



1 **Comparison of two near-by atmospheric CO₂ and CH₄ records** 2 **at the Mt. Cimone WMO/GAW global station (2165 m a.s.l.,** 3 **Italy)**

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18 **Abstract.** Long-term in situ atmospheric observations are essential for estimating surface fluxes and assessing
19 temporal and spatial variability of greenhouse gases (GHGs). Achieving the World Meteorological Organization
20 (WMO) compatibility goals for CO₂ and CH₄ dry mole fractions is critical for ensuring the accuracy of such
21 measurements. However, compliance with these goals can be challenging even at nearby sites due to
22 environmental and operational factors. This study presents a multi-year comparison of hourly atmospheric CO₂
23 and CH₄ dry mole fractions recorded by two independent monitoring programmes at the Mt. Cimone WMO/GAW
24 Global Station in Italy. The air inlets are positioned approximately 90 m horizontally and 50 m vertically apart,
25 and have different technical designs. Despite strong correlations and consistent seasonal and multiannual trends,
26 the two datasets exhibit significant deviations, often exceeding the WMO compatibility goals for CO₂ throughout
27 the year and for CH₄ primarily in winter and spring. Besides differences in data processing which led to large
28 deviations during episodes with high GHG dry mole fractions, the discrepancies appear to be possibly driven by
29 different factors. The different inlet positioning plays an important role. This is linked to measurement periods
30 characterised by high temporal variability and different sensitivity to local biogenic influences during the active
31 vegetative season. Additional contributors include the possible influence of human presence at the facilities.
32 Accounting for these factors reduces the seasonal CO₂ bias by roughly 40%, depending on the season, resulting
33 in a residual bias of 0.20 – 0.35 ppm. For CH₄, mean seasonal deviations within the WMO compatibility goal
34 occur from spring to autumn when periods characterised by low atmospheric variability and the absence of human
35 presence are selected. The installation of a drying system at the CAMM laboratory was associated with a
36 significant improvement in the agreement between the CAMM and CNR measurements. Finally, a preliminary
37 comparison conducted after the relocation of the CAMM inlet in early 2026 showed a further reduction in the
38 systematic differences, supporting the role of inlet configuration in the previously observed discrepancies. Our
39 findings emphasise the complexity of interpreting discrepancies in GHG observations at closely located stations
40 in mountainous environments and highlight the importance of standardised and centralised protocols, such as



41 those implemented within the ICOS Research Infrastructure, to improve data harmonisation and ensure
42 measurement compatibility.



43 1 Introduction

44 Long-term observations of greenhouse gas (GHG) atmospheric dry mole fractions are pivotal data for quantifying
45 long-term GHG trends, their latitudinal variability and global/regional fluxes using inverse modelling (e.g. World
46 Meteorological Organization, 2026). To determine net GHG fluxes at the Earth's surface, inverse models require
47 atmospheric measurements calibrated to a common scale because relative biases in the atmospheric dry mole
48 fractions lead to biases in the inferred fluxes (Bergamaschi et al., 2018). To ensure the high quality of GHG
49 observations, the World Meteorological Organization (WMO) has set compatibility goals for atmospheric CO₂
50 and CH₄ measurements to ± 0.1 ppm for CO₂ (± 0.05 ppm in the Southern Hemisphere) and ± 2 ppb for CH₄ (World
51 Meteorological Organization, 2026). This compatibility is ensured if individual laboratories keep accuracy of
52 measurements with respect to a common calibration scale within half of these goals, which corresponds to the so-
53 called internal reproducibility goal.

54 Usually, the compliance of the station network to the compatibility goal are assessed by the comparison of
55 travelling standards (Zellweger et al., 2016) by a World Calibration Center (WCC). Briefly, the travelling
56 standards are calibrated against laboratory reference standards traceable to Central Calibration Laboratories (e.g.,
57 Zellweger et al., 2019). The staff of the audited station analyse the travelling standards and report the dry mole
58 fractions, which are compared with the values assigned by the WCC. However, the travelling standard approach
59 cannot qualify all parts of the analytical system that may lead to a bias in a measurement. These parts include air
60 inlets, sampling lines and drying systems (Hazan et al., 2016; Zellweger et al., 2016). In addition, other factors,
61 such as data exposure to local emission/sink sources and the data flagging strategy/protocols adopted by the site
62 operators, may affect the final, fully quality-controlled time series of GHG dry mole fractions. Therefore, to limit
63 the impact of non-uniform protocols along the data generation of GHG dry mole fraction data, the Integrated
64 Carbon Observation System Research Infrastructure (ICOS-RI, see Heiskanen et al., 2022) adopted
65 standardised/centralised procedures for the generation of GHG data from in situ measurement sites.

66 There is some evidence that it may be operationally difficult to meet WMO compatibility goals at closely located
67 contiguous sites. Hoheisel et al. (2023) reported a 2-year comparison between CO, CO₂ and CH₄ measurements
68 carried out at the Environmental Research Station Zugspitze-Schneefemerhaus (ZSF), located approximately 300
69 m below the summit of Zugspitze in the German Alps, and measurements carried out at the nearby mountain ridge.
70 They showed that the ZSF measurements are influenced by local pollution events, mostly related to human
71 activities, and that even after removing the influence of these pollution events, a deviation of up to 0.24 ppm was
72 observed between the CO₂ time series at ZSF and the ridge during winter, although the station operators made
73 strenuous efforts to flag the contaminated data from the time series.

74 At the Schauinsland station (1205 m a.s.l., southwest Germany), CO₂ and CH₄ measurements from two intake
75 heights (12 m and 35 m) were compared over a 3-year period (Großmann et al., 2026). During summer daytime
76 diurnal mean CO₂ dry mole fractions at 35 m were up to 0.5 ppm higher, while night-time values were up to 1.1
77 ppm lower. Seasonal mean CO₂ are lowered by up to 0.36 ppm at 35 m relative to 12 m in summer, whereas no
78 significant differences are observed in winter. In summer, CH₄ spikes originating from nearby grazing cows were
79 frequently observed by the measurements at the 12 m intake. These spikes could increase hourly mean mole
80 amount at 12 m by up to 38 ppb with respect to measurements carried out at the 35 m intake (not affected by these
81 "local" emission events).



82 El Yazidi et al. (2018) showed that a small sewage treatment facility near the air intake of the mountain station
83 “Pic du Midi” (French Pyrenees) caused local CH₄ contamination exceeding several tenths of parts per billion.
84 After an experiment with a reference instrument located 200 m away from the original measurement site, the air
85 inlet was moved to avoid the impact of this local contamination.

86 Affolter et al. (2021) conducted a study comparing CO₂ measurements at the “Sphinx” laboratory on the
87 Jungfrauoch (Swiss Alps) (3580 m a.s.l.; JFJ) and a nearby site (3705 m a.s.l.) located approximately 1 km from
88 JFJ. They reported the presence of local short-term CO₂ variability, with diurnal peaks centred around noon in the
89 JFJ observations during summer. The observed anomalies, averaging +0.49 ppm during the day, were attributed
90 to the combined effects of different air mass origin from the planetary boundary layer (PBL) and local
91 anthropogenic sources. These sources were possibly related to visitors and tourism activities in the vicinity of the
92 sampling site.

93 These results emphasize the difficulties in achieving WMO compatibility goals, despite the implementation of
94 rigorous calibration and measurement protocols.

95 Laitinen et al. (2025) conducted a long-term study comparing atmospheric CO₂ and CH₄ measurements at the
96 Pallas-Sammaltunturi (PAL) station in Northern Finland. This station, which is part of both the ICOS and GAW
97 networks, utilises independent measurement systems. The study found that the average difference in CO₂
98 measurements between the two systems was less than 0.01 ppm, while the difference for CH₄ was 0.47 ppb. The
99 study also noted the impact of Nafion dryers used in the measurement systems, which improved the difference in
100 the CH₄ measurements. The findings underscore the importance of continuous quality control and the potential
101 influence of local environmental factors on measurement consistency.

102 Here, we present the results of a multi-year comparison (May 2018 – June 2024) of two in-situ atmospheric CO₂
103 and CH₄ datasets recorded independently by ICOS and GAW at the Mt. Cimone (CMN) WMO/GAW Global
104 Station (2,165 m a.s.l., Italy). This study focuses on characterising the degree of consistency between the CO₂ and
105 CH₄ time series recorded by the two measurement programmes, and discussing and attributing the observed
106 differences. The availability of contiguous CO₂ and CH₄ observations at this mountain site provides a unique
107 opportunity to compare completely independent measurements referring to the same international calibration
108 scales over an extended period of time, covering different seasons and meteorological conditions.



109 2 Measurement sites and methods

110 2.1 Site description

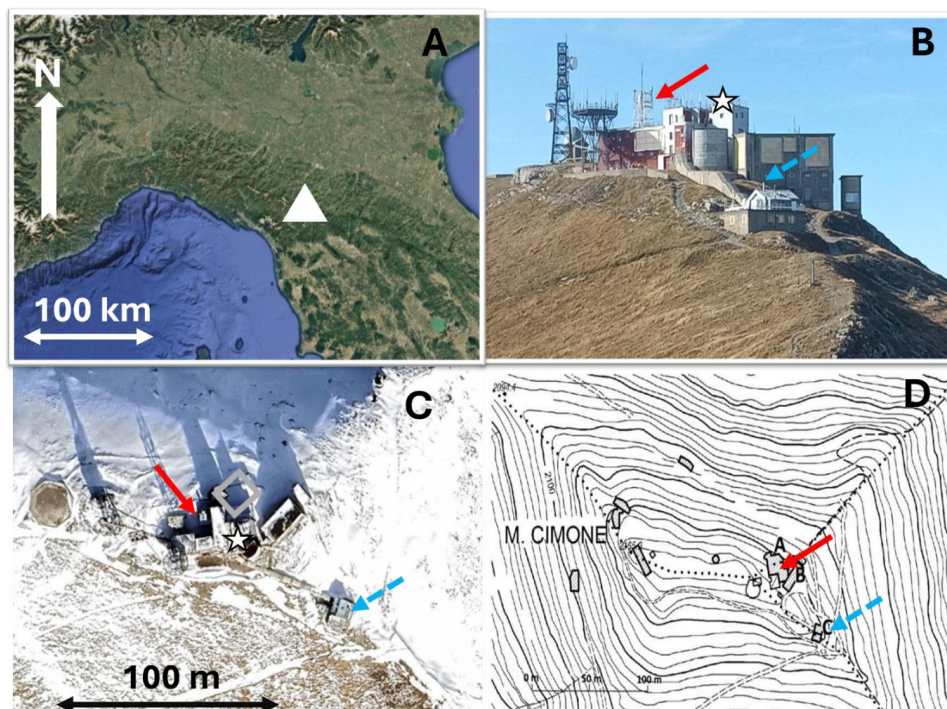


Figure 1: (A) Location of the Mt. Cimone WMO/GAW station (CMN) in northern Italy. (B) South-east view of the ridge with CAMM (solid arrow) and CNR (dashed arrow) inlets. (C) Locations (courtesy of © Google Earth) of CAMM (solid arrow) and CNR (dashed arrow) together with the water disposal tank (square). (D) Orography of the summit of Mt. Cimone with elevation line spacing by 5 m; the solid and dashed arrow indicate the location of the CAMM and CNR inlets, respectively. The star symbol on (B) and (C) denote the location of the new CAMM inlet adopted in February 2026. Base imagery for plates (A) and (C) are by Google Earth based on data by Google, Landsat/Copernicus, Data SIO, NOAA, U.S. Navy, NGA, GEBCO, GeoBasis-DE/BKG (© 2009) and Airbus.

Mt. Cimone is the highest peak (2165 m a.s.l., Fig. 1A) of the Italian Northern Apennines and is characterised by a 360° free horizon. The summit is above the tree line: it is mostly rocky, with patches of grass above ~1650 m a.s.l. (Fig. 1B). The slopes are usually covered in snow for ~6 - 7 months a year (November - May). CMN overlooks the highly industrialised Po basin (towards NW-SE) and northern Tuscany (towards S-NW). The nearest major urban areas are Modena (185 000 inhabitants, 50 km to N), Bologna (390 000 inhabitants, 60 km to N) and Florence (380 000 inhabitants, 55 km to the SE). Trace gas measurements of CO₂ have been carried out at Mt. Cimone since 1979 (Ciattaglia, 1983) by the Centro Aeronautica Militare di Montagna - CAMM (Italian Air Force), which also started continuous in-situ observations of CH₄ in 2015 (Fratticioli et al., 2023). Trace gas observations were performed by CAMM by a sampling inlet located on a telecommunication tower at the mountain ridge and embedded by the CAMM buildings, ~100 m to the East and ~10 m below the summit of the mountain (Fig 1C, D). Since 1996, continuous measurements of trace gases have also been carried out at the "O.



