

System and performance audit of Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide at the Global GAW Station Monte Cimone, Italy, September 2023

Submitted to the World Meteorological Organization by
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1. Executive Summary

The third WCC-Empa¹ system and performance audit at the Monte Cimone global GAW station (CMN) was conducted from 19 - 21 September 2023 in accordance with the WMO/GAW quality assurance system (WMO, 2017). A list of all WCC-Empa audits and the corresponding audit reports are available on the [GAW Empa website](#). The following people contributed to the audit:

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This report summarises the evaluation of the Monte Cimone GAW station in general and the measurements of surface ozone, methane, carbon dioxide and carbon monoxide in particular.

The report will be distributed to the Director of the [Italian Air Force Mountain Meteorological Centre \(CAMM\)](#), the [Institute of Atmospheric Sciences and Climate \(ISAC\)](#) of the [National Research Council of Italy \(CNR\)](#), the national focal point for GAW in Italy, and the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and made available on the [WCC-Empa website](#).

The recommendations found in this report are categorised as minor, important and critical, and are accompanied by a priority (** indicates high, * medium and * low priority) and a proposed completion date.

¹WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of Empa, the Swiss Federal Laboratories for Materials Science and Technology. Its mandate is to conduct system and performance audits at Global GAW stations on a mutually agreed basis.

2. Site Description and Operation

2.1 Station management

The Mt. Cimone GAW station facilities are owned by CAMM, and operated jointly by CAMM, CNR-ISAC, and the University of Urbino. Until June 2018, the station was permanently staffed by CAMM personnel. Since 15 June 2018, the station is staffed only during weekdays. Scientist and technicians from CNR-ISAC and the University of Urbino regularly visit the station for instrument maintenance and calibration.

Recommendation 1 (, important, ongoing)**

The operation of the CMN measurements is highly dependent on the infrastructure provided by CAMM. A long-term commitment as well as financial and logistical support is required for the sustainable operation of the CAMM/CMN GAW station.

2.2 Location and access

The CMN station (44.1934°N, 10.7009°E, 2165 m above sea level) is located on the highest peak of the Northern Apennines. The nearest inhabited areas are small villages 15 km away at an altitude of 1100 m below the station. Further information is available from the [CNR-ISAC](#), [CAMM](#) and the [GAWSIS](#) websites.

2.3 Station facilities

The CMN station offers spacious laboratory and office areas, complete with kitchen and sanitary facilities. The CAMM facilities are located in the main building, while the CNR-ISAC and University of Urbino laboratories are situated about 50 metres away in the Ottavio Vittori Observatory. The laboratories are air-conditioned and internet access is available. CMN is an excellent site for ongoing atmospheric research and large-scale measurement projects.

2.4 Measurement programme

CMN hosts a comprehensive measurement programme covering major focal areas of the GAW programme. An overview of the measured species is available on [GAWSIS](#). The monitoring activities of CMN are well embedded in international programmes and research infrastructures, such as [EMEP](#) (European Monitoring and Evaluation Programme), [ACTRIS](#) (The Aerosol, Clouds and Trace Gases Research Infrastructure), [ICOS](#) (Integrated Carbon Observation System) and [AGAGE](#) (Advanced Global Atmospheric Gases Experiment). CAMM measures CO₂ and CH₄, CNR-ISAC GHG and reactive gases as part of ICOS and ACTRIS, and the University of Urbino GHG as part of the AGAGE programme. A complete overview of all collaborations is available on the [CMN website](#).

The information available on GAWSIS was reviewed as part of the audit. The information was updated during the audit and is largely up to date. However, the station contacts need to be checked and corrected.

Recommendation 2 (, important, ongoing)**

It is recommended that GAWSIS is updated annually or when major changes occur. Some of the reviewed information needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface (e.g. deletion of station contacts).

2.5 Data submission

As of February 2024, the following CMN data within the scope of the audit were available at the World Data Centres:

CNR, submission to the World Data Centre for Reactive Gases (WDCRG):
O₃ (1996-2022).

