

Document reference: ATC-ML-TW-RP-18

**ICOS ATC Metrology Laboratory
Evaluation report
for the LICOR LI-7810 instrument**

Tests by L. Lienhardt
Approved by O. Laurent
Date: 2020-06-10

Document history

Version	Date	Actions
1.0	2020-06-10	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	Initialization Time	5
3	Warm restart	6
4	Cold restart	7
5	Continuous Measurement Repeatability (CMR) assessment	8
6	Short term stability and drift assessment	9
7	Short Term Repeatability (STR) assessment	10
8	Long Term Repeatability (LTR) assessment	11
8.1	First period	11
8.2	Second period	12
8.3	Third period	13
8.4	Fourth period	14
8.5	Fifth period	15
8.6	Sixth period	16
8.7	Over all Long Term Repeatability	17
9	Atmospheric pressure sensitivity	18
10	Inlet pressure sensitivity	19
11	Temperature sensitivity	21
12	Water vapor correction assessment	22
12.1	Factory correction	22
12.2	Determination of H ₂ O correction coefficients by the MLab	23
12.3	MLab correction	24
13	Calibration	25
14	Linearity	27
15	Rise Time and Fall Time	28
16	Laboratory inter-comparison	30
16.1	Without drying system	30
16.1.1	First period	30
16.1.2	Second period	33
16.1.3	Third period	36
16.1.4	Fourth period	39
16.1.5	Over all Laboratory inter-comparison	42
16.2	With drying system	45
16.2.1	First period	45
16.2.2	Second period	47
17	Summary	48

1 Instrument references

Owner	Reception Date	Departure date
LICOR	2019-09-23	2019-12-10

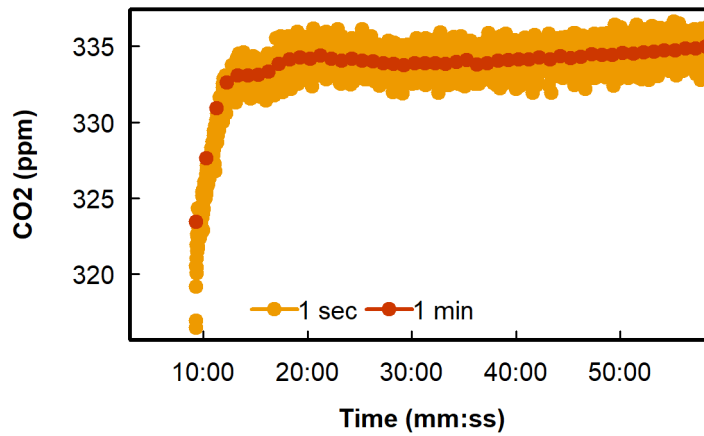
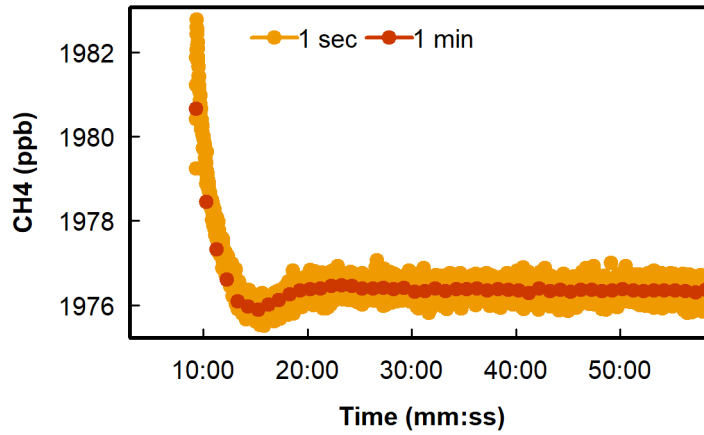
Brand	Model	S/N	Software release version
LICOR	LI-7810	TG10-01102	

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-1.3	2017-11
AD3	Incoming control sheet	ATC-ML-IT-IC-04	
AD4	Follow-up sheet	ATC-ML-IT-FS-09	2019-12-02

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 Initialization Time

Methodology: Measure continuously a tank filled with dry natural air after 1 hour of shutdown. No calibration applied. No rejected data. Target gas measured right after turning the instrument on.

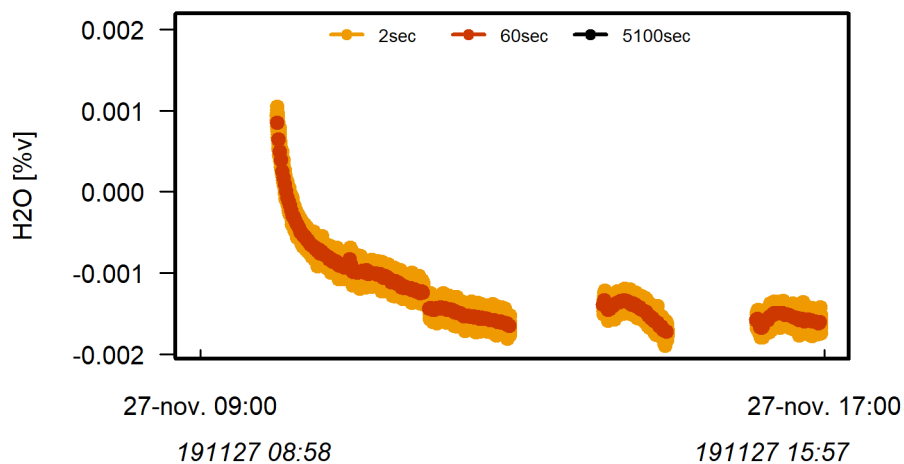
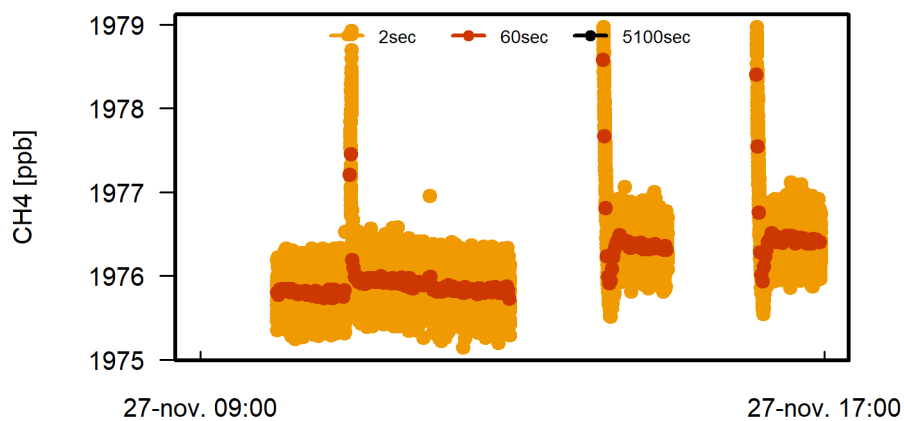
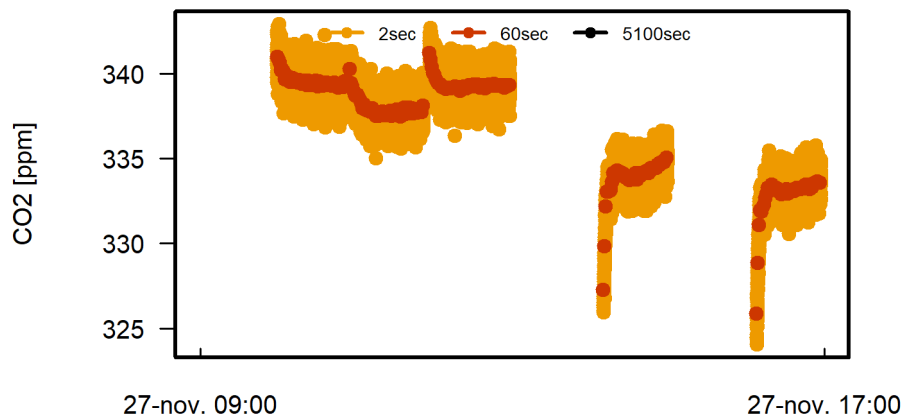


	CO2 (min)	CH4 (min)
Initialization time	20	20

3 Warm restart

Methodology: Measure continuously a tank filled with dry natural air after several restart. No calibration applied. No rejected data. Target gas measured right after turning the instrument on.

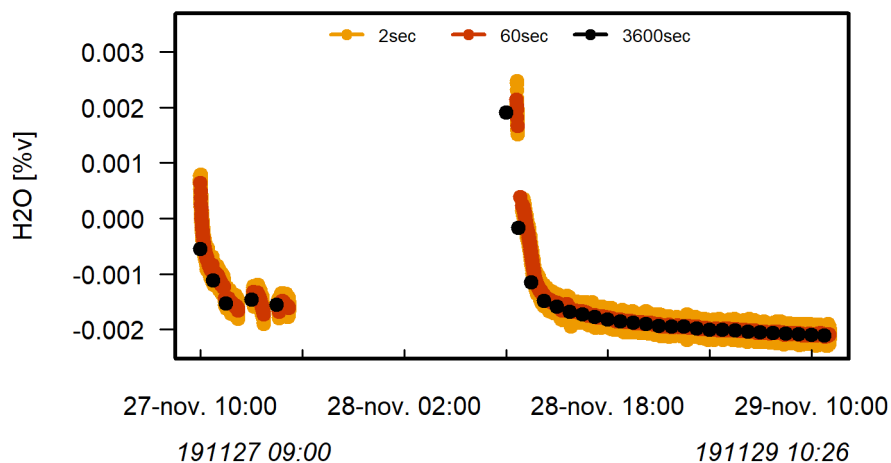
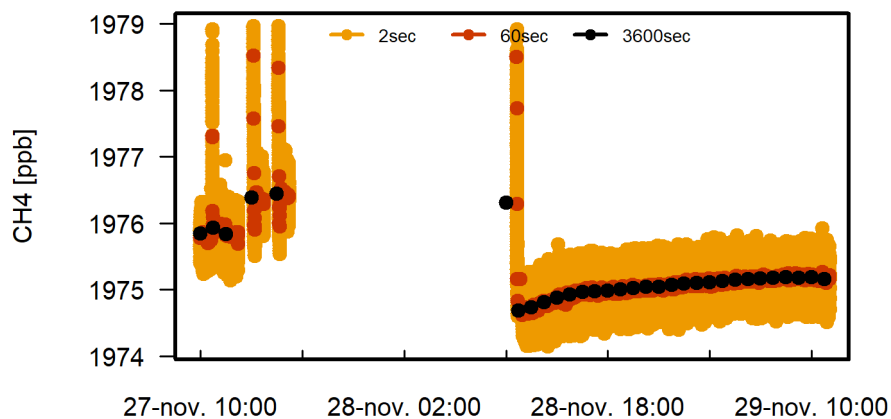
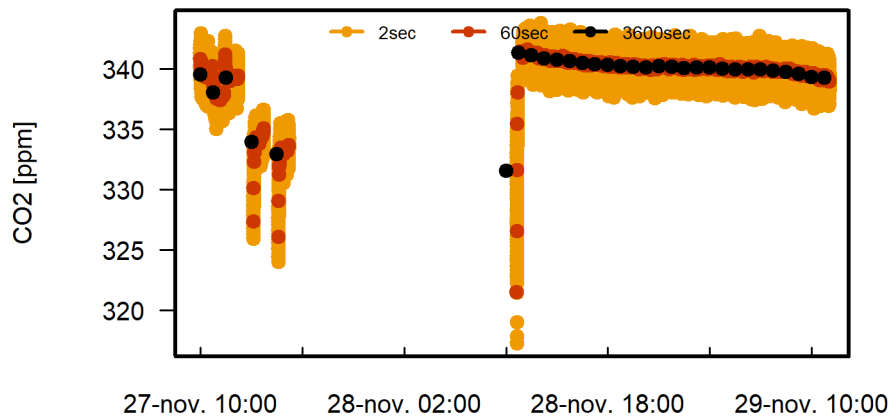
1 minute off then 1 hour on (3 times) ; 1 hour off then 1 hour on (2 times)



	CO2 [ppb]	CH4 [ppb]
Maximum offset between two successive restarts	6300	0.5

4 Cold restart

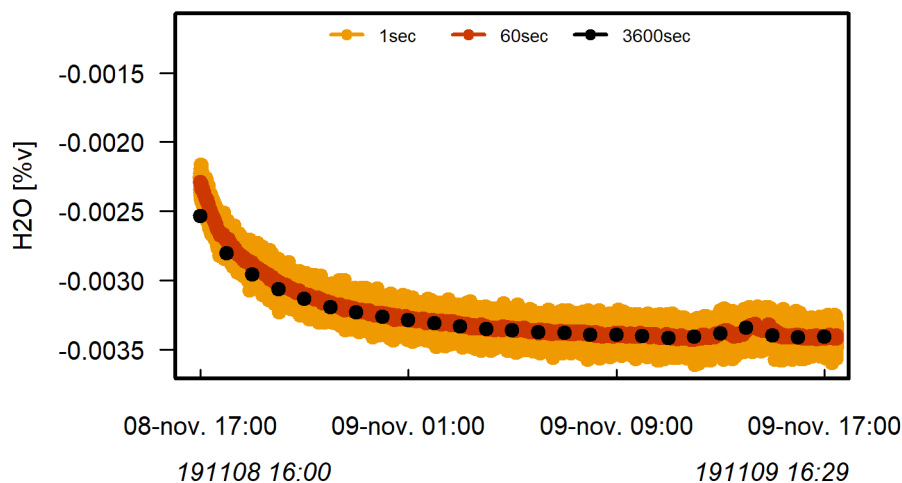
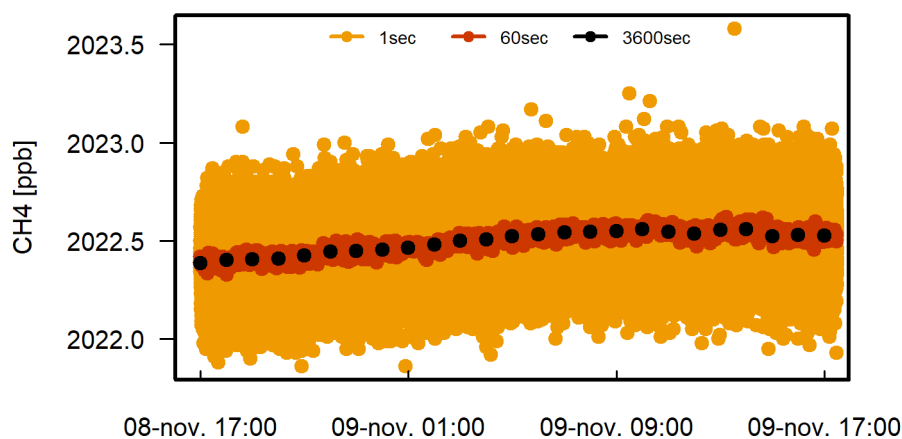
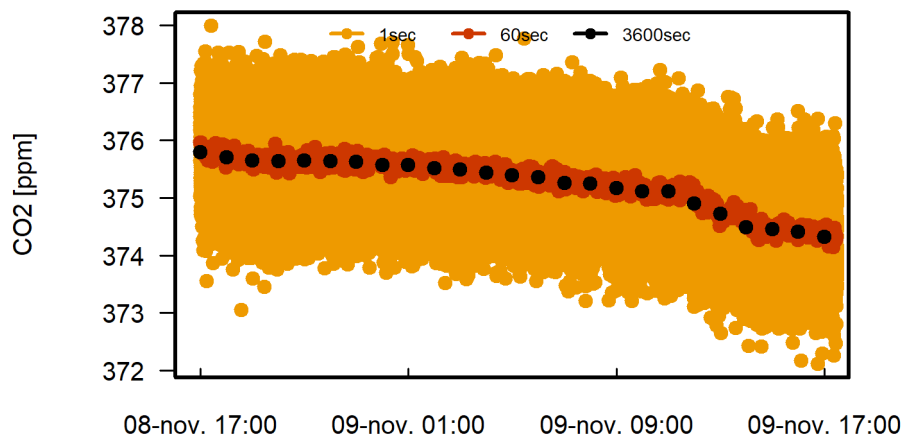
Methodology: Measure continuously a tank filled with dry natural air after 15 hours of shutdown. No calibration applied. No rejected data. Target gas measured right after turning the instrument on.



	CO2 [ppb]	CH4 [ppb]
Maximum offset between two successive restarts	7300	1.7

5 Continuous Measurement Repeatability (CMR) assessment

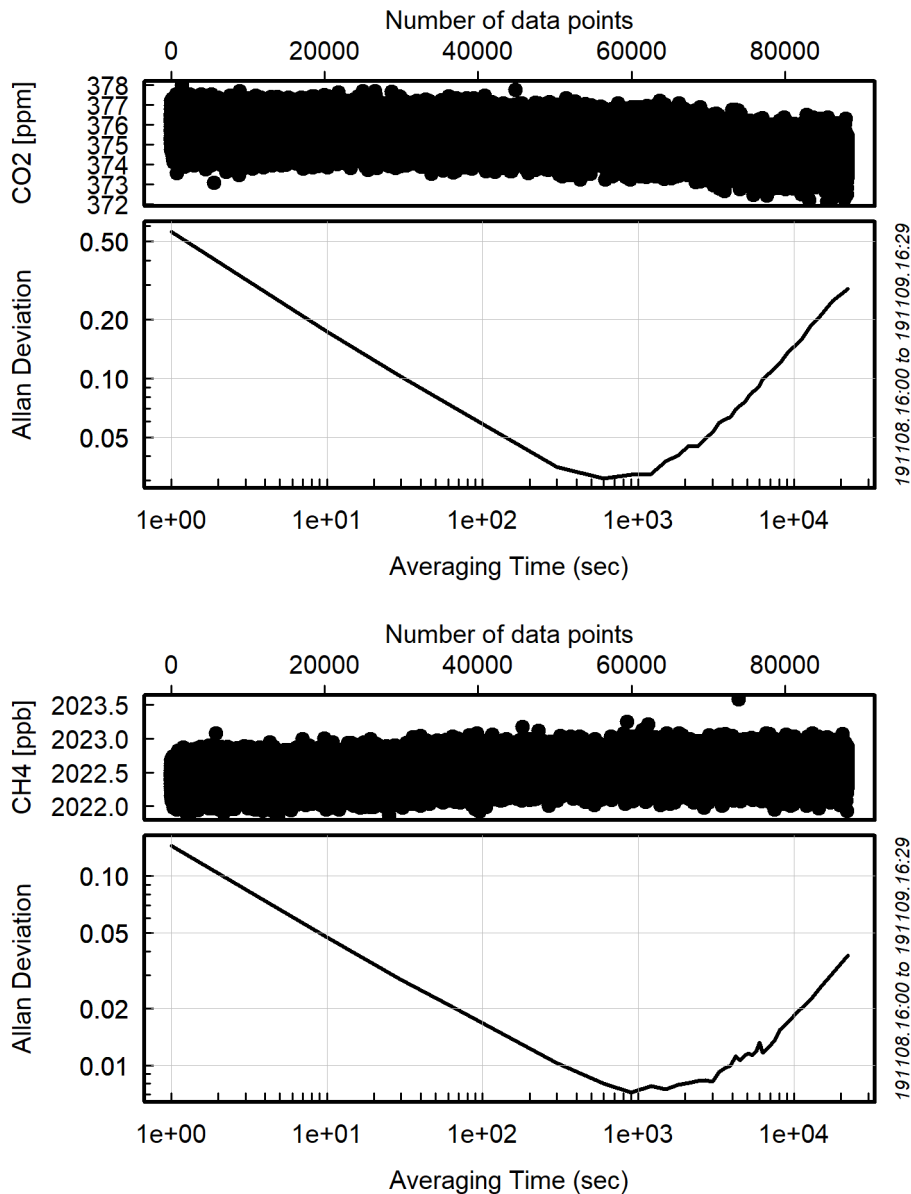
Methodology: Measure continuously a tank filled with dry natural air during at least 25 hours. Look at data distribution for different integration times. First hour not taken into account (stabilization time). No calibration applied.



