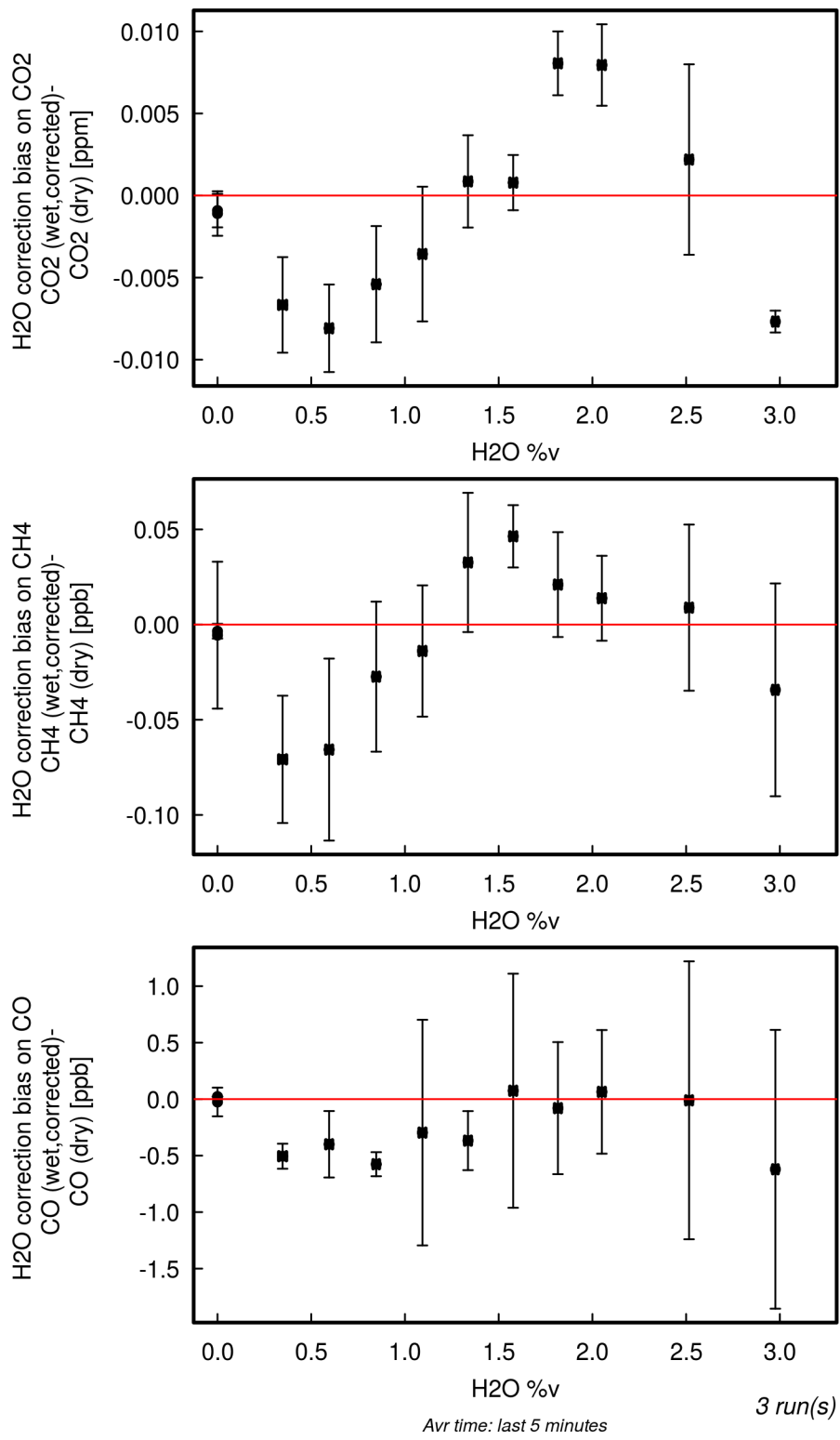


H₂O correction coefficients determined by ATC

	CO ₂	CH ₄
I1	-1.187e-02	-9.387e-03
I2	-2.681e-04	-2.434e-04

	CO
I1'	-2.435e-02
I2'	2.296e-03

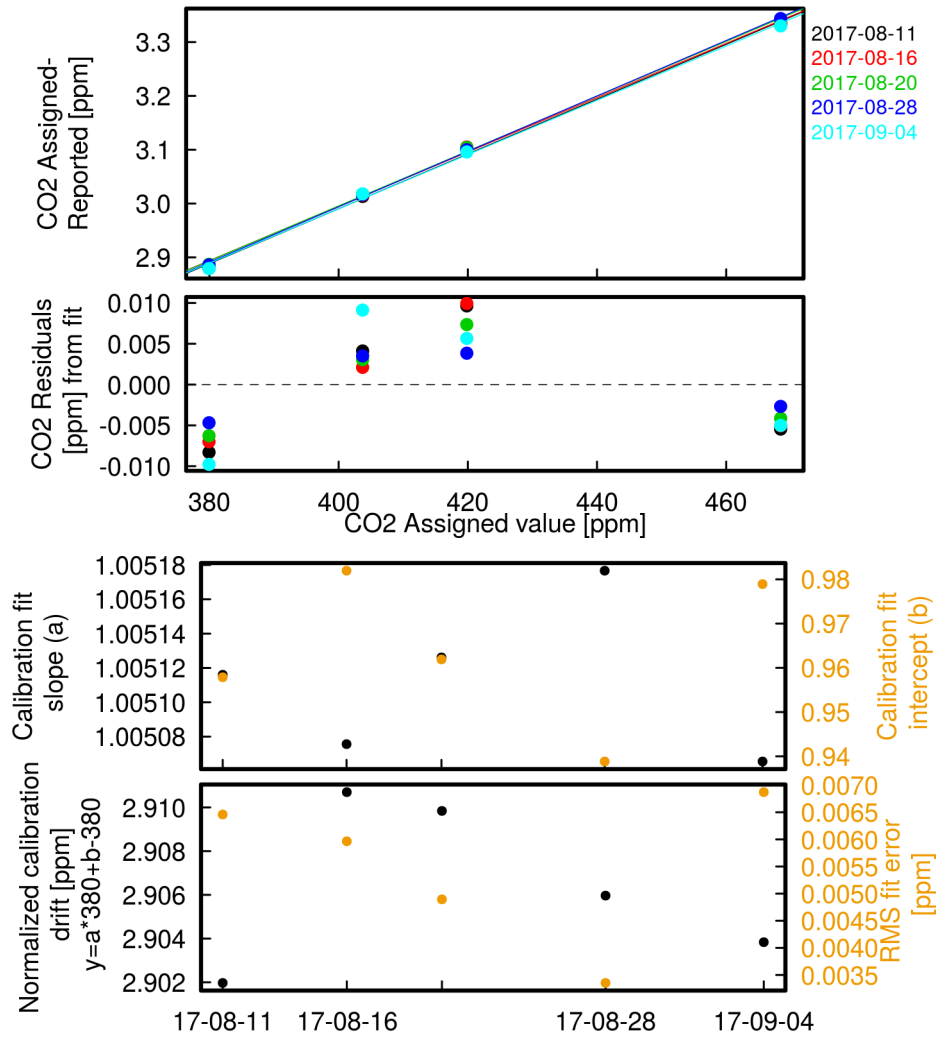
10.3 MLab correction



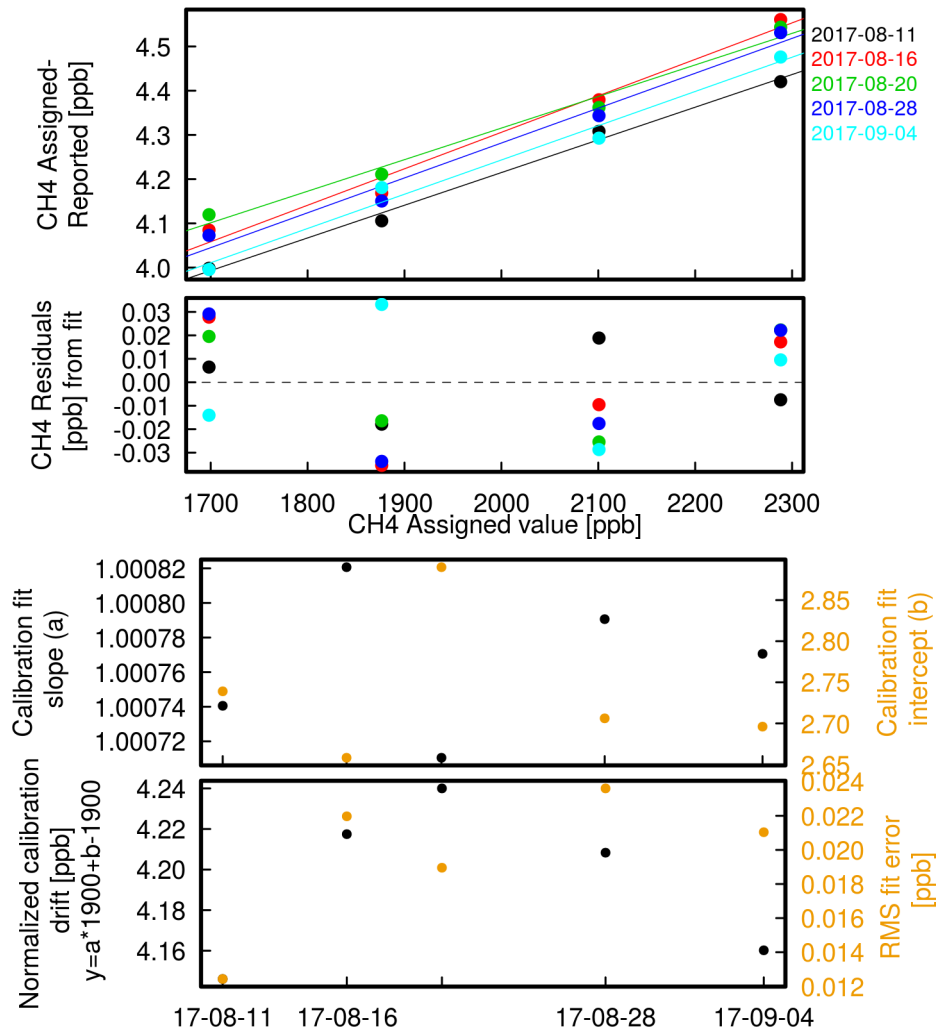
11 Calibration

Methodology: Measure 4 times (during 20 minutes each time) 4 standards filled with known CO₂, CH₄ and CO concentrations. Compare reported values from the instrument and assigned values. Determine calibration functions. The residuals shown are the residuals from the calibration fit ($C_{Assigned} - C_{Reported} = f(C_{Assigned})$). Check the instrument drift. The value in the table is evaluated by calculating the temporal regression of the average differences (Assigned-Reported) for each calibration episode.