CAMM, submission to WDCGG:
CH₄ (2015-2022), CO₂ (1979-2022)

CNR, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CO (2007-2016)

University of Urbino, submission to WDCGG:
CO (2008-2017), CH₄ (2008-2017), N₂O (2008-2017).

The University of Urbino stopped measuring CO, CH₄ and N₂O in 2018.

The CNR/ICOS GHG and CO data has not yet been submitted to WDCGG, but is available from the [ICOS Carbon Portal](#) (2018-2023, level 2 data, final, quality-checked ICOS RI dataset).

Recommendation 3 (*, critical, 2024)**

Data submission to the WMO/GAW data centres is mandatory for all GAW stations. It is recommended to submit data to the respective data centres at least once a year. Hourly data are required for all parameters. The ICOS GHG and CO data must be submitted to the WDCGG.

2.6 Data review

As part of the system audit, data within the scope of WCC-Empa available at WDCRG, WDCGG and the ICOS data portal was reviewed, and all accessed time series looked reasonable. Summary graphs and a brief description of the findings are provided in the Appendix.

2.7 Documentation

CNR-ISAC and University of Urbino:

Electronic logbooks and handwritten notes are available for all parameters. Instrument manuals are available on site and online. Standard Operating Procedures (SOPs) were prepared for the analysers operated by CNR-ISAC. The information was comprehensive and up to date.

CAMM:

Hand-written logbooks and notes are available. The information was mostly comprehensive and up to date.

Recommendation 4 (*, important, ongoing)**

Electronic logbooks, preferably server based, are recommended. Access to the information should be possible both in the field and from the office.

2.8 Air inlet system

The air inlets have not been modified since the last WCC-Empa audit in 2018.

CNR/ICOS inlet (for O₃, CO₂, CH₄, CO in Ottavio Vittori building):

The air intake is located 1.5 m above the roof of the building and consists of a glass manifold with a total length of 2.5 m and an internal diameter of 12 cm. It is protected from rain by an upside-down stainless steel bucket. The inlet is flushed by blower with a flow rate of 70 l/sec. This results in residence times of less than 2 seconds. From there, the individual instruments are connected by short lines. The inlet system is adequate and no modification is required.

CAMM inlet (for CO₂ and CH₄ in main building):

The inlet is located on a tower next to the main building. The air intake is approximately 12 m above the ground and 3-4 m above the height of the building. In total, about 30 m of 6 mm Synflex 1300 tubing is used. The air is sampled using a KNF pump, which is installed a few metres upstream of the instrument's calibration unit. Thus, air is passing through the pump prior to analysis, which can alter (contaminate or deplete) the sample and is a possible source of leakage. The flow rate is 3.3 l/min resulting in a residence time of less than 10 seconds. A stainless steel particulate filter is used to protect the instrument from particles.

Recommendation 5 (*, minor, 2024)

It is recommended to change the position of the air intake pump to the end of the system, after the calibration unit.

3. Performance Audit

3.1 Surface ozone measurements

Surface ozone measurements at CMN were established in 1996, and continuous time series are available since then.

Instrumentation. CMN is currently equipped with two Thermo Scientific 49i ozone analysers.

Standards. A Thermo Scientific 49i-PS with ozone standard traceability to a NIST SRP is available at CMN.

Data acquisition. A custom made data acquisition system programmed in LabVIEW is used. 1-min time resolution is available for ozone and ancillary data. Data is automatically transferred to a server and available in near real time. Time series and quality control plots can be accessed via the [NEXTDATA](#) (Naitza et al., 2020) web interface hosted by CNR.

Intercomparison (performance audit). The two CMN ozone analysers (OA) were compared to the WCC-Empa Travelling Standard (TS) with traceability to SRP#15. The internal ozone generator of the TS was used to generate a random sequence of ozone levels ranging from 0 to 250 nmol mol⁻¹. The result of the comparisons is summarised below in relation to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). Data were acquired using the WCC-Empa data acquisition system. The data were treated in the same way as ambient air measurements, and no further corrections were applied to the instruments readings.

