

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

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Table SM1: Water vapour correction coefficients for the G2401 CFKADS-2269; coefficients I_1 and I_2 refer to the correction of CO_2 and CH_4 with equation $C_{\text{wet}}/C_{\text{dry}} = 1 + I_1 \times \text{H}_2\text{O}_r + I_2 \times \text{H}_2\text{O}_r^2$; coefficients I_0' , I_1' and I_2' refer to the correction of CO with equation $\Delta\text{CO} = I_0' + I_1' \times \text{H}_2\text{O}_{\infty} + I_2' \times \text{H}_2\text{O}_{\infty}^2$. H_2O_r is the H_2O value reported by the instrument, $\text{H}_2\text{O}_{\infty}$ is H_2O using the spectroscopic peak close to the CO absorption line. In parenthesis, we reported the correction coefficient for the instrument G1301 CFADS-42.

	CO_2	CH_4	CO
I_1	-0.00187 (-0.01204)	-0.00939 (-0.01068)	
I_2	-0.0002681 (-0.0002277)	-0.0002434 (-0.0000798)	
I_0'			0.00051
I_1'			-0.024350
I_2'			0.0022960

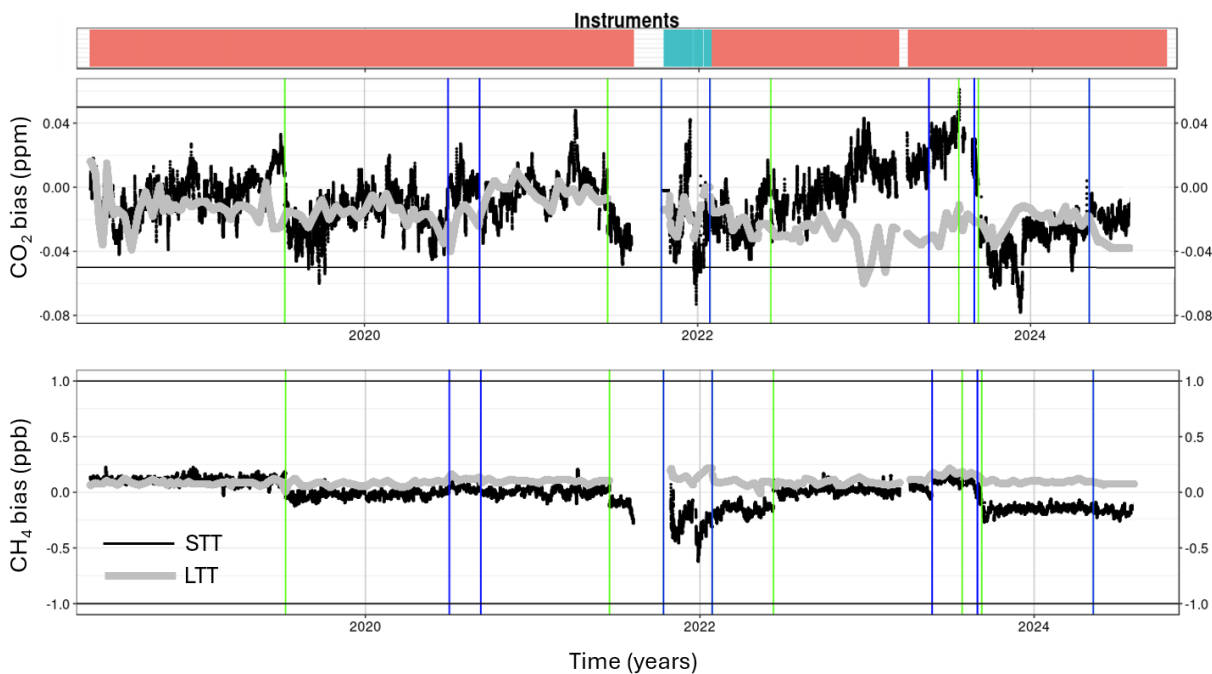


Figure SM1: Time series (May 2018 – June 2024) of the bias between STT and LTT analyses relative to the gas dry mole fractions assigned to each STT and LTT cylinder by the ICOS-FCL at the CNR observatory (data retrieved from the ATC website: <https://icos-atc.lsce.ipsl.fr/product/P0035.6.3/>). Green vertical lines mark changes of the STT cylinder, while blue lines indicate ‘calibration break’ events. The colored bar at the top shows the instrument operating periods (G2401: red; G1301: cyan; no measurements: white).