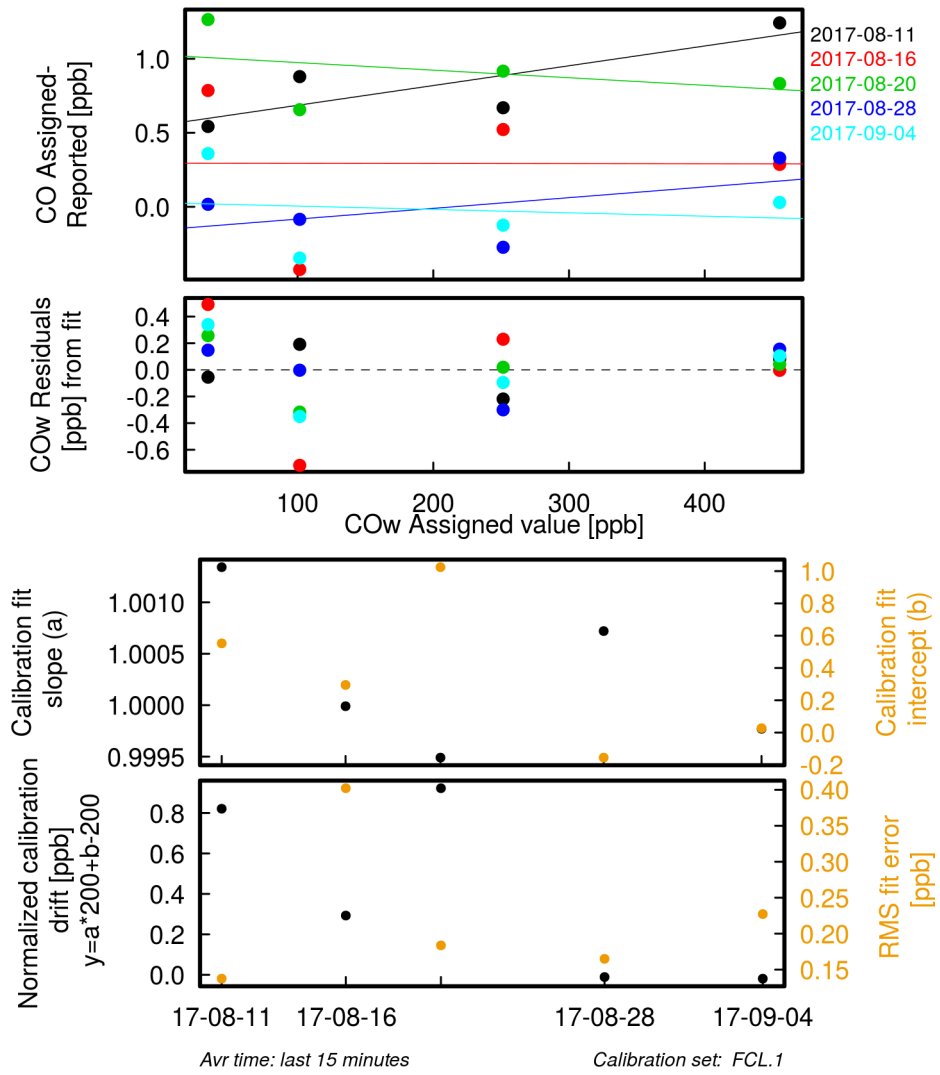
CO2



CH4



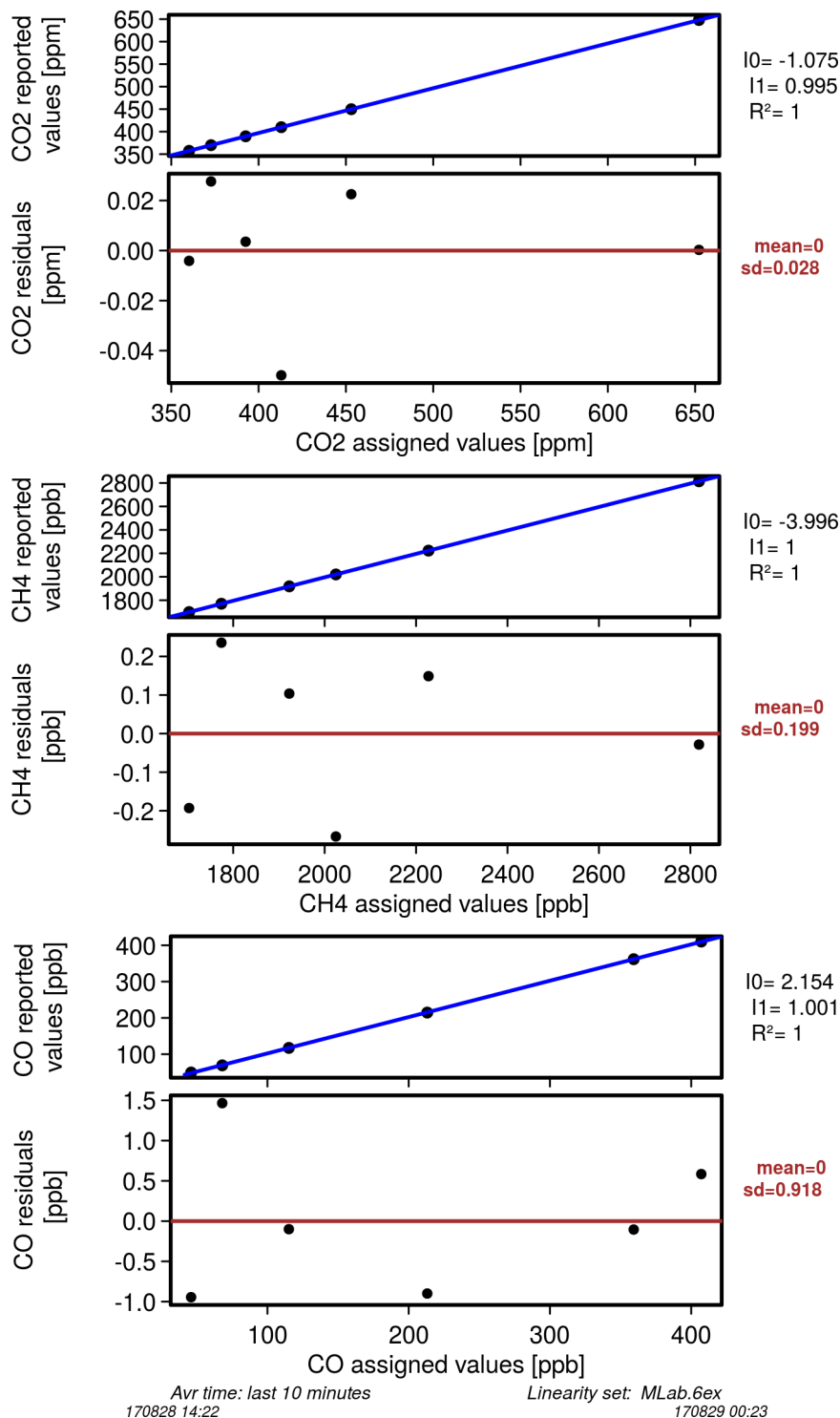
CO



	CO ₂	CH ₄	CO
Calibration drift trend (ppb/month)	-1.3	0.0	-1.1
Maximum residual from linear fit on calibration range [ppb]	10	0.0	0.7

12 Linearity

Methodology: Measure 4 times (during 20 minutes each time) 6 standards filled with known CO₂, CH₄ and CO concentrations within the range guaranteed by the manufacturer. The first minutes are not taken into account (stabilization time). No calibration applied.



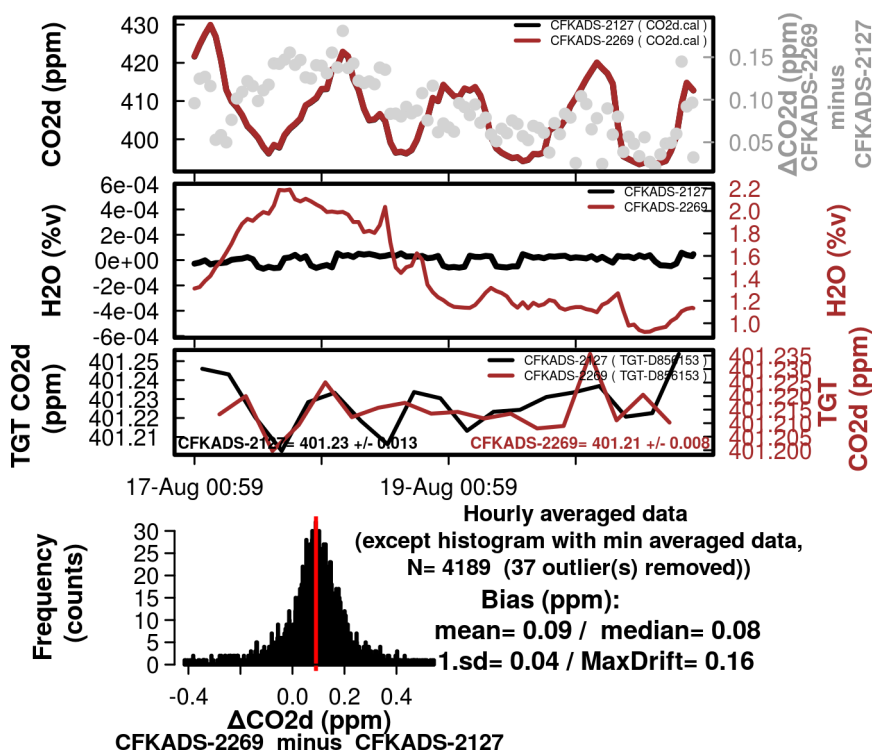
	CO ₂	CH ₄	CO
Maximum residual from linear fit on extended mole fraction range [ppb]	50	0.27	1.47
Maximum residual from linear fit on extended mole fraction range [%]	0.012	0.013	2.155

