ITINERIS

D4.3.2 REPORT ON THE OPERATION IN THE LABORATORY AND IN THE FIELD OF THE ACQUIRED INSTRUMENTS AT THE CNR ISAC LAMEZIA AND CALIBRATION/COMPARISON WITH REFERENCE METHODS.

[B14]

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1. INTRODUCTION

This document deals with the integration of Research Infrastructures within atmospheric domain through intersected approaches and developments in the context of the ITINERIS project. Specifically, Work Package 4 (Atmosphere). The contents of the report describe the current progress in the implementation of WP4.3 activities for the integration and harmonization of the local infrastructure with the broader Italian Network of Environment RIs. The goal of 4.3 activity is strengthening the observational capacity of the facilities in Lamezia Terme (LMT) and reinforce Italian contributions to the main Italian ICOS HUB activities. In particular, it is planned to reinforce the observation capabilities for green-house gases of the carbon cycle with ancillary isotopic fingerprints. The instrumental strengthening is focused on Climate Observatory in LMT and its integration with the ICOS Hub.

This document is organized in three different sections: the introduction, a description of the status and operativity of the Picarro G2201-i spectrometer at the LMT observation site, and the results of a measurement validation procedure. Only instruments installed and operative at the time of writing are discussed in this document.

2. STATUS AND OPERATIVITY OF THE INSTRUMENT CARBON ISOTOPE ANALYSER INSTALLED IN THE LABORATORY

The new data acquisition framework was planned to strengthen the capability of the LMT observatory regarding the continuous measurement of greenhouse gases and. Specifically, a carbon isotope analyzer meant to integrate the national network of carbon cycle monitoring has been implemented in July 2024. The instrument (Figure 1) is an online Picarro G2201-i analyzer. Compared to the Picarro G2401, the G2201-i performs measurements of δ^{13}C-CO$_2$ and δ^{13}C-CH$_4$, *i.e.* deviations from the Vienna Pee Dee Belemnite (VPDB) international standard in the ^{13}C/^{12}C ratio in each compound. The instrument also measures water vapor (%). The G2201-i (S/N: 2445) has been performing continuous measurements ever since its installation.

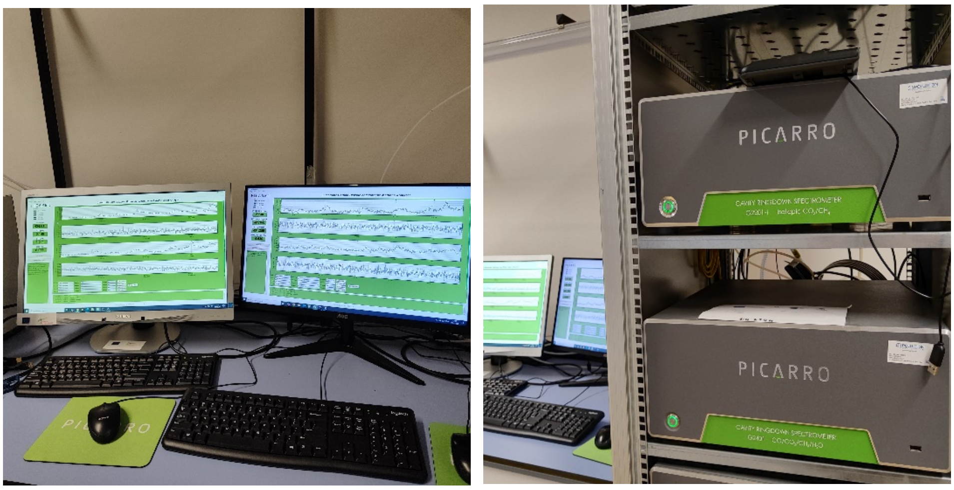


Figure 1. Operating Picarro G2201-i and G2401 analyzers.

The initial and experimental monitoring was carried out during the ITINERIS summer campaigns in the context of activities aimed at the identification of potential forest fire emissions.
Prior to these measurements, data processing efforts were aimed at isotopic data gathered at Lampedusa, a Mediterranean station operated by ENEA. These early evaluations were frequently discussed within the ICOS Atmosphere Italy group, comprised of ENEA, RSE, CNR-ISAC, CNR-IMAA, and other institutions. Considering the data output of the instrument, which is more complex than that of the G2401, discussions within the network have been particularly useful at selecting the parameters meant to be used in the consequent data evaluations. In fact, the instrument has an output of 59 parameters, all measured with a frequency of one measurement per second.

A description of the key parameters, relevant to isotopic measurements, follows:

HP_12CH4, HP_12CH4_dry, HP_13CH4: these parameters refer to "High Precision" (HP) measurement of CH_4's ^{13}C and ^{12}C isotopologues. As per the instrument's manual, the HP mode is recommended for standard atmospheric concentrations, c.a. 2 ppm.
HP_Delta_iCH4_Raw, HP_Delta_iCH4_30s, HP_Delta_iCH4_2min, HP_Delta_iCH4_5min: these are the isotopic delta parameters of CH_4, also accounting for moving averages at different time scales, ranging from 30 seconds to 5 minutes. In standard data analyses, only the "Raw" parameter should be used.
HR_12CH4, HR_12CH4_dry, HR_13CH4: these parameters constitute the "High Range" variant of CH_4 isotopologue measurements. As per the manual, these have to be used for high CH_4 concentrations only.
HR_Delta_iCH4_Raw, HR_Delta_iCH4_30s, HR_Delta_iCH4_2min, HR_Delta_iCH4_5min: HR measurements come with their own set of isotopic ratios. Considering that these values are based on HR isotopologue measurements, they are not used in standard evaluations.
12CO2, 12CO2_dry, 13CO2: parameters referring to CO_2's isotopologues. Unlike CH_4, CO_2 does not have a dual HP and HR mode.
Delta_Raw_iCO2, Delta_30s_iCO2, Delta_2min_iCO2, Delta_5min_iCO2: isotopic ratios of CO_2, also accounting for moving averages. Only the "Raw" parameter is used.

Preliminary results of G2201-i measurements at Lamezia Terme were presented during the 2024 ICOS Science Conference in Versailles, France **Error! Reference source not found.**, in conjunction with preliminary results from Lampedusa. Measurements performed between July and December 2024 were released as an uncalibrated dataset under the ITINERIS project **Error! Reference source not found.**.

More details on the instrumental configuration of both Picarro analyzers are shown in Fig. 2. The instruments operate at CNR-ISAC Lamezia Terme's laboratory, which is located 390 meters N/NE from the LMT observation site. Both Picarro analyzers, and other instruments, gather ambient air sampled at an elevation of c.a. 9 meters a.g.l. on the top of the building.