	CO2 [ppb]	CH4 [ppb]	H2O [%v]
Average of the standard deviations of raw data over a minute	556	0.14	0.0000
Minute averaged data CMR Precision (1σ)	433	0.06	0.0002
Hourly averaged data CMR Precision (1σ)	451	0.06	0.0002
Minute averaged data CMR MaxDrift (peak to peak)	1817	0.30	0.0011
Hourly averaged data CMR MaxDrift (peak to peak)	1469	0.17	0.0009

6 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.

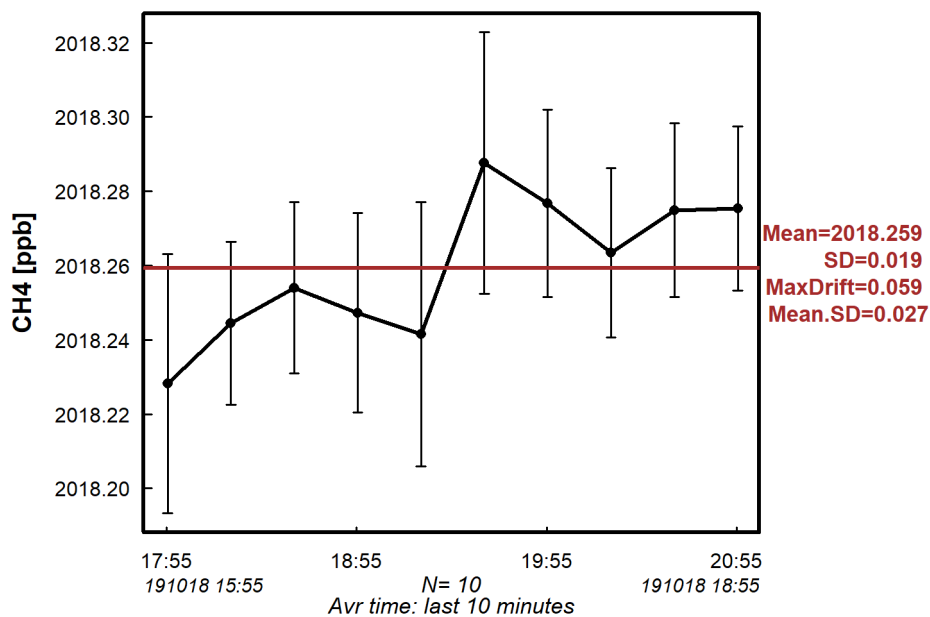
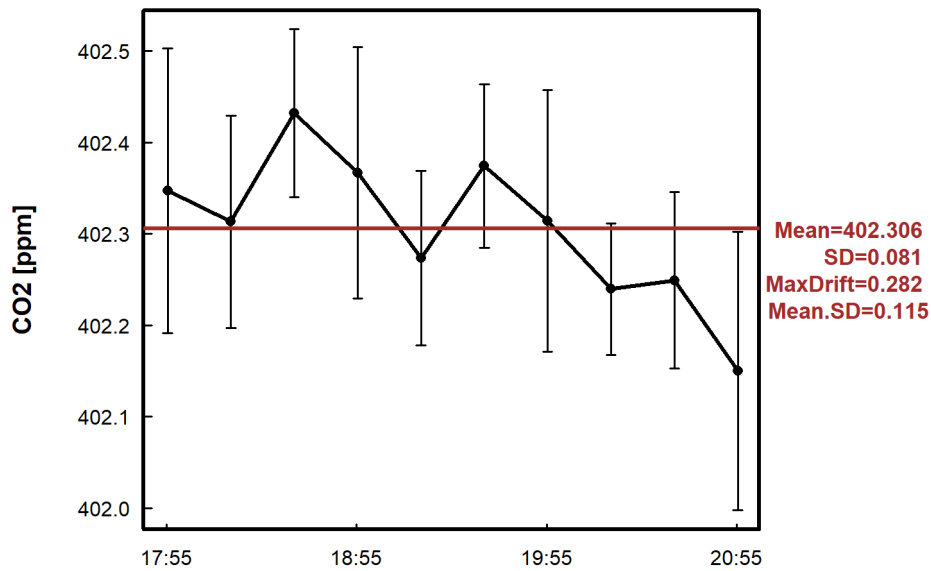


	CO2	CH4
Optimum Averaging time (s)*	600	900
Optimum Allan deviation [ppb]*	31	0.01
Allan deviation at 1 min [ppb]	74	0.02
Allan deviation at 5 min [ppb]	35	0.01
Allan deviation at 10 min [ppb]	31	0.01
Allan deviation at 15 min [ppb]	32	0.01
Allan Deviation at 1 hr [ppb]	62	0.01

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

7 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.

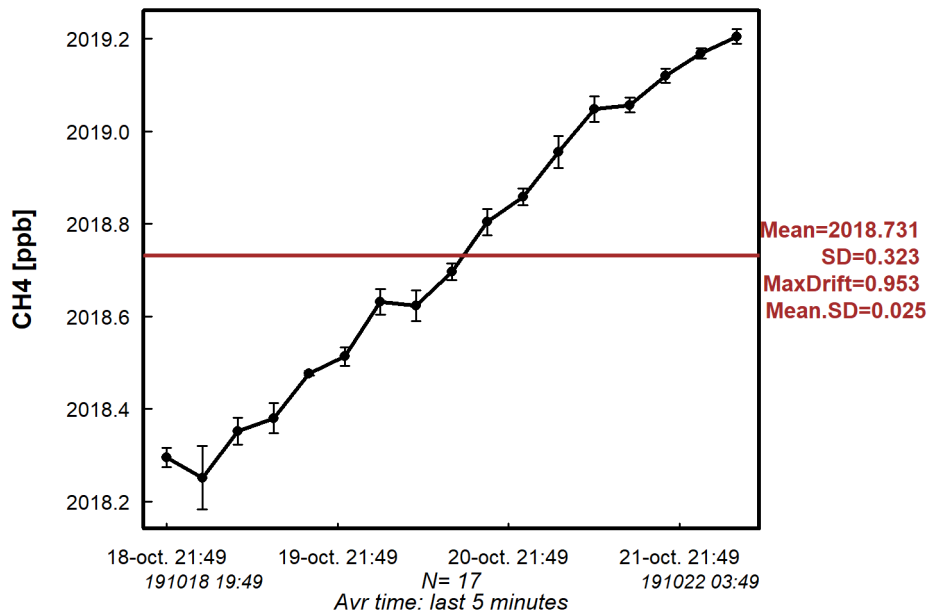
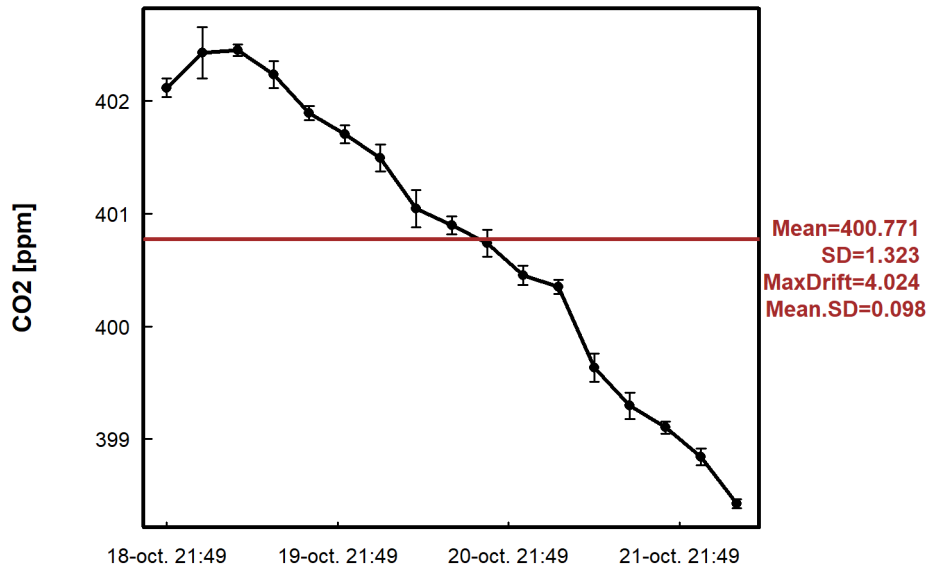


	CO2 [ppb]	CH4 [ppb]
Short term repeatability (1σ , 9 minute average raw data)	81	0.02
MaxDrift (peak to peak, 9 minute average raw data)	282	0.06

8 Long Term Repeatability (LTR) assessment

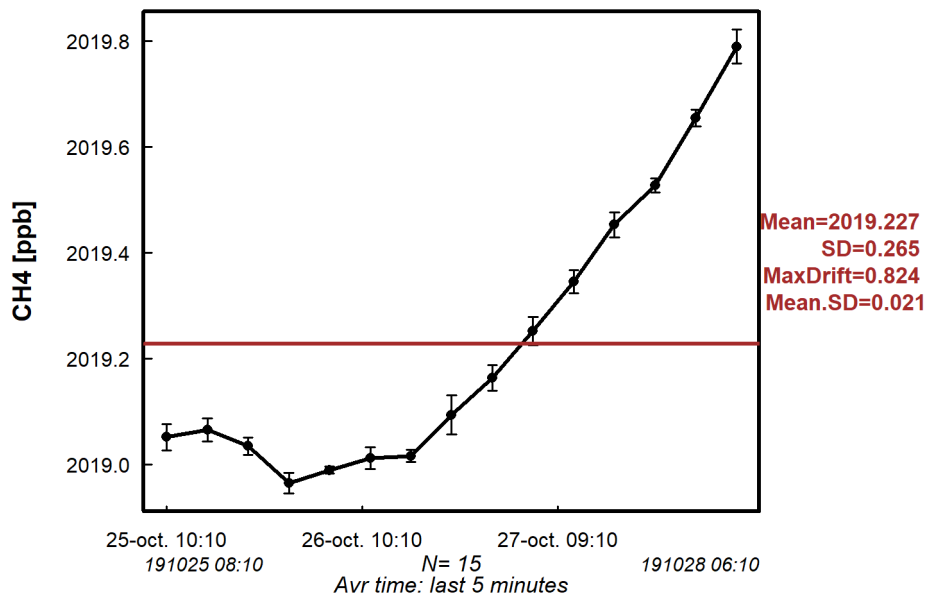
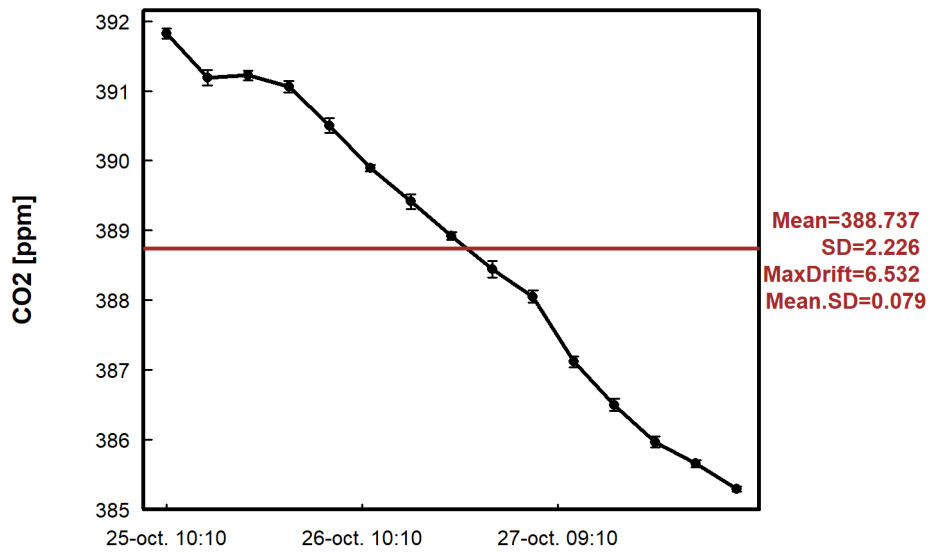
Methodology: Measure alternatively over 72 hours a tank filled with dry natural air for 30 minutes and 270 minutes of wet ambient air. For each period of tank measurement, calculate a mean value (discard the first minutes for stabilization). Look at the dispersion (1σ) of the mean values. No calibration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

8.1 First period



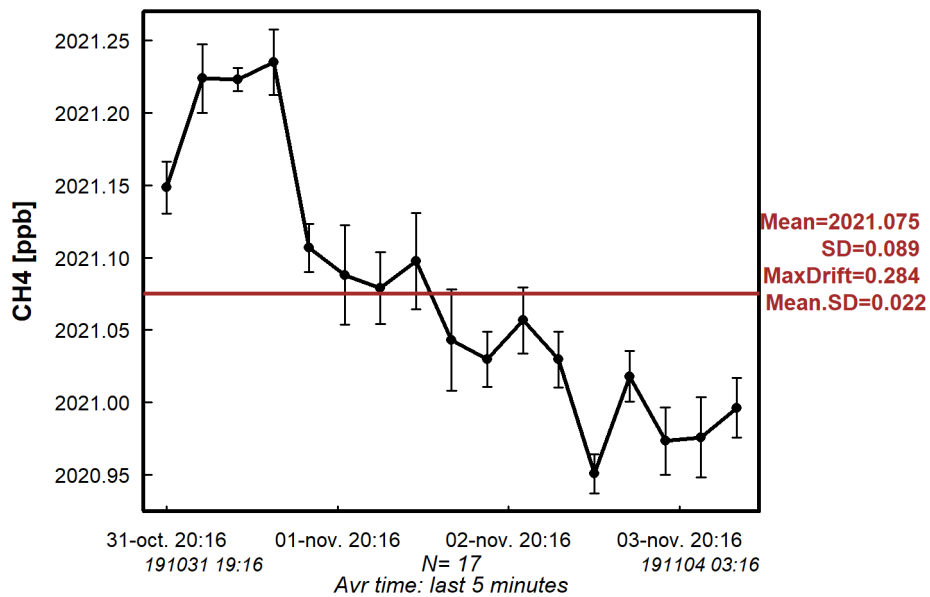
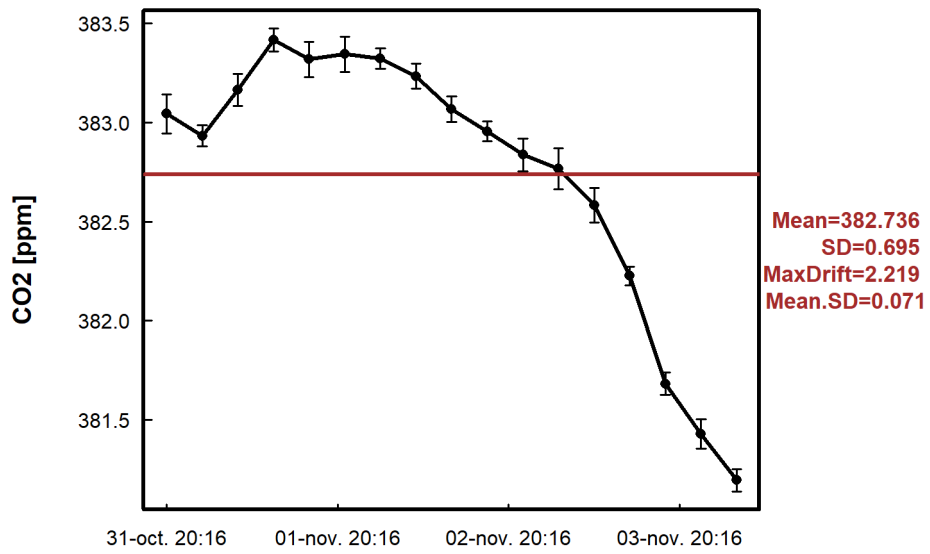
	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	1323	0.32
MaxDrift (peak to peak, 10 minute average raw data)	4024	0.95

8.2 Second period



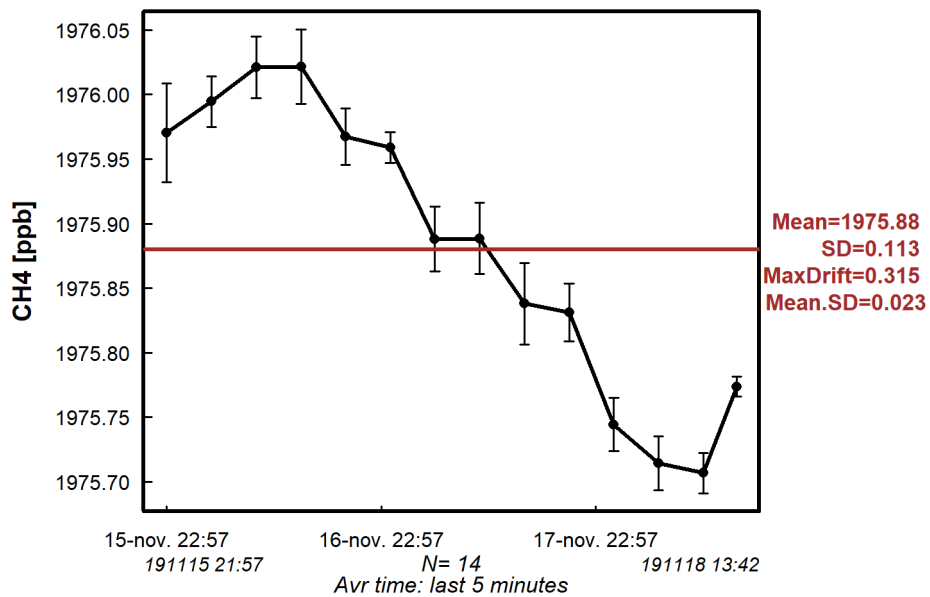
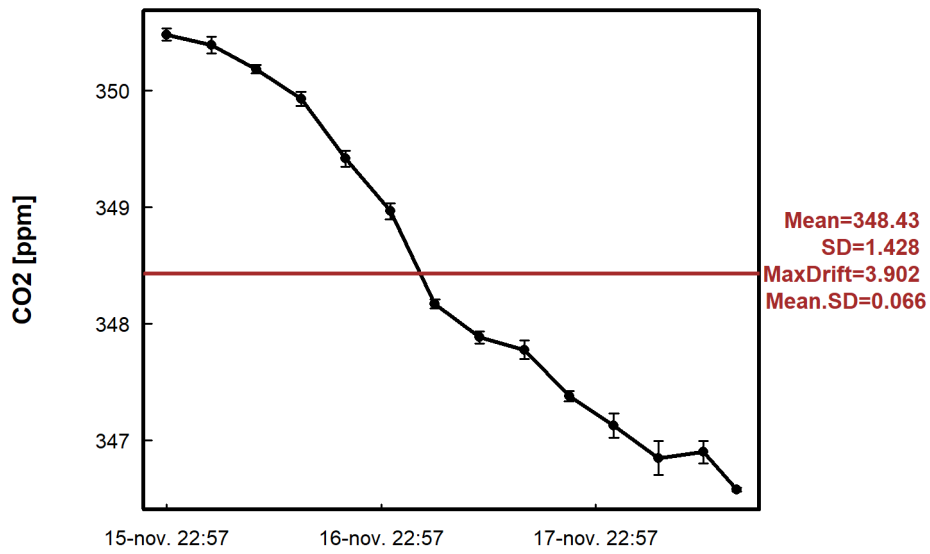
	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	2226	0.26
MaxDrift (peak to peak, 10 minute average raw data)	6532	0.82