131 Vittori" observatory, a scientific facility hosted by CAMM and managed by the National Research Council of Italy
132 - CNR (Cristofanelli et al., 2018). The "O. Vittori" observatory is located approximately 50 m below the summit
133 and 90 m to the South-East of the CAMM premises (Fig. 1B, C, D). Since April 2018, CNR has conducted
134 independent CO₂ and CH₄ measurements within ICOS-RI (Yver-Kwok et al., 2021). Both laboratories contributed
135 to the activities of the Mt. Cimone (CMN) WMO/GAW global station (Cristofanelli et al., 2018). Both CAMM
136 and CNR measurements are traceable to the WMO calibration scales: WMO X2019 for CO₂ and WMO X2004A
137 for CH₄.

138 At CMN, local sources of emissions include the tractors used to transport materials to the mountain top, helicopters
139 and diesel engines to provide emergency power at the CAMM observatory. A small effluent treatment tank is
140 located at the CAMM observatory, ~10 m from the tower where the air intakes are located (Fig 1C). Since 2020,
141 when CAMM automated the weather and GHG observations (controlled from the Air Force logistic base in
142 Sestola, 15 km from CMN), human presence at CMN has been limited to 2-3 people during normal working hours.
143 In previous years, at least four operators were also present 24 hours a day at the CAMM observatory. The "O.
144 Vittori" observatory is also completely automated and the CNR staff is only present for maintenance or
145 experiments. During the summer, tourists (about 500-600 persons per year for the period July-August) can access
146 the external platforms of the CAMM and "O. Vittori" observatories for educational activities.

147 2.2 Sampling systems and instruments

148 2.2.1 Mountain ridge (CAMM)

149 At the mountain ridge observatory, CAMM performs atmospheric CO₂ and CH₄ measurements since January 2015
150 by using an instrument based on the Cavity Ring Down Spectroscopy (CRDS) (G2301, Picarro, US). The CAMM
151 inlet was located on a tower next to the main station building (Fig. 2A). The air intake (not heated) was approx.
152 12 m above ground, and 3-4 m above the building height. In total, ~30 m of 6 mm (outer diameter) Synflex 1300
153 tubing is used from the inlet to the CRDS analyser. Ambient air was sampled using a pump (N89KTE, KNF,
154 France) installed a few meters upstream of the instrument's calibration unit (EMT2SD12MWE, Valco Vici,
155 Switzerland). The sampled air passed through the pump prior to analysis. The flow rate is 3.3 l/min, resulting in
156 a residence time of ~30 seconds. A Nafion air drying system (MD-070-144S-4, Permapure, US) was installed in
157 June 2023. Previously, the ambient air was not dried and a specific water vapour correction function was applied
158 to the data (Zellweger et al., 2018). A stainless steel particulate filter is used to protect the instrument from dust
159 and aerosol particles. The hourly averaged CO₂ and CH₄ data used in this work (Amendola et al., 2025a,b) have
160 been obtained from the World Data Center for Greenhouse Gases (WDCGG, <https://gaw.kishou.go.jp/>). CO₂ and
161 CH₄ measurements at CAMM were temporarily suspended at the end of June 2024 due to technical issues with
162 the CRDS analyser and the ambient air inlet. Measurements resumed in February 2026 after the air inlet was



relocated to the roof of the CAMM meteorological observatory (Fig. 1).

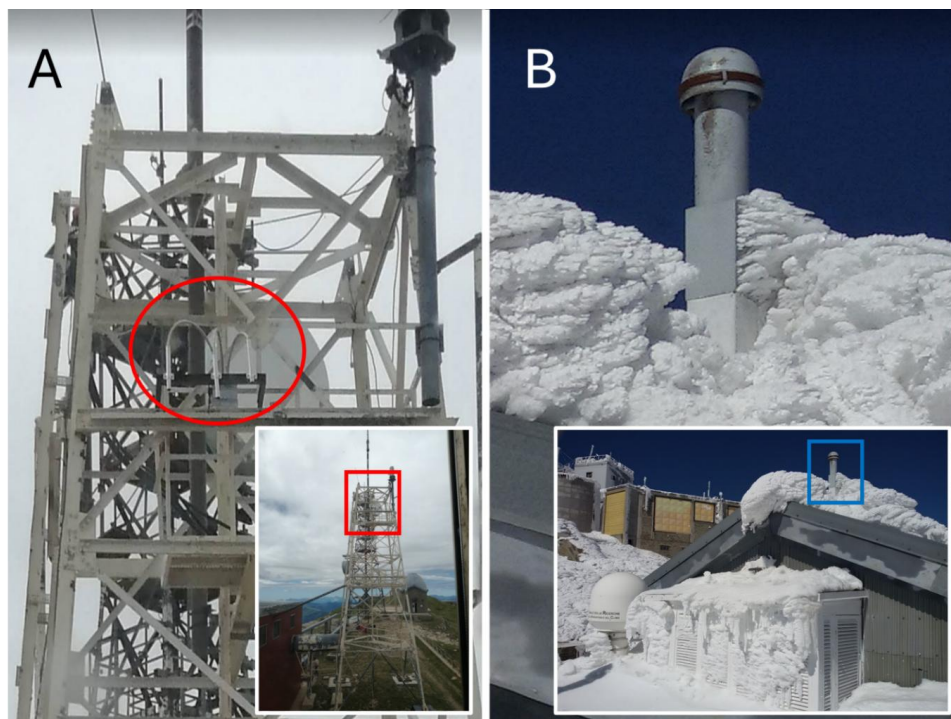


Figure 2: Ambient air inlets at CAMM (A) and CNR (B) observatories. The small inserts give an overall view of the inlet locations.

2.2.2 “O. Vittori” (CNR)

In May 2018, CNR started operational atmospheric CO₂ and CH₄ measurements at the “O. Vittori” observatory using a CRDS instrument (G2401, s/n: CFKADS-2269, Picarro, US). In August 2021, observations were temporarily suspended to allow important structural work to be carried out on the observatory building and the G2401 suffered an electronic board failure which required the instrument to be returned to the manufacturer. A backup CRDS instrument (G1301, s/n: CFADS-42, Picarro, US) was used from 18th October 2021 to 27th January 2022, when the G2401 was reinstalled. Both instrument were tested and characterised by the ICOS Atmospheric Thematic Center (ATC) before their commissioning at CMN (for more details about characterisation protocols, see Yver Kwok et al., 2015). The air intake, which is located 1.5 m above the roof of the CNR building (~8 m above the ground, see Fig. 2B), consists of a 2.5 m long glass manifold with an inner diameter of 12 cm. The external part of the inlet tube is equipped with a rain guard and it is heated to limit ice formation in freezing environmental conditions typical of Mt. Cimone. There was no flow control and the blower set-point was kept constant. This results in a residence time shorter than 2 seconds inside the manifold. A 1.5 m long Synflex 1300 tube (¼” O.D.) connects the manifold with a stainless steel 2 µm filter (SS-4FW-2, Swagelok). From there, stainless steel tubing (outer diameter: 1/8”) carries the air sample to a rotary valve (EMT2SD12MWE, Valco Vici, Switzerland) which controls the measurement schedule and the cycling between ambient air and calibration/target cylinder air. From 11 January 2020 onwards, the flow from the rotary valve passes through a Nafion drying system



184 (MD-110-7S2-4, Permapure, US). Prior to this date, residual interference from water vapour to the measurements
185 was corrected by an individual correction function determined by the ICOS Atmospheric Thematic Center (Tab.
186 SM1). Similarly, an instrument specific function for water vapour interference corrections (Tab. SM1) was used
187 from September 2022 to February 2023, when the G1301 was in use. The CO₂ and CH₄ data (Cristofanelli et al.,
188 2024a,b) used in this work have been obtained from the ICOS Carbon Portal (<https://icos-cp.eu/>).

189 **2.2.3 Meteorological measurements**

190 At CMN, meteorological measurements are carried out both by CAMM and CNR. In this work, we used the
191 dataset provided by CNR (Cristofanelli et al. 2024c). Wind speed and direction are observed on the roof of the
192 main structure of the CAMM observatory, while other measurements (air temperature, atmospheric pressure and
193 relative humidity) are recorded by a meteorological station located on the terrace of the “O. Vittori” observatory.

194 **2.3 CO₂ and CH₄ data processing**

195 **2.3.1 Mountain ridge (CAMM)**

196 As described by the metadata reported by WDCGG, hourly mean values are obtained by aggregating 10-minute
197 averages obtained from the 5-second data provided by the Picarro analyser. A “plausibility” screening is applied
198 to the 5-second data by rejecting CO₂ data higher than 475 ppm. A similar screening is adopted for CH₄ by
199 considering 1750 ppb as the lowest limit for “good” data and 2250 ppb as the highest limit (2050 ppb before June
200 2023). Before the final averaging, the 10-minute mean values underwent a manual screening by CAMM operators.
201 It should be noted that the CAMM data obtained from the WDCGG database (reported as UTC+1 time zone) have
202 been corrected to UTC.

203 **2.3.2 “O. Vittori” (CNR)**

204 The data processing that leads to the creation of hourly mean values is described by Hazan et al. (2016). The
205 processing of different types of gas (ambient air, calibration gases and target gases) follows the same general
206 scheme: quality control of raw data at native time resolution, followed by correction, filtering and time
207 aggregation. For each data point, both an automatic and a manual descriptive flag are available, with the manual
208 flag being set by the station operator and the automatic flag being set through the automated processing of the
209 data. To ensure data traceability and transparency, the flag information on the raw data is transferred to the
210 aggregated data (averaged over 1 minute or hourly). It is important to emphasise that any manual data invalidation
211 must be accompanied by codified reasons that can be traced and are not subjective.

212 **2.4 Calibrations and quality assurance**

213 **2.4.1 Mountain ridge (CAMM)**

214 The Picarro G2301 CRDS instrument is calibrated at least four times a year. The calibration is performed against
215 three NOAA laboratory standards whose dry mole fractions largely exceed the expected range for ambient air. All
216 cylinders are connected to a mass flow controller installed upstream of the Picarro, which regulates the gas flow
217 of the cylinders according to the calibration sequence.



218 The calibration sequence consists of a 1-minute gas injection for each cylinder, to check the gas flow rate, after
219 that the standard gas is injected 10 minutes for signal stabilization (these data are discarded) and 10 minutes for
220 measurement. This last cycle is repeated twice. The calibration data are then post-processed, and the calibration
221 coefficients are estimated through a linear fitting function. The resulting calibration parameters are used to correct
222 the in-situ air measurements. After applying the water vapor correction function, the calibration correction is
223 applied to the new measurements through a weighted average that considers the temporal proximity to the
224 calibration events. CAMM does not perform target gas measurements, even though they are currently under
225 implementation.

226 **2.4.2 “O. Vittori” (CNR)**

227 The dry mole fractions of CO₂ and CH₄ at the “O. Vittori” observatory are measured using the centralised and
228 standardised ICOS protocols. Only a general description of these protocols is given here, as they are described in
229 more detail elsewhere (Hazan et al., 2016; Yver-Kwok et al., 2021). After applying the water vapour correction
230 (Section 2.2.2), the raw data from the CRDS instrument is calibrated using a four-point calibration against
231 reference gases provided by the ICOS Flask and Calibration Laboratory (FCL). This links the ICOS data to the
232 WMO calibration scales. Calibration gas injection is performed every 14 days or when measurements are restarted
233 after instrument shutdown. Each calibration event consists of four cycles of 30-minute measurements for each
234 cylinder. A fitting function (Hazan et al., 2016) is then applied to the results of the calibration to define the
235 correction coefficients, which are applied to air and target gas measurements. The data are corrected using the
236 calibration equation which is closest in time to the data. As soon as there are calibration episodes before and after
237 the considered data, the correction is made with a linear interpolation of the enclosing calibration equations. When
238 the instrument has been switched off for a long time, or during major software updates or maintenance, a
239 “calibration break” event is introduced, i.e. the linear interpolation is not extended forward in time.

240 In addition to the calibration cylinders, short-term target gases are analysed every 10 hours, whereas long-term
241 target gases are measured after each calibration sequence (i.e. every 14 days). Target cylinders are treated as a
242 further tool for quality assurance. Their measured mole fractions are compared with the reference values assigned
243 by the ICOS Flask and Calibration Laboratory (FCL), and the resulting differences are expected to remain within
244 the WMO compatibility goals. If significant temporal drifts or abrupt step changes are detected, the station
245 principal investigators are required to identify their causes and apply appropriate corrective measures (Yver-Kwok
246 et al., 2021). The calibrated target measurements of CO₂ and CH₄ were stable over time within the WMO
247 compatibility goals and there was no significant difference in the bias between the G1301 and the G2401 (see Fig.
248 SM1, supplementary material).

249 Routine leak tests are also carried out. Every six months, the sampling and distribution elements upstream of the
250 analyser are checked for possible leaks. The test, known as the “shelter test” in the ICOS protocols, consists of
251 measuring a reference tank of dry natural air for 30 minutes after connecting it to the VICI-Valco distribution
252 valve and comparing the recorded data with those obtained after connecting the same tank upstream of the stainless
253 steel filter between the manifold and the rotary valve. If a bias greater than the intrinsic instrument bias calculated
254 by ATC during the instrument characterisation is detected, a potential leak may be present that requires specific
255 investigation. To date, no significant deviations between reference and test measurements has been detected at the
256 “O. Vittori” observatory. Further checks are carried out every time the operators visit the station: pure CO₂ is



257 blown to the fittings along the sampling system from the manifold to the instrument inlet to detect any leaks that
258 may occur during the period between two shelter tests.
259 As part of ICOS, other diagnostic parameters are monitored according to the quality assurance system described
260 by Yver-Kwok et al. (2021), e.g. temporal variability of continuous measurement repeatability, long-term
261 reproducibility, stabilization times during air injections from target and calibration tanks, temporal variability of
262 bias between measured air from these tanks and their assigned values (Fig. SM1).