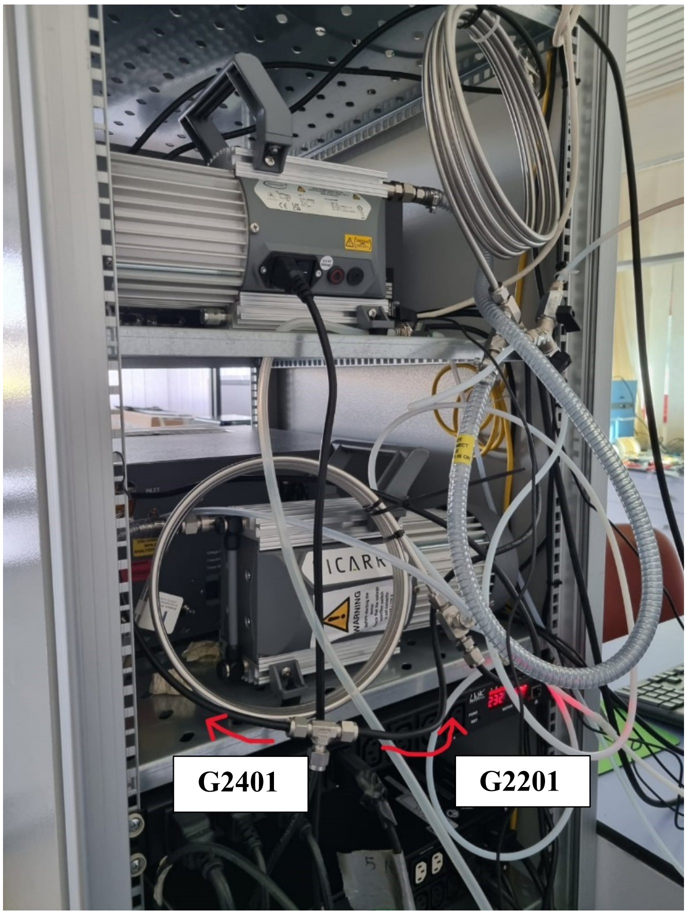
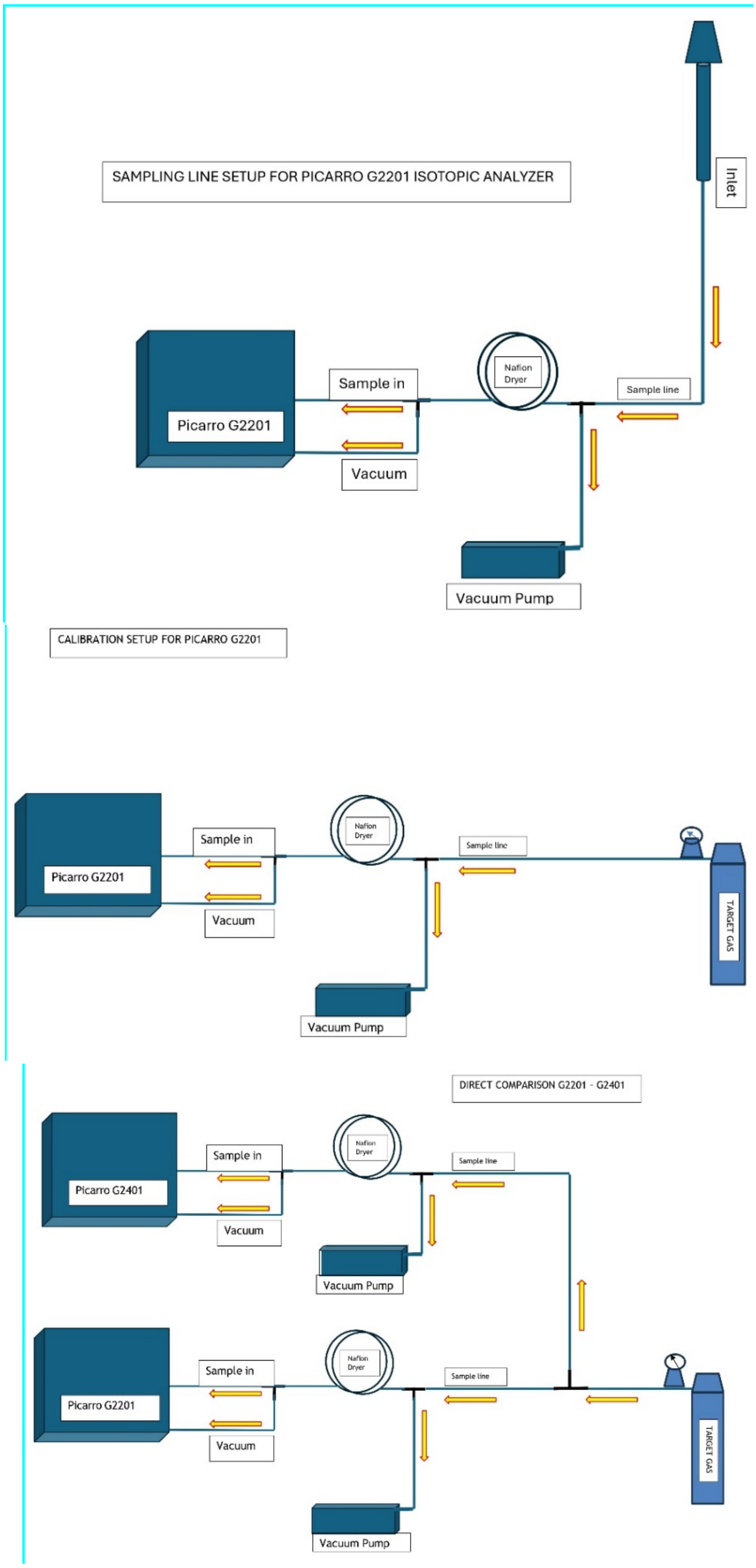


Figure 2. Details of the configuration currently in place at the Lamezia Terme laboratory. Both Picarro analyzers are connected to the main line sampling air from an elevation of c.a. 9 meters, on top of the building.



SAMPLING LINE SETUP FOR PICARRO G2201 ISOTOPIC ANALYZER

CALIBRATION SETUP FOR PICARRO G2201

DIRECT COMPARISON G2201 - G2401

Figure 3. Schemes showing in greater detail the employed configurations. Specifically, the main setup of the G2201-i is shown, as well as the combined setup used for direct comparisons between the measurements of both instruments (G2201-i and G2401).

3. VALIDATION PROCEDURE OF PICARRO G2201-I MEASUREMENTS AT THE LAMEZIA TERME SITE

At LMT, continuous measurements performed by a Picarro G2201-i are not subject to calibration due to the absence of a widely (and formally) accepted standard within the ICOS network. However, the presence of a G2401 (S/N: 2504) allows direct comparison with respect to the absolute *dry* mole fractions of CO_2 (ppm) and CH_4 (ppm), which are hereby used to validate G2201-i measurements. The following validation procedure is therefore based on the combined output of ^{12}C and ^{13}C isotopologues of both compounds and does not account for deltas.

Two target periods (Phases) within the calendar year 2025 have been selected for the validation procedure. Phase A is set as the time elapsed between January 1st (0000Z) and January 15th (0900Z), while Phase B falls in the February 1st (0000Z) to February 10th (1500Z) range. These periods have been selected to fully optimize the overlap of data from both instruments.

Although H_2O (%) is not the main scope of instrument data validation, it has also been considered in this procedure. The instruments yield different water vapor values over time which are hereby attributed to different degrees of water vapor reduction through each instrument's inlet caused by the Nafion dryer. Considering the much lower flow rate of the G2201-i (0.025 L/min compared to 0.260 L/min), we believe the Nafion dryer is much more efficient at reducing water vapor; the observed H_2O (%) is in fact effectively zero, with many negative values reported due to fluctuations in data recordings.