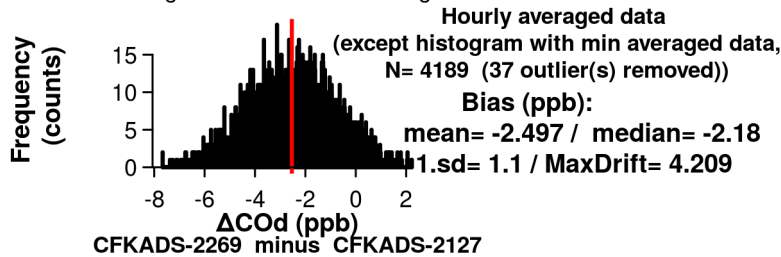
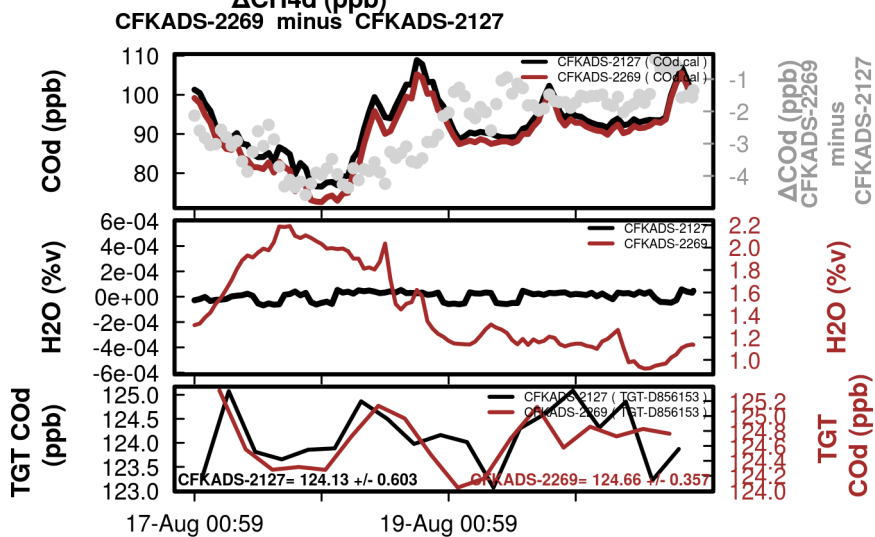
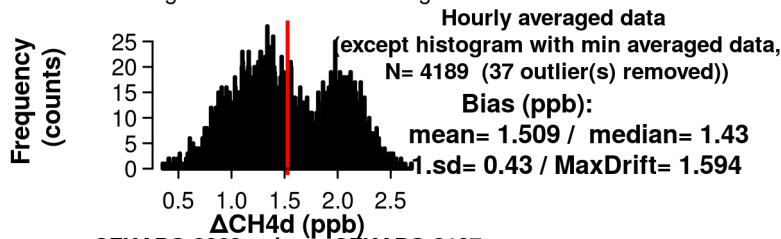
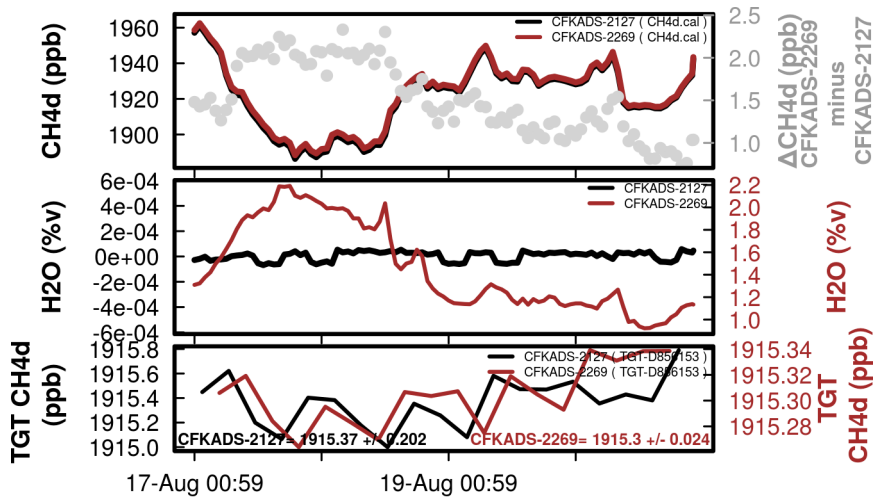
13 Laboratory inter-comparison

13.1 Without drying system

Methodology: Measure ambient air without drying system. Compare with a reference instrument with drying system. The 2 instruments are calibrated against the same set of calibration tanks. They are each equipped with a dedicated sampling line. If the MLab reference instrument is unavailable then the reference instrument is the instrument tested in parallel. In this case, they use the same sampling line and the ATC water vapor correction is applied to the reference. A target gas is measured on both instruments for quality control.

13.1.1 Factory water vapor correction

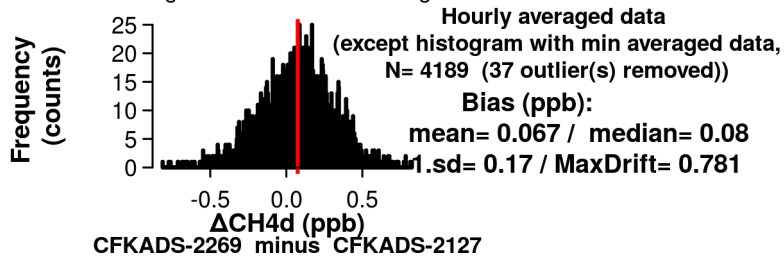
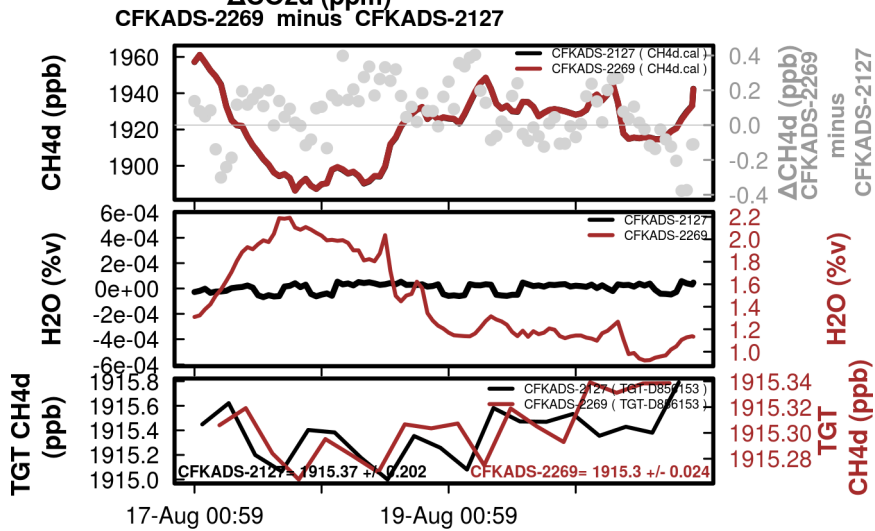
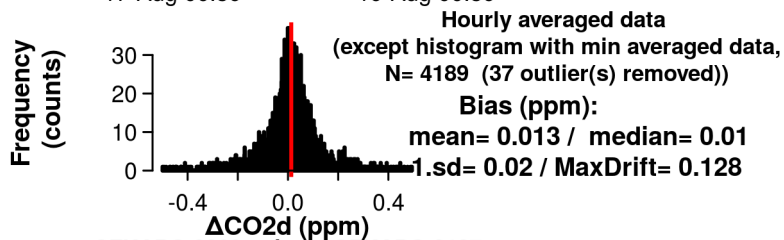
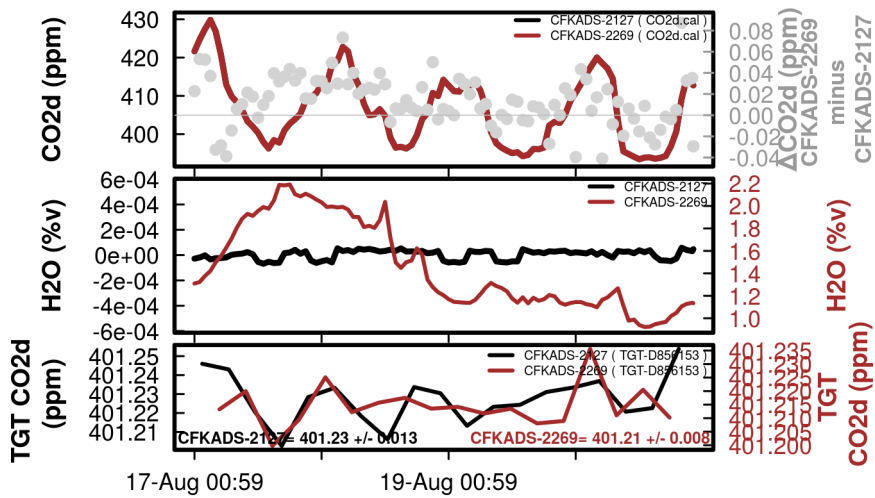