263 **3 Results**

264 **3.1 Time series comparison**

265 Since May 2018, the CO₂ and CH₄ dry mole fractions have been measured simultaneously at CMN by CAMM
266 (at the Air Force observatory located on the mountain ridge) and by CNR (at the "O. Vittori" observatory). Please
267 note that the potential travel time of the air masses between the two intake locations is not considered when
268 comparing the two time series. Fig. 3 shows the time series of 1-hour averages at both sites, together with
269 deviations between the hourly values recorded by CAMM and CNR, i.e. CAMM minus CNR (ΔCO_2 and ΔCH_4).
270 Negative deviations indicate lower values at the mountain ridge with respect to the "O. Vittori" observatory, while
271 positive deviations indicate higher values. Only hourly data for which simultaneous measurements are available
272 at both sites are included in the calculations. Overall, both the CO₂ and CH₄ time series appear to be consistent,
273 showing the same daily, seasonal and multi-annual variability. For both CO₂ and CH₄, the comparison between
274 the two datasets is robust overall according with t-test for Pearson correlation ($R = 0.99$, with $p < 0.01$ and $R =$
275 0.98 with $p < 0.01$, respectively). However, some data points deviate from the expected ~ 1 slope by more than 10
276 ppm for CO₂ and 100 ppb for CH₄ (Fig. SM2, supplementary material).

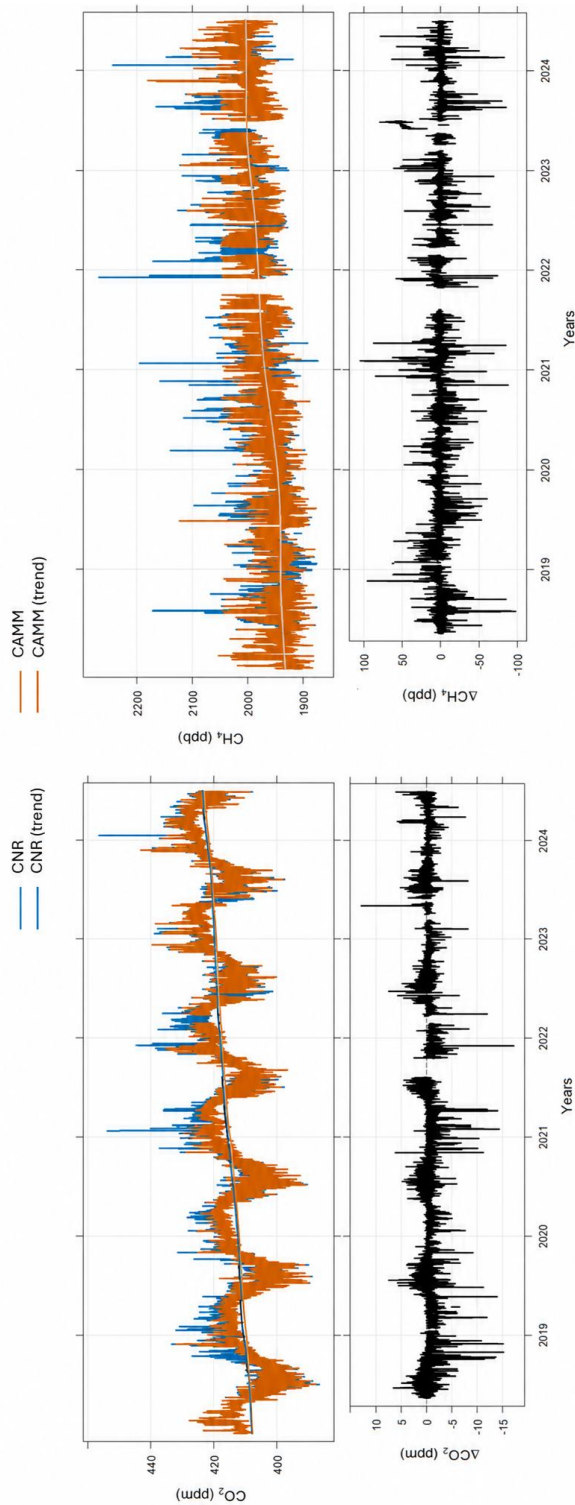


Figure 3: CO₂ and CH₄ dry mole fractions (top panels) in ambient air at the ‘O. Vittori’ observatory (CNR; blue) and along the mountain ridge (CAMM; red), together with the corresponding deviations (ΔCO₂ and ΔCH₄; bottom panels) between CAMM and CNR. Data shown are 1-hour means for the period May 2018–June 2024. The trend lines report the trend component of the time series deduced from the application of CCGRCV methodology (Section 3.1). Plots produced with the R package “Openair” (Carslaw and Ropkins, 2012).



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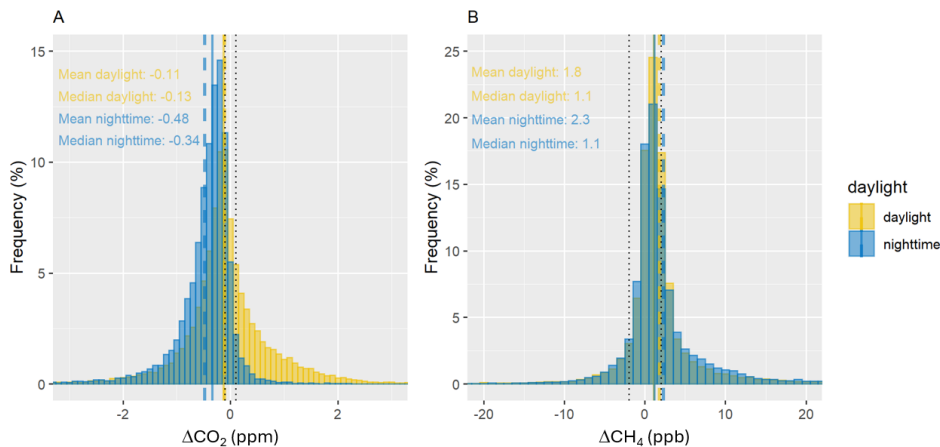
Location	CO ₂ (ppm yr ⁻¹)	CH ₄ (ppb yr ⁻¹)
Mountain ridge (CAMP)	2.75 ± 0.19	11.0 ± 1.9
“O. Vittori” (CNR)	2.86 ± 0.21	10.6 ± 1.6

282 **Table 1: CO₂ and CH₄ growth rates at CMN obtained by CAMP and CNR datasets (2018 – 2024). Uncertainties**
283 **represent the 2σ confidence intervals of the trend estimates.**

284

285 Fig. 3 also shows the trend lines for CO₂ and CH₄ calculated by using the Carbon Cycle Group CuRve (CCGRV)
286 signal decomposition method (Thoning et al., 1989) for the period 2018 - 2024. The average growth rates over
287 the considered period are consistent between the two measurement sites (Tab. 1). Nevertheless, the CO₂ and CH₄
288 data observed by CAMP appear to exhibit a lower range of variability than those observed by CNR (Fig. 3). One
289 contributing factor is the strict flagging strategy applied by CAMP, which led to the rejection of values exceeding
290 predefined thresholds or deemed not representative of background atmospheric conditions. In particular, the CH₄
291 data distribution in the CAMP – CNR scatterplot (Fig. SM2) reveals the presence of cutoffs for data higher than
292 2050 ppb in the CAMP data record, related to the “plausibility” screening adopted until June 2023. This has
293 resulted in the episodic occurrences of very large deviations in CH₄ (> 50 ppb, see Fig. SM3 in the supplementary
294 material) between the two laboratories. However, this data filtering does not appear to have been applied
295 consistently throughout the measurement period, as indicated by the presence of CH₄ values exceeding 2050 ppb
296 even before June 2023 (see Fig. 3). For this reason, the subsequent analyses for CH₄ include only data for which
297 the corresponding CNR values are below 2050 ppb (98.8% of the dataset).

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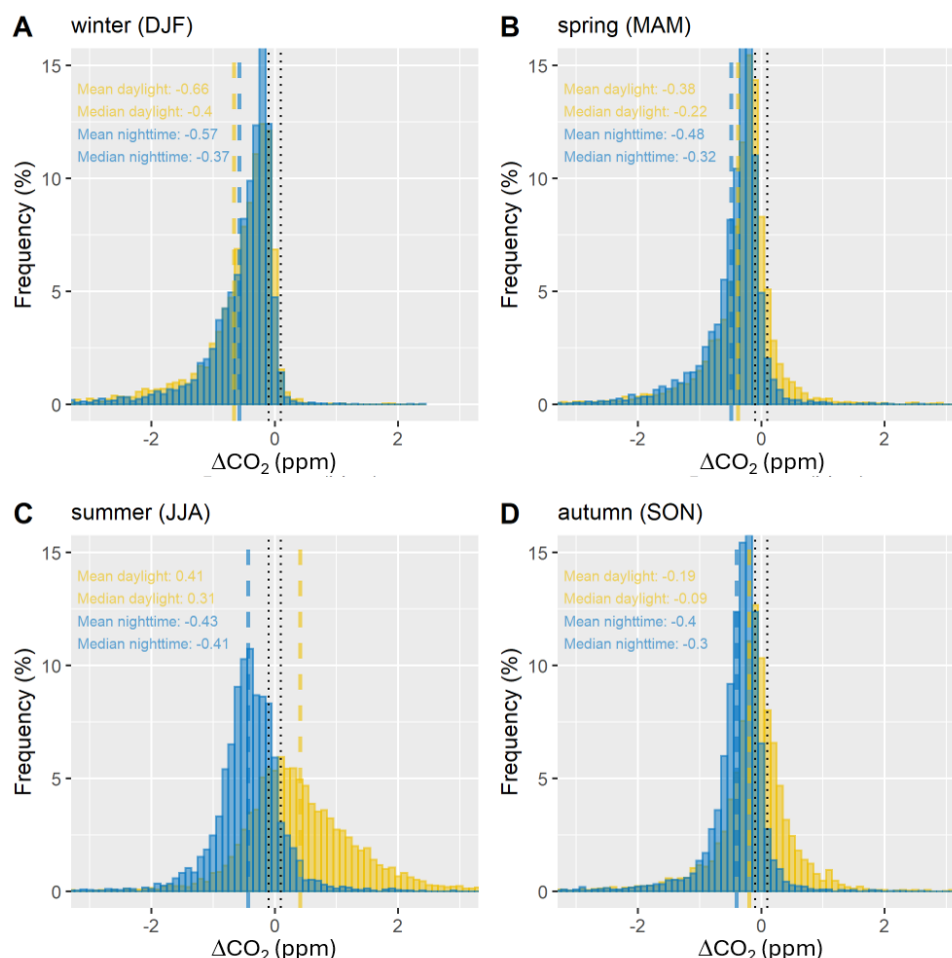
300 **Figure 4: Data frequency plots for ΔCO_2 (A) and ΔCH_4 (B), showing nighttime (sunset–sunrise) and daytime (sunrise–**
301 **sunset) values. Tick-dashed lines indicate mean deviations, and black dotted lines mark the WMO compatibility goals**
302 **(±0.1 ppm for CO₂; ±2 ppb for CH₄).**

303

304 Negative ΔCO_2 was predominantly observed over the entire comparison period (Fig. 4): during the night (Fig.
305 4A), the differences largely exceeded the WMO compatibility goal (mean = -0.48 ppm; median = -0.34 ppm),
306 while values close to the compatibility goal (mean = -0.11 ppm; median = -0.13 ppm) were observed during the



307 daytime. Additionally, the ΔCO_2 data distributions were skewed towards lower values at night. Overall, 13.1% of
 308 the 1-hour mean values fell within the WMO compatibility goal, while 28.2% of the data fell within the extended
 309 goal of ± 0.2 ppm. For ΔCH_4 , positive values were typically observed but with a normal distribution for both day
 310 and night (Fig. 4B) and mean (median) values of 1.8 ppb (1.1 ppb) and 2.3 ppb (+1.1 ppb) for day and night,
 311 respectively. Overall, 59.8% of the 1-hour mean values fell within the WMO compatibility goal, while 82.7% of
 312 the ΔCH_4 data fell within the extended goal of ± 5 ppb. For all years considered (see Fig. SM4 and SM5 in the
 313 supplementary material), the mean ΔCO_2 ranged from -0.6 ppm (in 2020 and 2021) to -0.3 ppm (in 2024) at night,
 314 and from -0.3 ppm (2021) to +0.1 ppm (in 2023) during the day. The mean ΔCH_4 values were higher at night
 315 (from 1.3 ppb in 2023 to 3.3 ppb in 2019) than during the day (from 0.8 ppb in 2018 to 2.8 ppb in 2021).
 316