Using dplyr and tidyverse algorithms in R, measurements performed by both compounds have been aggregated on a 10-minute basis (6 aggregations per hour). In addition to averaged parameters, standard deviations have also been computed as an indicator of data variability through time. 10-minute aggregates have been arbitrarily chosen in this validation procedure as a compromise between hourly and per-minute aggregates, as the former would not be sufficient to record short-term variations, while the latter would be subject to significant fluctuations that may affect the agreement between the two instruments. This choice is also based on the temporary lack of a standard that could be used for a time span sufficient to assess the Allan Variance (or Deviation, ADEV) of the instrument. Later in the experimental evaluation phase however, the ADEV was calculated by measuring two standard cylinders for 24 continuous hours.

The Picarro G2201-i CRDS analyzer does not provide total mole fractions of CO_2 and CH_4. These have been calculated via a sum of $^{12}CO_2$-$^{13}CO_2$ (defined as "CO2_2201") and HP$^{12}CH_4$-HP$^{13}CH_4$ ("CH4_2201") values, respectively.

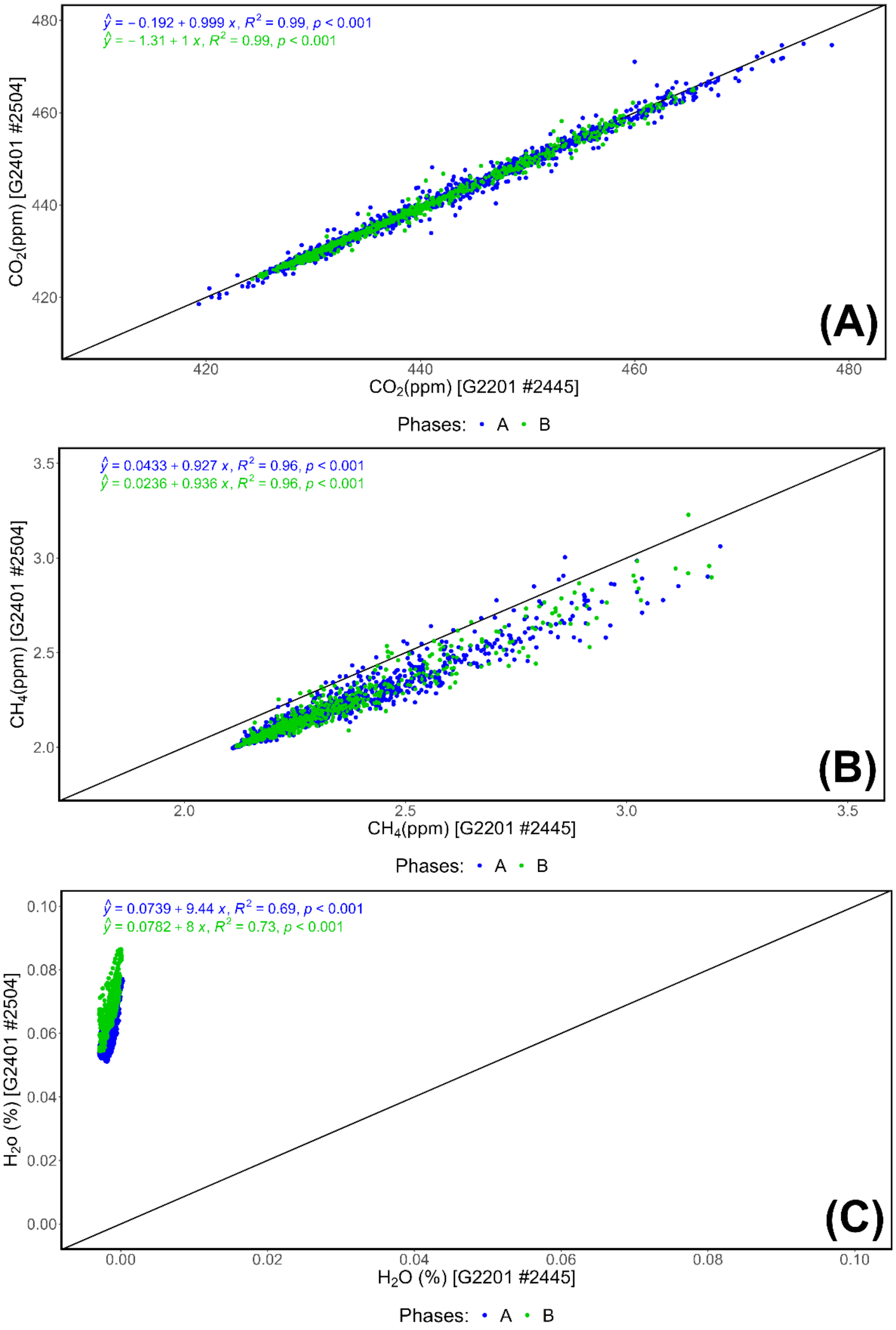


Figure 4. Linear regression, with equations and related statistical parameters, of 10-minute aggregated data for A: CO_2 (ppm), B: CH_4 (ppm), C: H_2O (%).

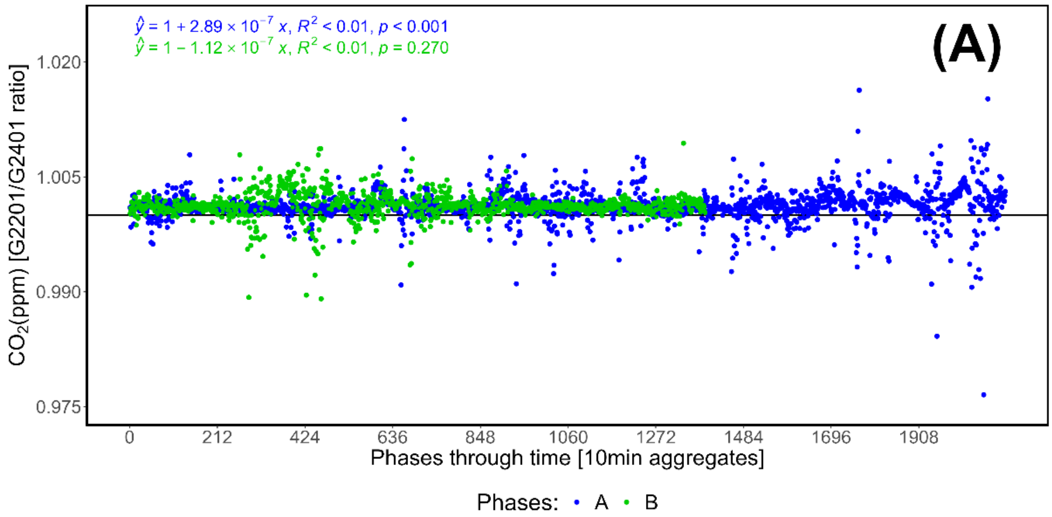
The previous figures, grouped in **Error! Reference source not found.** and depicting 10-minute aggregated data, allow a direct comparison. The key parameters and statistics of the computed linear regression are also shown. Both compounds have yielded statistically relevant (*p*-value < 0.001) linear correlations, however, the R^2 values differ (0.99 for CO_2, 0.96 for CH_4). The plots also underline the presence of a possible bias in CH_4 measurements, which will be subject to more detailed evaluation. H_2O shows a significant correlation, although the two measurements differ for the reasons explained earlier in this section.