The following equations characterise the bias of the instruments and the remaining uncertainty after compensation of the bias. Uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). As the measurements refer to a conventionally agreed value of the ozone absorption cross section of 1.1476x10⁻¹⁷ cm² (Hearn, 1961), the uncertainties reported below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #1225011092, main analyser (BKG +0.0 nmol mol⁻¹, COEF 1.001):

$$\text{Unbiased O}_3 \text{ amount fraction } X_{\text{O}_3} \text{ (nmol mol}^{-1}\text{): } X_{\text{O}_3} = ([\text{OA}] + 0.30 \text{ nmol mol}^{-1}) / 1.0054 \quad (1)$$

$$\text{Standard uncertainty } u_{\text{O}_3} \text{ (nmol mol}^{-1}\text{): } u_{\text{O}_3} = \text{sqrt}(0.30 \text{ nmol mol}^{-1} + 2.13\text{e-}05 * X_{\text{O}_3}^2) \quad (2)$$

Thermo Scientific 49i #1182780003, backup analyser (BKG +0.0 nmol mol⁻¹, COEF 1.012):

$$\text{Unbiased O}_3 \text{ amount fraction } X_{\text{O}_3} \text{ (nmol mol}^{-1}\text{): } X_{\text{O}_3} = ([\text{OA}] - 0.53 \text{ nmol mol}^{-1}) / 1.0124 \quad (3)$$

$$\text{Standard uncertainty } u_{\text{O}_3} \text{ (nmol mol}^{-1}\text{): } u_{\text{O}_3} = \text{sqrt}(0.29 \text{ nmol mol}^{-1} + 2.08\text{e-}05 * X_{\text{O}_3}^2) \quad (4)$$

Thermo Scientific 49i-PS #1118511036 (BKG -0.3 nmol mol⁻¹, COEF 1.013):

$$\text{Unbiased O}_3 \text{ amount fraction } X_{\text{O}_3} \text{ (nmol mol}^{-1}\text{): } X_{\text{O}_3} = ([\text{OA}] - 0.22 \text{ nmol mol}^{-1}) / 1.0062 \quad (5)$$

$$\text{Standard uncertainty } u_{\text{O}_3} \text{ (nmol mol}^{-1}\text{): } u_{\text{O}_3} = \text{sqrt}(0.29 \text{ nmol mol}^{-1} + 2.05\text{e-}05 * X_{\text{O}_3}^2) \quad (6)$$