317
 318 **Figure 5: Seasonal frequency distribution of ΔCO_2 , with nighttime (blue) and daytime (yellow) values. Tick-dashed**
 319 **lines show mean deviations, while black dotted lines indicate the WMO compatibility goal (± 0.1 ppm).**
 320

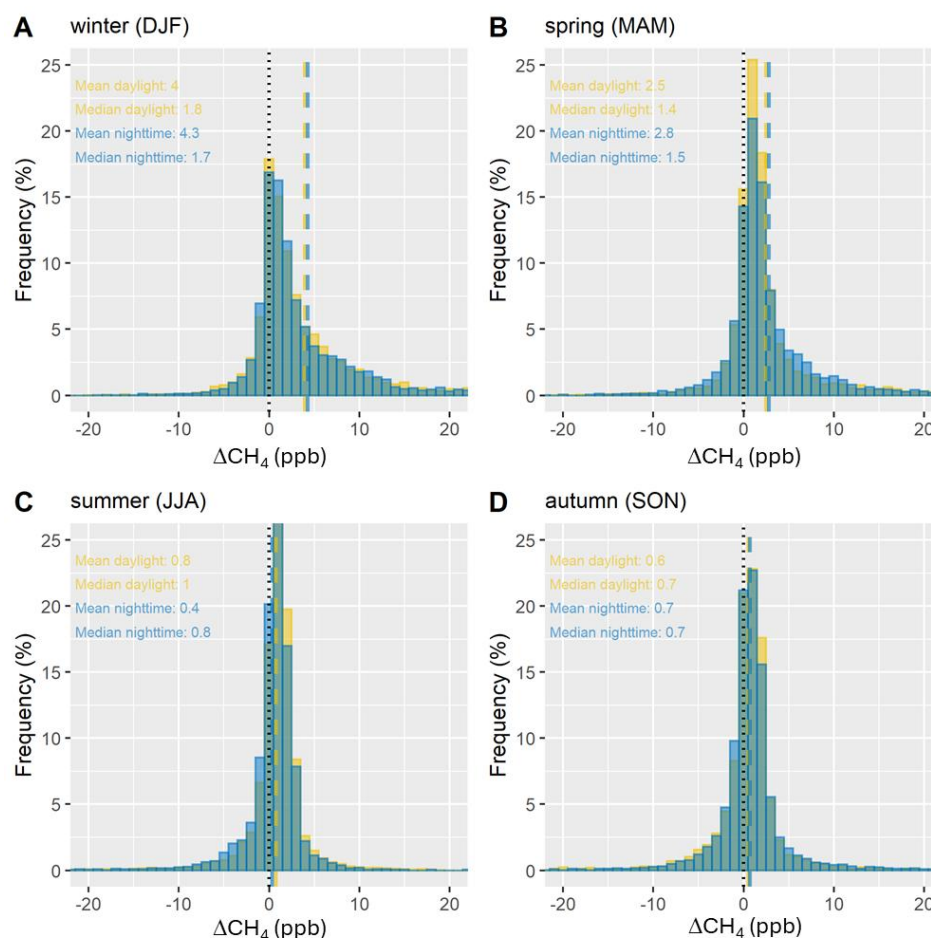


Figure 6: Seasonal frequency distribution of ΔCH_4 , with nighttime (blue) and daytime (yellow) values. Tick-dashed lines show mean deviations, while black dotted lines indicate the WMO compatibility goal (± 2 ppb).

Figures 5 and 6 show the seasonal distribution of ΔCO_2 and ΔCH_4 data for all measurement years. Skewed data distributions are observed for both ΔCO_2 and ΔCH_4 in winter (towards negative and positive values, respectively), with no significant differences emerging between nighttime and daytime, which exhibit similar mean values (-0.57 ppm and -0.66 ppm for ΔCO_2 ; 4.0 ppb and 4.3 ppb for ΔCH_4). Similar data frequency distributions and seasonal means are observed from spring to autumn for ΔCH_4 , while clear differences emerge for ΔCO_2 across the seasons. Notably, the nighttime ΔCO_2 data distribution in summer appeared to be normally distributed, centred around a mean value of -0.43 ppm, while the daytime distribution was skewed towards positive values (i.e., higher CO_2 at CAMM with respect to CNR), with an average value of +0.41 ppm.



3.2 Seasonal and diurnal cycles in ΔCO_2 and ΔCH_4

As shown above, the CAMM (mountain ridge) and CNR (“O. Vittori”) datasets show comparable multiannual CO_2 and CH_4 trends, and both time series follow the same seasonal variations. However, two datasets show notable deviations that often exceed the WMO compatibility goals. In order to better characterise these differences, and to assess impacts on the temporally aggregated data, we have analysed and compared the seasonal and diurnal cycles of ΔCO_2 and ΔCH_4 for each individual measurement year.

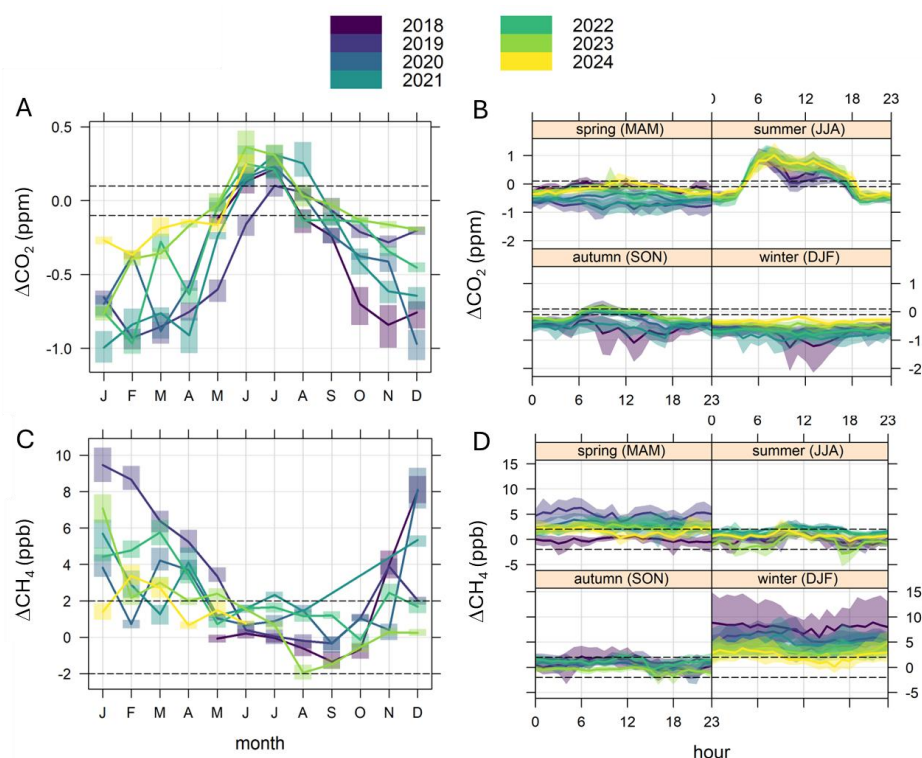


Figure 7: Monthly mean values (A) and annual diel cycles (B) of ΔCO_2 , with 95% confidence intervals shown as vertical bars (A) and shaded areas (B). Horizontal dashed lines indicate the WMO compatibility range. Colours denote the years. Panels (C) and (D) show the corresponding results for ΔCH_4 . Plots produced with the R package “Openair” (Carslaw and Ropkins, 2012).

The monthly averaged ΔCO_2 (Fig. 7A) typically exceeded the upper limit of the WMO compatibility goal during the summer months (mean value: 0.12 ppm), whereas it was below the lower limit from late autumn to spring (mean value: -0.43 ppm). The seasonal diel cycles of ΔCO_2 show no variations during wintertime, except in 2018 when a minimum is evident in the middle of the day (Fig. 7B). Please note that only December data is available for the winter months of 2018. A clear diurnal cycle emerges in summer, with CAMM reporting higher CO_2 values (up to +1 ppm) during daytime and lower values (down to -0.5 ppm) during nighttime (Fig. 7B). In 2018-2019, CO_2 deviations within the WMO compatibility goal were present in the central part of the day. This summertime behaviour has already been pointed out by the WMO/GAW World Calibration Center for Surface Ozone, Carbon



Monoxide, Methane and Carbon Dioxide during system and performance audits conducted at the CMN (Zellweger et al., 2018; Zellweger et al., 2024) and was tentatively attributed to the different locations of the air inlets of the two laboratories. To obtain further insight into the process that can lead to the appearance of the summer ΔCO_2 diurnal cycle, we analysed the diurnal variability of atmospheric equivalent black carbon (eqBC) from 2018 to 2024 (Fig. 8A). The eqBC concentrations were derived from the aerosol absorption coefficients measured at 637 nm using a multi-angle absorption photometer (MAAP, Model 5012, Thermo Scientific), following the methodology described in Marinoni et al. (2008) and Zanatta et al. (2026). A wavelength correction factor of 1.05 is applied, as recommended by Müller et al. (2011), and the result is multiplied by the nominal mass absorption cross-section of the instrument ($6.6 \text{ m}^2/\text{g}$). The data used in this work are based on the dataset “Equivalent black carbon product dataset collection over Monte Cimone, Italy 2007-2024” (Zanatta et al., 2025) which is publicly available on the ITINERIS-HUB data repository (<https://hub.itineris.cnr.it/datasets/>).

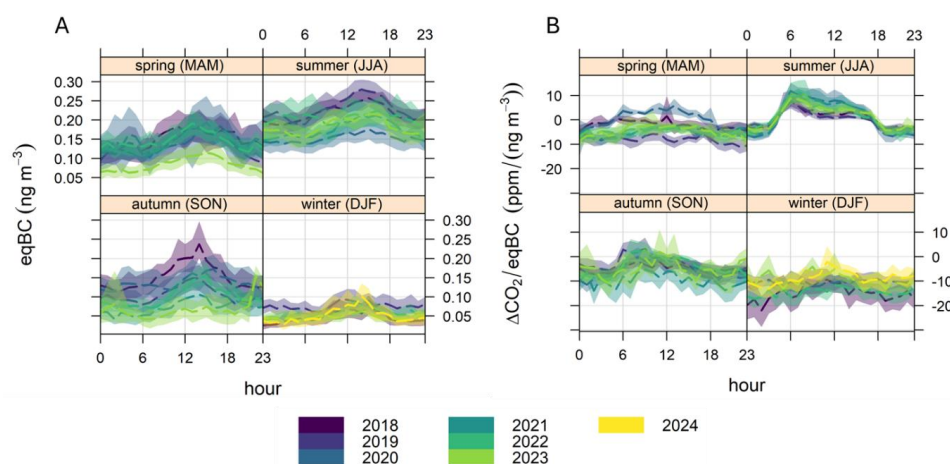


Figure 8: Seasonal diurnal cycles of eqBC (A) and $\Delta\text{CO}_2/\text{eqBC}$ ratio (B) at the “O. Vittori” observatory. The shaded areas represent the 95% confidence interval. Colours denote the calendar years. Plots produced with the R package “Openair” (Carslaw and Ropkins, 2012).

The diurnal cycles of eqBC generally follow a similar pattern to those observed at other mountain stations in Europe (Sun et al., 2021), with the seasonal diurnal cycles primarily influenced by the planetary boundary layer (PBL) height and convective upslope winds. Since air from the PBL is enriched in eqBC, higher values are typically measured during the day from spring to autumn. As reported by previous studies (e.g., Colombo et al., 2000; Trisolino et al., 2021), the diurnal CO_2 cycle at CMN is also affected by the thermal transport of PBL air masses up to the mountain peak. Daytime thermal winds bring CO_2 depleted air masses to the measurement site due to the vegetation sink within the PBL. This effect is further enhanced by the presence of forests on the slopes of the mountain (Colombo et al., 2000).

To better understand the diurnal variability of summer ΔCO_2 , we calculated the diurnal cycle of the $\Delta\text{CO}_2/\text{eqBC}$ ratio (Fig. 8B). Assuming that air masses transported from the PBL were the only source of diurnal variability for eqBC and CO_2 with a similar degree of air mass mixing and dilution, we would expect a constant $\Delta\text{CO}_2/\text{eqBC}$ ratio. However, the observed increase in the $\Delta\text{CO}_2/\text{eqBC}$ ratio (Fig. 8B) during the hours from 3:00 to 20:00 UTC



in summer and, albeit less evident and robust, from 5:00 to 18:00 UTC in autumn indicates that a process other than the transport of air masses from the PBL determines the observed deviations. As the daily increase in ΔCO_2 coincides with the sunrise in summer and autumn and it occurs earlier than the daily increase in eqBC (Fig. 8A), it is likely that the CO_2 uptake by the grasslands near the mountain top plays a role, as already suggested by Zellweger et al. (2018; 2024). As the CNR observatory is located on a mountain slope with a lower air intake height than CAMM, the CNR observations are likely to be more influenced by CO_2 uptake by mountain meadows. This is further supported by the reduced $\Delta\text{CO}_2/\text{eqBC}$ diurnal cycle in spring (except in 2020), when the slopes of Mt. Cimone were still snow-covered and the impact of local biospheric activity was therefore less likely. ΔCH_4 monthly mean values showed positive values largely exceeding 2 ppb during winter and early spring (i.e. from December to April) and on May and November (2019 – 2018 and 2022), with the mean monthly values remained within the ± 2 ppb compatibility goal during the rest of the year (Fig. 7C). The ΔCH_4 seasonal diel cycles (Fig. 7D) do not show systematic variability although negative and positive peaks can be observed, reflecting episodic CH_4 deviations between the two measurement sites.