8.3 Third period



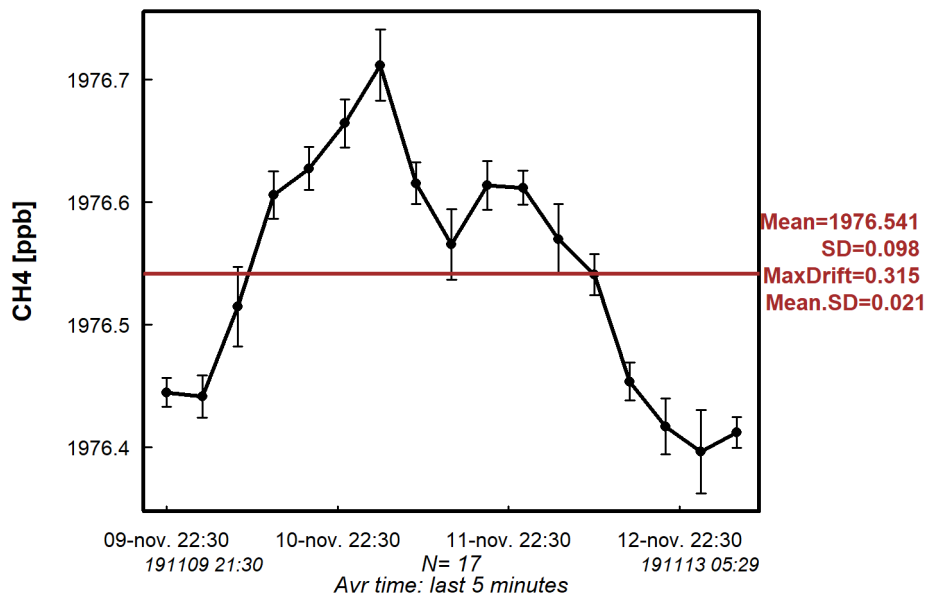
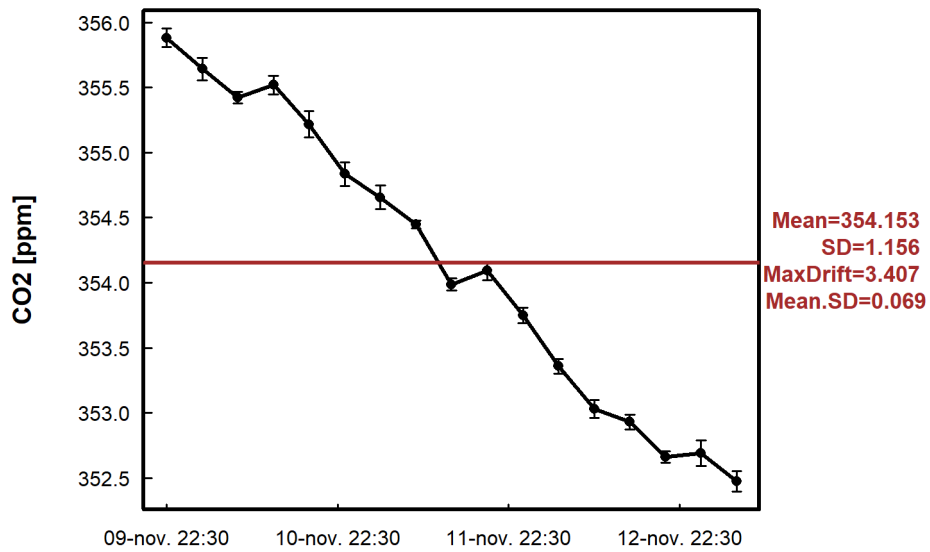
	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	695	0.09
MaxDrift (peak to peak, 10 minute average raw data)	2219	0.28

8.4 Fourth period



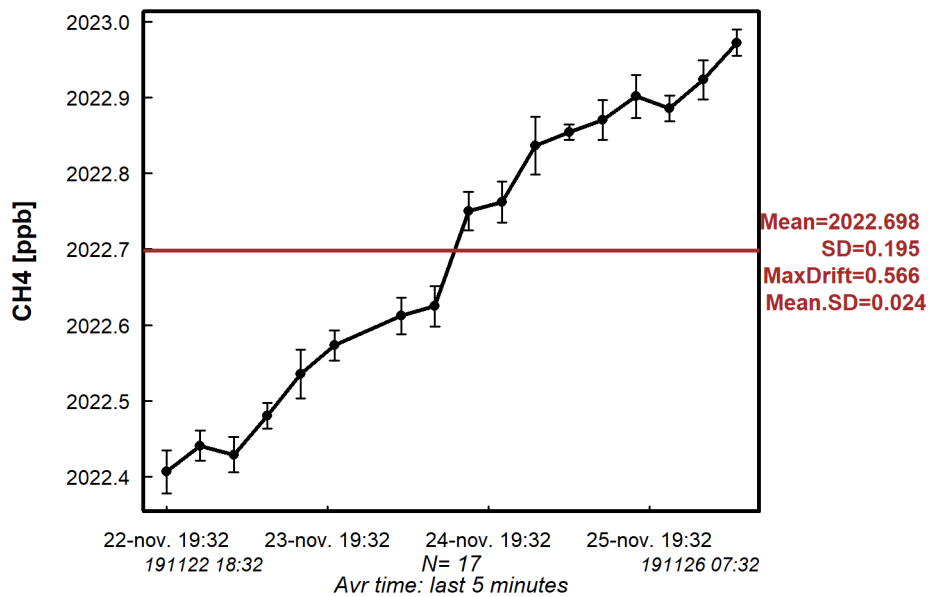
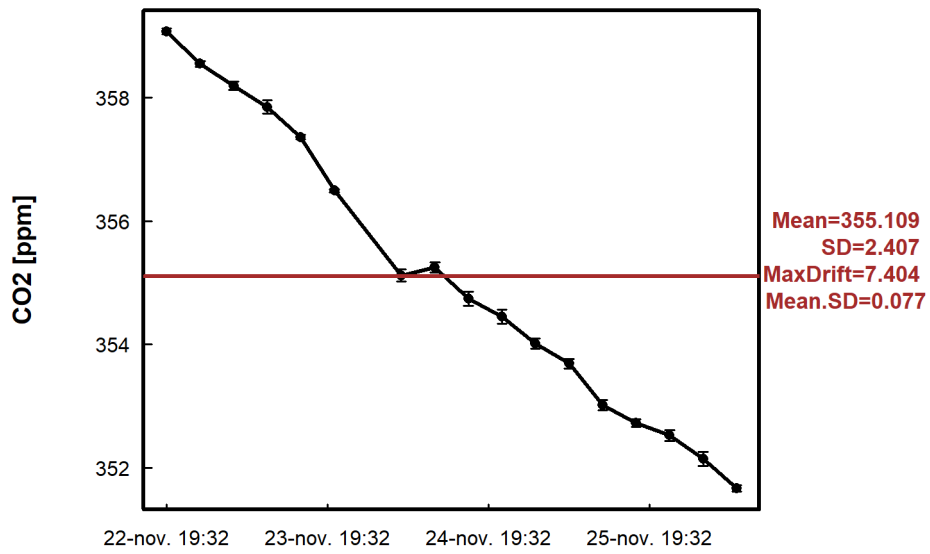
	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	1428	0.11
MaxDrift (peak to peak, 10 minute average raw data)	3902	0.32

8.5 Fifth period



	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	1156	0.10
MaxDrift (peak to peak, 10 minute average raw data)	3407	0.32

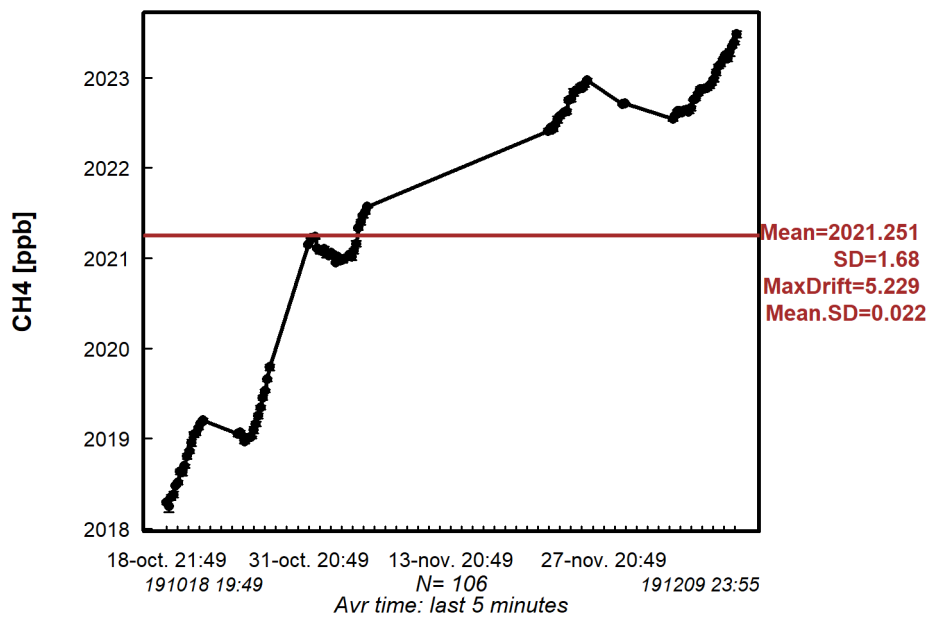
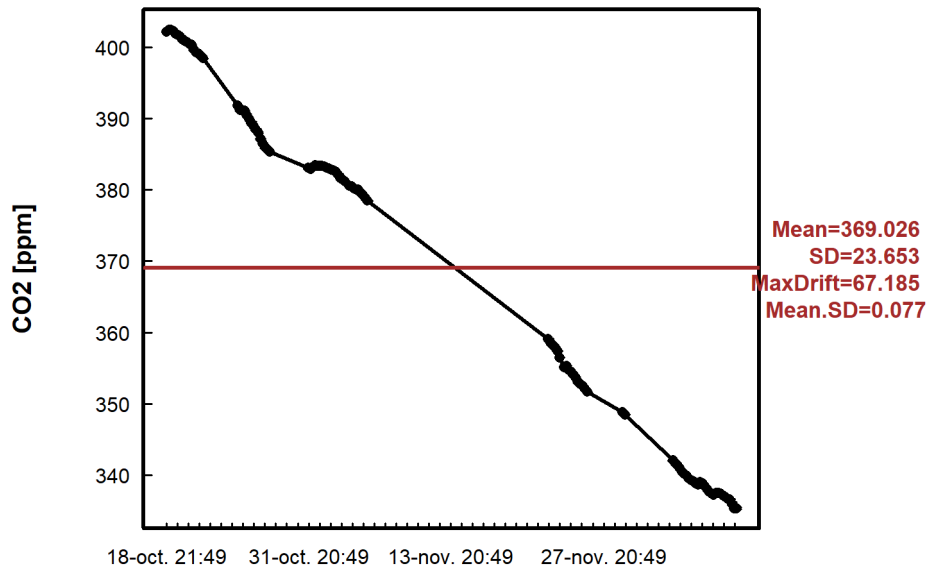
8.6 Sixth period



	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	2407	0.20
MaxDrift (peak to peak, 10 minute average raw data)	7404	0.57

8.7 Over all Long Term Repeatability

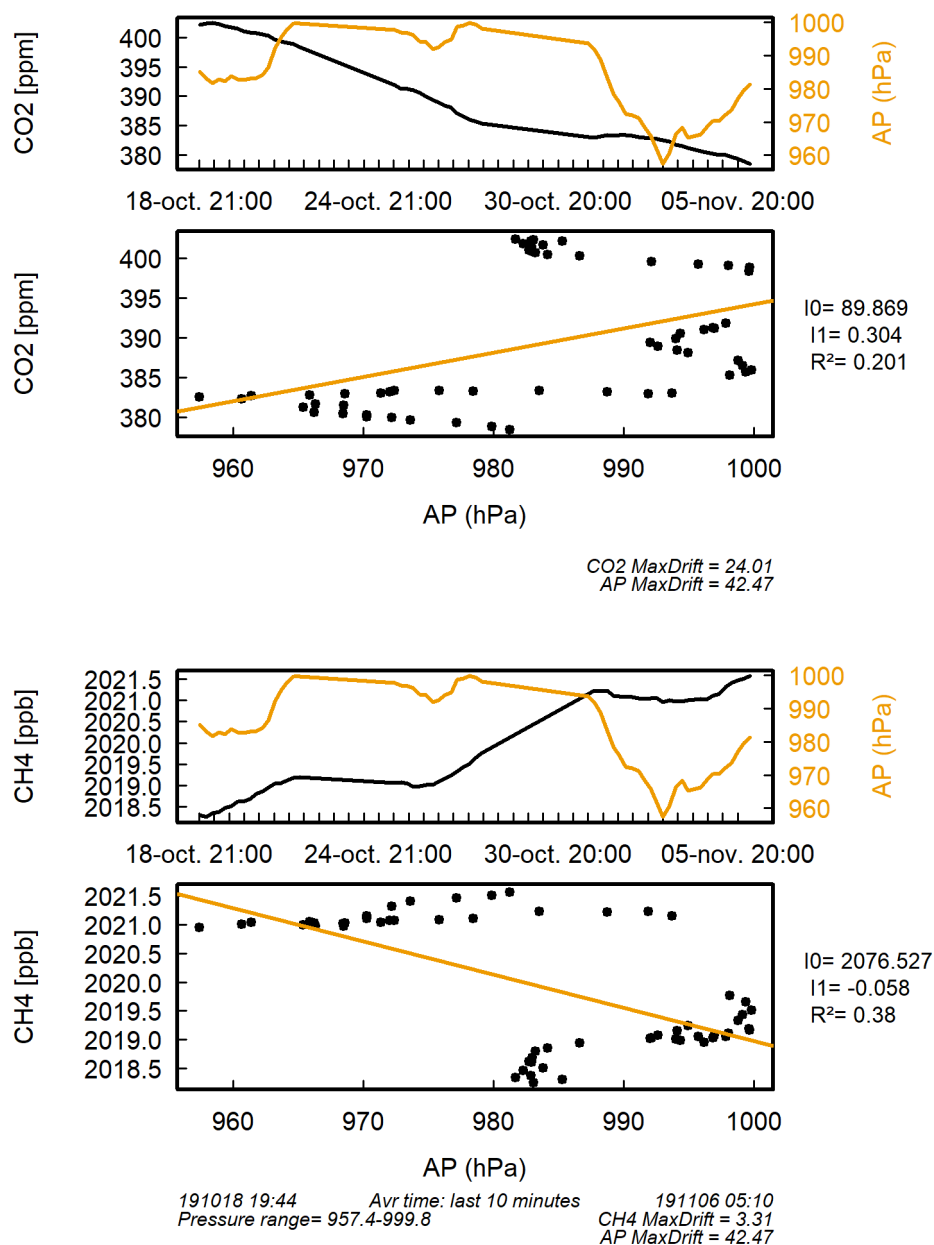
Restarts performed from November 27th to 28th



	CO2 [ppb]	CH4 [ppb]
Long term repeatability (1σ , 10 minute average raw data)	23653	1.68
MaxDrift (peak to peak, 10 minute average raw data)	67185	5.23

9 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.