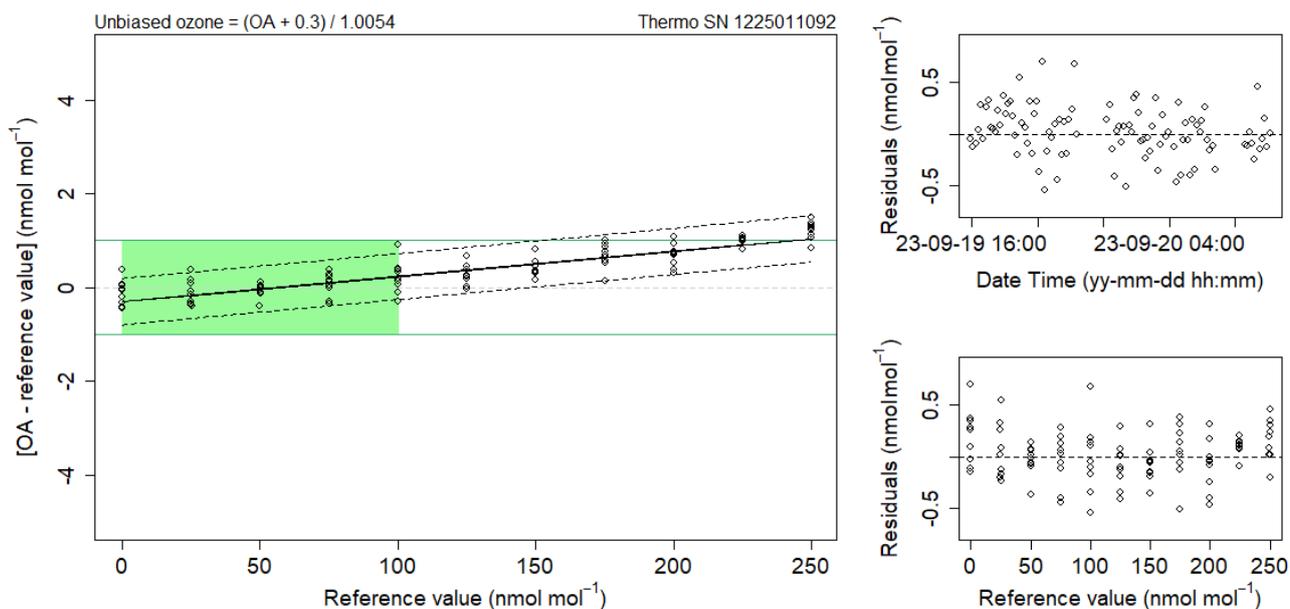


Figure 1. Left: Bias of the CMN ozone analyser (Thermo Scientific 49i #1225011092, BKG $0.0 \text{ nmol mol}^{-1}$, COEF 1.001) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated by green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).

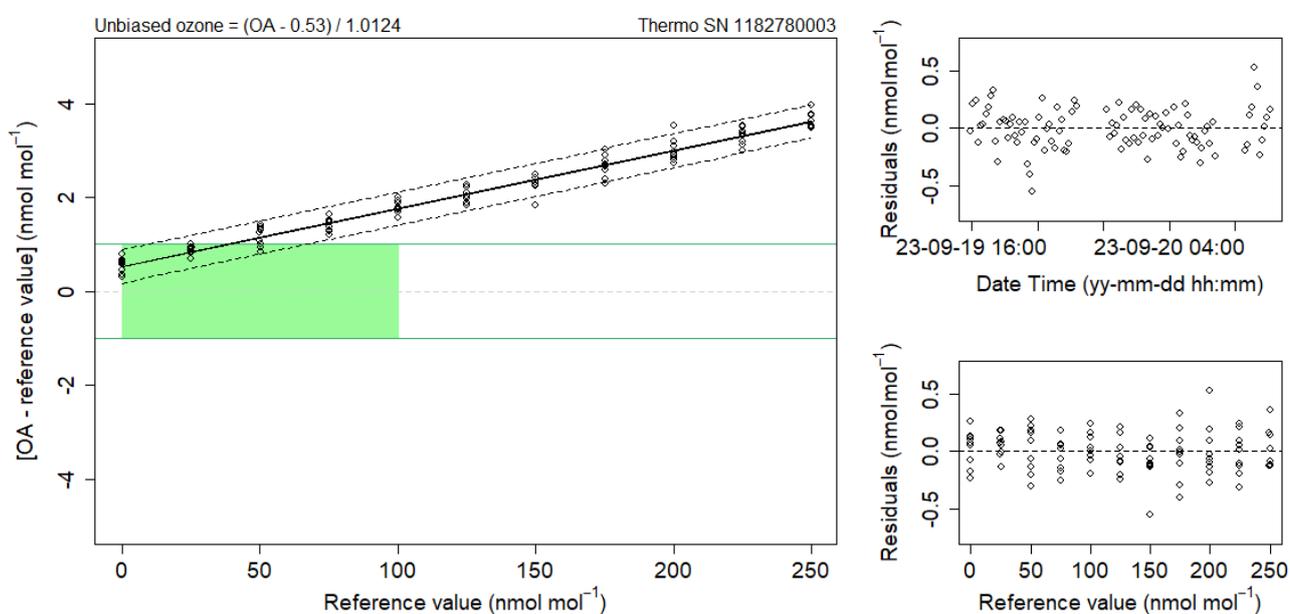


Figure 2. Left: Bias of the CMN ozone analyser (Thermo Scientific 49i #1182780003, BKG $0.0 \text{ nmol mol}^{-1}$, COEF 1.012) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated by green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).