3.3 Dependency of ΔCO_2 and ΔCH_4 by local wind regime

In order to determine whether local sources or sinks could be responsible for the observed deviations, we examined the dependence of ΔCO_2 and ΔCH_4 depend on local wind speed and direction. For this purpose, we categorized the 1-hour mean deviations as a function of season (winter and summer) and time of day (daytime and nighttime).

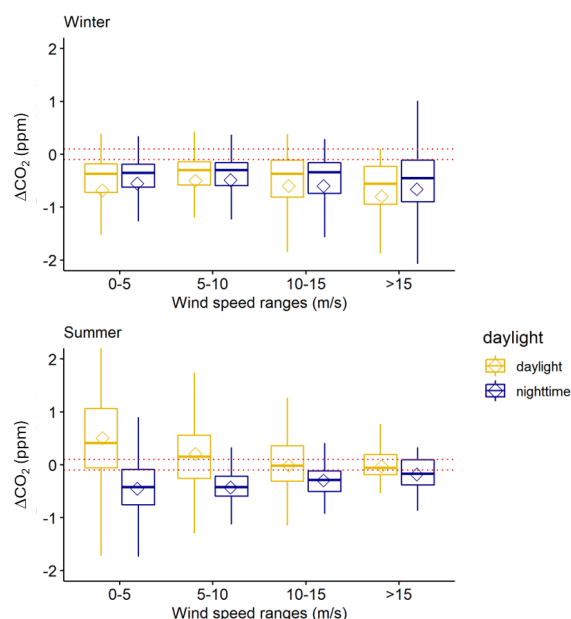
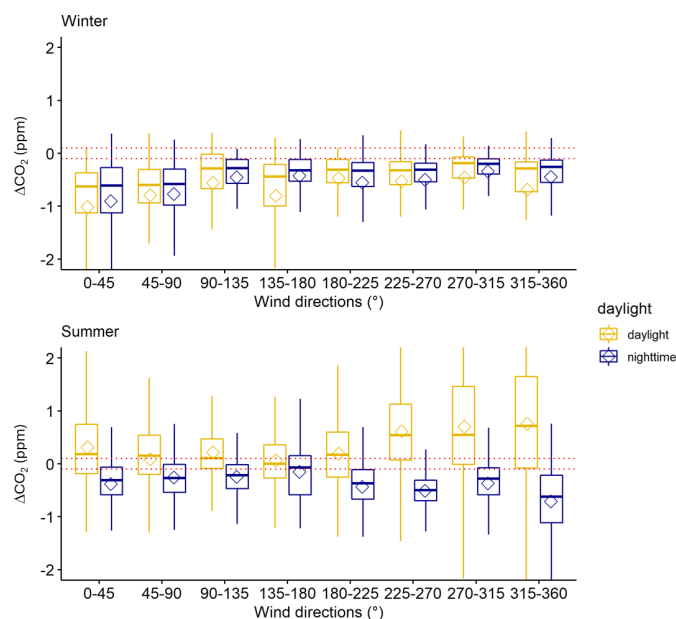


Figure 9: ΔCO_2 as a function of wind speed ranges, season (Winter, Summer) and period of day (daytime, nighttime). For each wind speed rang, the boxes report the 25th and 75th with median values (tick horizontal lines). The whiskers indicate data range falling within 1.5 times the interquartile range.



404 As demonstrated in Fig. 9, no clear correlation between the mean ΔCO_2 and wind speed was observed during the
405 winter months. During the summer months, a higher spread of ΔCO_2 values was observed for low wind speeds ($<$
406 5 m s^{-1}) at nighttime. Furthermore, an increasing tendency for better agreement (i.e. ΔCO_2 converging to WMO
407 goal) was observed with rising wind speed. A clear dependence on wind speed can be observed during the summer
408 daytime: for wind speeds above 5 m s^{-1} , the average ΔCO_2 was near or within the WMO goals, and the ΔCO_2
409 spread decreased. The fact that there was better agreement between the CAMM and CNR data in ambient
410 conditions characterised by higher wind speeds would suggest the presence of local sources affecting the
411 measurements at night and sinks affecting the measurements during the day. In particular, local biospheric activity
412 may explain some of the CO_2 deviations observed between the two datasets during the summer months.
413



414
415 **Figure 10: ΔCO_2 as a function of wind-direction sectors, seasons (winter, summer), and time of day (daytime,**
416 **nighttime).** For each wind sector, boxplots show the 25th–75th percentiles with median values (thick horizontal lines),
417 while whiskers represent data within 1.5 times the interquartile range.

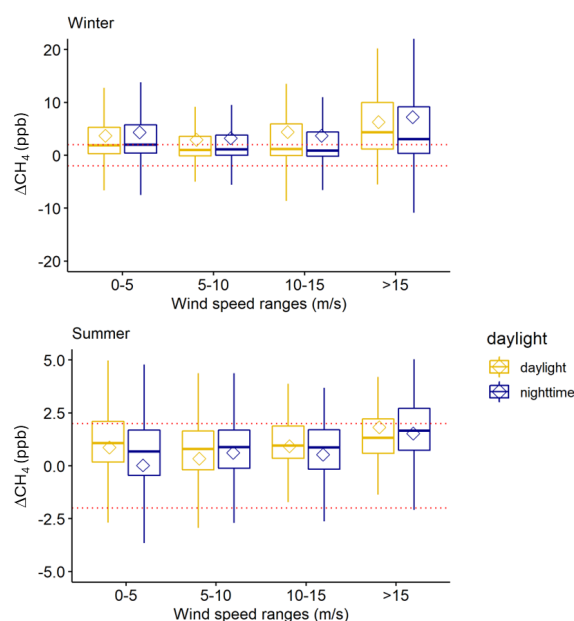
418

419 During the winter, a clear dependence of ΔCO_2 values on wind direction was observed, with the lowest values
420 occurring during northeasterly winds (Fig. 10).

421 In summer, we also observed an increase in deviations under certain wind directions. For winds from 225° to
422 360° , the ΔCO_2 values deviated more from the WMO goal, with different trends observed between nighttime and
423 daytime. The ΔCO_2 was more negative at night and more positive during the day. These findings, together with
424 the analysis of the diurnal variability of the $\Delta\text{CO}_2/\text{eqBC}$ ratio, suggest that CNR observations were more affected
425 by local biospheric influences than CAMM observations. This may be due to the lower sampling height used at
426 the CNR observatory. However, the representativeness of the two sampling sites cannot be ruled out as a possible
427 cause of the difference. As Vitali et al. (2024) recently argued, the wind field at the CAMM site could be affected



428 by disturbances related to the presence of structures or obstacles on the mountaintop, as well as by a sheltering
429 effect of the mountaintop for winds from the south/southwest. According to Vitali et al. (2024), upslope valley
430 winds associated with south-westerly winds may be particularly effective in funnelling air masses affected by
431 biospheric activity related to Apennine vegetation to the CMN. Given the lack of dependence of ΔCH_4 on the
432 local wind regime in summer, it is reasonable to conclude that observations at the CNR site are more susceptible
433 to local or regional biospheric signals than those conducted at the CAMM mountain ridge laboratory.
434



435
436 **Figure 11: Same as figure 9 but for ΔCH_4 .**

437
438 In winter (Fig. 11), the mean ΔCH_4 exceeded the WMO compatibility goal, with increased mean values and
439 variability (note the high interquartile range) at high wind speeds ($>15 \text{ m s}^{-1}$). There was also a slight tendency
440 for ΔCH_4 to increase with wind speed in summer; however, the mean deviations remained within the WMO goal
441 for both daytime and nighttime data (Fig. 11).
442

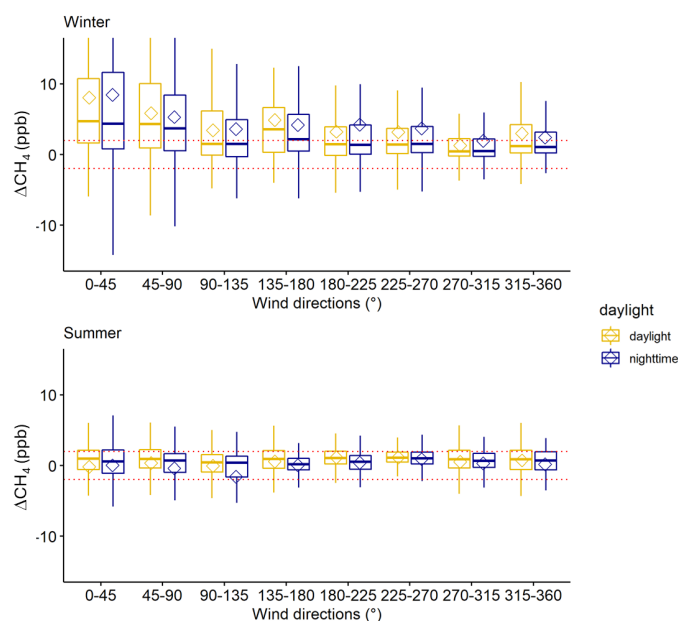


Figure 12: As figure 10 but for ΔCH_4 .

Wind direction significantly impacts ΔCH_4 in winter (Fig. 10), with the highest deviations (CAMM values higher than CNR) occurring for wind directions between 0° and 180° . This trend mirrors that observed for CO_2 (Fig. 7), where the largest (though negative) deviations occurred also in the same wind direction sectors. The discrepancies between the two sampling sites are difficult to attribute. It should be noted that a wastewater treatment tank is located ~ 10 m north-east of the tower housing the CAMM sampling inlet (see Fig. 1). However, no such CH_4 signal is observed in summer, despite the higher air temperature and reduced snow cover, which would be expected to result in increased microbiological emissions. Therefore, it seems unlikely that the wastewater tank is the actual source of CH_4 for the CAMM observations, nor can it explain the large ΔCO_2 values observed for this wind sector in winter.

As reported in Section 2, the horizontal distance between the CAMM and CNR air intakes is 90 m, and the vertical distance is 50 m. Another point to investigate is whether, under highly variable atmospheric conditions, the differing sampling locations could lead to systematic discrepancies between CAMM and CNR measurements. Wind sectors between 0° and 90° correspond to one of the main wind directions observed at CMN (see Fig. SM6 in the supplementary material). Especially in winter, these sectors exhibit strong temporal variability in CO_2 and CH_4 , as indicated by the analysis of the 1-hour standard deviation values (see Fig. SM7 in the supplementary material). The next section therefore examines the possible impact of CO_2 and CH_4 temporal variability on ΔCO_2 and ΔCH_4 investigating whether the disagreement between the two measurement sites in winter can be attributed to the slightly different locations of the CAMM and CNR inlets.



3.4 Impact of atmospheric variability on ΔCO_2 and ΔCH_4

In order to quantify the amount of disagreement between the two measurements that can be attributed to different sampling locations, we examined changes in CO_2 and CH_4 deviations as a function of hourly standard deviations, which were calculated from 1-minute CNR measurements. We assume that low standard deviation values are representative of low atmospheric variability, under which the degree of agreement between measurements taken at close sampling locations would be maximised. This approach is inspired by the strategy used by Levin et al. (2020), who applied an hourly standard deviation threshold to identify measurement periods characterised by low atmospheric variability for the purpose of comparing continuous and flask measurements for quality control purposes. For this test, different standard deviation thresholds corresponding to the 25th and 50th percentile of the CO_2 (0.14 ppm and 0.44 ppm, respectively) and CH_4 (0.9 ppb and 3.0 ppb) data population were adopted.

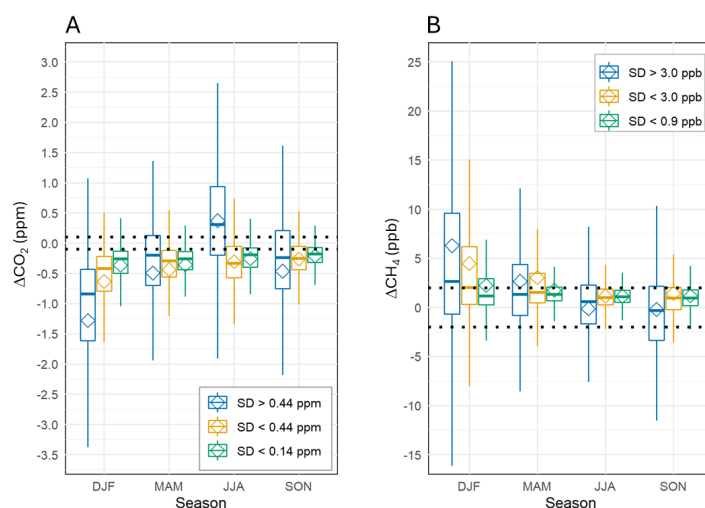


Figure 13: Seasonal distributions and mean values (diamonds) of ΔCO_2 (A) and ΔCH_4 (B) after applying different threshold values to CO_2 and CH_4 standard deviations. Whiskers represent data within 1.5 times the interquartile range.