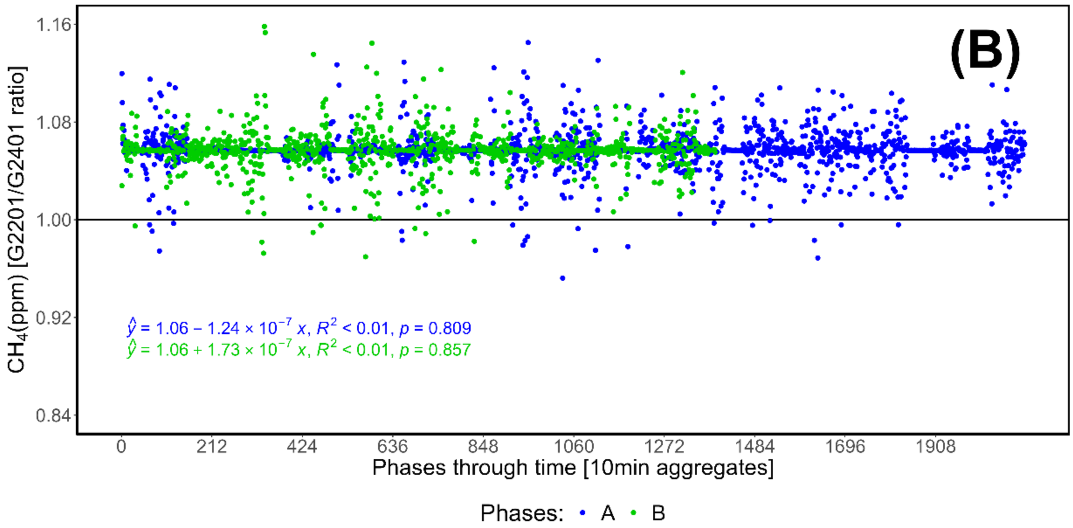
As reported in **Error! Reference source not found.**, ratios (G2201-i/G2401) of all CO_2, CH_4, and H_2O pairs have been calculated. On average, the ratios of G2201-i and G2401 measurements diverge by 0.1% in the case of CO_2. However, the value reaches a peak of 5.7% for CH_4. H_2O's negative ratio is due to the same fluctuations that have been previously reported. Covariance and standard deviations have been calculated to compute a linear correlation coefficient, which is higher for CO_2 at 0.997 (99.7%).

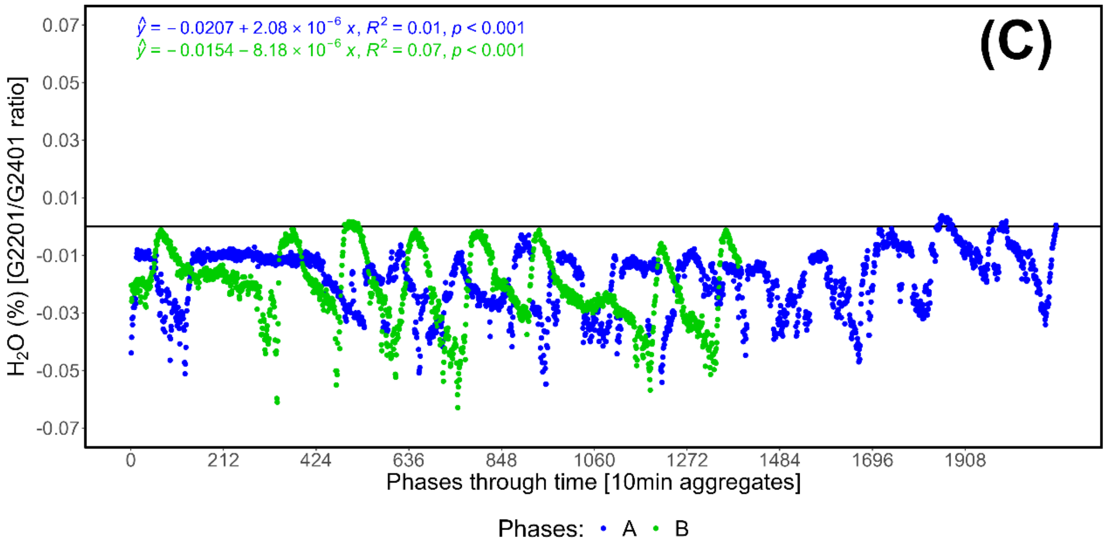
Table 1 (G2201-i/G2401) Ratios of CO_2, CH_4, and H_2O species.

	Phase	
	A	**B**
Avg. CO_2	1,001	1,001
Avg. CH_4	1,057	1,057
Avg. H_2O	-0,018	-0,021
Max. CO_2	1,016	1,009
Max. CH_4	1,145	1,158
Max. H_2O	0,004	0,002
Min. CO_2	1,016	1,009
Min. CH_4	1,145	1,158
Min. H_2O	0,004	0,002
CO_2 correlation	0,997	0,997
CH_4 correlation	0,978	0,979

Changes in the ratios of G2201 to G2401 measurements through time have also been considered. In the plots from **Error! Reference source not found.**, the x-axis shows 10-minute aggregates through time for each phase, while the y-axis shows variability in the ratios themselves. In these plots, we report for instance that CO_2 (Figure 3A) and CH_4 (Figure 3B) differs in terms of agreement between the two instruments. H_2O's ratios and their variability, considering the efficiency of a Nafion dryer combined with the low flow rate of the G2201 which results in near-zero H_2O, are more representative of changes through time in the measured water vapor content of the G2401, as the G2201 equivalent could in fact be considered static (Figure 3C). This cyclic pattern is typical of Nafion dryer implementation under these circumstances, as previously discussed within the ICOS ATM Italy network. Although the validation procedure is not aimed at isotopic deltas from the VPDB standard, the ratios of CO_2 (Figure 3D) and CH_4 (Figure 3E) from the two instruments have been compared with their respective $\delta^{13}C$ values to assess a possible dependence of the G2401-G2201 measurement ratio on the isotopic deltas.


(A)
ŷ = 1 + 2.89 × 10^−7 x, R² < 0.01, p < 0.001
ŷ = 1 − 1.12 × 10^−7 x, R² < 0.01, p = 0.270
CO2(ppm) [G2201/G2401 ratio]
1.020
1.005
0.990
0.975
0
212
424
636
848
1060
1272
1484
1696
1908
Phases through time [10min aggregates]
Phases: • A • B


(B)
CH4(ppm) [G2201/G2401 ratio]
1.16
1.08
1.00
0.92
0.84
ŷ = 1.06 − 1.24 × 10^−7 x, R² < 0.01, p = 0.809
ŷ = 1.06 + 1.73 × 10^−7 x, R² < 0.01, p = 0.857
0
212
424
636
848
1060
1272
1484
1696
1908
Phases through time [10min aggregates]
Phases: • A • B


(C)
ŷ = − 0.0207 + 2.08 × 10^−6 x, R² = 0.01, p < 0.001
ŷ = − 0.0154 − 8.18 × 10^−6 x, R² = 0.07, p < 0.001
H2O (%) [G2201/G2401 ratio]
0.07
0.05
0.03
0.01
-0.01
-0.03
-0.05
-0.07
0
212
424
636
848
1060
1272
1484
1696
1908
Phases through time [10min aggregates]
Phases: • A • B