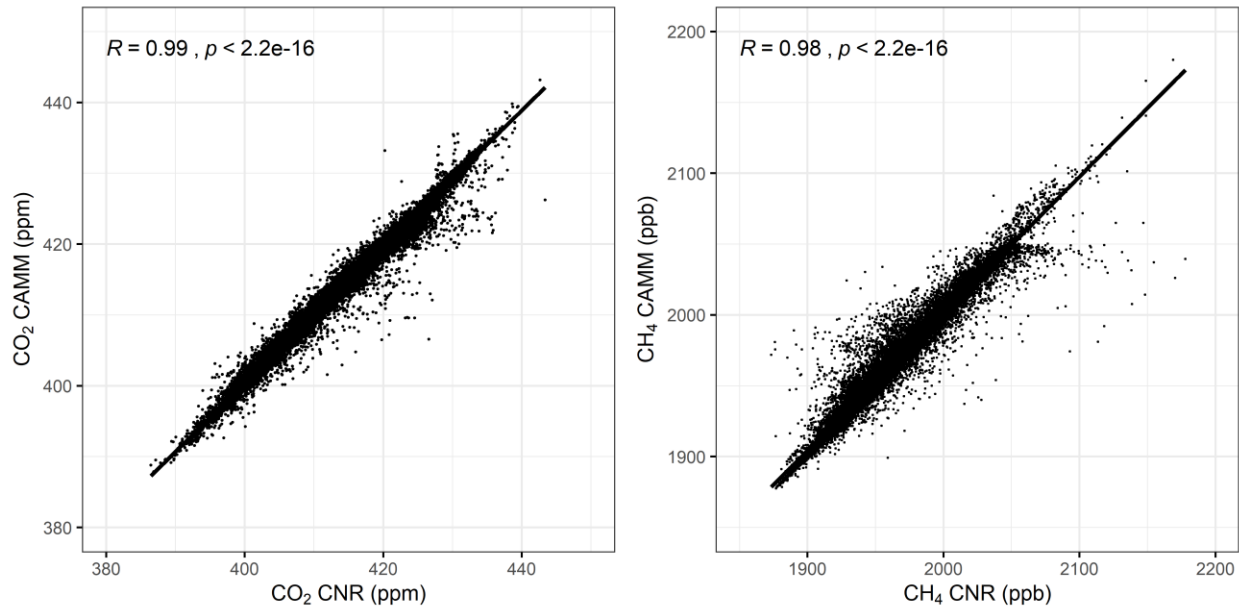
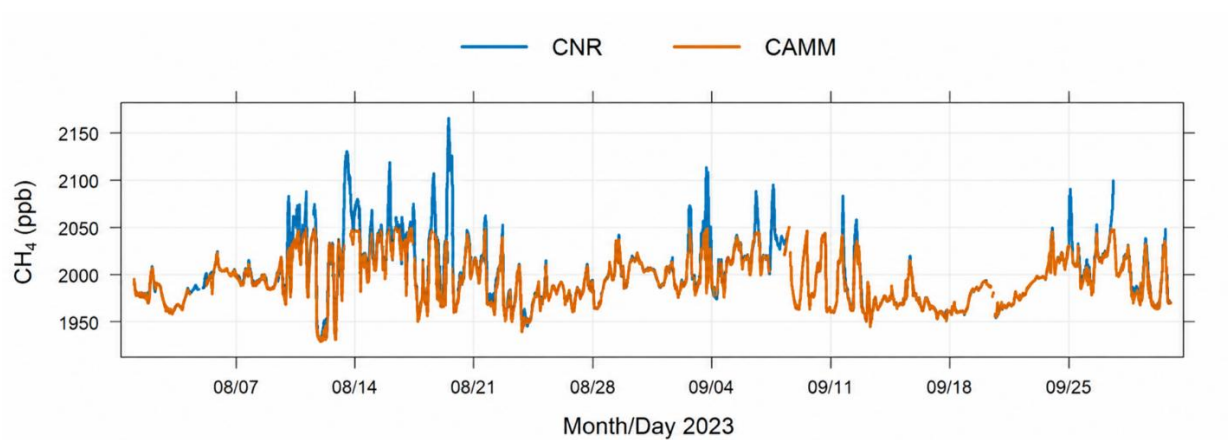


Figure SM2: CAMM versus CNR CO₂ and CH₄ dry mole fractions based on 1 hour average values over the period March 2018 – June 2024.

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43 **Figure SM3: Time series of CH₄ dry mole fractions recorded at the mountain ridge (CAMM) and “O. Vittori” observatory**
44 **(CNR) during August – September 2023.**