Notable convergence of ΔCO_2 and ΔCH_4 values was observed across all seasons when the data were screened for conditions of low atmospheric variability (Fig. 13). After adopting a threshold value of 0.44 ppm (0.14 ppm), the mean ΔCO_2 reduced to -0.63 ppm (-0.36 ppm) in winter, -0.44 ppm (-0.36 ppm) in spring, -0.31 ppm (-0.26 ppm) in summer and -0.26 ppm (-0.21 ppm) in autumn, with respect to the remaining data. Screening the data for low atmospheric variability (hourly standard deviation < 0.9 ppb), resulted in mean seasonal ΔCH_4 values that met the WMO goals for all seasons except in winter (+2.2 ppb). Deviations occurring in winter for winds from the North-East, in particular, show an evident reduction of the bias when considering data characterized by low atmospheric variability. For this wind sector, when the winter data were selected for a low hourly standard deviation of CO_2 (CH_4), the mean ΔCO_2 (ΔCH_4) shifted from -1.62 ppm to -0.39 ppm (from +9.7 ppb to +3.2 ppb).



3.5 Possible influence of local human presence on ΔCO_2 and ΔCH_4

Previous studies have shown that local anthropogenic activities can influence GHG measurements at mountain stations (Affolter et al., 2021; El Yazidi et al., 2018; Hoheisel et al., 2023). We therefore explored whether differences between the CAMM and CNR observations varied between days with and without recorded access to the CNR observatory. The analysis covered January 2021–June 2024 and included 191 access days. Because no equivalent access record was available for CAMM, and access occurrence may covary with meteorological conditions, this analysis should be regarded as exploratory rather than as a direct attribution of the observed differences to human presence.

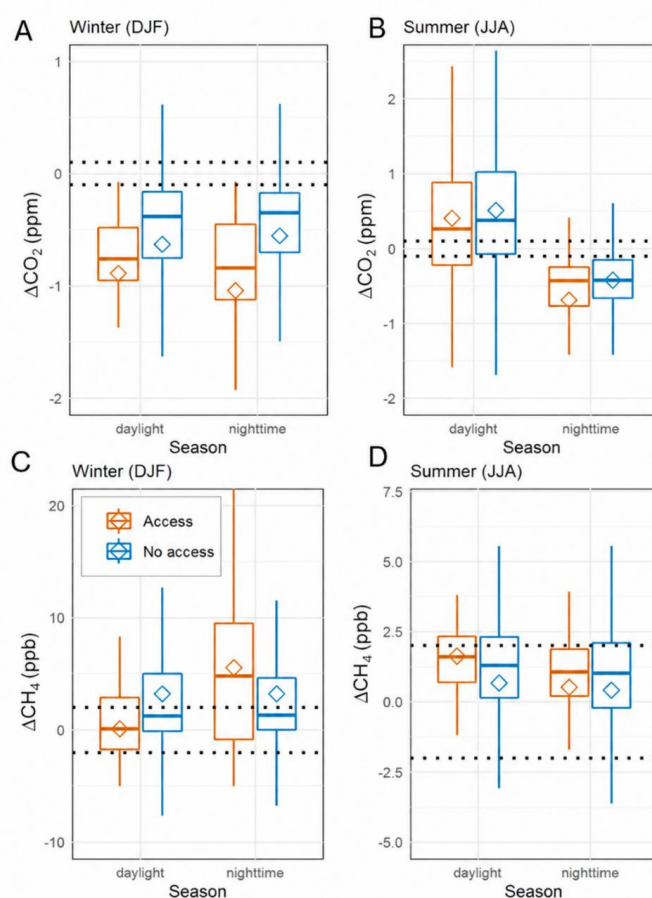


Figure 14: Seasonal distributions of ΔCO_2 (A, B) and ΔCH_4 (C, D) during winter (A, C) and summer (B, D), comparing periods with ("Access") and without ("No access") operators, external users or visitors at the CNR observatory. Boxplots represent the 25th–75th percentile range, with median values shown by thick horizontal lines. Diamonds indicate arithmetic means and whiskers extend to 1.5 times the interquartile range. Dotted horizontal lines indicate the WMO compatibility goals.

For ΔCO_2 , access days were associated with a shift towards lower CAMM–CNR differences in all daytime categories (Fig. 14; Table 2). The mean "Access–No access" differences amounted to -0.26 ppm during winter



daytime and -0.48 ppm during winter nighttime, while smaller decreases were observed during summer (-0.10 ppm during daytime and -0.25 ppm during nighttime; Table 2). To gain additional insight into the possible origin of these differences, we separately examined the residual dry mole fractions at CAMM and CNR obtained after the application of CCGRCV (Fig. SM8, supplementary material). Figure SM8 shows that CO_2 residuals generally increased at both observatories during “Access” days. During winter daytime the increase was substantially larger at CNR ($+1.6$ ppm) than at CAMM ($+0.7$ ppm), whereas nighttime increases were more similar ($+0.8$ and $+0.5$ ppm, respectively). The fact that larger increases of CO_2 residuals were observed during the daytime at the CNR observatory suggests that anthropogenic activities near the CNR inlet could interfere with CO_2 observations, and that this interference was also detected at the CAMM inlet, albeit to a lesser extent. This is somewhat expected, given that the analysed accesses took place at the CNR facility, which is 90 m away from the CAMM inlet. During summer daytime, the two laboratories observed a comparable increase in CO_2 residuals for days with accesses of 1.9 ppm (CAMM) and 1.8 ppm (CNR). During the night a larger increase was observed for CNR (0.9 ppm) than CAMM (0.3 ppm). The better agreement in CO_2 residuals during daytime in the summer months can be tentatively explained by the fact that, during that season, accesses were mostly represented by groups of tourists who visited both the CNR and CAMM terraces on the same day.

Table 2: Comparison between the effects of access conditions at the “O. Vittori” observatory on ΔCO_2 and ΔCH_4 .

Season	Period	ΔCO_2 (Access – No access) (ppm)	ΔCH_4 (Access – No access) (ppb)
Winter	Daytime	-0.26	-2.1
Winter	Nighttime	-0.48	$+5.3$
Summer	Daytime	-0.10	$+0.9$
Summer	Nighttime	-0.25	$+0.1$

No comparably consistent pattern was found for CH_4 . “Access–No access” differences were small in summer, whereas in winter their sign depended on the daytime category (Fig. 14, Table 2). The analysis of CH_4 residuals (Fig. SM8) shows a shift to higher values for both the observatories in winter during “Access” conditions, especially evident for CNR during daytime. On the opposite, during “Access” conditions, a shift towards lower values characterised both the observatories in summer with CNR showing a larger decrease during daytime with respect to CAMM. The available observations do not allow the access-related perturbations to be uniquely attributed to emissions occurring at either observatory.

Overall, the analysis indicates that local human presence might contribute slightly to the variability of the CAMM–CNR CO_2 differences, while the evidence is weaker and less coherent for CH_4 . Other factors associated with access days, particularly meteorological and transport conditions, may also explain part of the observed differences.

3.6 Impact of the calibration corrections on ΔCO_2 and ΔCH_4

Two system and performance audits were conducted at CMN by the WMO/GAW “World Calibration Center for Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide” (hereafter referred to as WCC-Empa) in June 2018 (Zellweger et al., 2018) and September 2023 (Zellweger et al., 2024). During these audits, the CMN instruments were repeatedly challenged with randomised CO_2 and CH_4 levels from the WCC-Empa



539 travelling standards. These standards are traceable to the primary reference standards maintained by the Central
540 Calibration Laboratory (CCL) hosted by NOAA/GML.
541

Year	Laboratory	a	B
2018	CAMM	1.00252	-0.96
	CNR-ISAC	1.00114	-0.43
2023	CAMM	1.00049	-0.22
	CNR-ISAC	1.00047	-0.21

542
543 **Table 3: Coefficients of the equations “Unbiased CO₂ dry mole fraction (ppm) = CO₂ * a (ppm) + b (ppm) for CAMM**
544 **and CNR-ISAC instrument during the audits in 2018 and 2023.**
545

Year	Laboratory	a	B
2018	CAMM	1.00644	-11.77
	CNR-ISAC	1.00140	-2.70
2023	CAMM	1.00331	-6.92
	CNR-ISAC	1.00140	-3.00

546
547 **Table 4: Coefficients of the equations “Unbiased CH₄ dry mole fraction (ppb) = CH₄ * a (ppb) + b (ppb) for CAMM**
548 **and CNR-ISAC instrument during the audits in 2018 and 2023.**
549

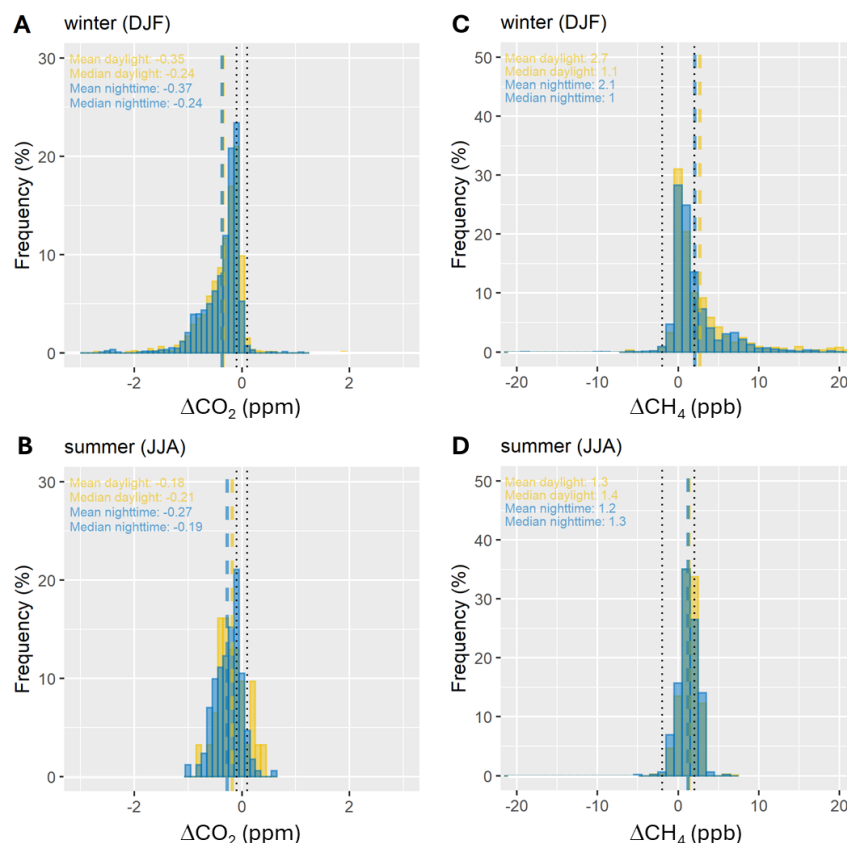
550 Tables 3 and 4 show the coefficients of the equations describing the biases of the CMN instruments compared to
551 the WCC-Empa travelling standards. As detailed in the audit reports (Zellweger et al., 2018; 2024), the CMN
552 instruments demonstrated agreement with the travelling standard during both intercomparisons, aligning with the
553 WMO compatibility goal for CO₂ and CH₄. Agreement between the CAMM and CNR-ISAC instruments was
554 excellent for the 2023 intercomparison; however, a not negligible deviation was observed for the 2018
555 intercomparison. The calculated equations, shown in Tables 3 and 4, implied a negative bias of the CAMM
556 instrument with respect to CNR of half of the WMO compatibility goal for CO₂ dry mole fractions above 425
557 ppm and for CH₄ dry mole fractions above 2000 ppb, roughly representing the 23% of the original data.
558 The coefficients obtained during the audits describe the instrumental behaviour only at the time of the
559 intercomparisons. Since the performance of the analysers can change between audits, their calibration state is not
560 guaranteed to remain constant over multi-year periods. For this reason, we did not retroactively correct ΔCO₂ or
561 ΔCH₄ using constant parameters.

562 3.7 Bias reassessment after considering impact of the atmospheric variability and human accesses

563 To get an overall picture of the potential impact of all the various contributors on hourly changes in CO₂ and CH₄,
564 for the period 2021 – 2024 (the choice of this shorter time period is related to the availability of access data to the
565 CNR laboratory), we recalculated the deviations after: (a) considering only data characterised by low atmospheric
566 variability (i.e. hourly CO₂ standard deviation lower than 0.13 ppm and hourly CH₄ standard deviation lower than
567 0.9 ppb), (b) selecting the data for which there was no concurrent person access at the CNR observatory. The
568 implementation of these selections led to the rejection of about 75% of the hourly data. Here, we present the



569 results for the winter and summer seasons, and the full analysis can be found in the supplementary material (Fig.
570 SM9).