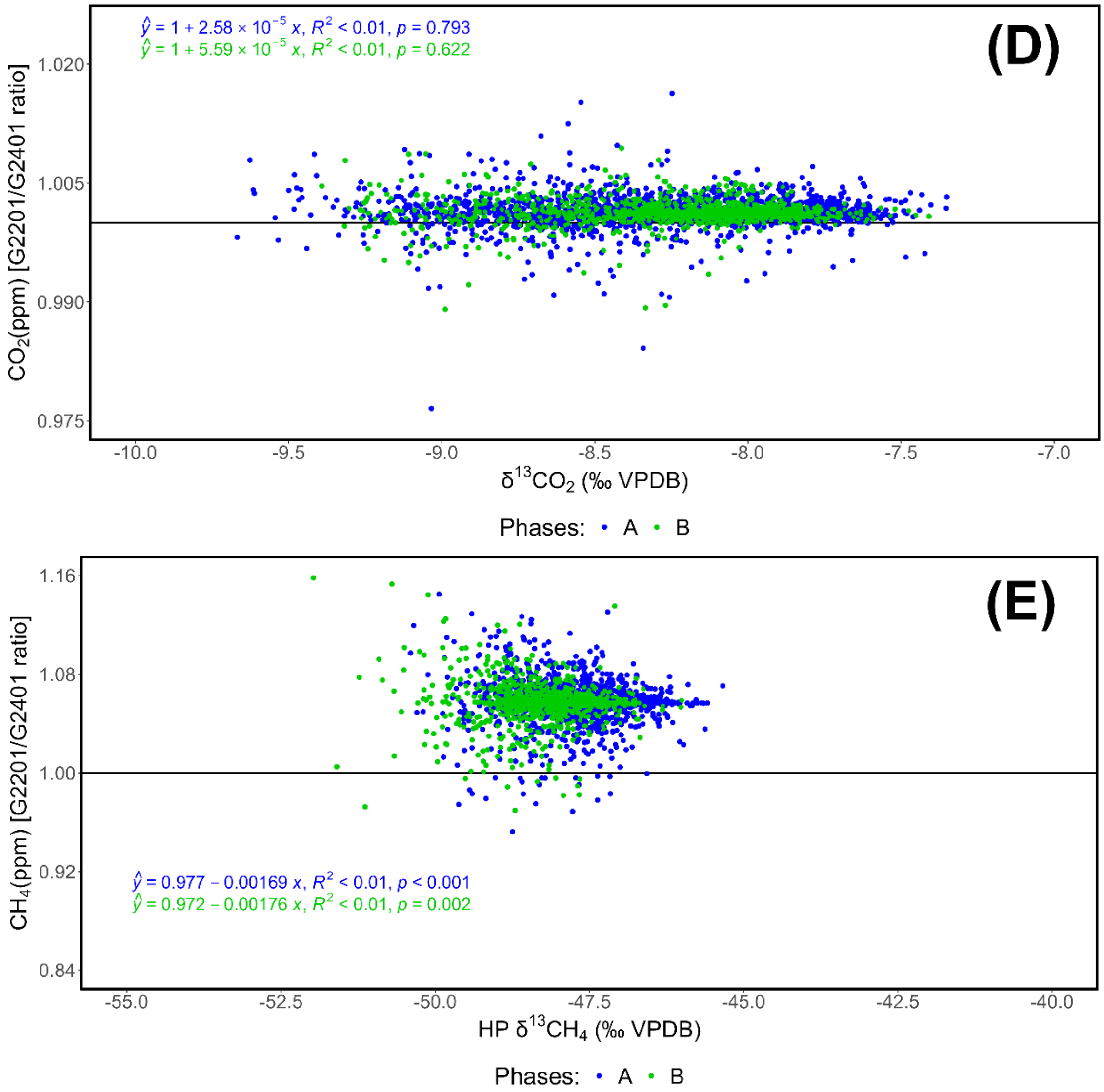


Figure 5. Variability in the observed ratio of CO_2 (A), CH_4 (B), and H_2O (C) between G2201-i measurements at the site and their G2401 counterparts. These ratios have also been compared with the isotopic deltas of CO_2 (D) and CH_4 (E).

Under both circumstances, no clear correlation emerges, meaning that isotopic deltas are not affected by the G2201 measuring considerably higher (or lower) absolute concentrations of both compounds compared to the G2401.

It is worth mentioning that this assessment does not validate δ^{13}C-CO_2 and δ^{13}C-CH_4 measurements, in the sense that it does not provide an alternate calibration procedure within the ICOS Atmosphere network.

In the late stages of Phase A, the variability of CO_2's ratio tends to increase and reaches its peaks (Figure 3A). This occurrence coincides with the ratio of water vapor turning positive, thus indicating measurements yielding higher water vapor content for the G2401, compared to their G2201-i counterparts. This could be interpreted as influence of water vapor on the measurements, even when accounting for dry mole fractions and isotopologues.

In addition to tested linear correlations, a more detailed comparison has been made based on the Bland & Altman (1986) **Error! Bookmark not defined.** methodology and its recent updates. With over 42.000 citations in the literature, the method is widely used to compare two instruments via an analysis of their measurements of a given parameter. In this case, the method is used to compare CO_2 dry and CH_4 dry mole fractions measured by the Picarro G2401 with the sum of ^{12}C and ^{13}C isotopologues measured by the G2201. As stated above, only High Precision (HP) modes are considered for CH_4.

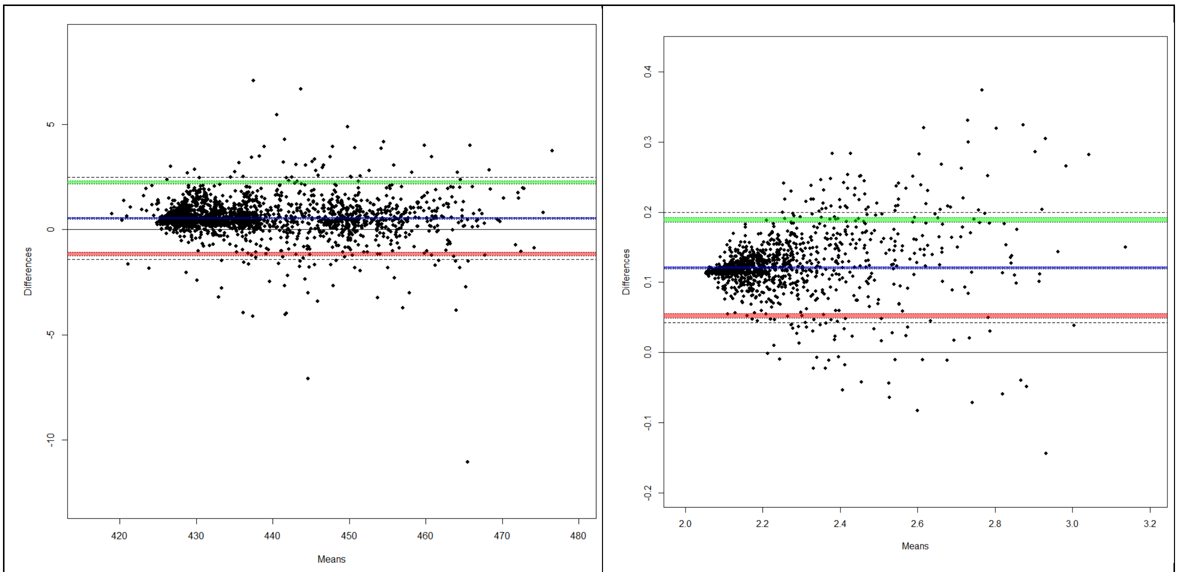
In addition to tested linear correlations, a more detailed comparison has been made based on the Bland & Altman (1986) method **Error! Reference source not found.**. Via the blandr package in R **Error! Reference source not found.**, several statistical parameters have been computed and their results are shown in Table 2. The selected level of significance for these outputs was 0.975 (97.5%), however, several outputs are based on the 95% threshold which is a default value for the method described in the original paper **Error! Reference source not found.**.
The output provides details on a number of key statistical parameters, such as the Bias between measurements, CI (confidence intervals), LoAs (Limits of Agreement), and combinations of these parameters. The "t" value in particular refers to the result of a Student's T test evaluation; during both phases, t yields higher values for CH_4 compared to CO_2, thus indicating the presence of a consistent (and statistically significant, as evidenced by $p < 0.001$) bias between the two measurements. The same bias was graphically noticeable in Figures 2 and 3.