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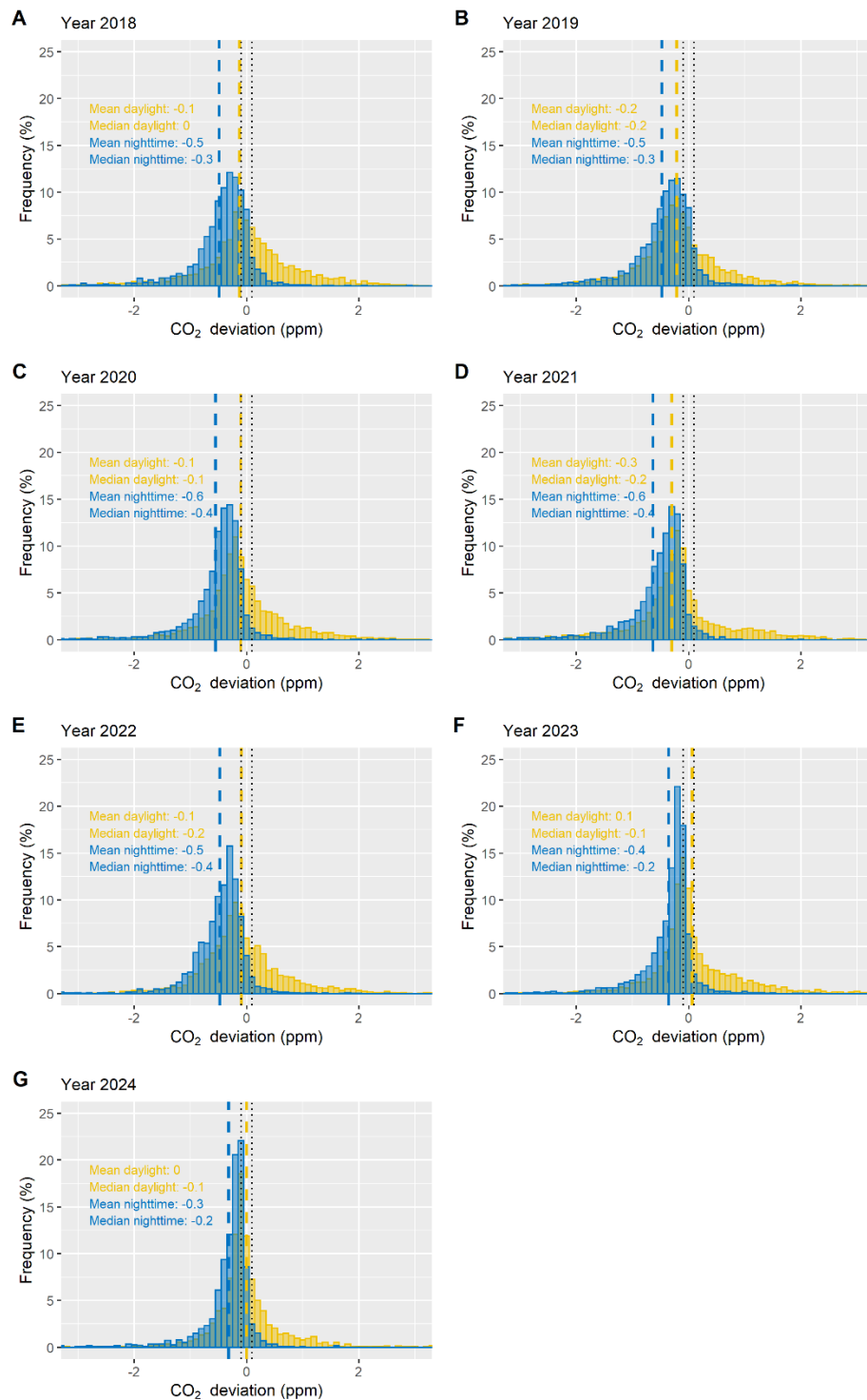


Figure SM4: Data frequency plot for ΔCO_2 over single calendar years. Nighttime (blue) and daytime (yellow) value are reported. Tick dashed lines represent the mean deviations, while the black dotted lines indicated the WMO compatibility goal (± 0.1 ppm).