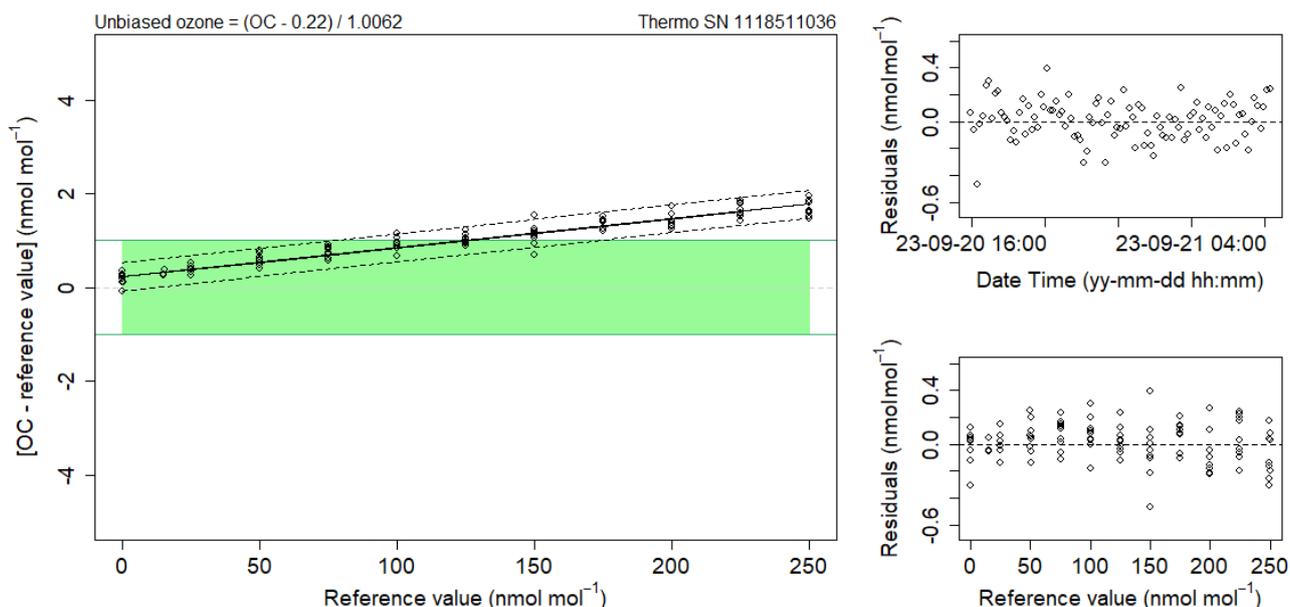


Figure 3. Left: Bias of the CMN ozone calibrator (Thermo Scientific 49i-PS # 1118511036, BKG $-0.3 \text{ nmol mol}^{-1}$, COEF 1.013) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated by green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).

The results of the comparisons can be summarised as follows:

Thermo Scientific 49i #1225011092: This instrument is currently used as the main CMN ozone analyser and data from this instrument will be used for data submission. It is in a good working condition and fully complies within the WMO/GAW quality objectives in the relevant amount fraction range.

Thermo Scientific 49i #1182780003: This instrument serves as a backup analyser and read slightly higher than the WCC-Empa reference. The instrument is in a good working condition, but calibration is recommended.

Recommendation 6 (*, minor, 2024)

It is recommended that the Thermo Scientific 49i #1182780003 ozone analyser be calibrated using the CMN ozone calibrator if it is to be used as the primary analyser.

Thermo Scientific 49i-PS #1118511036: The CMN ozone calibrator was reading slightly higher than the WCC-Empa reference. This is in good agreement with a calibration carried out at the WCC-Empa calibration laboratory in 2022. It is recommended to compensate for the bias when using the instrument to calibrate of ozone analysers.

Recommendation 7 (*, minor, ongoing)

The bias of the Thermo Scientific 49i-PS #1118511036 ozone calibrator must to be compensated when it is used for ozone calibration.

In conclusion, the CMN ozone measurements are within the WMO/GAW quality objectives, and the redundant measurements with two ozone instruments support the long-term quality of the CMN ozone data. It is recommended to continue with the current practice, and no immediate action is required.