Table 2. Details of the statistical evaluations based on the Bland & Altman (1986) methodology.

Bland & Altman (1986) Statistics				
Statistical parameter	**Phase A**		**Phase B**	
	CO_2	CH_4	CO_2	CH_4
t	28.886	158.53	30.659	126.82
df	2116	2116	1391	1391
p-value	< 0.001	< 0.001	< 0.001	< 0.001
Number of comparisons	2117	2117	1392	1392
Maximum value for average measures	476.5147	3.136864	465.3321	3.862669
Minimum value for average measures	418.9356	2.052759	424.1383	2.060195
Maximum value for difference in measures	7.076946	0.3737717	4.081837	0.5463744
Minimum value for difference in measures	-11.03653	0.1435314	5.001406	0.08863081
Bias	0.5463767	0.1207591	0.5548342	0.1206938
Bias Standard Deviation	0.8702774	0.03504954	0.6751934	0.03550836
Bias Standard Error	0.01891461	0.0007617665	0.01809708	0.0009517239
Standard Error for Limits of Agreement (LoA)	0.0354523	0.001427805	0.03392297	0.001784006
Bias-upper 95% CI	0.5888022	0.1224678	0.595441	0.1228293
Bias-lower 95% CI	0.5039513	0.1190505	0.5142274	0.1185583
Upper LoA	2.25212	0.1894562	1.878213	0.1902902
Upper LoA upper 95% CI	2.33164	0.1926588	1.954331	0.1942932
Upper LoA lower 95% CI	2.172601	0.1862536	1.802096	0.1862872

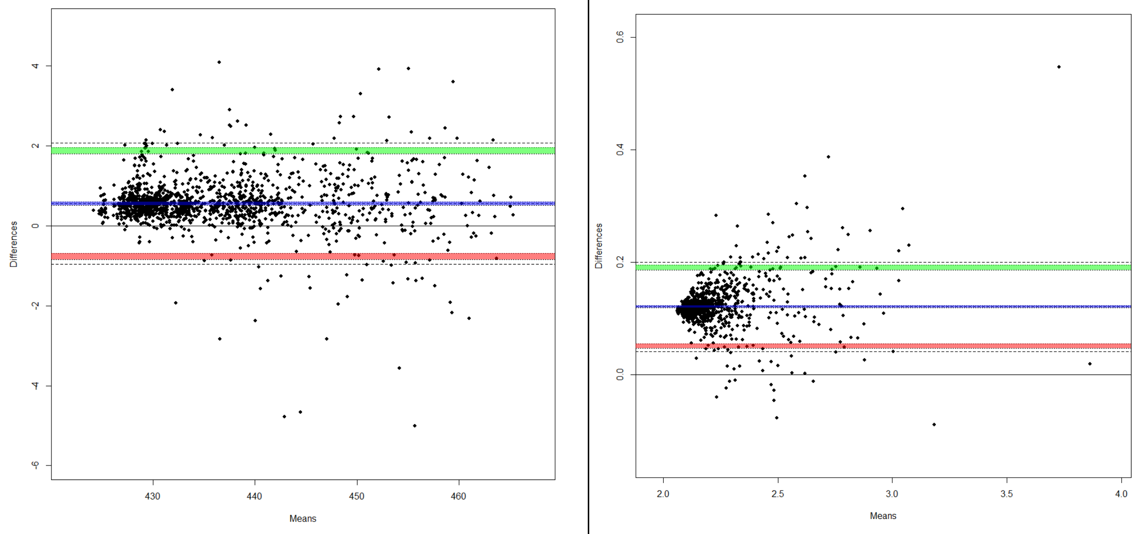
Lower LoA	-1.159367	0.05206202	0.7685448	0.05109745
Lower LoA upper 95% CI	-1.079848	0.05526458	0.6924273	0.05510046
Lower LoA lower 95% CI	-1.238887	0.04885945	0.8446622	0.04709444
Mean of differences/means	0.1251638	5.52329	0.1273469	5.510578
Point estimate of bias as proportion of the lowest average	0.1304202	5.882772	0.1308145	5.858371
Point estimate of bias as a proportion of the highest average	0.1146611	3.849677	0.119234	3.124623
Spread of data between lower and upper LoAs	3.411488	0.1373942	2.646758	0.1391928
Bias as a proportion of LoA spread	16.01579	87.89244	20.96279	86.70985
Bias	0.5463767 (0.5039513 to 0.5888022)	0.1207591 (0.1190505 to 0.1224678)	0.5548342 (0.5142274 to 0.595441)	0.1206938 (0.1185583 to 0.1228293)
Upper Level of Agreement (ULoA)	2.25212 (2.172601 to 2.33164)	0.1894562 (0.1862536 to 0.1926588)	1.878213 (1.802096 to 1.954331)	0.1902902 (0.1862872 to 0.1942932)
Lower Level of Agreement (LLoA)	-1.159367 (-1.238887 to -1.079848)	0.05206202 (0.04885945 to 0.05526458)	-0.7685448 (-0.8446622 to -0.6924273)	0.05109745 (0.04709444 to 0.05510046)

The method can also be visualized, as shown in the following plots. X-axes show the means of data pairs from both instruments, while Y-axes show their difference. A bias in these plots (Figure 4) appears as data lining up diagonally, which indeed occurs in the case of CH_4 (right column). According to the Bland & Altman methodology, this pattern is representative of either instrument (in this case, G2401 or G2201-i measurements) yielding results which depend on the magnitude of measurements. The colored bands identify confidence level intervals; the two measurements are deemed in accordance if most data fall within these bands. The first row refers to Phase A, while the second row refers to Phase B.



CO_2 (ppm) – Phase A

CH_4 (ppb) – Phase A



CO_2 (ppm) – Phase B

CH_4 (ppb) – Phase B

Figure 6. Distribution of means and differences of CO_2 and CH_4 measurements, of both phases, with respect to the confidence intervals and LoAs (Levels of Agreement) defined by the Bland & Altman (1986) methodology. Please refer to Table 2 for statistical details concerning these comparisons. The upper (green) and lower (red) band show LoAs (Limits of Agreement), which are defined in the mean ± 1.96 SD interval. The mean value is reported by the horizontal blue line.

Three calibration standards used at LMT in addition to the main NOAA cylinders have been used to perform a cycle of data validation. CO and CH_4 standards are diluted in molecular nitrogen (N2), while the CO_2 standard is a pure one, up to 99.995%.