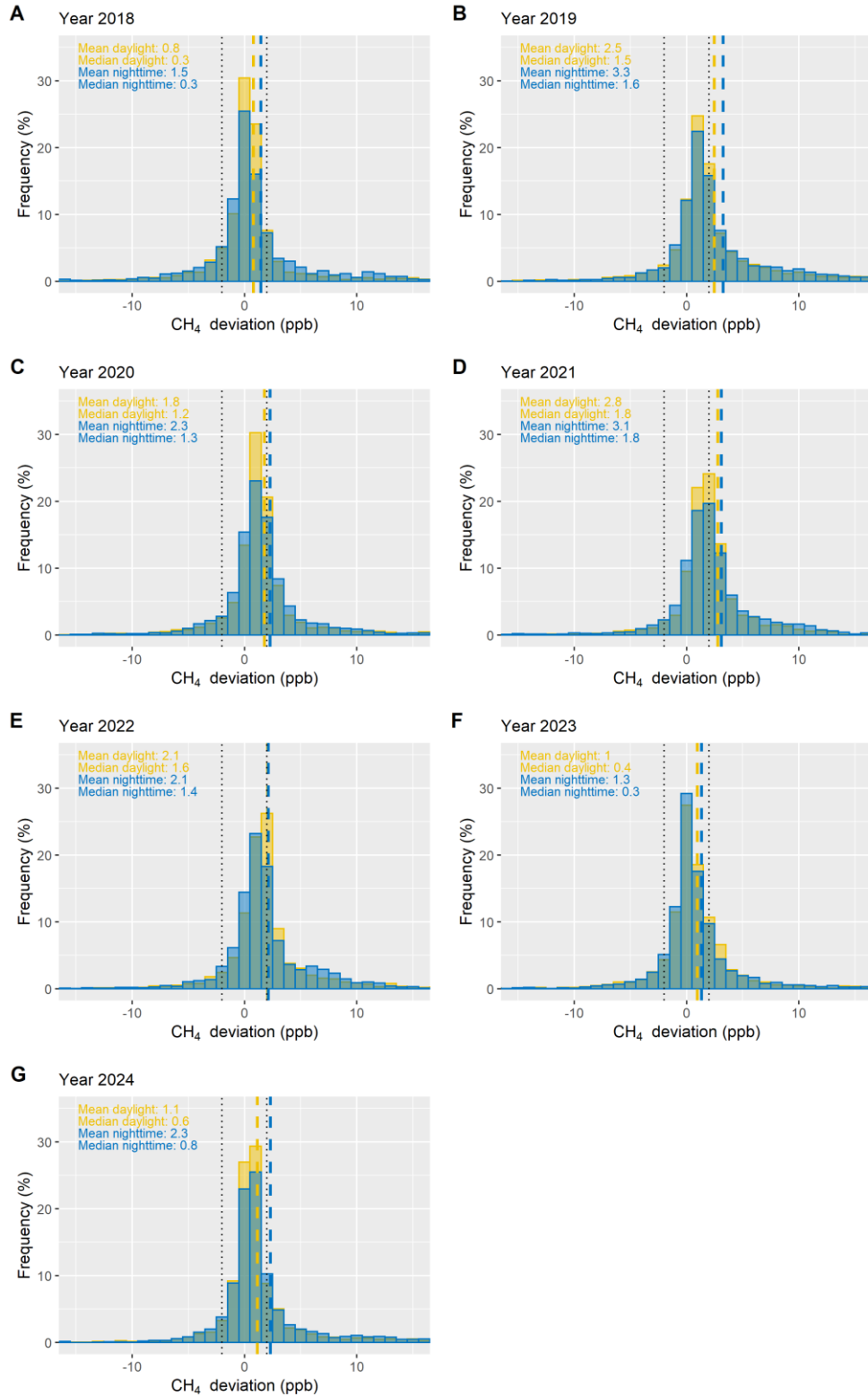


Figure SM5: Data frequency plot for ΔCH_4 over single calendar years. Nighttime (blue) and daytime (yellow) value are reported. Tick dashed lines represent the mean deviations, while the black dotted lines indicated the WMO compatibility goal (± 2 ppb).