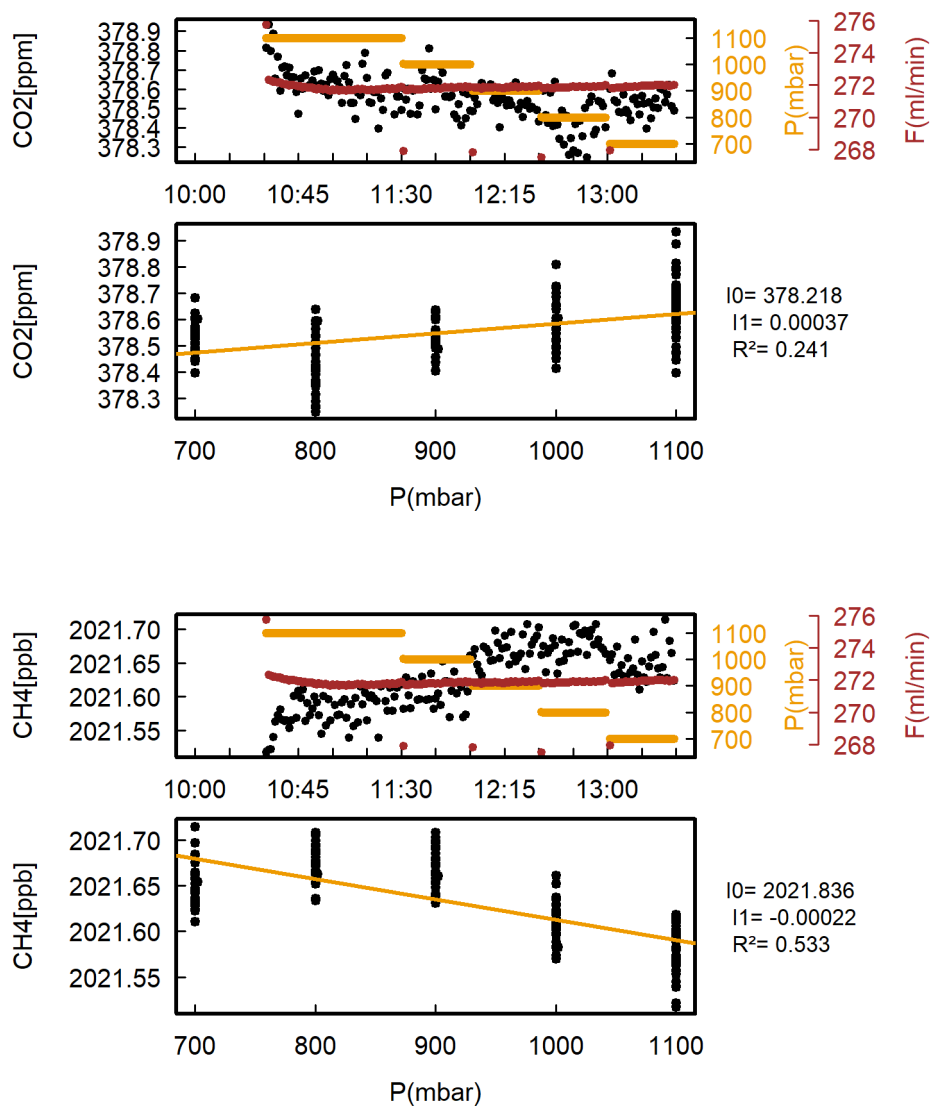


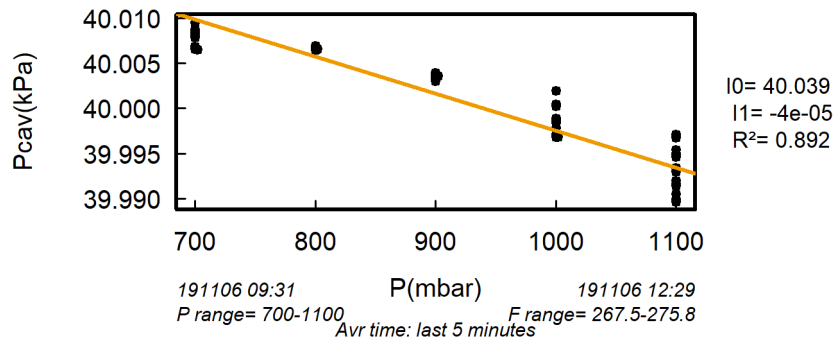
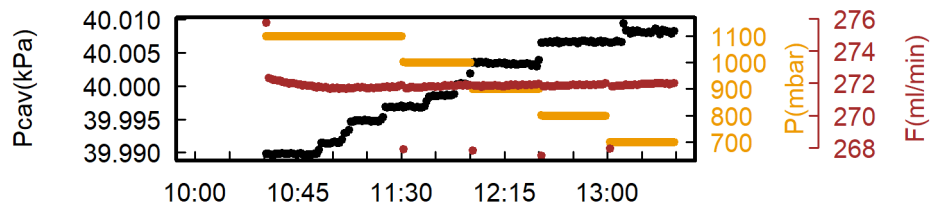
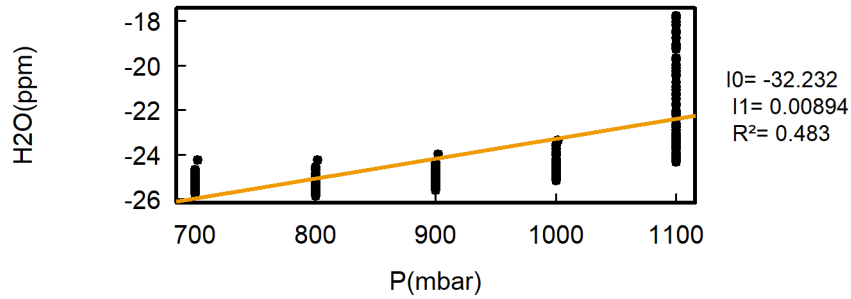
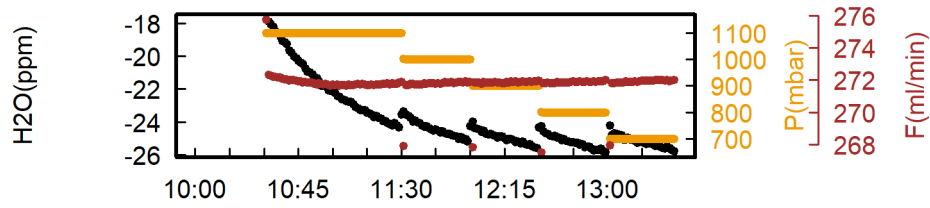
	CO ₂	CH ₄
Atmospheric pressure sensitivity (ppb/hPa)	NS	NS

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

10 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 20 minutes) the instrument inlet pressure (maximum range from 1200 mbar absolute to 600 mbar absolute) thanks to the pressure controller. The valid range is evaluated as the range where CO₂ mixing ratios are pm 0.02ppm from the mixing ratio at atmospheric pressure..



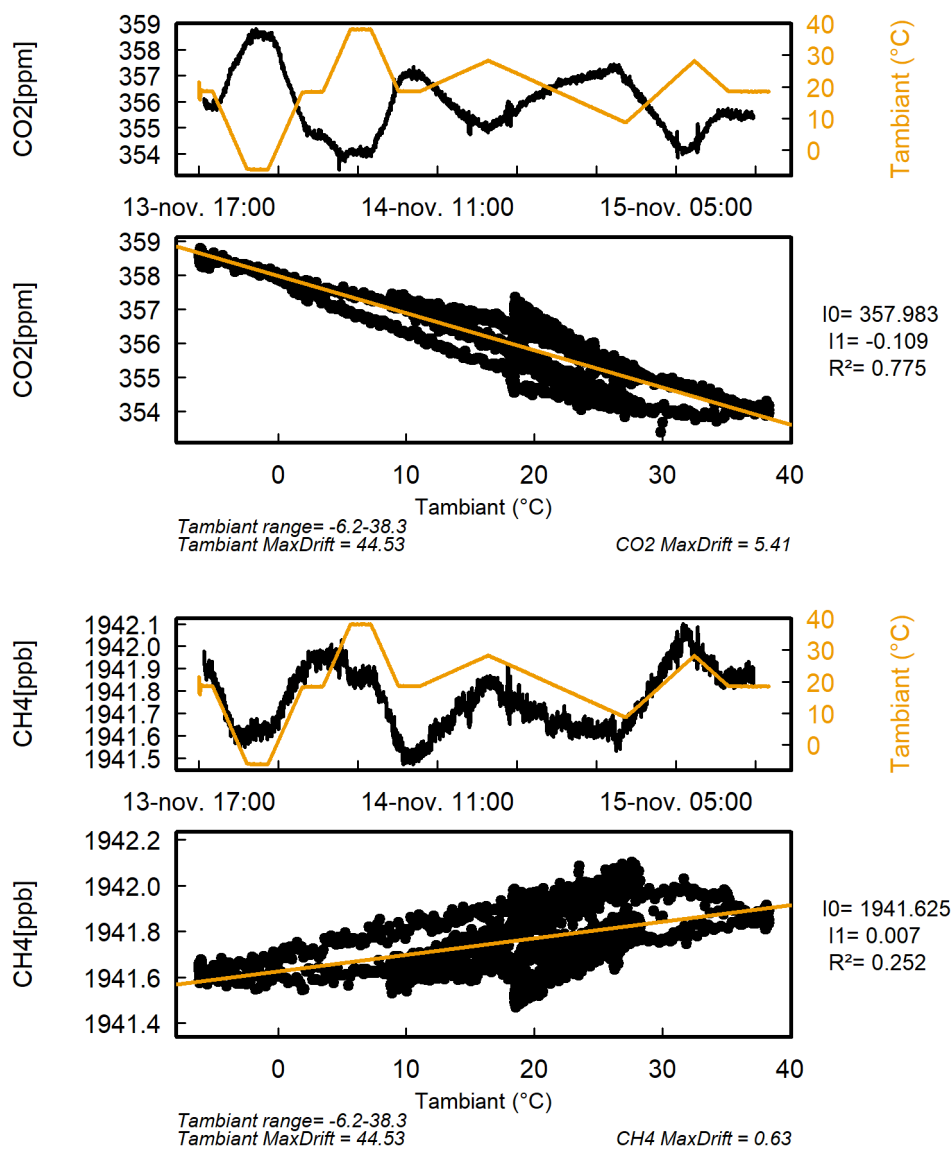


	Min	Max
Valid inlet pressure range (mbar absolute)	700	1100

11 Temperature sensitivity

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

Drift of the CH₄ measurement corrected using the target value at 20 °C at the beginning and end of the test



	CO ₂	CH ₄
Ambient temperature sensitivity (ppb/°C)	-109.241	NS

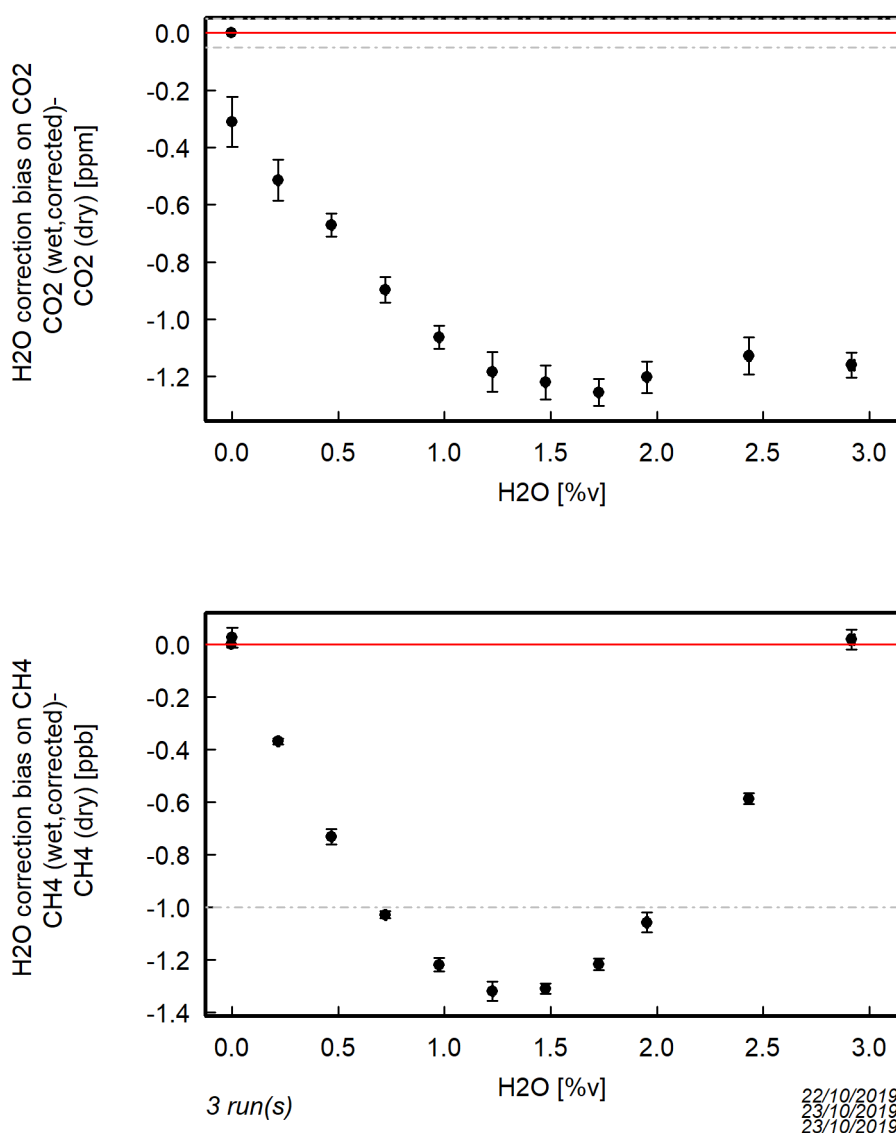
Not significant (NS) if $R^2 < 0.45$ or the absolute value of the slope lower than 5 and 0.1 ppb/°C for CO₂ and CH₄ respectively

12 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.

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

12.1 Factory correction

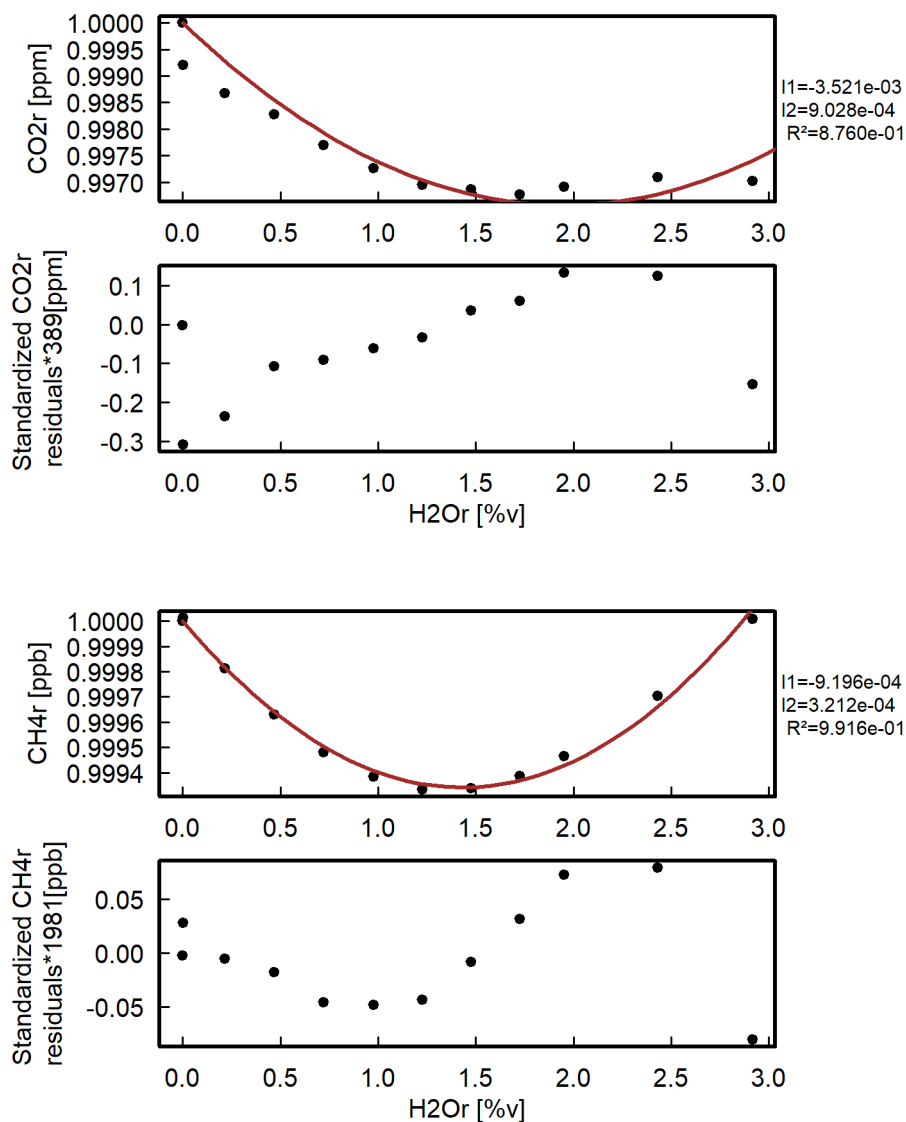


12.2 Determination of H₂O correction coefficients by the MLab

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

with H₂O_r: Instrument reported value (not calibrated). The “calibrated” H₂O value is:

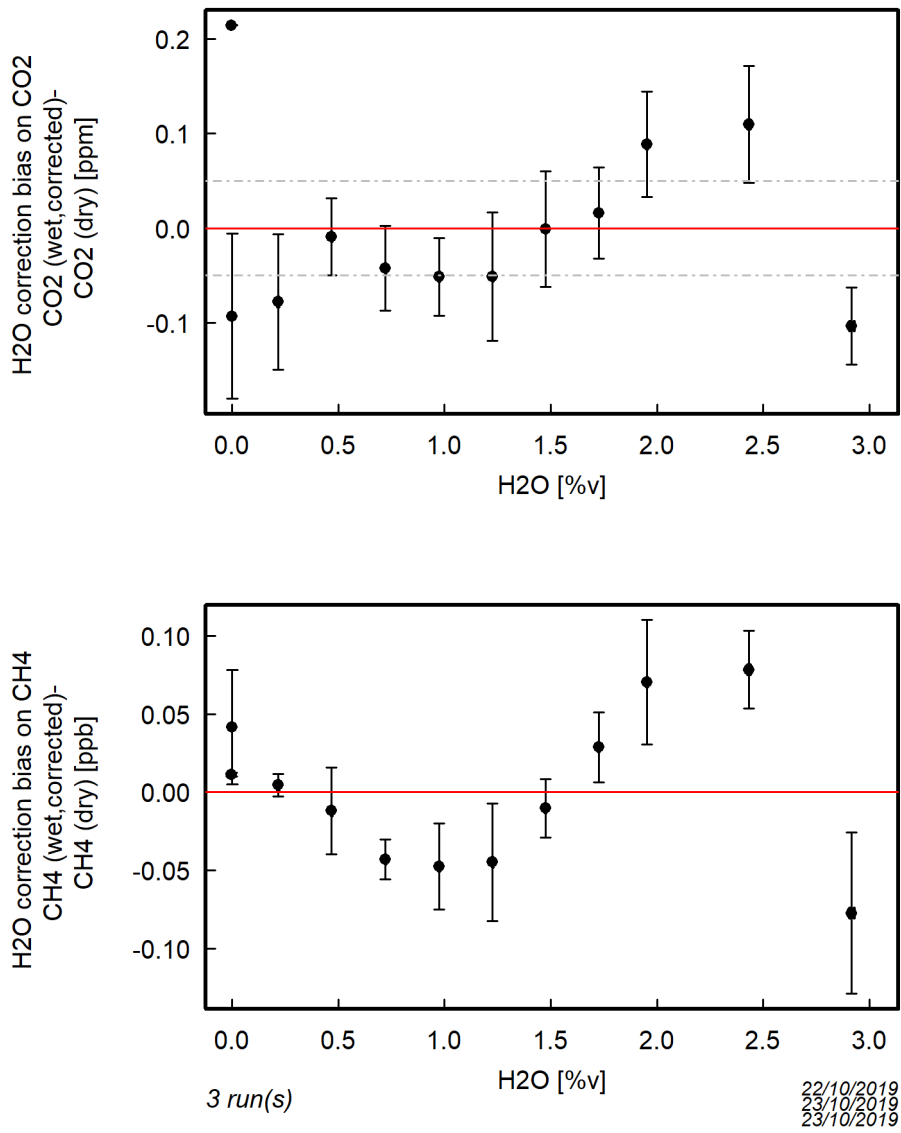
$$H_2O = 0.772 * H_2O_r + 0.019493 * H_2O_r^2 \quad (3)$$