571
572 **Figure 15: Data frequency plots for ΔCO_2 (A - B) and ΔCH_4 (C - D) for summer and winter seasons after (a) considering**
573 **only data characterised by low atmospheric variability, (b) selecting the data for which there was no concurrent person**
574 **access at the CNR observatory. Nighttime (blue) and daytime (yellow) value are reported. Tick dashed lines represent**
575 **the mean deviations, while the black dotted lines indicated the WMO compatibility goals (± 0.1 ppm for CO_2 , ± 2 ppb**
576 **for CH_4).**

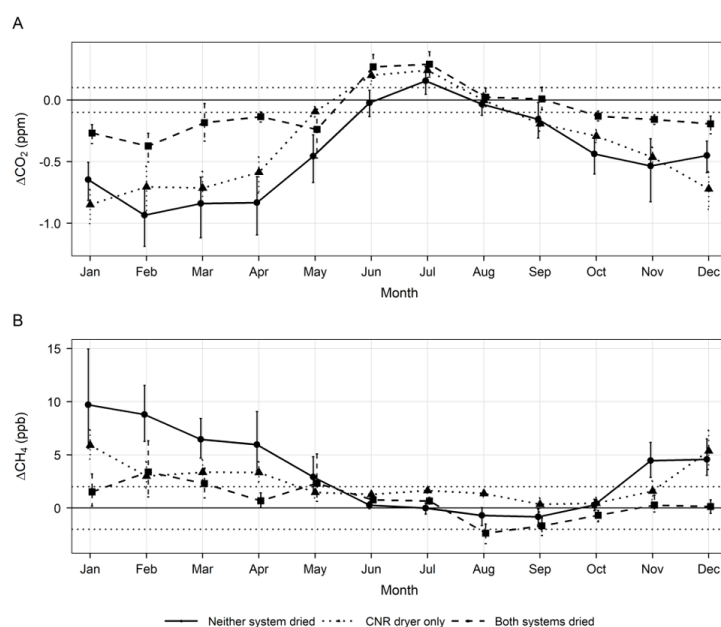
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578 For ΔCO_2 , the results (Fig. 15 A, B) showed a narrowing of the data distribution and mean deviation values,
579 approaching the WMO goals for both winter and summer. In particular, the range of the mean ΔCO_2 value was -
580 0.35 ppm (daytime) to -0.37 ppm (nighttime) in winter, and -0.18 ppm (daytime) to -0.27 ppm (nighttime) in
581 summer. After implementing the recalculations, these values represent a percentage increase in ΔCO_2 of +41% in
582 winter and +40% in summer for the same reference period. For ΔCH_4 , an improvement of the deviations between
583 CAMM and CNR was observed for winter with mean ΔCH_4 decreasing to 2.4 ppb (-41 %), see Fig. 15C. Also for
584 spring mean ΔCH_4 decreased with respect to the whole data selection, with values within the WMO compatibility
585 goals (Fig. SM9).



3.8 Potential influence of Nafion sample drying on ΔCO_2 and ΔCH_4

Previous work has shown that the use of Nafion sample dryers can improve the consistency between co-located GHG measurement systems, particularly for CH_4 observations, by reducing systematic differences and increasing the proportion of measurements fulfilling the WMO compatibility goals (Laitinen et al., 2025). Because the CAMM and CNR laboratories adopted Nafion sample dryers at different times (June 2023 for CAMM and January 2020 for CNR), the study period considered in this work encompassed three distinct instrumental configurations: (i) neither laboratory operating a Nafion dryer (March 2018 - December 2019), (ii) only the CNR system equipped with a Nafion dryer (January 2020 – May 2023), and (iii) both laboratories operating Nafion dryers (June 2023 – June 2024). This progressive harmonization of the sampling configurations provided the opportunity to investigate whether changes in the drying strategy were associated with systematic variations in the magnitude, variability and seasonal behaviour of ΔCO_2 and ΔCH_4 between CAMM and CNR. For period (ii), data collected while CNR was temporarily operating the G1301 analyser were excluded to ensure consistency in the instrumental configuration.



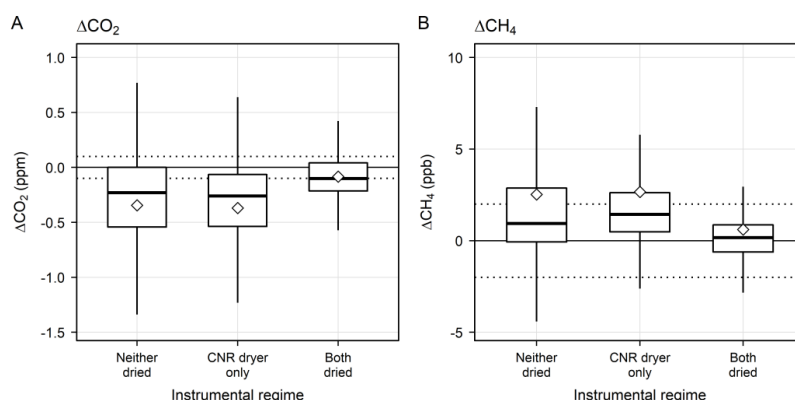
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Figure 16: Monthly climatology of the daily differences between CAMM and CNR measurements for ΔCO_2 (A) and ΔCH_4 (B) under the three instrumental configurations: neither sampling system equipped with a Nafion dryer ("Neither system dried"), only the CNR sampling line equipped with a Nafion dryer ("CNR dryer only"), and both sampling systems equipped with Nafion dryers ("Both systems dried"). Symbols represent monthly mean differences, while error bars denote the 95% bootstrap confidence intervals of the monthly means. Horizontal solid lines indicate zero difference, whereas dotted lines denote the WMO compatibility goals (± 0.1 ppm for CO_2 and ± 2 ppb for CH_4).

The monthly climatologies of the CAMM–CNR differences for the three instrumental configurations are shown in Figure 16. For ΔCO_2 (Fig. 16A), the largest differences are observed when neither sampling lines were equipped with a Nafion dryer. For this period, the monthly mean differences range from -0.93 ppm in February to 0.15 ppm



in July, corresponding to a yearly mean ΔCO_2 of -0.43 ppm. For the period January 2020 – May 2023, when the Nafion dryer was only installed on the CNR sampling line, the yearly mean ΔCO_2 increase to -0.35 ppm, ranging from -0.84 ppm in January to 0.24 ppm in July. In contrast, when both laboratories operated Nafion dryers (June 2023 – June 2024), the ΔCO_2 seasonal cycle became noticeably flatter, with monthly mean values ranging from -0.37 ppm (February) to 0.30 ppm (July), corresponding to a yearly mean value of -0.09 ppm. Consequently, the peak-to-peak seasonal ΔCO_2 amplitude decreased to 0.66 ppm, corresponding to a reduction of approximately 40% relative to the initial instrumental configuration. The behaviour of CH_4 (Fig. 16B) exhibited both similarities and notable differences. The largest positive differences occurred during winter and early spring during the first measurement period, with monthly mean values approaching 10 ppb in January and progressively decreasing towards WMO compatibility goals in summer (yearly mean value: 3.5 ppb). After the installation of the Nafion dryer at CNR, the winter enhancement was substantially reduced (monthly mean maximum of 5.9 ppb in January), while summer differences remained close to zero and the yearly mean ΔCH_4 value was equal to 2.4 ppb. A further reduction in the ΔCH_4 values was observed after the installation of the Nafion drier at CAMM, which remained below 3.4 ppb in February and resulting in a yearly mean ΔCH_4 of 0.6 ppb.



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Figure 17: Distribution of the mean daily ΔCO_2 (A) and ΔCH_4 (B) under the three instrumental configurations. Boxplots show the interquartile range (25th–75th percentiles), the horizontal line within each box represents the median, whiskers extend to 1.5 times the interquartile range, and open diamonds indicate the arithmetic mean. Outliers are omitted for clarity. Horizontal solid lines indicate zero difference, while dotted lines denote the WMO compatibility goals (± 0.1 ppm for CO_2 and ± 2 ppb for CH_4).

Figure 17 reports the overall distributions of the daily mean CAMM–CNR differences. For ΔCO_2 (Fig. 17A), the progressive harmonization of the sampling systems was accompanied by a marked reduction in both systematic bias and measurement variability. The mean daily difference decreased from -0.37 ppm when only the CNR system employed Nafion drying to -0.08 ppm after both laboratories adopted identical drying configurations. At the same time, the standard deviation was reduced from 0.70 to 0.35 ppm, while the interquartile range decreased from 0.47 to 0.26 ppm, indicating a substantially tighter distribution of daily differences. A corresponding



improvement is also evident in terms of WMO compatibility, with the percentage of observations falling within the WMO compatibility goal increasing from 13.6% to 28.5%. A similar behaviour was observed for ΔCH_4 (Fig. 17B). The mean CAMM–CNR difference decreased from 2.66 ppb to 0.61 ppb between the second and third instrumental configurations, accompanied by reductions in both the standard deviation (5.4 to 4.0 ppb) and the interquartile range (2.1 to 1.5 ppb). The fraction of observations satisfying the WMO compatibility goal also increased substantially, from 61.0% to 77.9%.

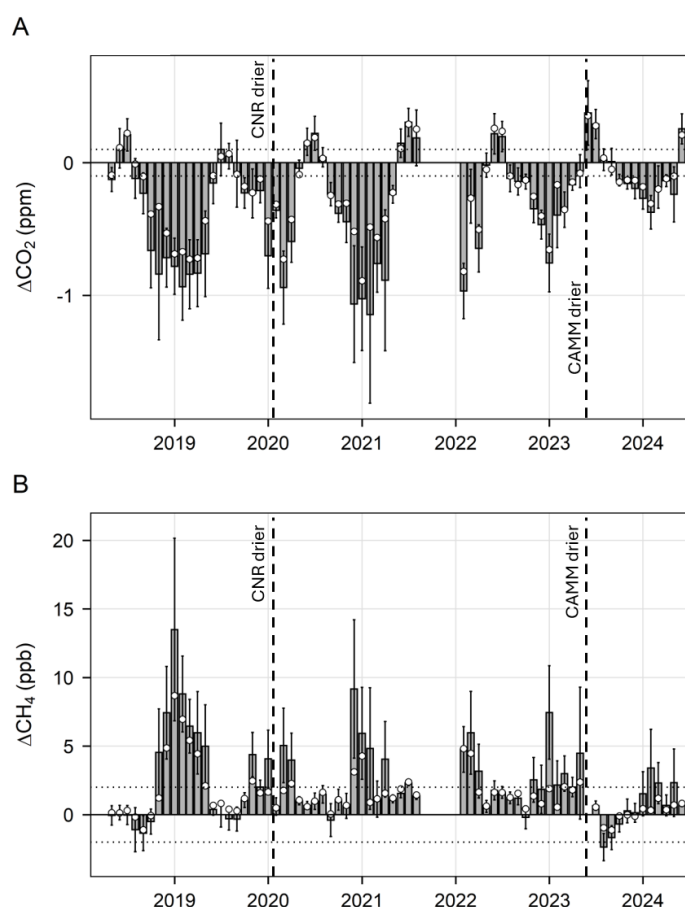


Figure 18: Daily differences between CAMM and CNR measurements for (A) ΔCO_2 and (B) ΔCH_4 over the study period. Vertical grey bars represent the monthly mean values, the thin bars show the 95% confidence level of monthly mean values, while the white dots represent the median values. Dashed lines indicate the installation dates of the Nafion dryers at CNR (January 2020) and CAMM (June 2023). Horizontal solid lines indicate zero difference, whereas dotted lines denote the WMO compatibility goals (± 0.1 ppm for CO_2 and ± 2 ppb for CH_4).

The monthly time series of ΔCO_2 and ΔCH_4 (Fig. 18) further shows that for both GHGs, a progressive improvements of the differences CAMM–CNR occurred during the whole period and that the periods following the installation of the Nafion dryers are characterized by a visibly reduced dispersion of the daily CAMM–CNR



differences. In particular, after June 2023, when both laboratories operated equivalent drying systems, the ΔCO_2 and ΔCH_4 values remained generally closer to zero than during the preceding years. To investigate whether the apparent improvement observed after June 2023 simply reflected the continuation of an already existing long-term evolution, we compared successive 12-month periods (June – May) preceding the installation of the Nafion dryer at CAMM using two complementary non-parametric approaches. First, differences between annual mean CAMM–CNR biases were estimated together with their 95% bootstrap confidence intervals obtained by non-parametric resampling with replacement (Efron, 1979; Efron and Tibshirani, 1994). Bootstrap confidence intervals were estimated by resampling the monthly mean CAMM–CNR differences within each annual period. Second, the statistical significance of the observed changes was evaluated using the Wilcoxon signed-rank test (Wilcoxon, 1945). Monthly values were paired according to the corresponding calendar month (e.g. June versus June, July versus July), thereby accounting for the seasonal cycle in the CAMM–CNR differences. The Wilcoxon signed-rank test was preferred over parametric alternatives because it does not require normally distributed differences and is robust for small paired samples, making it well suited for the present comparison of annual monthly means.