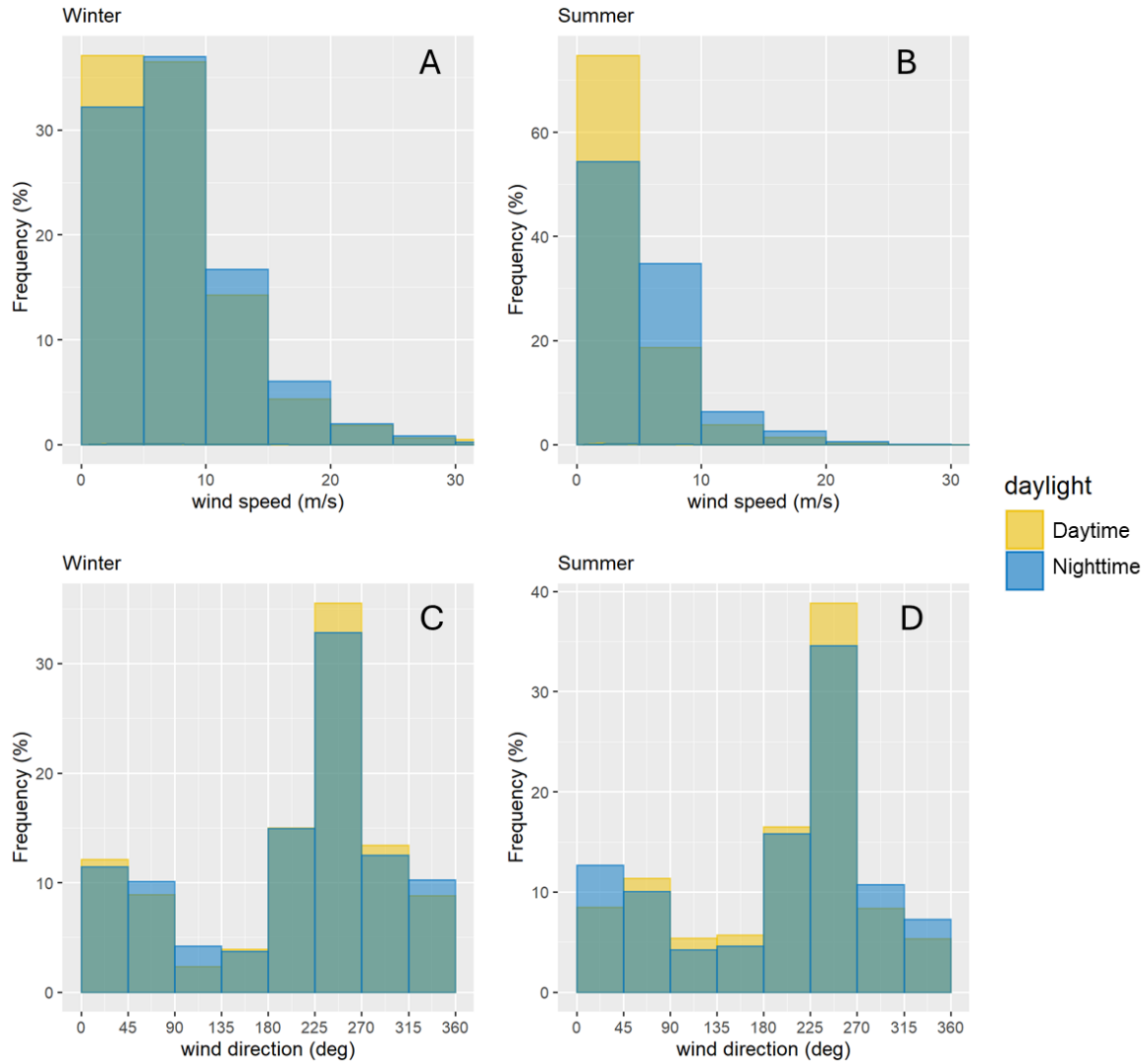


Figure SM6: Frequency of wind speed and wind direction occurrence at CMN for winter (A, C) and summer (B, D) seasons.

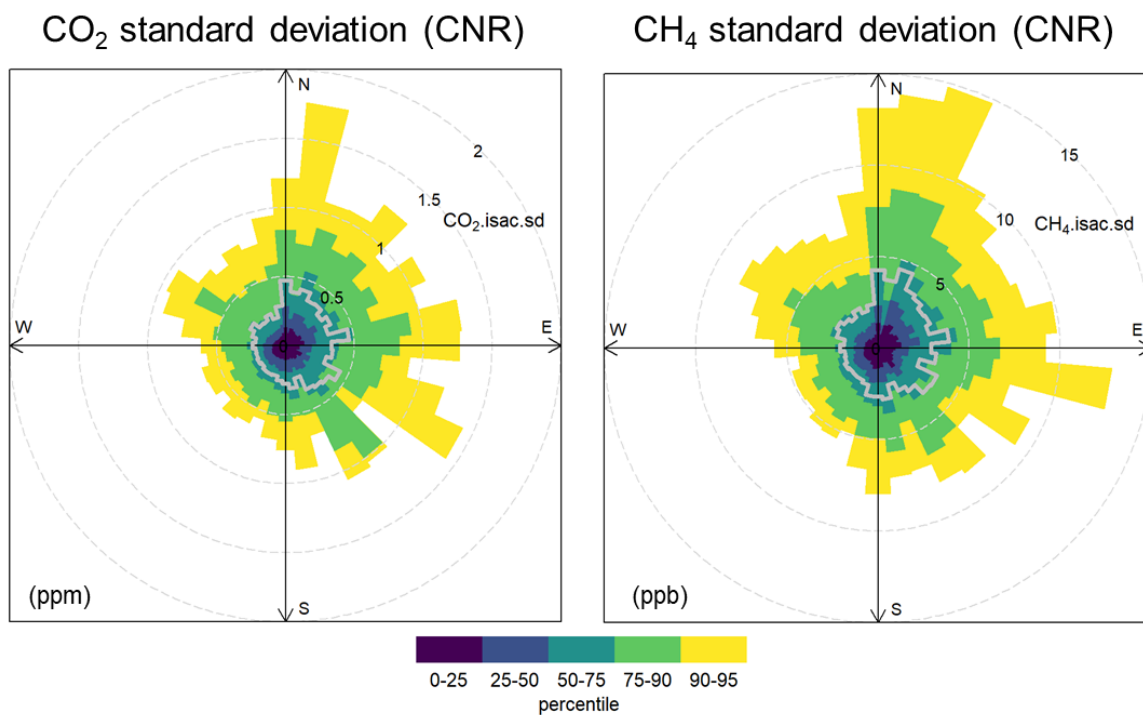


Figure SM7: Percentile values (colored stacks) and mean values (tick lines) of the 1-hour values of CO₂ (right) and CH₄ (left) at CMN during winter.