The CO standard has a concentration of 40.3 ppm, while the CH_4 cylinder has a concentration of 2950 ppb. CO and CO_2 standards have been diluted in their concentration to 100 ppb and 665 ppm, respectively. In order to dilute these gases, a Thermo Scientific 146i multi gas calibrator was employed. The output was consequently channeled towards the inlet of both Picarro instruments, set up in parallel with a ¼ Swagelok. In order to prevent anomalous increases in pressure, a vent yielding an overflow of 500 mL per minute was set up and maintained constant throughout the entire cycle.

The cycle is defined in three stages, each aimed at the measurement of one compound. In order, CO, CO_2, and CH_4 standards have been analyzed. The measurement of CO was limited to the G2401.

Table 3. Results of the first stage, aimed specifically at CO. This compound is not analyzed by the G2201-i.

	CO (100 ppb)	
10-minute blocks	**G2401**	**G2201-i**
1	0.098 ± 0.003	N/A
2	0.100 ±0.003	N/A
3	0.099 ± 0.002	N/A
4	0.100 ± 0.003	N/A
5	0.100 ± 0.003	N/A
6	0.100 ± 0.003	N/A

The second stage was aimed at CO_2. The compound is analyzed by both instruments, so a direct comparison is possible. The isotopic delta has also been considered; it is worth mentioning however that the cylinder does not have a certified standard in terms of isotopic fingerprint, as it's limited to the absolute CO_2 concentration alone.

Table 4. Results of the second stage, aimed specifically at CO_2.

	CO_2 (665 ppm)		
10-minute blocks	**G2401**	**G2201-i**	**$\delta^{13}C\text{-}CO_2$**
1	663.221 ± 6.181	662.193 ± 4.085	-39.492 ± 0.773
2	667.197 ± 5.043	665.913 ± 2.781	-39.450 ± 0.677
3	669.048 ± 5.503	668.511 ± 2.736	-39.446 ± 0.792

The third stage covered CH_4, also accounting for its isotopic delta. The G2201-i's overestimation of CH_4, previously reported via direct comparisons between the two instruments, is also confirmed by a comparison with the standard.

Table 5. Results of the third stage, aimed specifically at CH_4.

	CH_4 (2955 ppb)		
10-minute blocks	**G2401**	**G2201-i (HP)**	**$\delta^{13}C\text{-}CH_4$**
1	2.966 ± 0.001	3.020 ± 0.403	-49.099 ± 4.526
2	2.967 ± 0.000	3.134 ± 0.001	-49.635 ± 3.627
3	2.966 ± 0.000	3.134 ± 0.001	-50.022 ± 3.933
4	2.966 ± 0.000	3.134 ± 0.001	-49.750 ± 3.703
5	2.966 ± 0.000	3.134 ± 0.001	-49.336 ± 3.501
6	2.963 ± 0.038	3.134 ± 0.001	-48.829 ± 3.301

Overall, phases A and B demonstrate a good level of agreement between the two instruments, especially for CO_2, thus validating the new Picarro G2201-i analyzer in use at the LMT laboratory. The cycle based on standard cylinders has demonstrated the presence of a minor bias for CH_4, which indicates that the instruments – which have been performing continuous measurements for months – will have to be subject to calibration procedures once these become available.

A further analysis was performed by measuring air from two distinct cylinders, used at the LMT observation site for quality assurance purposes under conventional G2401 data gathering. The first cylinder has a known concentration of 2955 ppb (CH_4), while the second cylinder has a concentration of 335 ppm (CO_2). The instrument has measured air from each cylinder for c.a. 24 hours, thus allowing the measurements to be subject to an Allan deviation analysis (Fig. 6). It is worth mentioning that measured CO_2 concentrations are below the instrument's range for isotopic CO_2 (380 ppm), and may therefore explain the observed behavior of the Allan deviation.

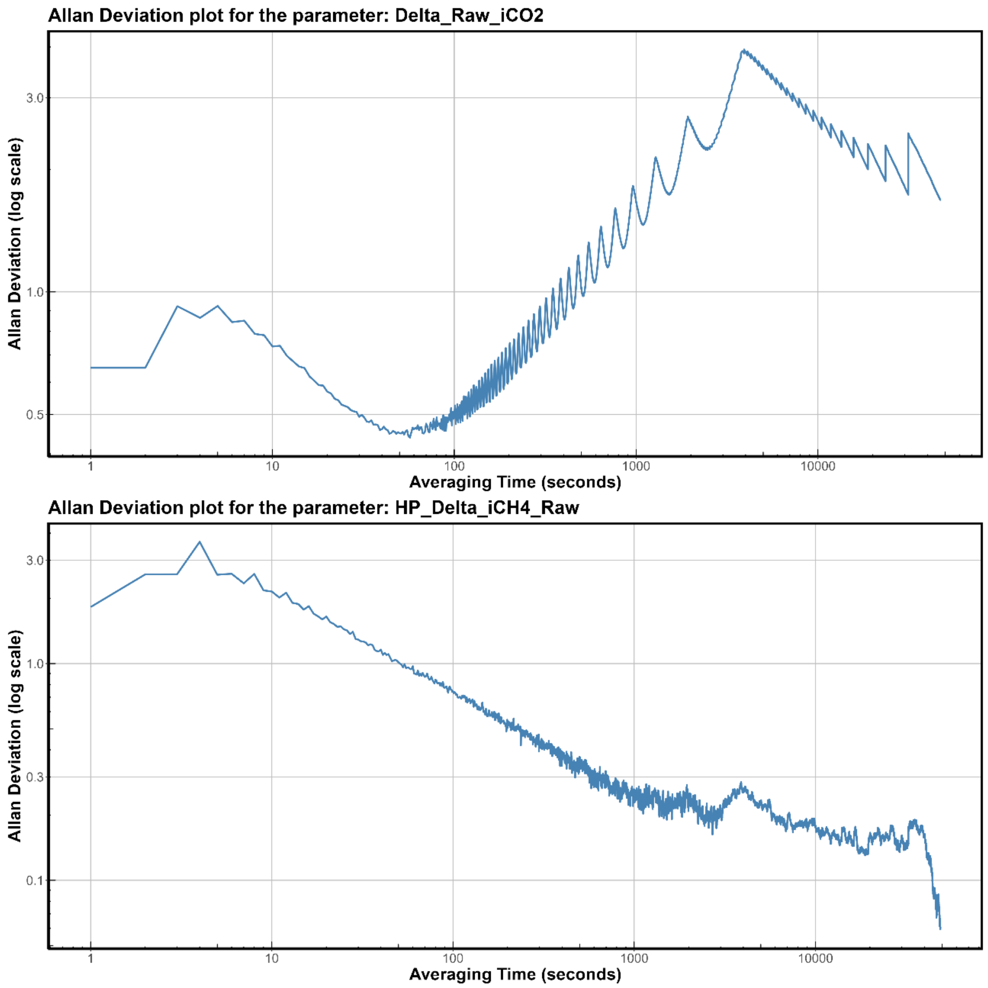
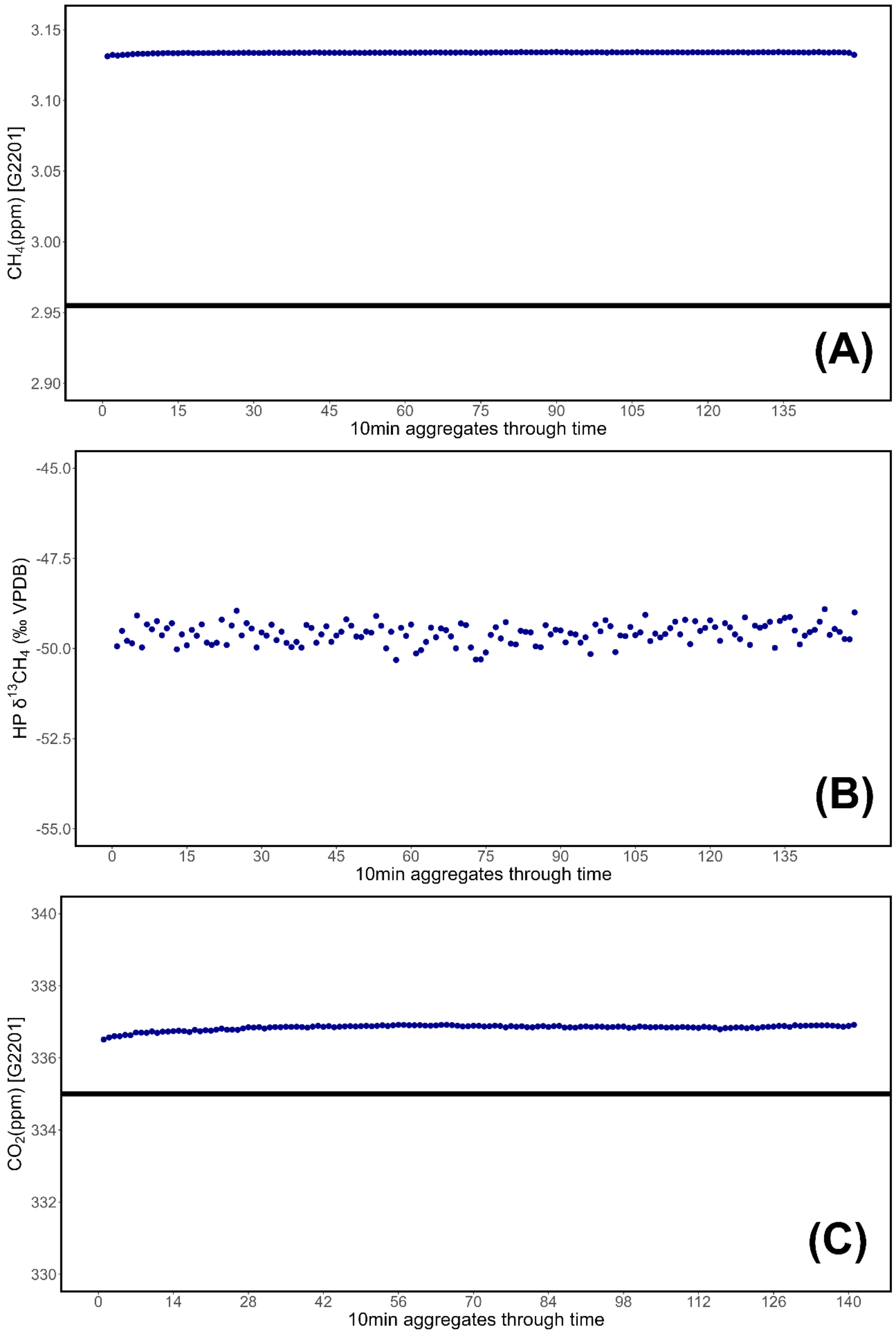