H₂O correction coefficients determined by ATC

	CO ₂	CH ₄
I1	-3.521e-03	-9.196e-04
I2	9.028e-04	3.212e-04

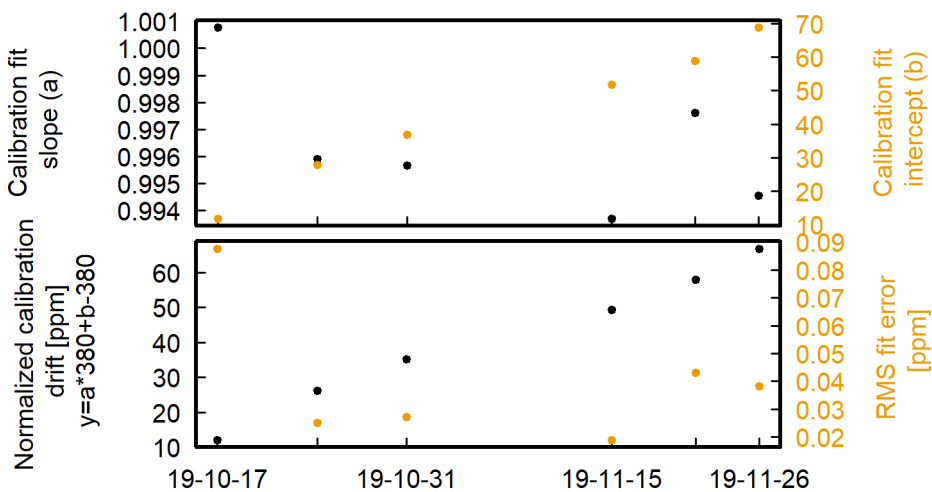
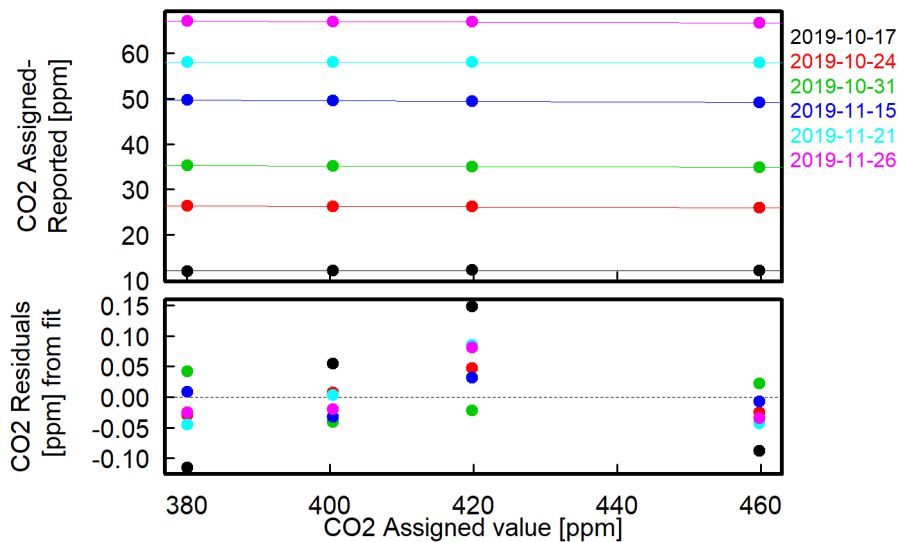
12.3 MLab correction



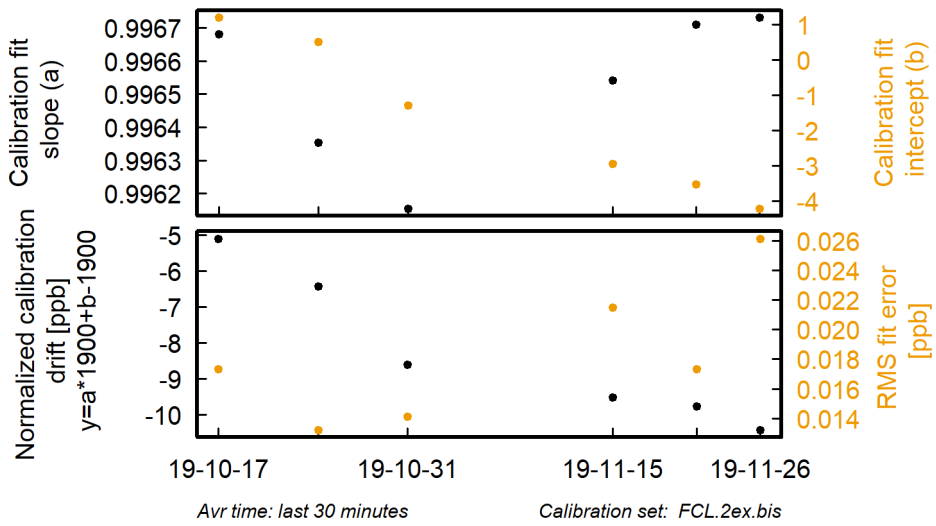
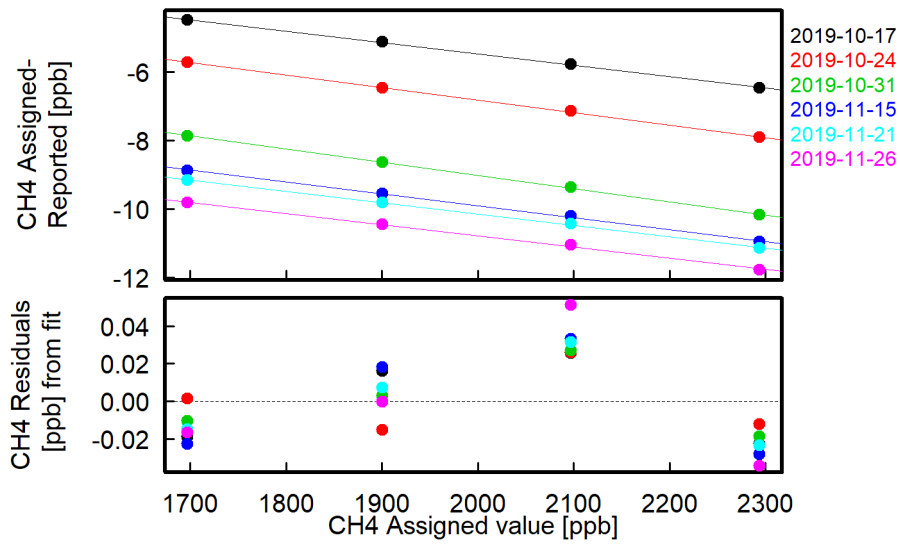
13 Calibration

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



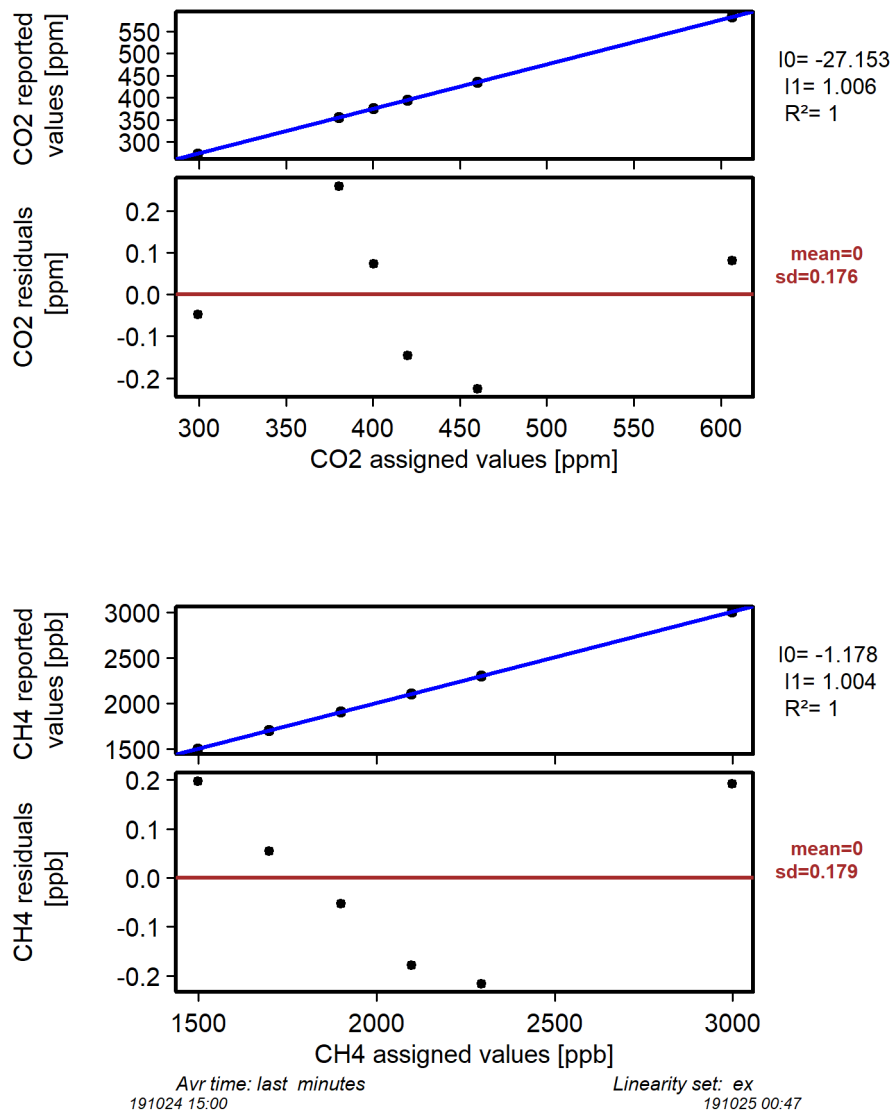
CH4



	CO2	CH4
Calibration drift trend (ppb/month)	37919.1	-3.7
Maximum residual from linear fit on calibration range [ppb]	148	0.1

14 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.



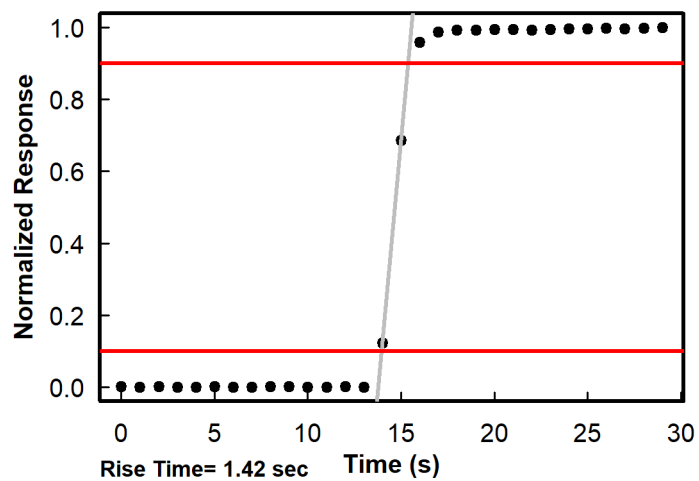
	CO ₂	CH ₄
Maximum residual from linear fit on extended mole fraction range [ppb]	261	0.22
Maximum residual from linear fit on extended mole fraction range [%]	0.069	0.009

15 Rise Time and Fall Time

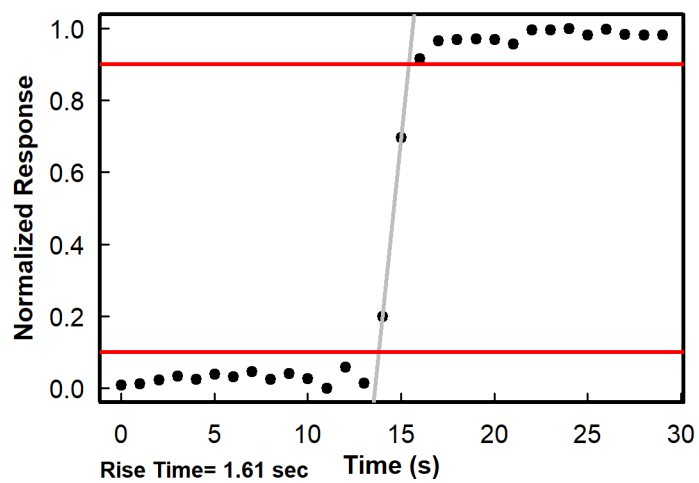
Methodology: Measure the rise time and fall time between two different tanks during a calibration.

Rise time : Time taken for the response to rise from 10% to 90% of its final normalized value

LI-7810: CH4 Rise Time

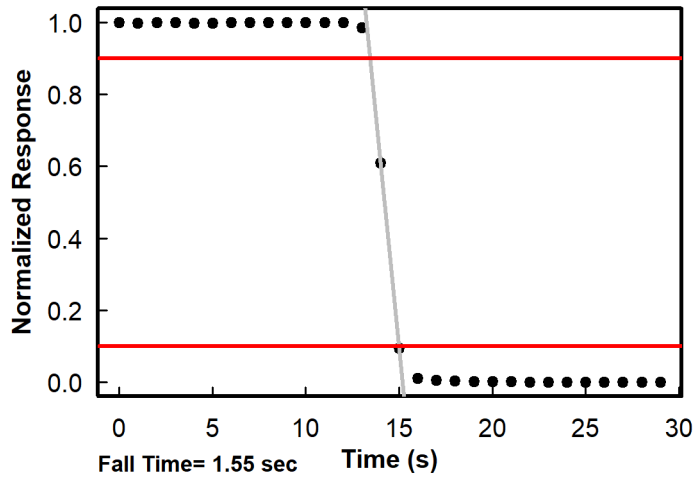


LI-7810: CO2 Rise Time

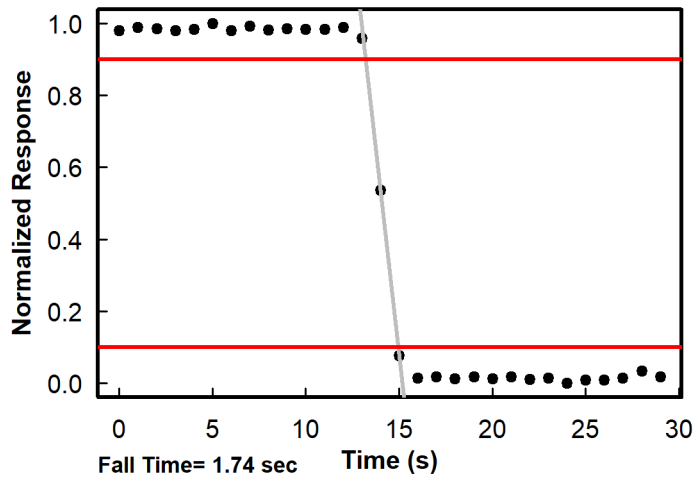


Fall time : Time taken for the response to fall from 90% to 10% of its final normalized value

LI-7810: CH4 Fall Time



LI-7810: CO2 Fall Time



	CO2 (sec)	CH4 (sec)
Rise time	<2	<2
Fall time	<2	<2

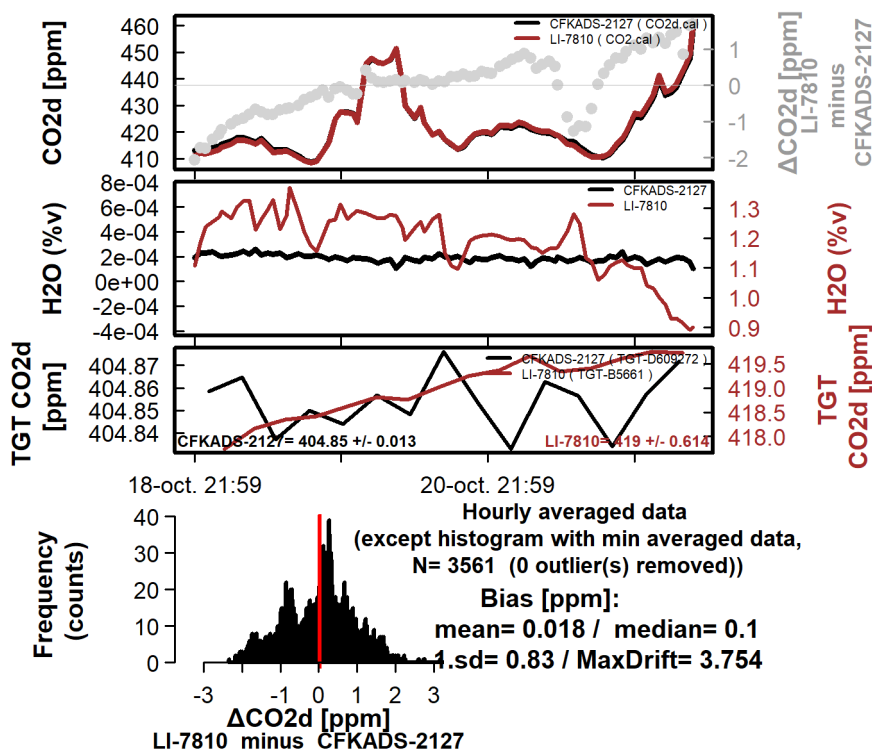
16 Laboratory inter-comparison

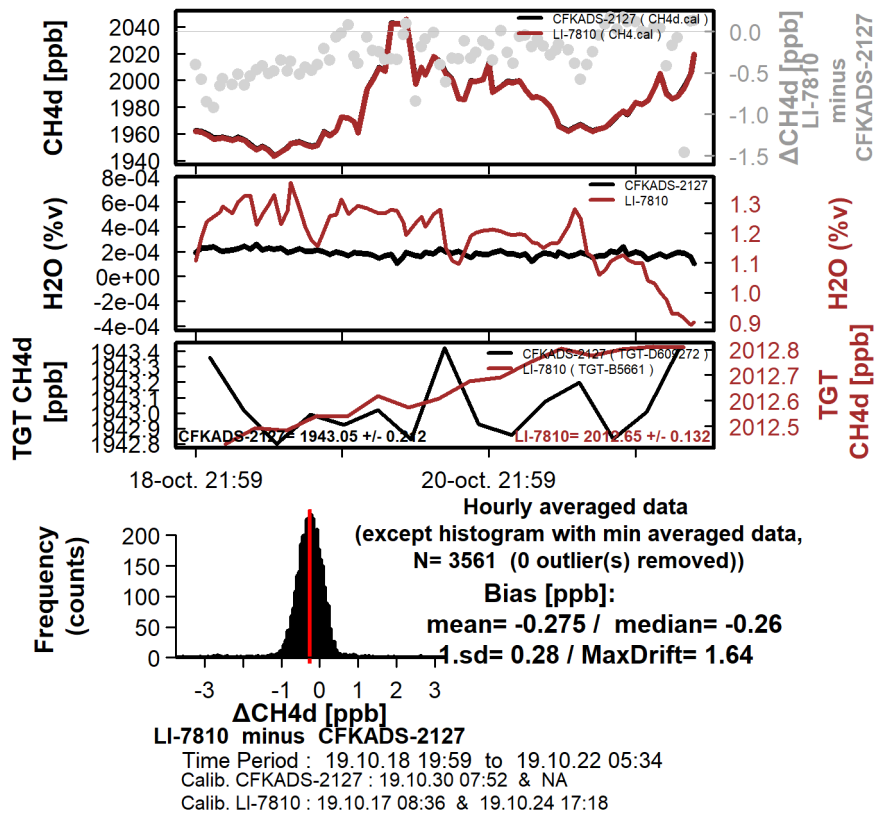
16.1 Without drying system

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.