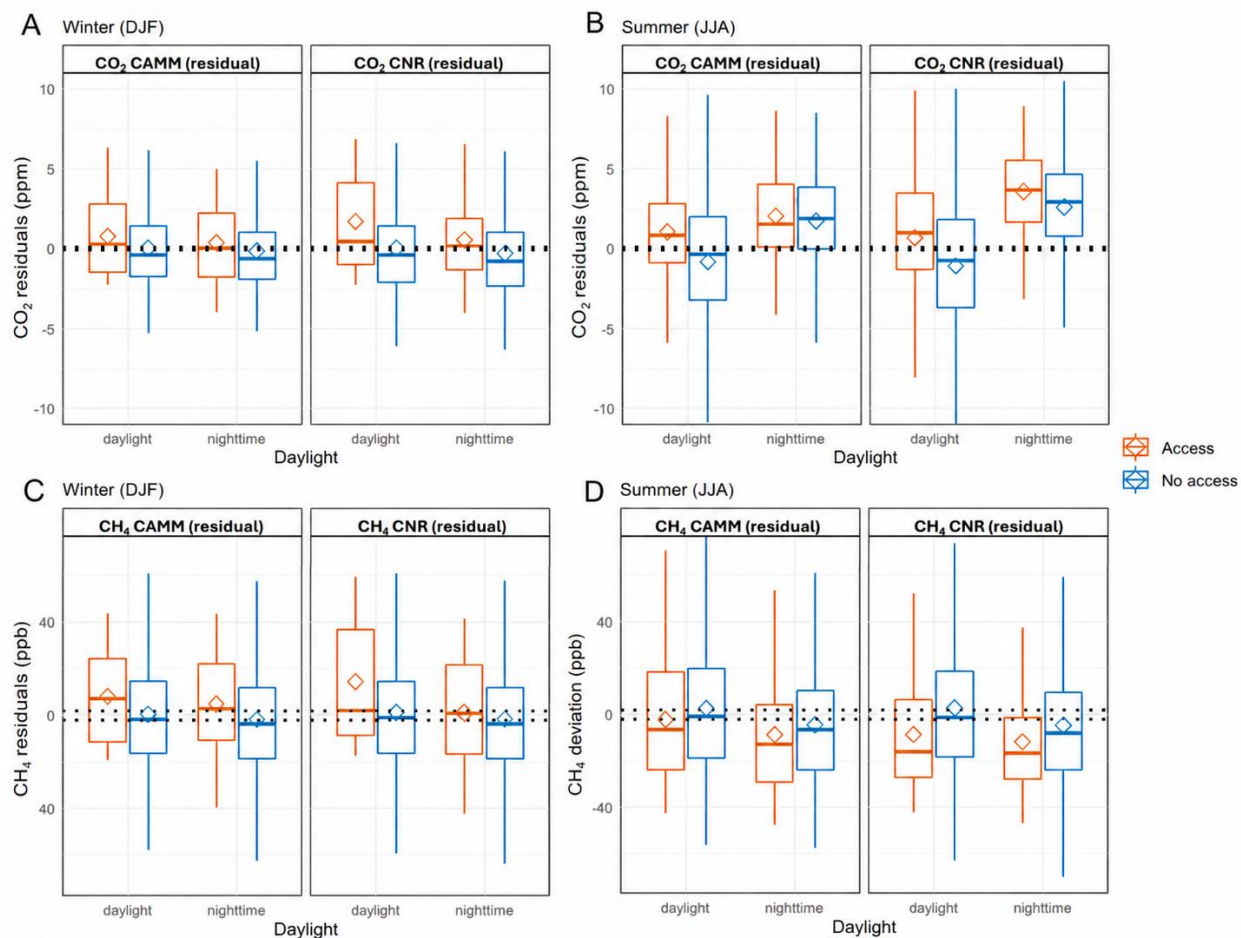


Figure SM8: Seasonal (summer, winter) distribution of CO₂ (A, B) and CH₄ (C, D) residuals for winter (A, C) and summer (B, D) for periods with ("Access") and without ("No access") users or operators at the CNR observatory. The boxes report the 25th and 75th with median values (tick horizontal lines). The whiskers indicate data range falling within the 1.5 times the interquartile range. For comparison purposes the dotted horizontal lines represent the WMO compatibility goals.