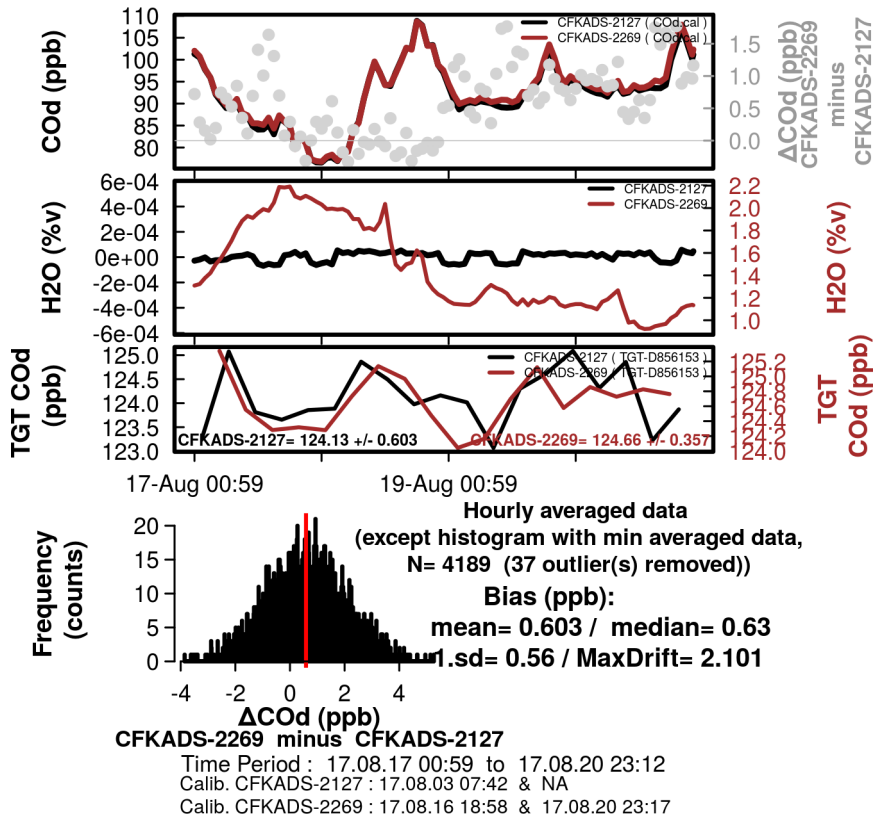


CFKADS-2269 minus CFKADS-2127
Time Period : 17.08.17 00:59 to 17.08.20 23:12
Calib. CFKADS-2127 : 17.08.03 07:42 & NA
Calib. CFKADS-2269 : 17.08.16 18:58 & 17.08.20 23:17

	CO ₂ [ppb]	CH ₄ [ppb]	CO [ppb]
Observed bias in ambient air:			
mean difference (CFKADS-2269 - Ref Instrument)	90	1.51	-2.50
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (1.5 %v H ₂ O)	107	1.67	-3.28
Remaining bias (not related to H ₂ O correction)	-17	-0.16	0.78
Observed bias on TGT (dry air):			
mean difference (CFKADS-2269 - Ref Instrument)	-13	-0.06	0.53