3.2 Carbon monoxide measurements

Continuous measurements of CO at CMN started in 2007 using gas chromatography / flame ionisation detection (GC/FID). A non-dispersive infrared (NDIR) instrument was additionally installed by CNR-ISAC in 2012. Since 2017, CO is measured as part of the ICOS programme with a Picarro G2401 CRDS instrument, and the other CO measurements are now discontinued.

Instrumentation. Picarro G2401 (near-IR CRDS). The air is dried using a Nafion dryer (MD-070-144S-4). To account for the residual effect of water vapour, a correction function using coefficients from a water bench test conducted in 2017 by the ICOS Atmospheric Thematic Center (ATC, ref: ATC-ML-IT-RP-93-1.0_IT_590) is applied to the data production chain by the ICOS Atmospheric Thematic Center (ATC, ref: ATC-ML-IT-RP-93-1.0_IT_590).

Standards. Several NOAA CCL and ICOS FCL standards are available for the calibration of the CO instruments. An overview of available standards is given in Table 13 in the Appendix.

Calibration. The following calibration sequence is used for the CNR-ISAC/ICOS instrument: 570 min ambient air, followed by 4 repetitions of the 4 calibration tanks for 30 min each, 30 min long term target tank, and 20 min short term target tank. Then a sequence of 570 min ambient air / 20 min short term target tank is repeated 35 times. The sequence then starts again from the beginning.

Intercomparison (performance audit). The comparison consisted of repeated challenges of the CMN instrument with randomly selected levels of carbon monoxide, using the WCC-Empa travelling standards.

The following equations characterise the instrument bias, and the result is further illustrated in Figure 4 with respect to the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020):

Picarro G2401 #2871-CFKADS2269:

Unbiased CO mixing ratio: $X_{CO} \text{ (nmol mol}^{-1}\text{)} = (\text{CO} - 5.36 \text{ nmol mol}^{-1}) / 0.9681$ (7)

Remaining standard uncertainty: $u_{CO} \text{ (nmol mol}^{-1}\text{)} = \text{sqrt}(3.2 \text{ nmol mol}^{-1} + 1.01\text{e-}04 * X_{CO}^2)$ (8)