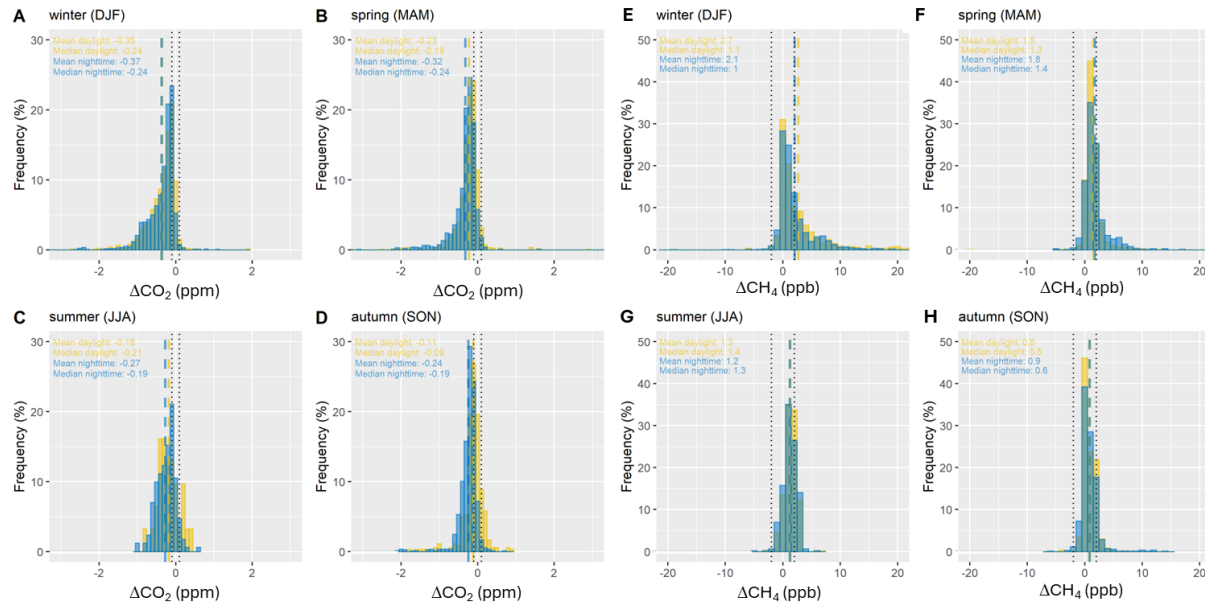


Figure SM9: Data frequency seasonal plots for ΔCO_2 (A - D) and ΔCH_4 (E - H) for period January 2021 – June 2024 after (a) considering only data characterized by low atmospheric variability, (b) selecting the data for which there was no concurrent person access at the CNR observatory. Nighttime (blue) and daytime (yellow) value are reported. Tick dashed lines represent the mean deviations, while the black dotted lines indicated the WMO comparability goals (± 0.1 ppm for CO_2 , ± 2 ppb for CH_4).

SM1.1 Impact to ΔCO_2 and ΔCH_4 of the different residence times along the sampling lines

As reported in Section 3, the CAMM sampling system was characterised by a 27 s residence time in the sampling line from the ambient inlet to Picarro G2301. To assess whether this time shift between the CAMM and CNR systems would affect the observed differences for CO_2 and CH_4 , we recalculated the “O. Vittori” 1-minute mean CO_2 and CH_4 values for a full year (i.e., 2020) by shifting the raw data by -27 s to match the mountain ridge measurements. After applying the time shift, the mean differences between the ridge and “O. Vittori” measurements were -0.32 ppm (ΔCO_2) and +1.9 ppb (ΔCH_4), which are only slightly different from the mean differences calculated when considering the original CNR data (ΔCO_2 : -0.32 ppm; ΔCH_4 : +2.0 ppb). Figure SM9 shows, the monthly mean values of CO_2 and CH_4 deviations between measurements at the mountain ridge and at the “O. Vittori” observatory, calculated for the original data as well as by considering CNR data with a time shift of -27 s. While no differences were detected for CO_2 , for some specific months (i.e. March and December 2020) the detected differences decreased by 1 ppb for CH_4 when the CNR time-shifted data were considered. Please note that the high monthly deviations reported for December 2020 (higher than 7 ppb) were due to the flagging out of CH_4 data higher than 2050 ppb in the CAMM dataset (see also Fig. 2).