13.1.2 Water vapor correction coefficients determined by ATC

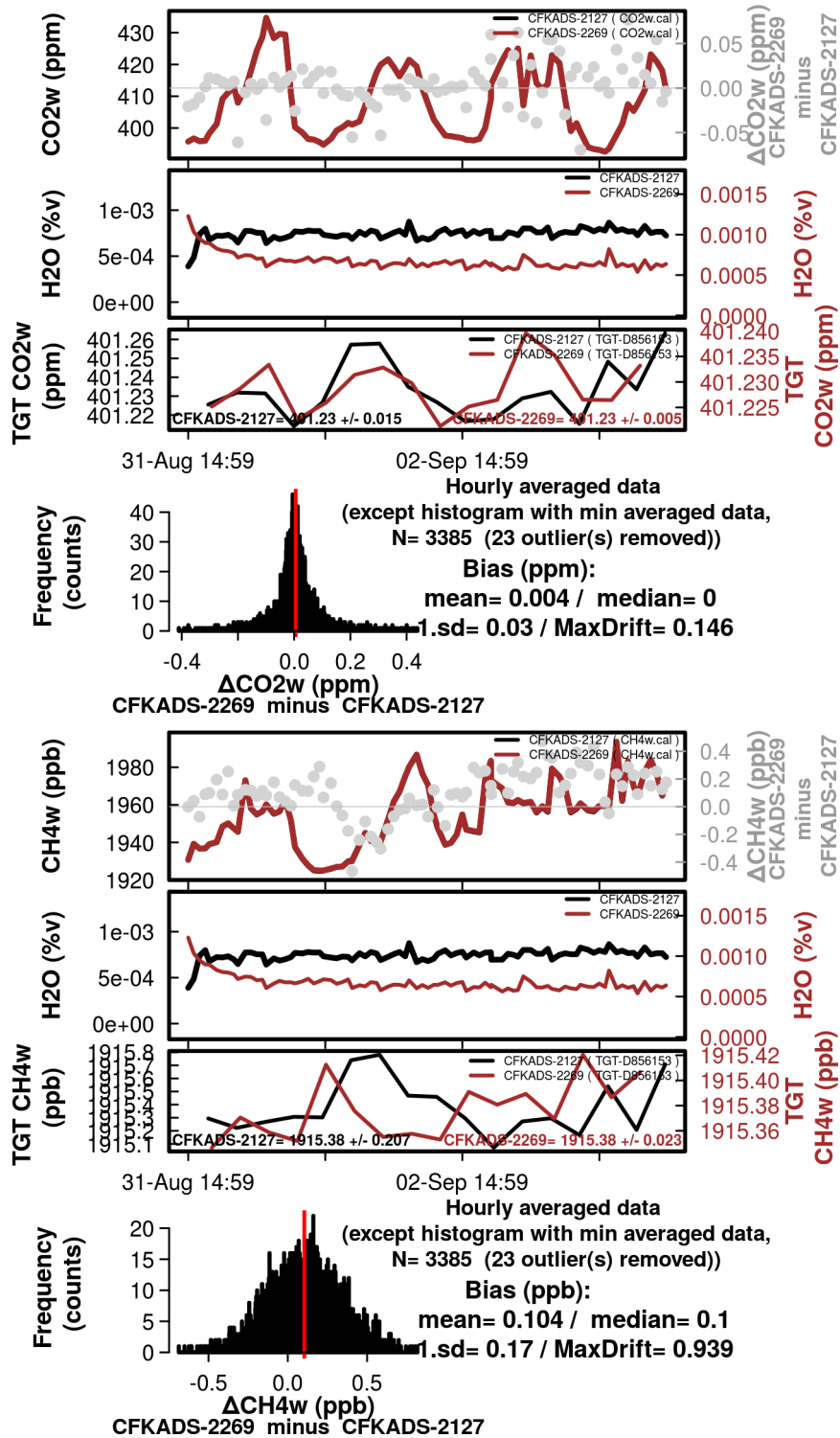


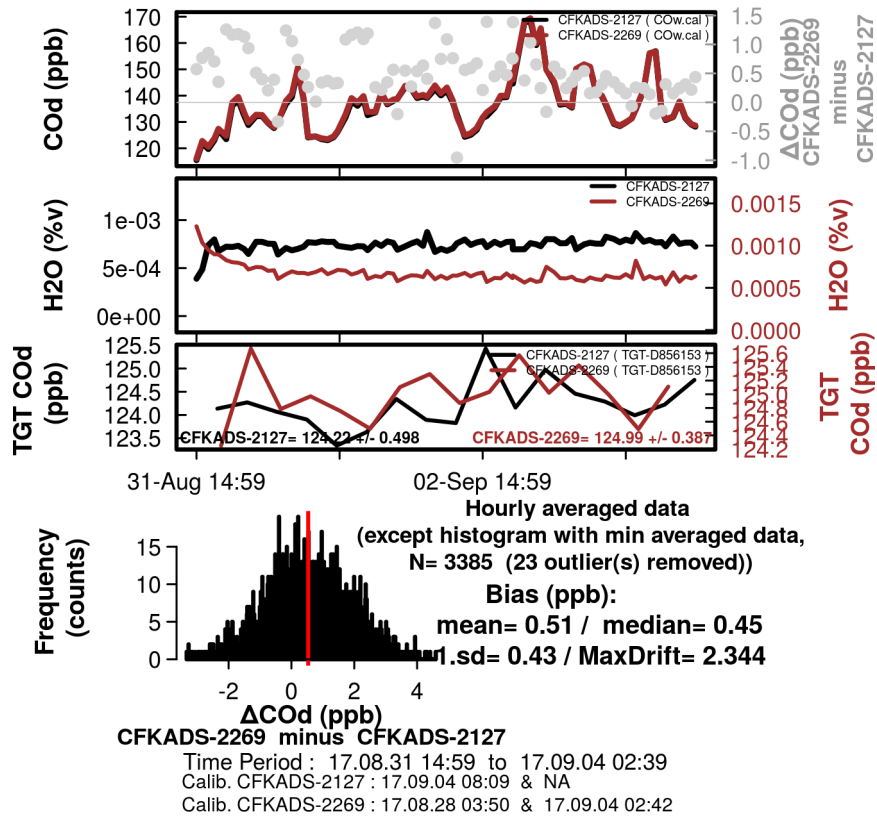


	CO ₂ [ppb]	CH ₄ [ppb]	CO [ppb]
Observed bias : mean difference (CFKADS-2269 - Reference)	13	0.07	0.60
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (1.5 %v H ₂ O)	1	0.05	0.07
Remaining bias (not related to H ₂ O correction)	12	0.02	0.53
Observed bias on TGT (dry air): mean difference (CFKADS-2269 - Ref Instrument)	-13	-0.06	0.53

13.2 With drying system

Methodology: Measure ambient air with drying system. Compare with a reference instrument. The 2 instruments are calibrated against the same set of calibration tanks. They are equipped with a dedicated sampling line. If the MLab reference instrument is unavailable then the reference instrument is the instrument tested in parallel. In this case, they use the same sampling line. A target gas is measured on both instruments for quality control.





	CO ₂ [ppb]	CH ₄ [ppb]	CO [ppb]
Observed bias : mean difference (CFKADS-2269 - Reference)	4	0.10	0.51
Intrinsic bias estimated in wet air conditions (ATC correction)	12	0.02	0.53
Observed bias on TGT (dry air): mean difference (CFKADS-2269 - Ref Instrument)	-4	0.00	0.77