Table 5: Comparison of annual periods before and after the adoption of Nafion sample dryers. *Italic characters denote p-values < 0.1.*

Species	Comparison periods	Mean difference	Bootstrap 95% Confidence level	Wilcoxon signed-rank test (<i>p</i>)
ΔCO_2 (ppm)	Jun 2022–May 2023 vs Jun 2021–May 2022 ¹	+0.08	−0.13 to +0.31	0.938
	Jun 2023–May 2024 vs Jun 2022–May 2023	+0.13	−0.06 to +0.32	<i>0.016</i>
	Jun 2022–May 2023 vs Jun 2021–May 2022 ¹	−0.5	−1.9 to +1.2	0.469
	Jun 2023–May 2024 vs Jun 2022–May 2023	−1.9	−3.0 to −0.9	<i>0.0068</i>

¹September 2021–January 2022 were excluded because CNR was temporarily operating the G1301 analyser without Nafion drying.

Table 5 summarizes the comparison of consecutive 12-month periods spanning the installation of the Nafion sample dryer at the CAMM station in June 2023. For both CO_2 and CH_4 , the comparison between the two annual periods preceding the installation (June 2021–May 2022 and June 2022–May 2023) revealed no statistically significant changes. ΔCO_2 decreased from −0.29 to −0.21 ppm; however, the bootstrap confidence interval included zero and the Wilcoxon signed-rank test did not indicate a significant shift ($p = 0.938$). Similarly, the reduction in the mean ΔCH_4 difference from 3.0 to 2.4 ppb was not statistically significant ($p = 0.469$). In contrast, the comparison between the period June 2022–May 2023 and the first year after the installation of the Nafion dryer at CAMM (June 2023–May 2024) showed a markedly different behaviour. The mean ΔCO_2 further decreased from −0.211 to −0.082 ppm. Although the bootstrap confidence interval for the difference in the annual means still marginally overlapped zero, the paired Wilcoxon signed-rank test detected a significant reduction in the monthly differences ($p = 0.016$).



An even stronger signal emerged for CH₄. Following the installation of the Nafion dryer at CAMM, the mean Δ CH₄ decreased from 2.4 to 0.6 ppb. Both statistical analyses consistently supported the significance of this reduction: the bootstrap 95% confidence interval for the difference between annual means did not include zero, and the Wilcoxon signed-rank test indicated a highly significant decrease ($p = 0.0068$).

Overall, the statistical analyses indicate that the largest and most consistent improvements in the agreement between the two measurement systems occurred only after both sampling systems employed Nafion sample dryers. While these analyses do not by themselves establish causality, the absence of statistically significant changes during the two years preceding the CAMM upgrade, together with the significant reductions observed immediately afterwards, is consistent with the hypothesis that harmonization of the sample configurations was a major contributor to the improved agreement between the CAMM and CNR observations.

Overall, the observed changes are notably larger, but broadly consistent, with the improvements between parallel measurement systems detected by Laitinen et al. (2025) after the implementation of Nafion driers. Nevertheless, the period during which both laboratories operated Nafion dryers at CMN spans only approximately one annual cycle, preventing a definitive attribution of all observed improvements to the implementation of the dryers alone. Additional observations collected over longer periods under identical sampling configurations would be required to isolate the specific contribution of sample drying from other sources of long-term instrumental variability.

3.9 Follow-up comparison after relocation of the CAMM sampling inlet

In February 2026, atmospheric sampling at CAMM resumed after the relocation of the air inlet from its previous position. This modification provided an opportunity to perform a preliminary follow-up assessment of the agreement between the CAMM and CNR observations under a different inlet configuration. Figure 19 presents the monthly distributions of the hourly CAMM–CNR differences from February to June 2026, separately for daytime and nighttime conditions.

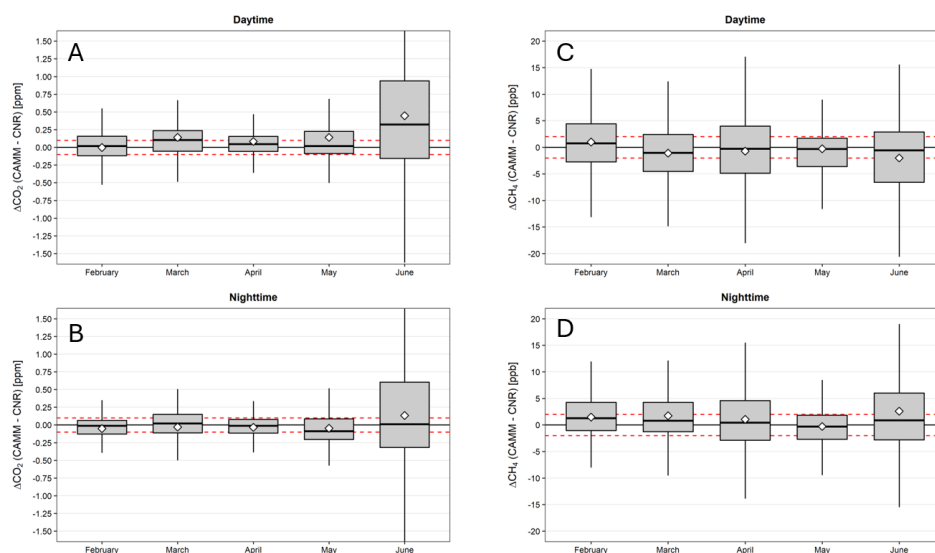


Figure 19: Monthly distributions of hourly CAMM–CNR differences following the relocation of the CAMM sampling inlet: Δ CO₂ during daytime (A) and nighttime (B), and Δ CH₄ during daytime (C) and nighttime (D), from February to



June 2026. Boxes represent the interquartile range, horizontal lines indicate median values, whiskers extend to 1.5 times the interquartile range, and open diamonds denote arithmetic means. Outliers are omitted for clarity. Horizontal solid lines indicate zero difference, while red dotted lines denote the WMO compatibility goals (± 0.1 ppm for CO_2 and ± 2 ppb for CH_4).

For CO_2 , the differences observed between February and May were generally centred close to zero during both daytime and nighttime (Fig. 19A–B). This represents a clear improvement compared with the systematic negative winter differences found during the historical comparison, when mean ΔCO_2 values frequently ranged between approximately -0.5 and -1.0 ppm. The monthly mean differences during the first four months following the inlet relocation remained close to the WMO compatibility interval, although the distributions of the hourly observations continued to extend beyond the ± 0.1 ppm goal. A larger positive difference and a broader distribution emerged in June, particularly during daytime. This behaviour may reflect the increasing influence of spatially heterogeneous biospheric fluxes and thermally driven transport during the transition towards summer, consistently with the seasonal and diurnal patterns discussed in Sections 3.2 and 3.3.

The CH_4 comparison also showed generally small monthly mean differences following the relocation (Fig. 19C–D). From February to May, the mean daytime and nighttime ΔCH_4 values were close to or within the ± 2 ppb WMO compatibility interval, without the pronounced positive winter differences observed during the earlier comparison period. In June, the distributions became wider and the mean differences showed opposite signs during daytime and nighttime. Nevertheless, the absence of a persistent positive bias across the five-month period indicates substantially improved agreement between the two datasets. These recent observations provide additional evidence that the previous CAMM inlet configuration was an important contributor to the CAMM–CNR differences, particularly to the systematic winter biases. Together with the improvement observed after harmonising the Nafion drying systems (Section 3.8), the results indicate that sampling-system configuration played a major role in determining the historical differences between the two measurement systems. However, the February–June 2026 record is too short to establish whether the observed improvement is robust and persistent. The CAMM–CNR differences will therefore continue to be monitored under the new inlet configuration to obtain a more comprehensive assessment over longer periods and across individual seasons.

4. Conclusions

In this study, we analyse deviations in CO_2 and CH_4 observations from two nearby sampling sites belonging to the Mt. Cimone WMO/GAW Global station in Italy. One site (CAMM) is located on the mountain ridge (~ 100 m east and ~ 10 m below the summit), while the other (CNR, “O. Vittori” observatory) is situated on the south-eastern flank. Although separated by only ~ 90 m horizontally and ~ 50 m vertically, the sites operate in a complex mountainous environment and employ different sampling-system configurations. The two laboratories also apply distinct protocols for data flagging, temporal aggregation and quality assurance, including calibration-correction procedures for referencing measurements to WMO scales.

A multi-year comparison (May 2018–June 2024) of 1-hour averaged data shows a strong correlation between the datasets, with consistent long-term trends and seasonal cycles in both CO_2 and CH_4 . However, significant deviations are present. For hourly values, 86.5% (71.9%) of CO_2 data and 42.5% (19.4%) of CH_4 data exceed the



744 WMO (extended) compatibility goals. Monthly mean differences range from -1.0 ppm (CO_2 , winter) to $+0.2$ ppm
745 (summer) and from $+10$ ppb (CH_4 , winter) to ± 2 ppb (summer).
746 The largest deviations were related to the different flagging strategies. CNR follows ICOS-RI protocols, removing
747 data only when documented issues affect data quality. In contrast, CAMM applies stricter criteria designed to
748 exclude data potentially influenced by non-background conditions, including threshold-based rejection of raw
749 values. The application and magnitude of such thresholds are not fully consistent through time, preventing
750 reconstruction of a harmonised dataset for the full period.
751 Sampling-location effects play a key role. During the vegetation period, differing exposures to local and regional
752 biogenic fluxes lead to distinct diurnal CO_2 modulations, with CNR being more sensitive to these signals. The
753 influence of the sampling locations is also apparent when separating observations according to high/low
754 atmospheric CO_2 variability, particularly in winter. Although our analysis did not explicitly account for the travel
755 time of air masses between the two sampling inlets or for differences in local airflow, the dependence of the
756 observed biases on hourly atmospheric variability suggests that the two systems may have sampled slightly
757 different air masses. The possible impact of the different residence times within the sampling lines between
758 CAMM and CNR measurements (see Section 3) has been explored but no evident effects have been detected on
759 the hourly mean values (Section SM1.1 of the supplementary material). Additional deviations could arise from
760 human activities at the CNR observatory, as suggested through access-log analysis. Accounting for these effects
761 yields up to a 40% reduction in mean seasonal CO_2 and CH_4 differences between the sites.
762 Differences in calibration-correction implementation can also contribute. WCC-Empa audits in June 2018
763 (Zellweger et al., 2018) reported CAMM biases amounting to half of the WMO compatibility goal for high CO_2
764 (>425 ppm) and CH_4 (>2000 ppb). While audit-derived coefficients can only reflect instrument behaviour at the
765 time of intercomparison, they provide an estimate of potential calibration-related biases.
766 Additional factors may also affect the comparison. These include unidentified local sources or reduced inlet
767 efficiency during extreme winter conditions at CMN, where wind speeds can exceed 20 m s^{-1} . Continuous flow
768 monitoring is not available for CAMM, whereas CNR installed flow-control capability only in October 2024. The
769 presence of condensed liquid water in inlet lines is another possible contributor. Since CMN is frequently affected
770 by clouds (Fig. SM11), water on inlet surfaces may absorb CO_2 and introduce negative biases. We also investigated
771 the potential influence of sample drying on the observed CAMM–CNR differences. The progressive
772 harmonization of the sampling systems, culminating in the installation of a Nafion sample dryer at CAMM in
773 June 2023, was accompanied by a statistically significant improvement in the agreement between the two
774 measurement systems, particularly for CH_4 but also for CO_2 . Finally, a preliminary follow-up comparison
775 conducted after the relocation of the CAMM inlet in early 2026 showed a further reduction in the systematic
776 winter differences, providing additional evidence that the previous inlet configuration at CAMM was an important
777 contributor to the observed discrepancies together with lack of a drying system.
778 Overall, this study highlights the difficulty of meeting WMO compatibility goals when independent measurements
779 are performed at nearby but not fully equivalent locations, especially in harsh high-mountain environments. The
780 results demonstrate that inconsistencies may arise from a combination of site representativeness, data-processing
781 strategies, temporal synchronization, calibration implementation and sampling-system configuration. Adoption of
782 standardized measurement, processing and QA/QC procedures, such as those implemented within ICOS-RI,



783 would substantially improve the capability to identify, attribute and reduce inconsistencies in long-term GHG
784 observations across different monitoring sites.

785 **Data availability**

786 Hourly mean CO₂ and CH₄ data from CNR are can be accessed under CC-BY license from the ICOS Carbon
787 Portal (<https://www.icoscp.eu/data-products>, Carbon Portal, 2026). Hourly mean CO₂ and CH₄ data from CAMM
788 can be accessed from the World Data Center for Greenhouse Gases (WDCGG, <https://gaw.kishou.go.jp/>).

789 **Author contribution**

790 PC and CZ contribute to the study conceptualization. PC and PT designed the methodology and carried out the
791 formal analysis. PC, CZ, FM, DP and PT contribute to the study investigation. FM, FD, FC, FR, MB, AM, LR,
792 MZ, SM contributed to the data curation. CRC contributed to the funding acquisition. PC prepared the original
793 manuscript, all the co-authors contributed to the review and editing.

794 **Competing interests**

795 The authors declare that they have no conflict of interest.

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