16.1.1 First period

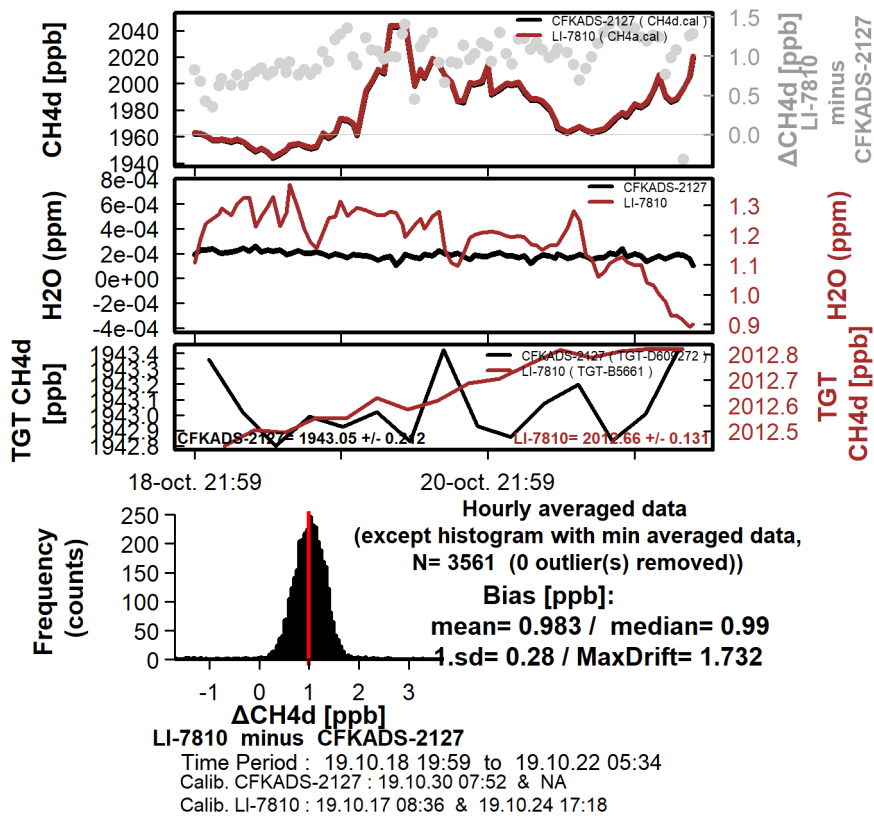
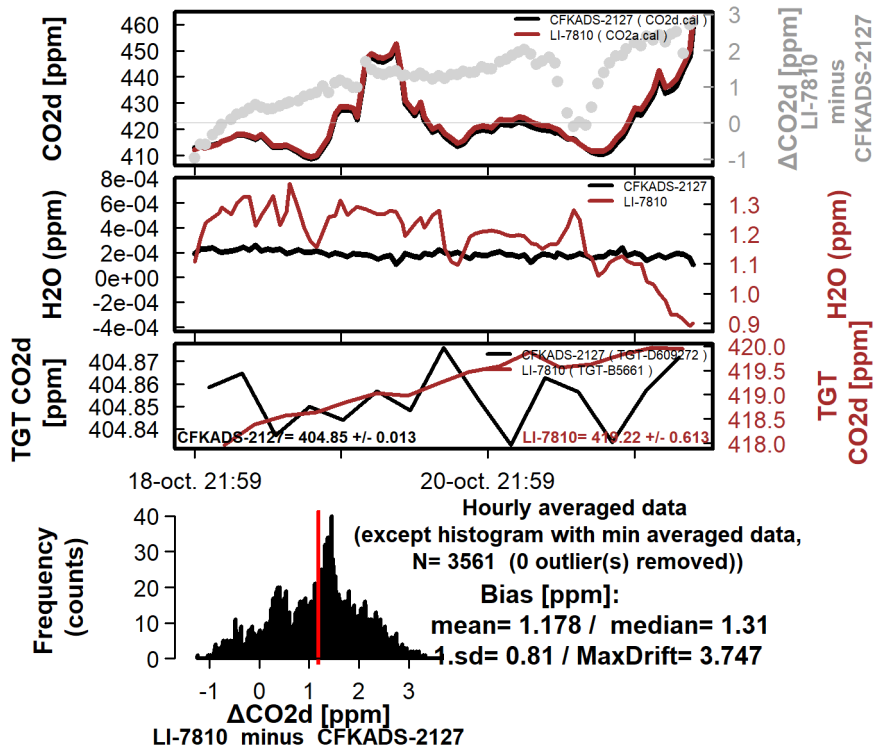
16.1.1.1 Factory water vapor correction





	CO2 [ppb]	CH4 [ppb]
Observed bias in ambient air:		
mean difference (LI-7810 - Ref Instrument)	18	-0.28
H ₂ O correction bias estimated by ATC		
for the mean H ₂ O during the test (11910 ppm H ₂ O)	-1184	-1.32
Remaining bias (not related to H ₂ O correction)	1202	1.05

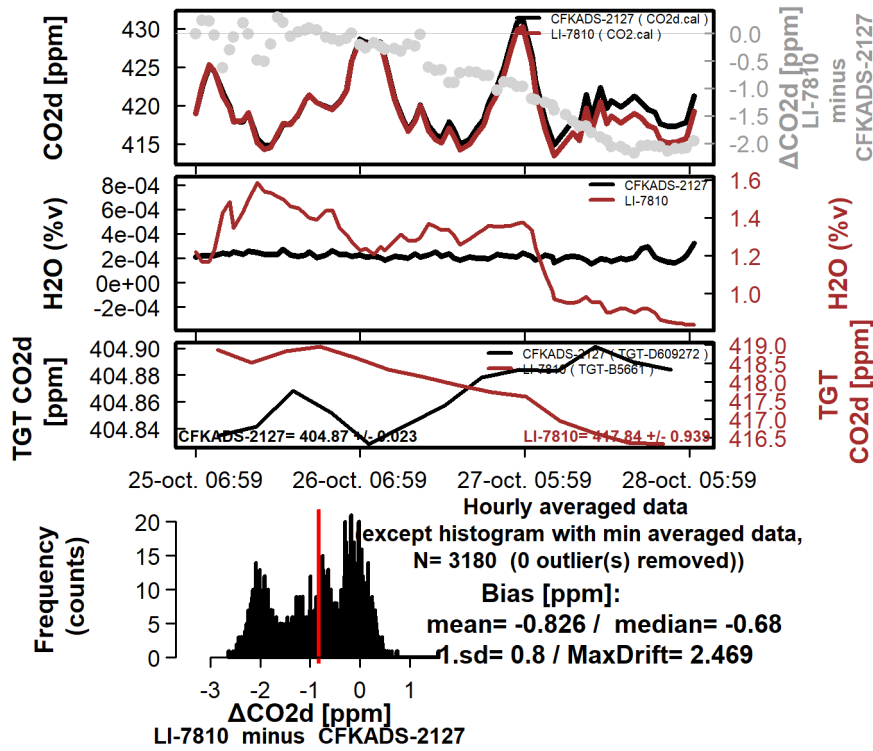
16.1.1.2 Water vapor correction coefficients determined by ATC

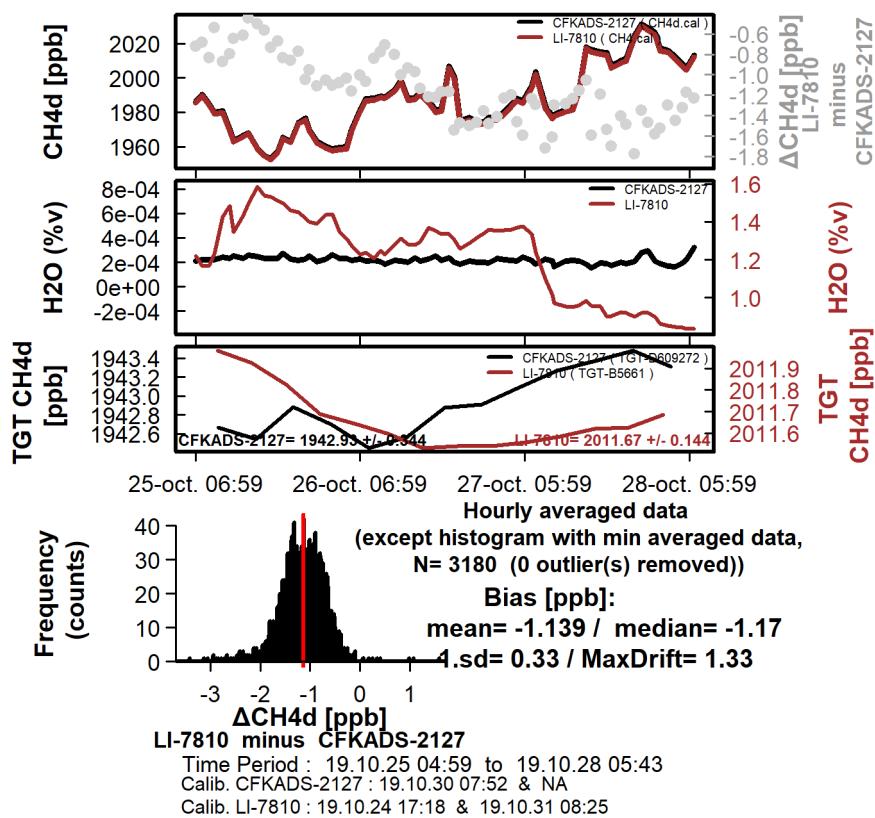


	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	1178	0.98
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (11910 ppm H ₂ O)	-51	-0.04
Remaining bias (not related to H ₂ O correction)	1229	1.03

16.1.2 Second period

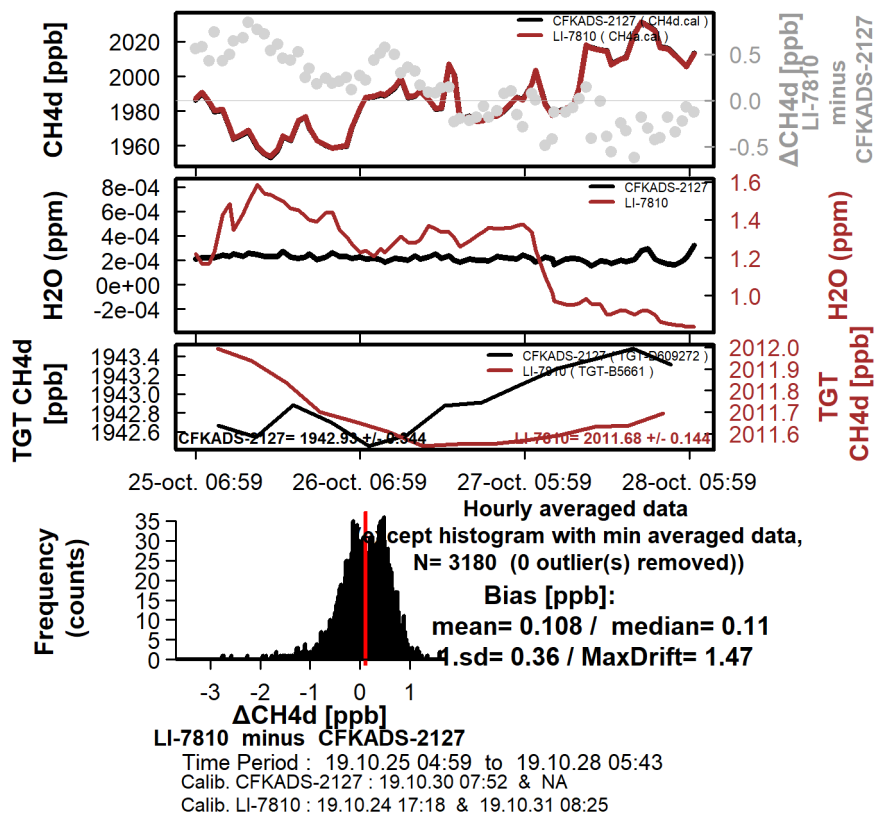
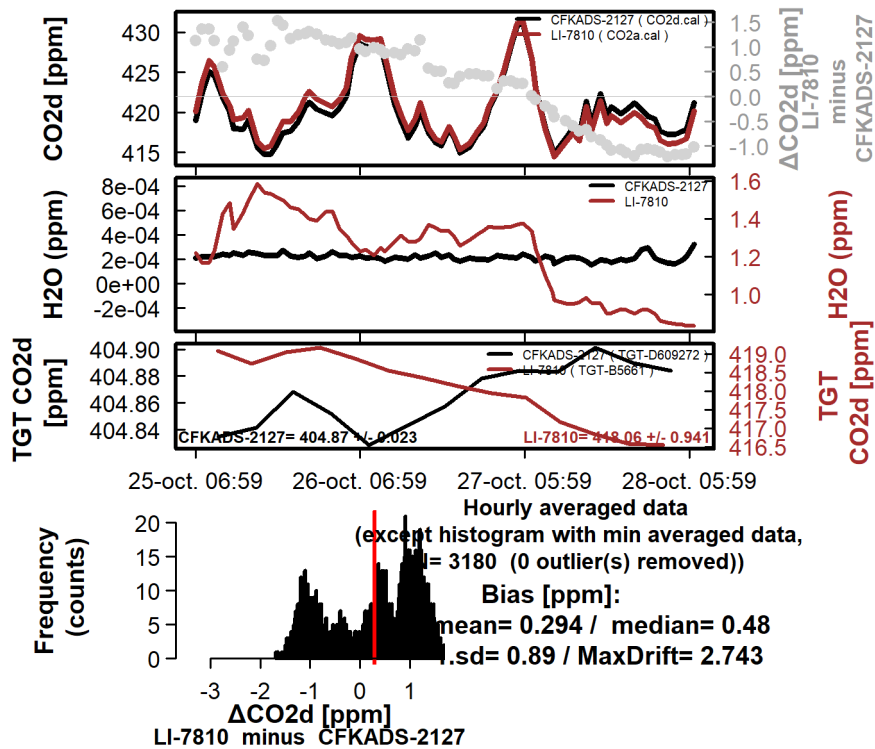
16.1.2.1 Factory water vapor correction





	CO2 [ppb]	CH4 [ppb]
Observed bias in ambient air:		
mean difference (LI-7810 - Ref Instrument)	-826	-1.14
H ₂ O correction bias estimated by ATC		
for the mean H ₂ O during the test (12143 ppm H ₂ O)	-1184	-1.32
Remaining bias (not related to H ₂ O correction)	358	0.18

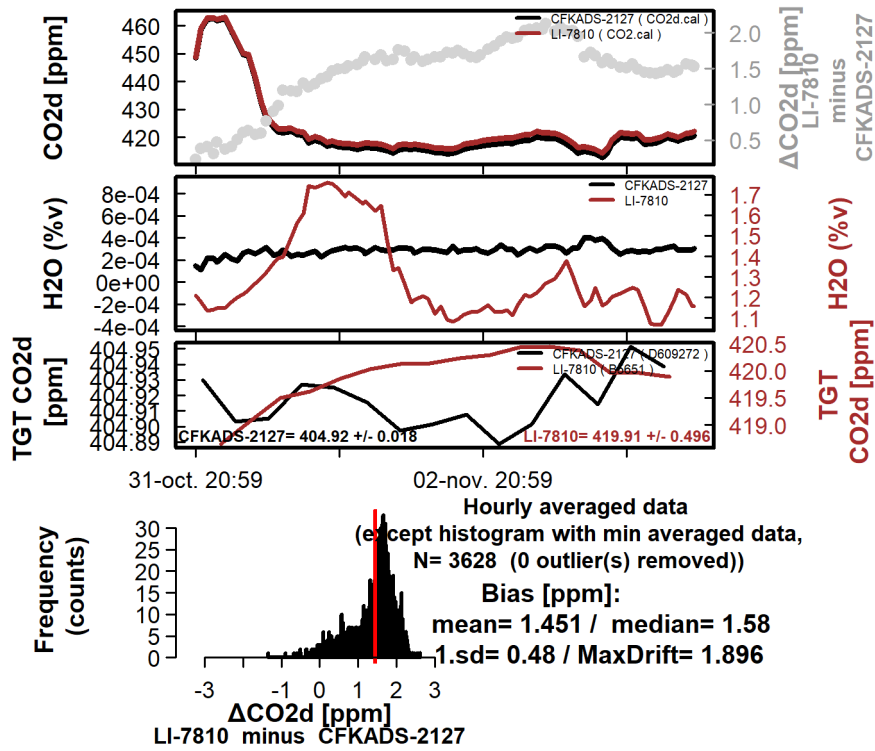
16.1.2.2 Water vapor correction coefficients determined by ATC

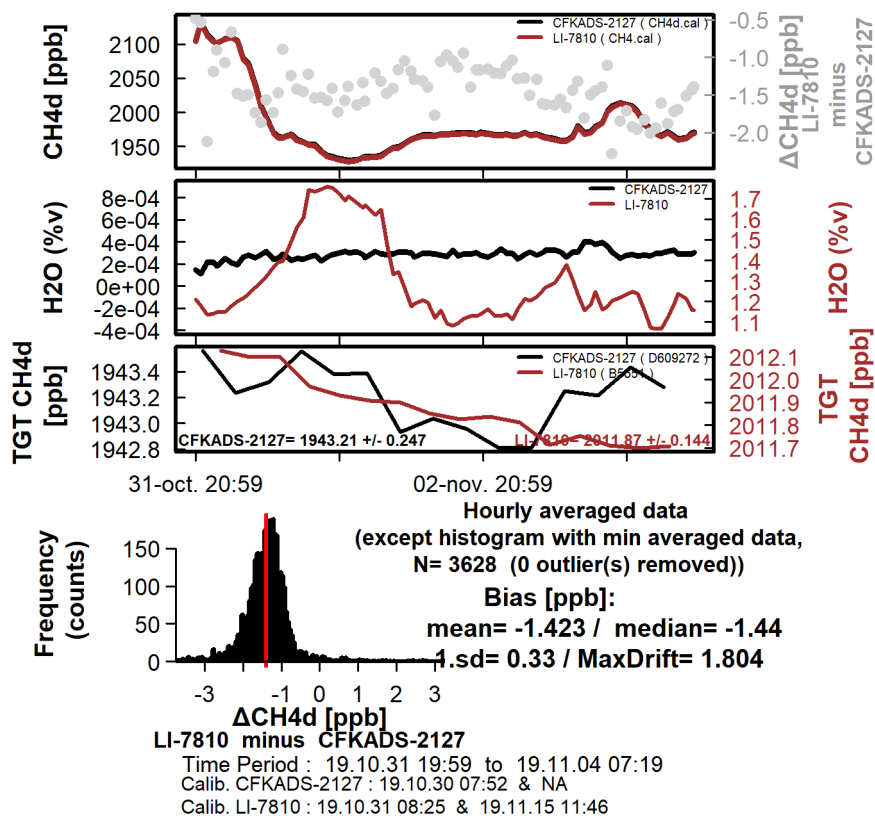


	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	294	0.11
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (12143 ppm H ₂ O)	-51	-0.04
Remaining bias (not related to H ₂ O correction)	345	0.15