14 Summary

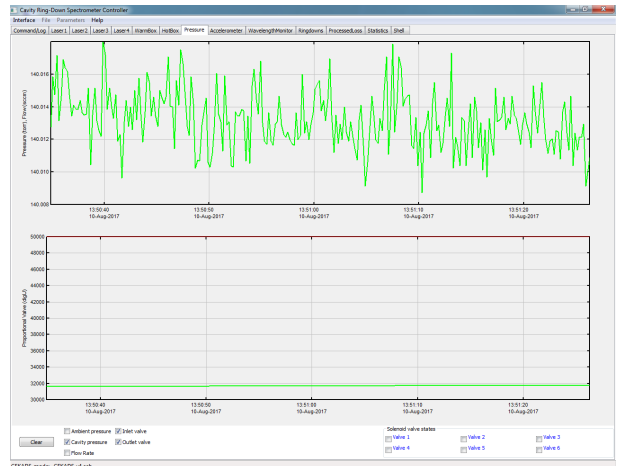
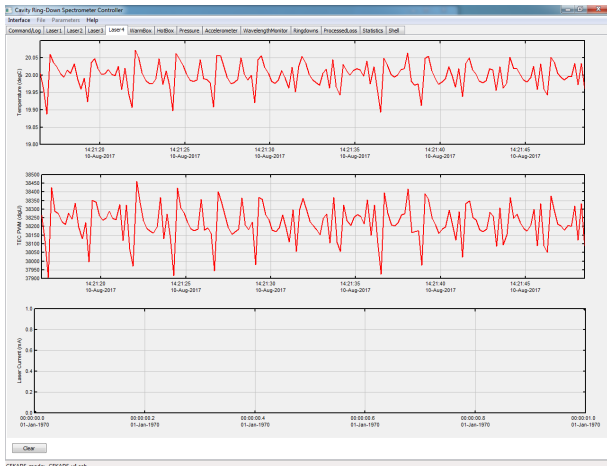
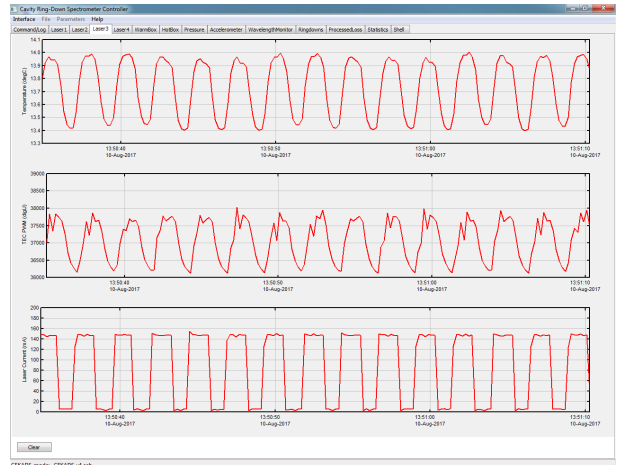
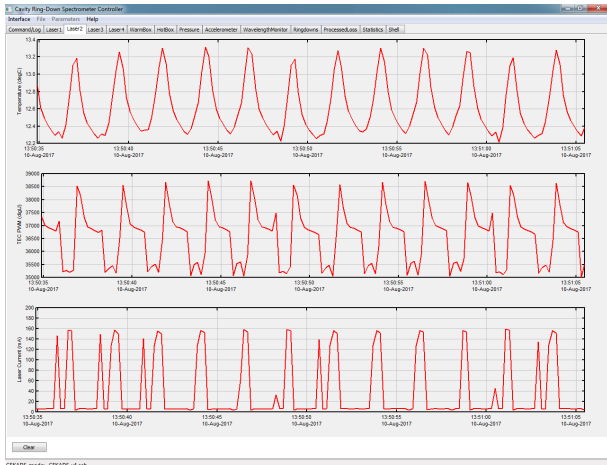
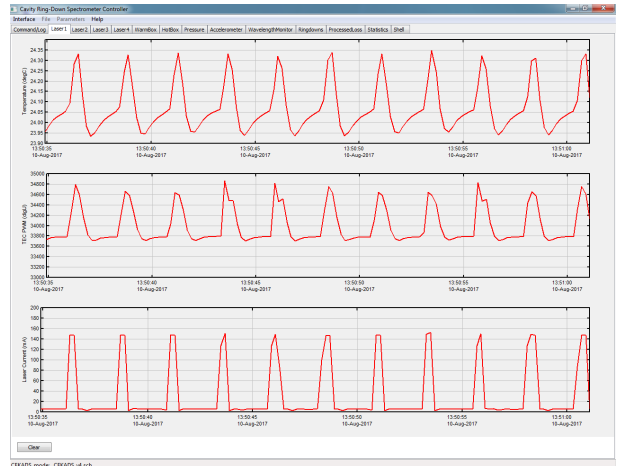
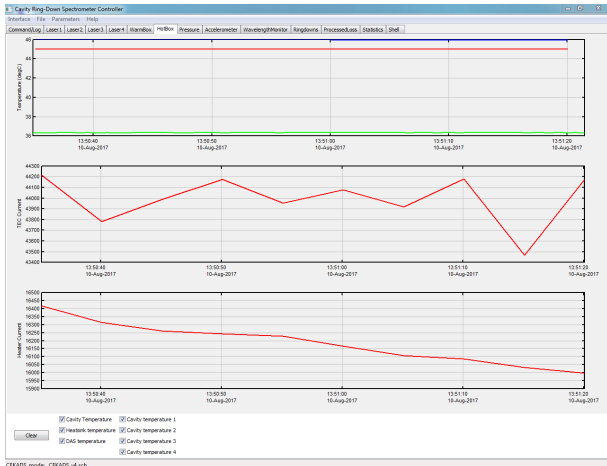
For legibility purposes, the results are split into tables by species.
Only status in bold are taken into account for the final status.

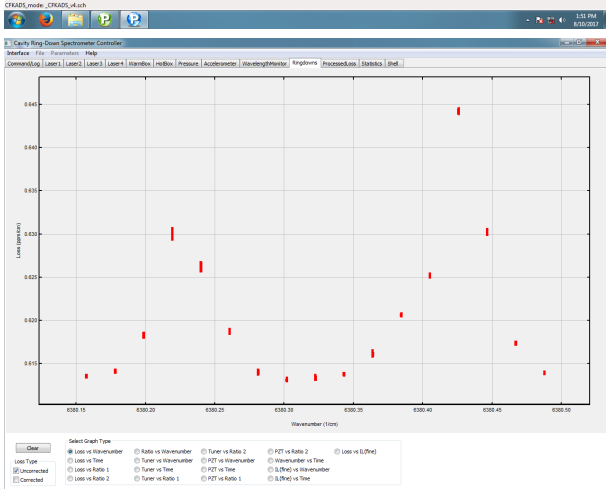
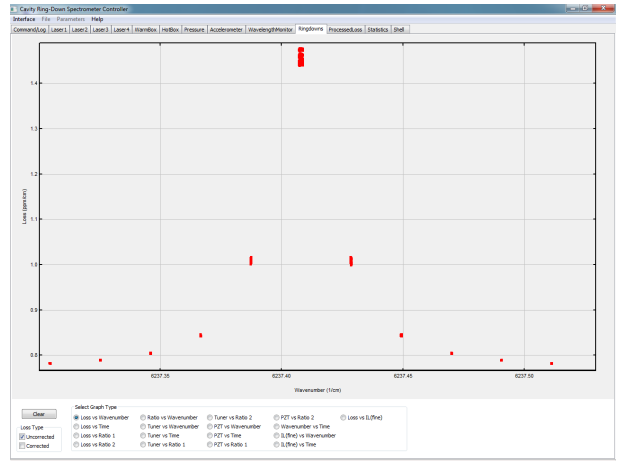
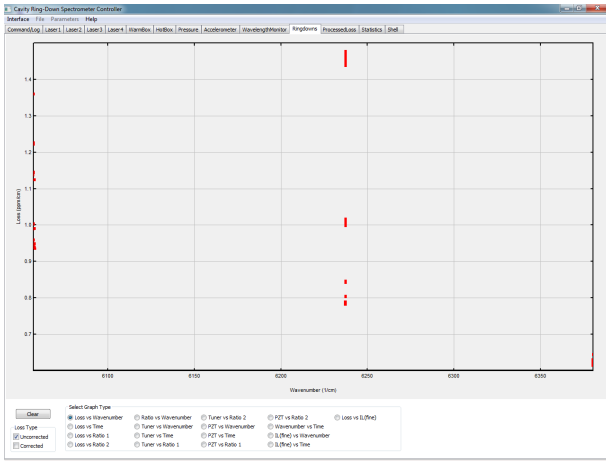
	CO ₂			
	Spec	ATC	Unit	Status
Field CMR (average on min sd)	-	17	ppb	-
Minute CMR (1σ)	<50	6	ppb	Pass
Hourly CMR (1σ)	<25	2	ppb	Pass
Minute CMR MaxDrift (peak to peak)	<200	40	ppb	Pass
Hourly CMR MaxDrift (peak to peak)	<150	12	ppb	Pass
LTR (1σ, 10 min avr raw data)	<50	10	ppb	Pass
LTR MaxDrift (peak to peak)	<200	30	ppb	Pass
STR (1 σ , 9 min avr raw data)	-	8	ppb	-
Atm. pressure sensitivity	-	NS	ppb/hPa	-
Temperature sensitivity	-	NS	ppb/°C	-
Max res from fit in cal range	-	10	ppb	-
Max res from fit in extended range	-	50	ppb	-
Max res from fit in extended range 2	-	0.012	%	-
Calibration drift trend	-	-1.3	ppb/month	-
Water vapor corr: max bias ATC	-	0.01	ppb	-
Water vapor corr: max bias Factory	-	0.19	ppb	-
Water vapor correction I1	-	-1.187e-02	-	-
Water vapor correction I2	-	-2.681e-04	-	-