Figure 7. Allan deviation of δCO_2 (top) and δCH_4 (bottom). The different behaviors are hereby attributed to concentration dependence of the measurements, as the analyzed CO_2 cylinder has a reported concentration below the instrument's range of 380 ppm.

In addition to the Allan deviation, 10-minute aggregates have been directly compared to the standard known concentrations of both cylinders for the entire duration of the 24-hour measurement cycle (Fig. 7). The cylinders do not have a characterized isotopic fingerprint. The plots show the presence of drifts compared to employed standards, but the measurements are stable.



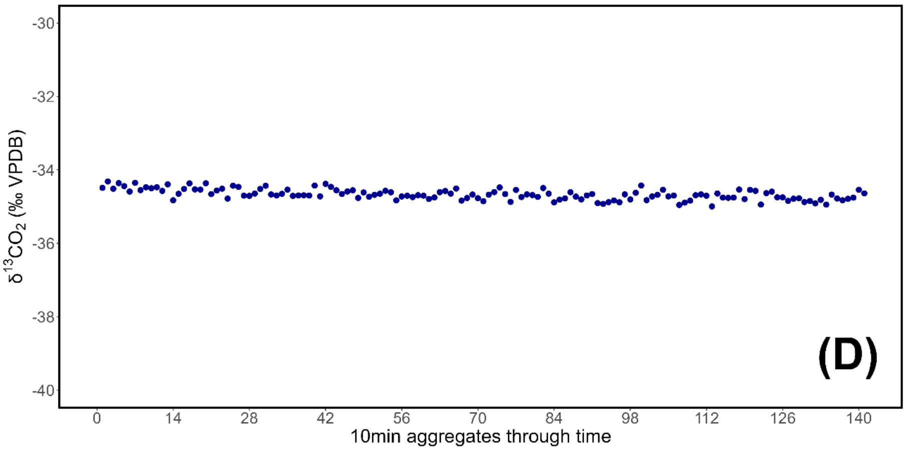


Figure 8. Comparison between the standard concentrations of analyzed CH4 (A) and CO2 (C) cylinders and 10-minute aggregates of measurements. Standard concentrations are shown as horizontal lines. The behavior of δCH_4 (B) and δCO_2 (D) 10-minute aggregates is also shown.

The results confirm the presence of a drift in CH_4 concentrations which will be corrected once calibration procedures become available. Measured CO_2 mole fractions deviate by less than 2 ppm from the standard and will also be subject to a calibration procedure. The behavior of CO_2's Allan deviation, which differs from that of CH_4, is attributed to the operational limitations of the instrument (min. 380 ppm, while the measured standard has a concentration of 335 ppm).

References

(1) D'Amico, F. *et al.*, Continuous CH_4 carbon isotope measurements in Italy: preliminary results from the Lampedusa observatory (Strait of Sicily) and general outline of the developing cross-country network. ICOS Science Conference 2024, Versailles. https://fileshare.icos-cp.eu/apps/onlyoffice/s/cpQxAYrtQECEZFa?fileId=4089959.

(2) Calidonna, C.R., D'Amico, F., Ammoscato, I., Malacaria, L., Gulli, D., Lo Feudo, T., Sinopoli, S., De Benedetto, G., Mona, L., Dema, C., Ripepi, E. (2025). Continuous $\delta^{13}C\text{-}CO_2$ and $\delta^{13}C\text{-}CH_4$ measurements in the atmosphere – data gathered at Lamezia Terme (Calabria, Southern Italy) between July and December 2024 (Version 1) [Data set]. ITINERIS HUB. https://doi.org/10.71763/CNR-IMAA/ITINERIS/CNR-ISAC-LT/CARBON_ISOTOPES_LMT_2024.

(3) Bland, J.M., Altman, D. (1986). Statistical methods for assessing agreement between two methods of clinical measurement. The Lancet, 327(8476), 307-310. http://dx.doi.org/10.1016/S0140-6736(86)90837-8.

(4) Datta, D. (2017). Blandr: a Bland-Altman Method Comparison package for R (Version 0.6.0). https://www.doi.org/10.5281/zenodo.824514.