16.1.3 Third period

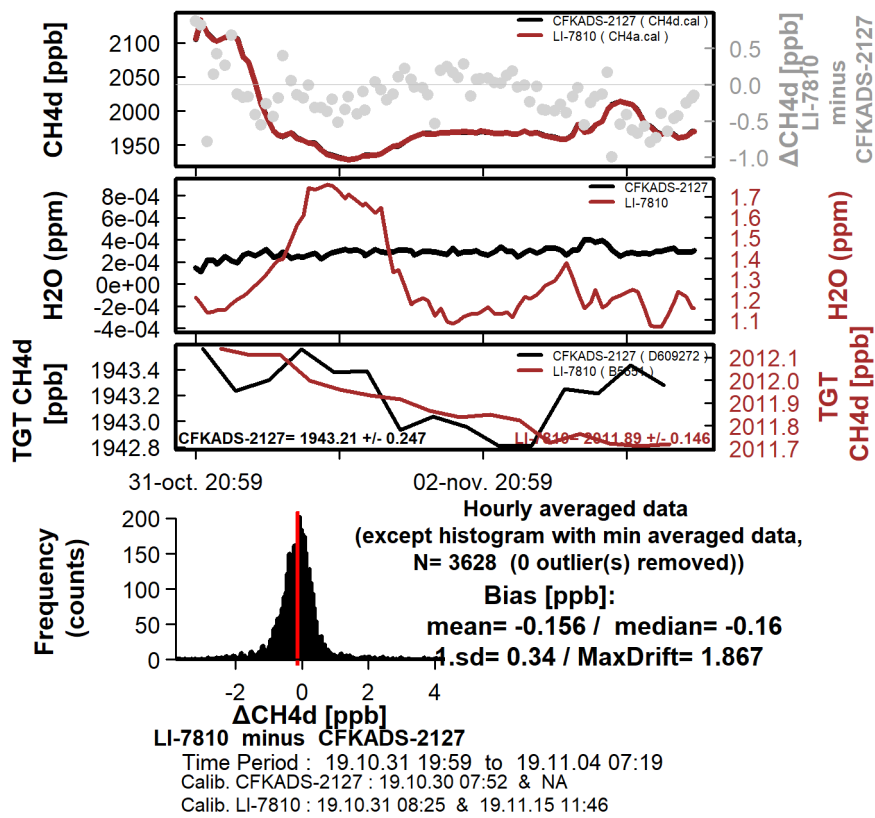
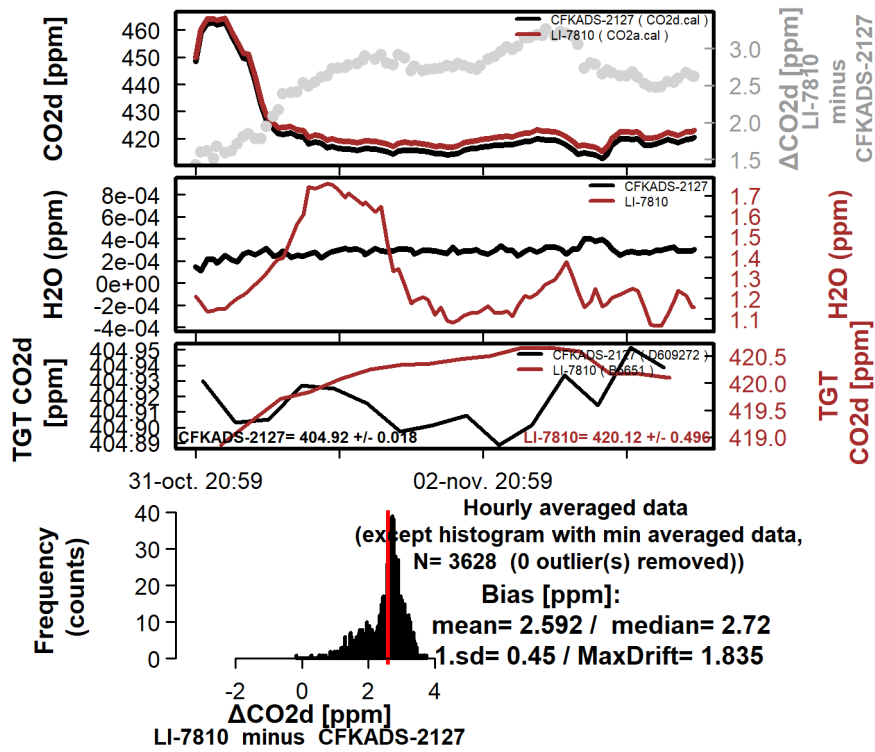
16.1.3.1 Factory water vapor correction





	CO2 [ppb]	CH4 [ppb]
Observed bias in ambient air:		
mean difference (LI-7810 - Ref Instrument)	1451	-1.42
H ₂ O correction bias estimated by ATC		
for the mean H ₂ O during the test (12931 ppm H ₂ O)	-1184	-1.32
Remaining bias (not related to H ₂ O correction)	2635	-0.10

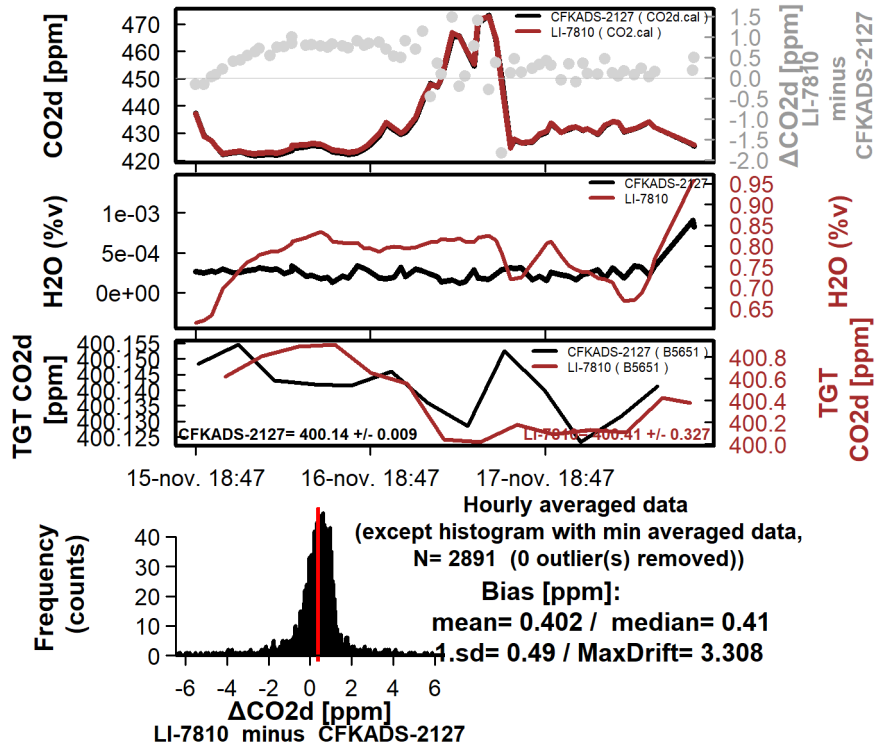
16.1.3.2 Water vapor correction coefficients determined by ATC

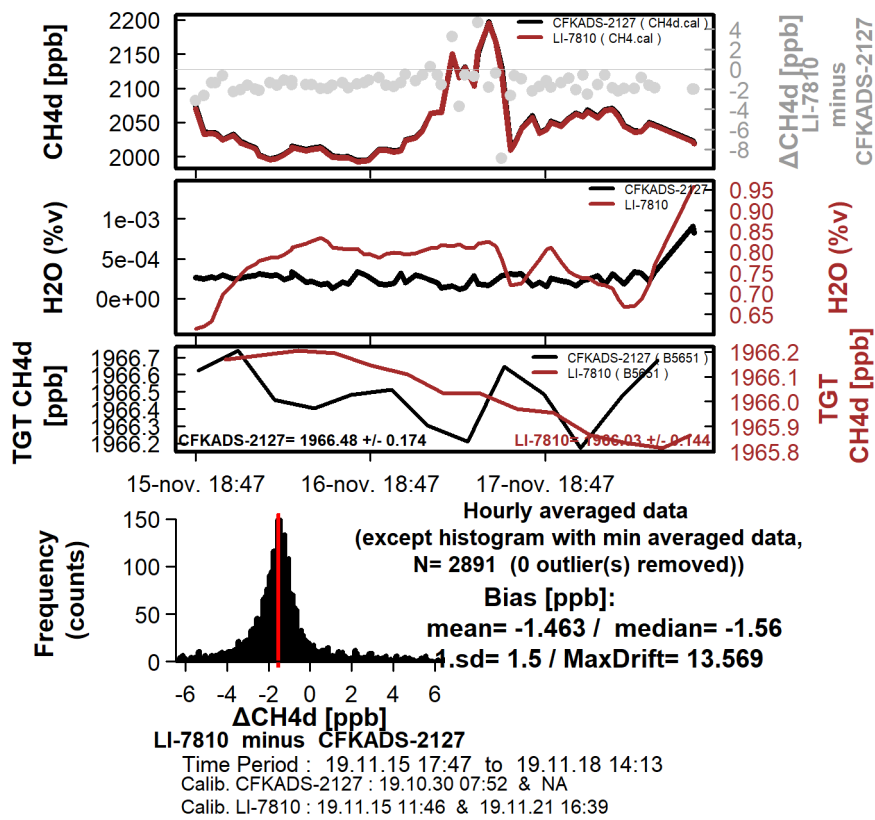


	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	2592	-0.16
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (12931 ppm H ₂ O)	-51	-0.04
Remaining bias (not related to H ₂ O correction)	2643	-0.11

16.1.4 Fourth period

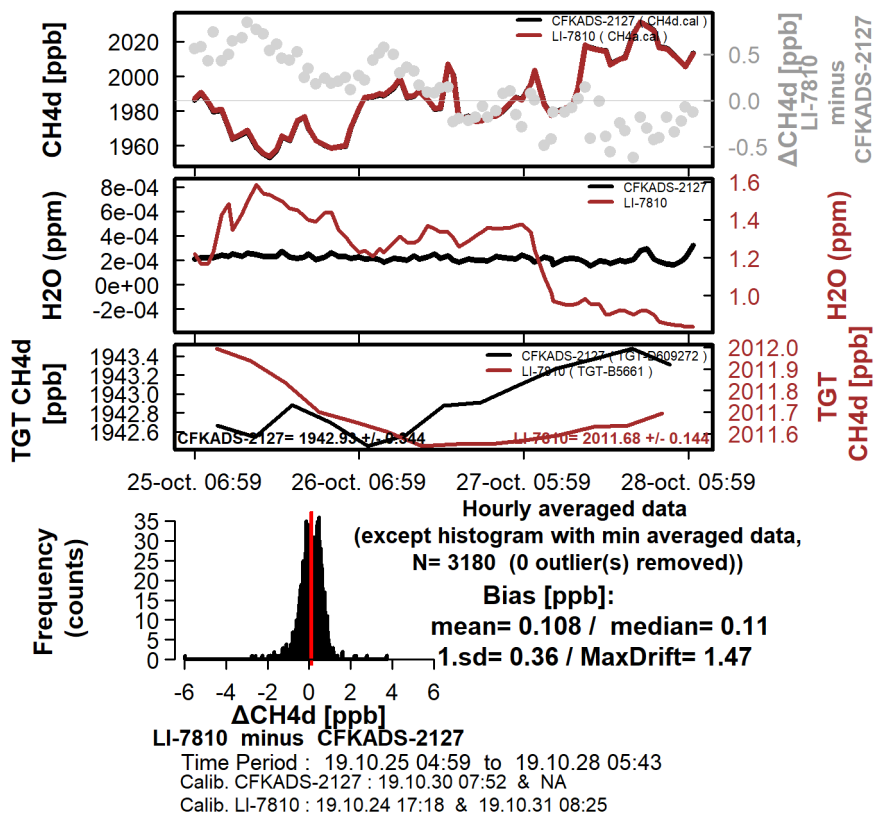
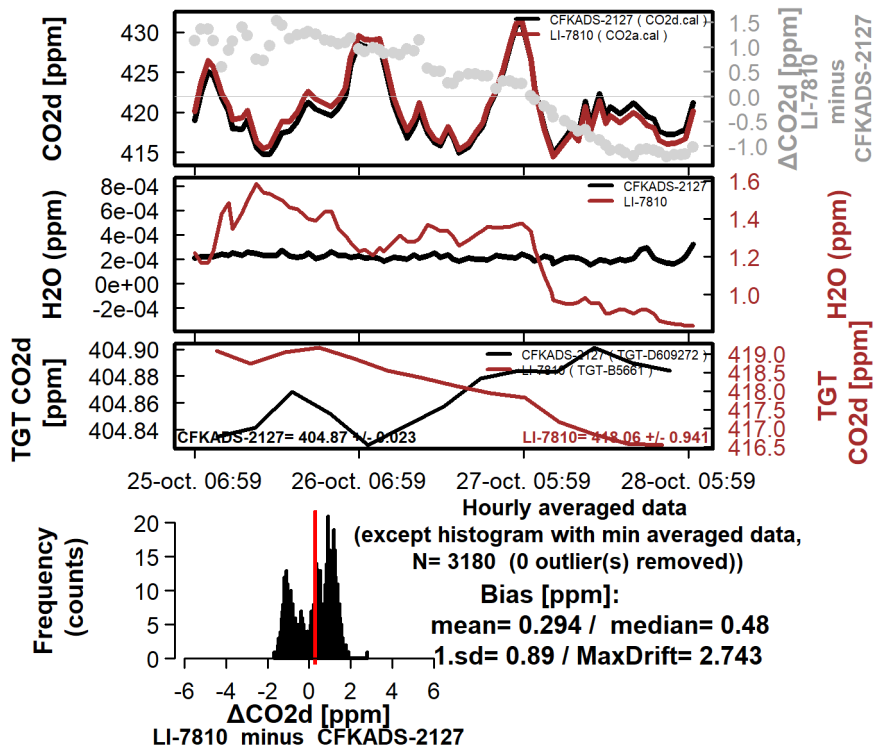
16.1.4.1 Factory water vapor correction





	CO2 [ppb]	CH4 [ppb]
Observed bias in ambient air:		
mean difference (LI-7810 - Ref Instrument)	402	-1.46
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (7687 ppm H ₂ O)	-897	-1.03
Remaining bias (not related to H ₂ O correction)	1299	-0.43
Observed bias on TGT (dry air):		
mean difference (LI-7810 - Ref Instrument)	274	-0.45

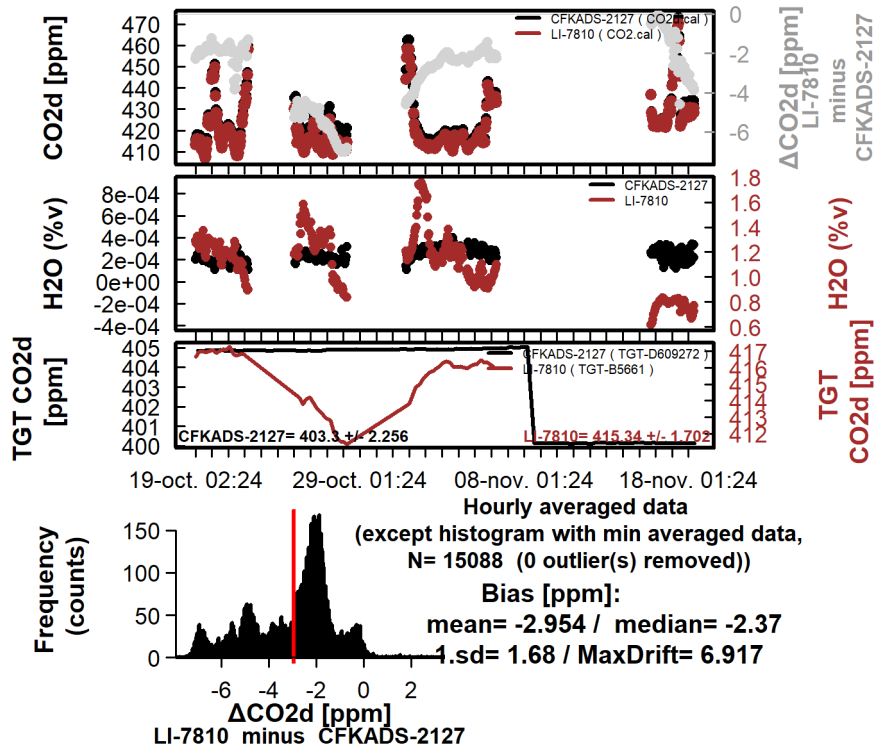
16.1.4.2 Water vapor correction coefficients determined by ATC

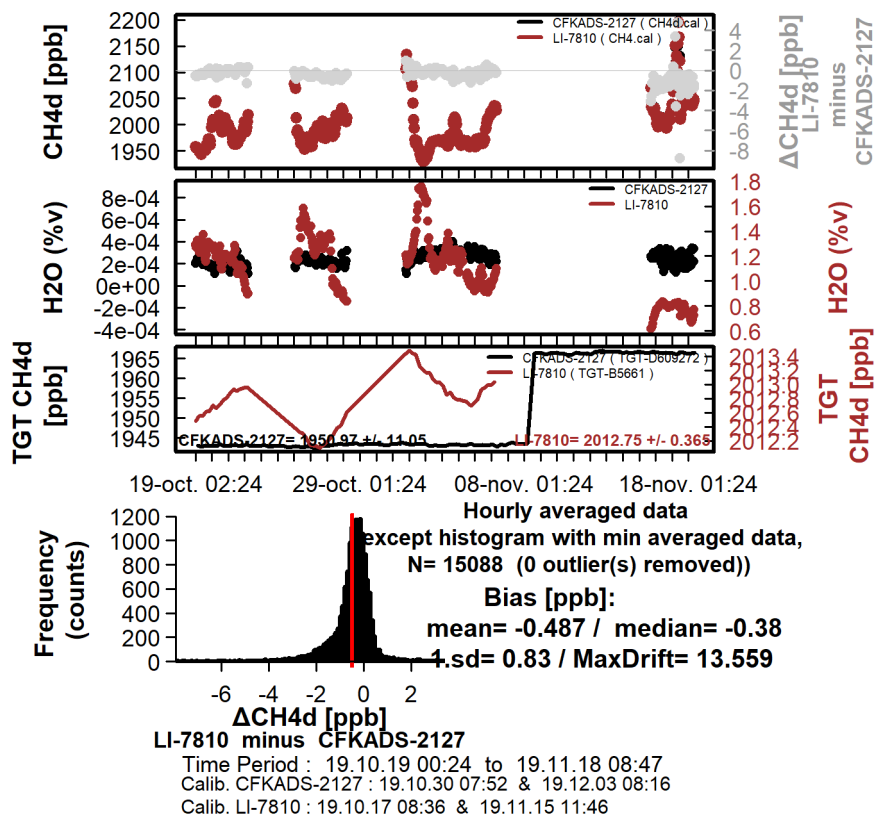


	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	294	0.11
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (12143 ppm H ₂ O)	-51	-0.04
Remaining bias (not related to H ₂ O correction)	345	0.15