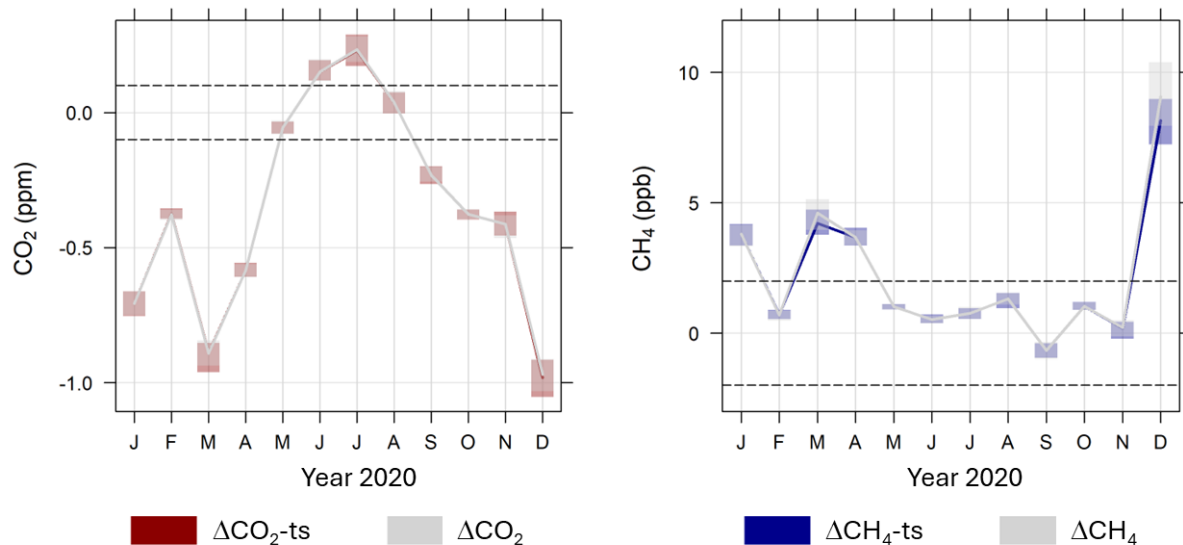


Figure SM10: For the year 2020, monthly mean values of CO_2 and CH_4 deviations between measurements at the ridge and at the “O. Vittori” observatory. The vertical bars indicate the 95% confidence level. The horizontal dashed lines indicate the interval of the WMO comparability target. Grey lines and bars indicate the deviations from the original data, while dark red ($\Delta\text{CO}_2\text{-ts}$) and dark blue ($\Delta\text{CH}_4\text{-ts}$) indicate the deviations calculated after applying a time shift of -27 s to the raw “O. Vittori” measurements.

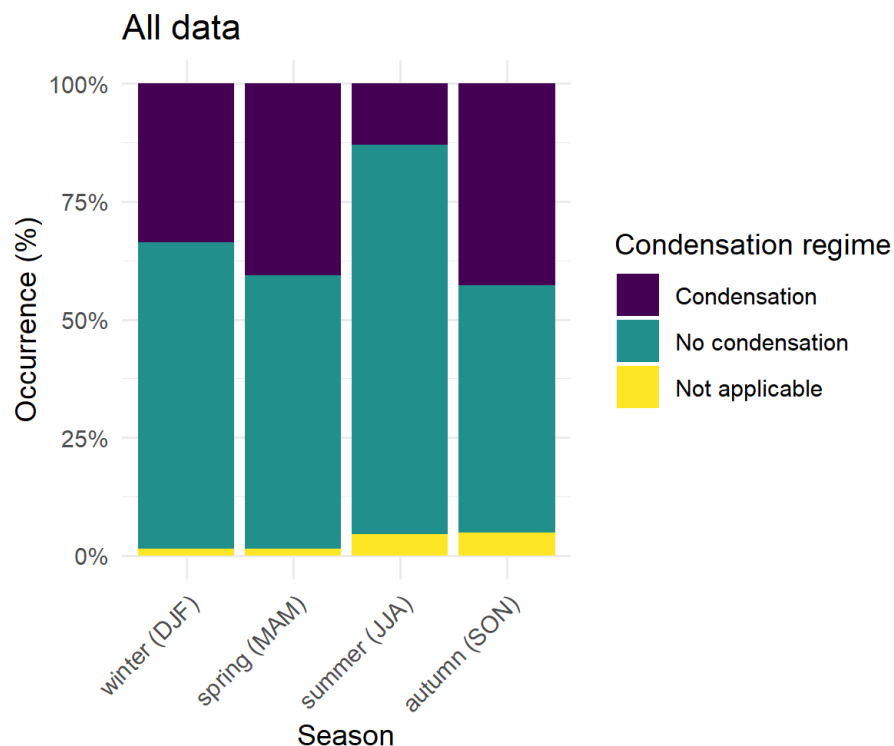


Figure SM11: Seasonal occurrence of condensation regimes at CMN (based to the air-temperature and relative humidity values recorded at the CNR observatory). In order to identify the presence of environmental conditions that could lead to the occurrence of water condensation in the ambient air, we calculated the dew point temperature (Tdew) from the ambient temperature (TA) and relative humidity measurements. As summarized by Lawrence (2005), different approaches can be used to derive TD in different temperature and RH regimes. We used the formula and relative constants ($A1 = 17.625$, $B1 = 243.04^{\circ}\text{C}$, and $C1 = 610.94 \text{ Pa}$) proposed by Alduchov and Eskridge (1996), which gives Tdew values with a relative error lower than 0.4% for the temperature range at CMN ($-15^{\circ}\text{C} < \text{TA} < 24^{\circ}\text{C}$). The hourly variability of Tdew was used to identify and classify potential condensation conditions. Each single hour was classified as “no condensation” condition when $\text{TA} > (\text{Tdew} + 1^{\circ}\text{C})$ and as “condensation” when $\text{TA} \leq (\text{Tdew} + 1^{\circ}\text{C})$.

107 **References**

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