	CH ₄			
	Spec	ATC	Unit	Status
Field CMR (average on min sd)	-	0.11	ppb	-
Minute CMR (1σ)	<1	0.04	ppb	Pass
Hourly CMR (1σ)	<0.5	0.01	ppb	Pass
Minute CMR MaxDrift (peak to peak)	<2	0.22	ppb	Pass
Hourly CMR MaxDrift (peak to peak)	<1.5	0.06	ppb	Pass
LTR (1σ, 10 min avr raw data)	<0.5	0.05	ppb	Pass
LTR MaxDrift (peak to peak)	<2	0.19	ppb	Pass
STR (1 σ , 9 min avr raw data)	-	0.02	ppb	-
Atm. pressure sensitivity	-	NS	ppb/hPa	-
Temperature sensitivity	-	NS	ppb/°C	-
Max res from fit in cal range	-	0.0	ppb	-
Max res from fit in extended range	-	0.27	ppb	-
Max res from fit in extended range 2	-	0.013	%	-
Calibration drift trend	-	0.0	ppb/month	-
Water vapor corr: max bias ATC	-	0.03	ppb	-
Water vapor corr: max bias Factory	-	2.93	ppb	-
Water vapor correction I1	-	-9.387e-03	-	-
Water vapor correction I2	-	-2.434e-04	-	-

	CO			
	Spec	ATC	Unit	Status
Field CMR (average on min sd)	-	3.27	ppb	-
Minute CMR (1σ)	<2	0.76	ppb	Pass
Hourly CMR (1σ)	<1	0.30	ppb	Pass
Minute CMR MaxDrift (peak to peak)	<15	4.90	ppb	Pass
Hourly CMR MaxDrift (peak to peak)	<2	0.90	ppb	Pass
LTR (1σ, 10 min avr raw data)	<1	0.34	ppb	Pass
LTR MaxDrift (peak to peak)	<3	1.44	ppb	Pass
STR (1 σ , 9 min avr raw data)	-	0.21	ppb	-
Atm. pressure sensitivity	-	NS	ppb/hPa	-
Temperature sensitivity	-	NS	ppb/°C	-
Max res from fit in cal range	-	0.7	ppb	-
Max res from fit in extended range	-	1.47	ppb	-
Max res from fit in extended range 2	-	2.155	%	-
Calibration drift trend	-	-1.1	ppb/month	-
Water vapor corr: max bias ATC	-	0.62	ppb	-
Water vapor corr: max bias Factory	-	6.23	ppb	-
Water vapor correction I1	-	-2.435e-02	-	-
Water vapor correction I2	-	2.296e-03	-	-

15 Screenshots





Picarro CRDS (S/N: 2871-CFKADS2269)

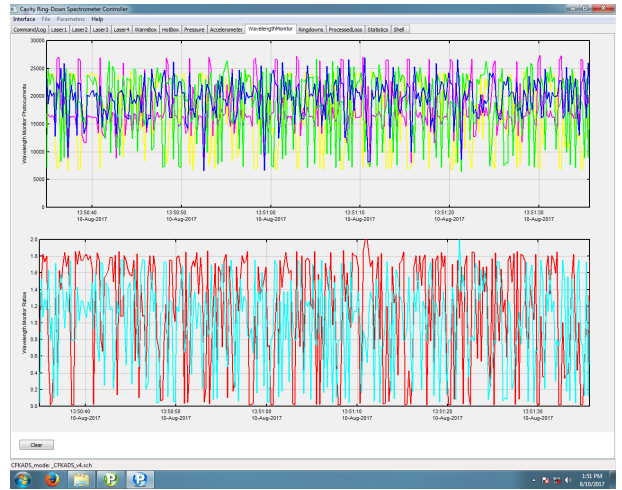
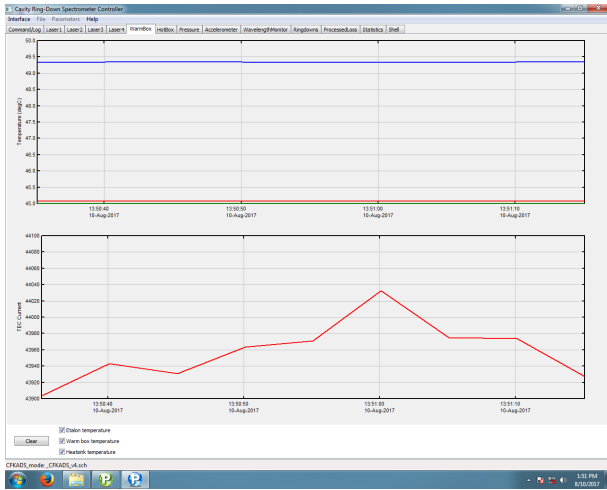
SOFTWARE RELEASE VERSION : g2000-1.6.0.14 (473fd9b)

Web site : www.picarro.com
 Technical support : 408-962-3900
 E-mail : techsupport@picarro.com

(c) 2005-2017, Picarro Inc.

Version strings:
 config - app version no : 1.0.1
 config - common version no : 1.0.9
 config - instr version no : 1.0.0
 interface : 1

OK



Certificate of Compliance

Certificate n°: ATC-ML-IT-CoC-93-1.0_IT_590

Issued to the instrument 590 (PICARRO 2871-CFKADS-2269)

Tested by: C. Philippon from 2017-08-09 to 2017-09-11

Tests	CO ₂			CH ₄			CO			Test definition
	ICOS Spec	ATC test results	Status	ICOS Spec	ATC test results	Status	ICOS Spec	ATC test results	Status	
Minute CMR (1 σ , [ppb])	<50	6	Pass	<1	0.04	Pass	<2	0.76	Pass	Measure continuously a tank filled with dry natural air during at least 25 hours. Look at data dispersion (1 σ) for minute average. First hour not taken into account (stabilization time). No calibration applied.
Hourly CMR (1 σ , [ppb])	<25	2	Pass	<0.5	0.01	Pass	<1	0.30	Pass	Measure continuously a tank filled with dry natural air during at least 25 hours. Look at data dispersion (1 σ) for hourly average. First hour not taken into account (stabilization time). No calibration applied.
LTR (1 σ , 10 min avr raw data, [ppb])	<50	10	Pass	<0.5	0.05	Pass	<1	0.34	Pass	Measure alternatively over 72 hours a tank filled with dry natural air for 30 minutes and 270 minutes of ambient air (not dry). For each period of tank measurement, calculate a mean value (last 10 minutes). Look at the dispersion (1 σ) of the mean values. No calibration applied.

ICOS status: COMPLIANT with the ICOS specifications

Date issued: 2017-09-18



Olivier Laurent
Metrology laboratory manager
ICOS ATC
France