16.1.5 Over all Laboratory inter-comparison

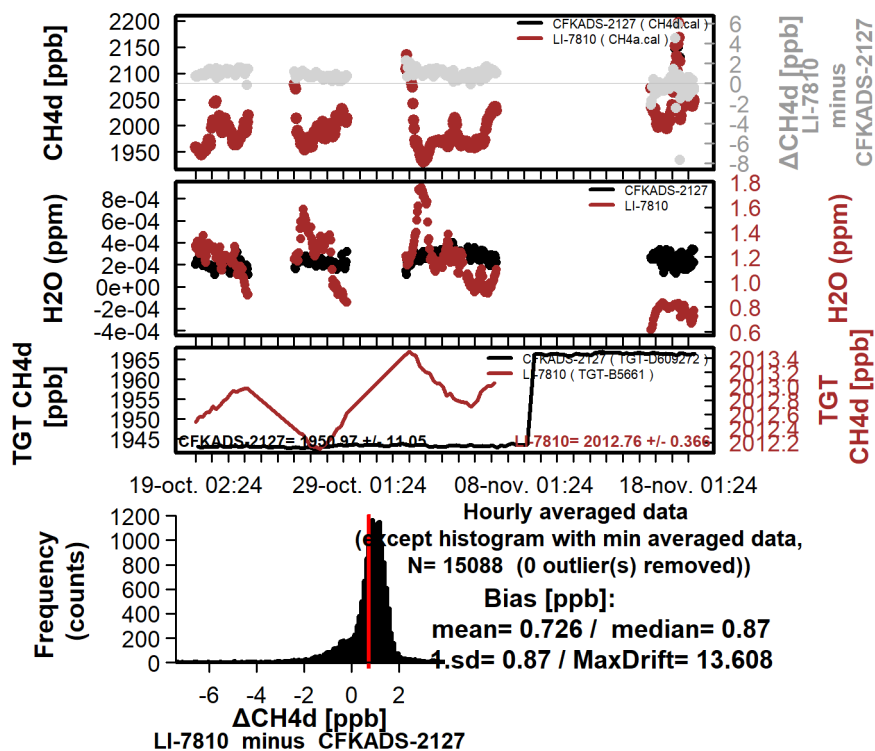
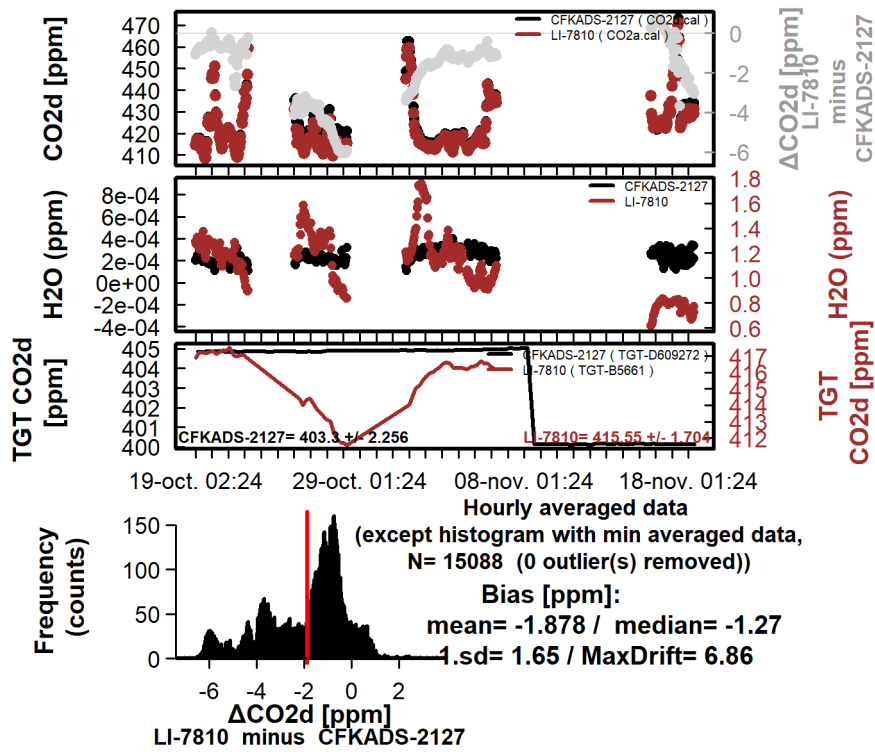
16.1.5.1 Factory water vapor correction





	CO2 [ppb]	CH4 [ppb]
Observed bias in ambient air:		
mean difference (LI-7810 - Ref Instrument)	-2954	-0.49
H ₂ O correction bias estimated by ATC		
for the mean H ₂ O during the test (11144 ppm H ₂ O)	-1184	-1.32
Remaining bias (not related to H ₂ O correction)	-1770	0.83

16.1.5.2 Water vapor correction coefficients determined by ATC



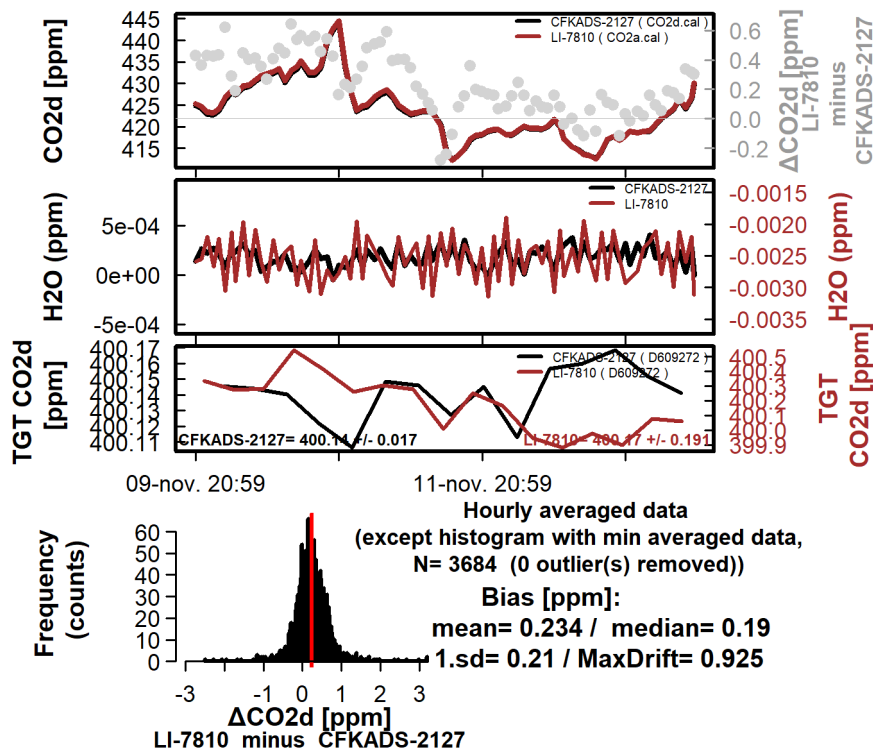
Time Period : 19.10.19 00:24 to 19.11.18 08:47
 Calib. CFKADS-2127 : 19.10.30 07:52 & 19.12.03 08:16
 Calib. LI-7810 : 19.10.17 08:36 & 19.11.15 11:46

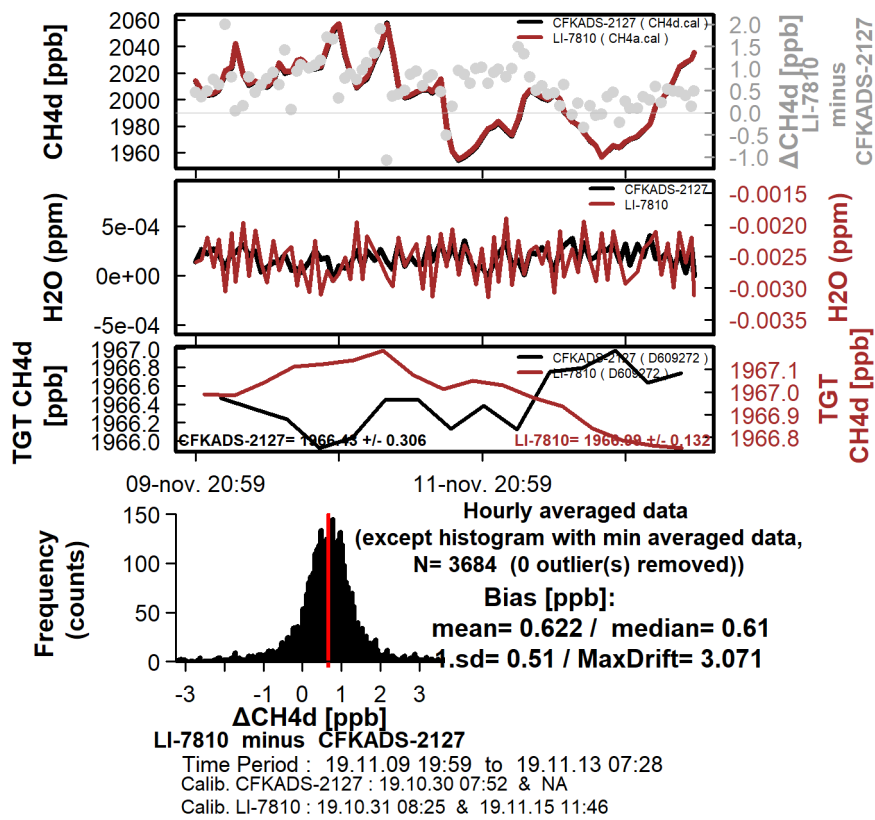
	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	-1878	0.73
H ₂ O correction bias estimated by ATC for the mean H ₂ O during the test (11144 ppm H ₂ O)	-51	-0.04
Remaining bias (not related to H ₂ O correction)	-1827	0.77

16.2 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. In this case, they use the same sampling line. A target gas is measured on both instruments for quality control.

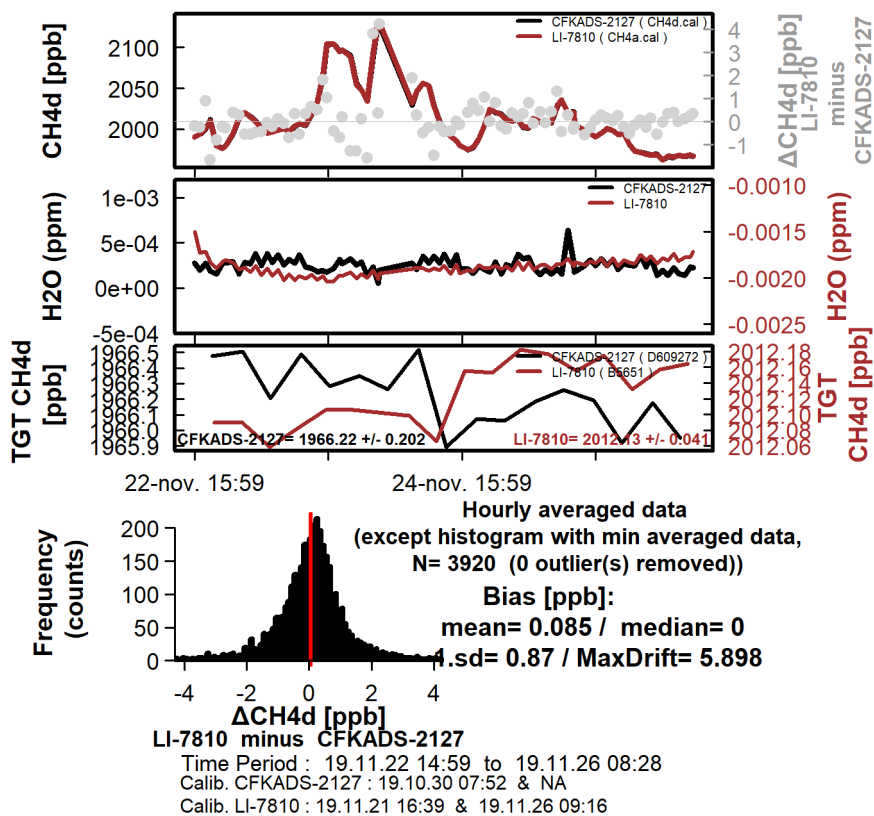
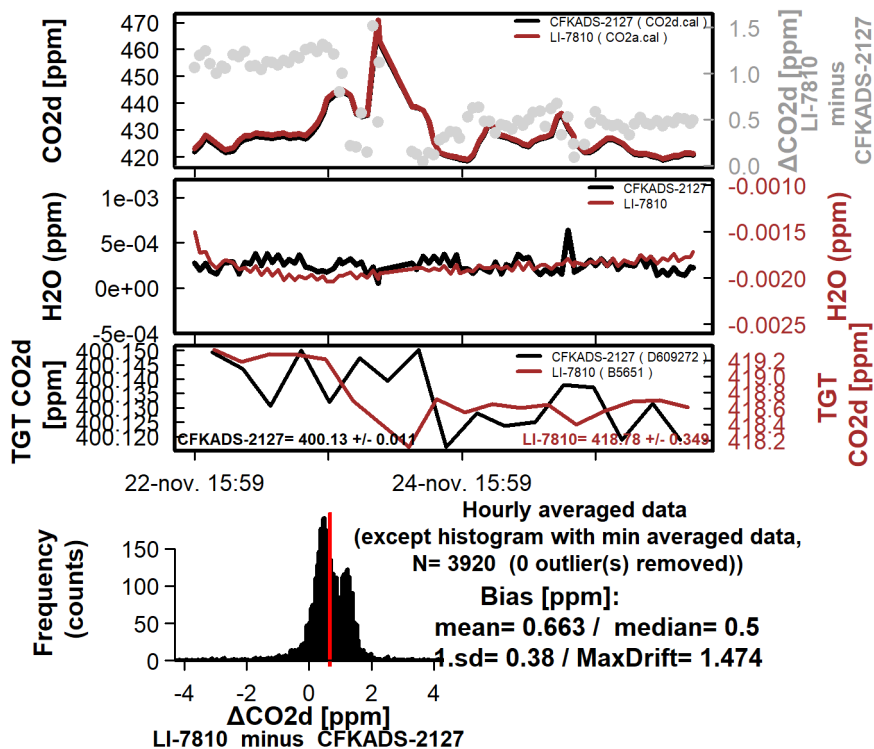
16.2.1 First period





	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	234	0.62
Intrinsic bias estimated in wet air conditions (ATC correction)	-1827	0.77
Observed bias on TGT (dry air):		
mean difference (LI-7810 - Ref Instrument)	33	0.56

16.2.2 Second period



	CO2 [ppb]	CH4 [ppb]
Observed bias : mean difference (LI-7810 - Reference)	663	0.08
Intrinsic bias estimated in wet air conditions (ATC correction)	-1827	0.77

17 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)	-	556	ppb	-
Minute CMR (1σ)	<50	433	ppb	Fail
Hourly CMR (1σ)	<25	451	ppb	Fail
Minute CMR MaxDrift (peak to peak)	<200	1817	ppb	Fail
Hourly CMR MaxDrift (peak to peak)	<150	1469	ppb	Fail
LTR-1 (1σ, 10 min avr raw data)	<50	1323	ppb	Fail
LTR-1 MaxDrift (peak to peak)	<200	4024	ppb	Fail
LTR-2 (1σ, 10 min avr raw data)	<50	2226	ppb	Fail
LTR-2 MaxDrift (peak to peak)	<200	6532	ppb	Fail
LTR-3 (1σ, 10 min avr raw data)	<50	695	ppb	Fail
LTR-3 MaxDrift (peak to peak)	<200	2219	ppb	Fail
LTR-4 (1σ, 10 min avr raw data)	<50	1428	ppb	Fail
LTR-4 MaxDrift (peak to peak)	<200	3902	ppb	Fail
STR (1 σ , 9 min avr raw data)	-	81	ppb	-
Atm. pressure sensitivity	-	NS	ppb/hPa	-
Temperature sensitivity	-	-109.241	ppb/°C	-
Max res from fit in cal range	-	148	ppb	-
Max res from fit in extended range	-	261	ppb	-
Max res from fit in extended range 2	-	0.069	%	-
Calibration drift trend	-	37919.1	ppb/month	-
Water vapor corr: max bias ATC	-	214.14	ppb	-
Water vapor corr: max bias Factory	-	1255.87	ppb	-
Water vapor correction I1	-	-3.521e-03	-	-
Water vapor correction I2	-	9.028e-04	-	-

	CH ₄			
	Spec	ATC	unit	Status
Field CMR (average on min sd)	-	0.14	ppb	-
Minute CMR (1σ)	<1	0.06	ppb	Pass
Hourly CMR (1σ)	<0.5	0.06	ppb	Pass
Minute CMR MaxDrift (peak to peak)	<2	0.30	ppb	Pass
Hourly CMR MaxDrift (peak to peak)	<1.5	0.17	ppb	Pass
LTR-1 (1σ, 10 min avr raw data)	<0.5	0.32	ppb	Pass
LTR-1 MaxDrift (peak to peak)	<2	0.95	ppb	Pass
LTR-2 (1σ, 10 min avr raw data)	<0.5	0.26	ppb	Pass
LTR-2 MaxDrift (peak to peak)	<2	0.82	ppb	Pass
LTR-3 (1σ, 10 min avr raw data)	<0.5	0.09	ppb	Pass
LTR-3 MaxDrift (peak to peak)	<2	0.28	ppb	Pass
LTR-4 (1σ, 10 min avr raw data)	<0.5	0.11	ppb	Pass
LTR-4 MaxDrift (peak to peak)	<2	0.32	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	-	0.1	ppb	-
Max res from fit in extended range	-	0.22	ppb	-
Max res from fit in extended range 2	-	0.009	%	-
Calibration drift trend	-	-3.7	ppb/month	-
Water vapor corr: max bias ATC	-	0.08	ppb	-
Water vapor corr: max bias Factory	-	1.32	ppb	-
Water vapor correction I1	-	-9.196e-04	-	-
Water vapor correction I2	-	3.212e-04	-	-