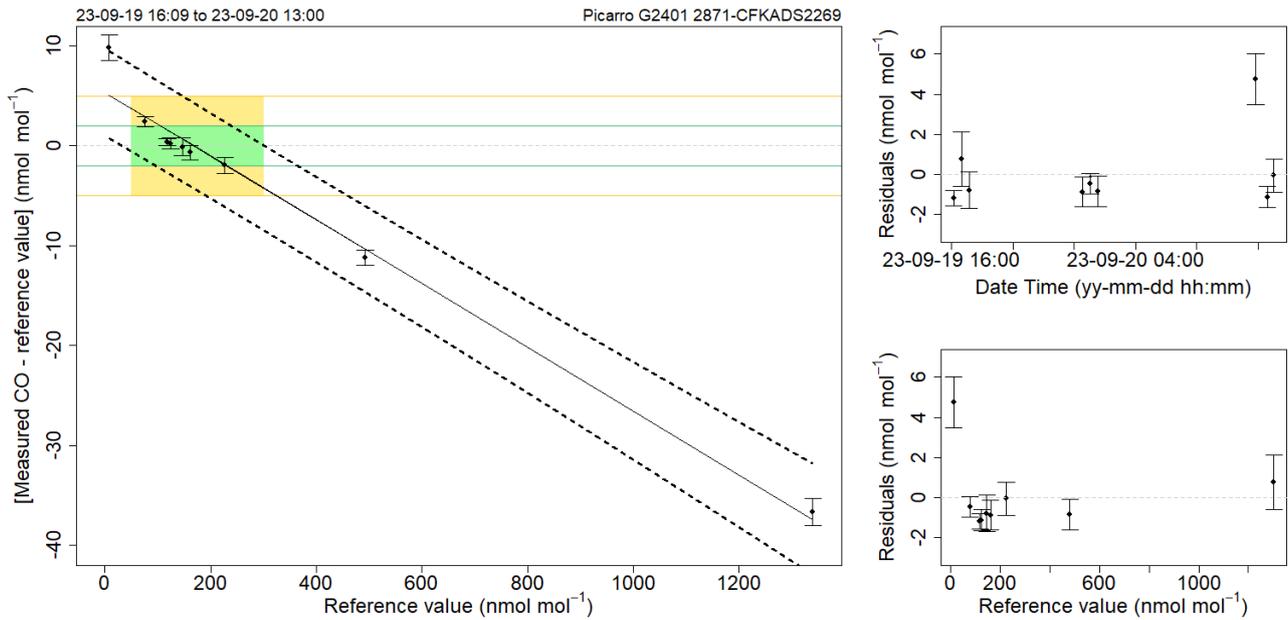


Figure 4. Left: Bias of the CMN Picarro G2401 #2871-CFKADS2269 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CMN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).

The result of the comparison can be summarised as follows:

Agreement between the CMN CO measurements and WCC-Empa within the extended WMO/GAW network compatibility goal was found in the relevant amount fraction range. However, a strong linear relationship of the bias was found. It is recommended to investigate on the cause of the bias at the zero CO level.

Recommendation 8 (, important, 2024)**

It is recommended to characterise the zero offset and the linearity of the CO instrument between 0 and 1000 nmol mol⁻¹ CO. High purity nitrogen (grade 6.0) can be used to characterise the zero air response of the instrument.

3.3 Methane measurements

Continuous measurements of CH₄ at CMN started in 2007 using GC / Flame Ionisation Detection (FID). In 2015 CAMM installed a Picarro G2301 CRDS instrument and in 2017 another CRDS analyser was added by CNR-ISAC/ICOS. Continuous time series are available since 2007.

Instrumentation. CNR: Picarro G2401 (near-IR CRDS). The air is dried with a Nafion dryer (MD-070-144S-4). CAMM: Picarro G2301 (near-IR CRDS), Nafion dryer (MD-070-72S-4).

Standards. Several NOAA CCL and ICOS FCL standards are available for the calibration of the CH₄ instruments. An overview of available standards is given in Table 13 in the Appendix.

Calibration. CNR-ISAC/ICOS: see CO.

CAMM: Calibrations against the NOAA laboratory standards are performed manually four times a year. In addition, working and target standards are available, but these are not measured regularly and have not been considered to correct for instrument drift.

Recommendation 9 (, important, 2024)**

For the CAMM system, it is recommended to use the measurements of the working standards to apply a drift correction. The results of the target tank measurements should be used for quality control.

Data acquisition. CAMM: The internal data acquisition of the CRDS analyser is used, and the highest resolution (1-2 s resolution) raw data files are stored. A backup of the data is available at the CAMM headquarters in Sestola. CNR-ISAC/ICOS: See CO.

Recommendation 10 (*, critical, 2024)**

It was noted that the CAMM data were provided in UTC+2, which corresponds to European summer time. In addition, a time difference of 9 minutes was observed with respect to synchronised clocks. The time needs to be regularly synchronised with a time server and data should be acquired in either UTC or local standard time (UTC+1) throughout the year.

Intercomparison (performance audit). The comparison consisted of repeated challenges of the CMN instruments with randomly selected CH₄ levels from travelling standards.

The following equations characterise the instrument bias. The results are further illustrated in Figures 5 and 6 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G2401 #2871-CFKADS2269 (CNR):

$$\text{Unbiased CH}_4 \text{ mixing ratio: } X_{\text{CH}_4} \text{ (nmol mol}^{-1}\text{)} = (\text{CH}_4 - 3.00 \text{ nmol mol}^{-1}) / 0.9986 \quad (9)$$

$$\text{Remaining standard uncertainty: } u_{\text{CH}_4} \text{ (nmol mol}^{-1}\text{)} = \text{sqrt}(0.1 \text{ nmol mol}^{-1} + 1.30\text{e-}07 * X_{\text{CH}_4}^2) \quad (10)$$

Picarro G2301 #2017-CFADS2374 (CAMM):

$$\text{Unbiased CH}_4 \text{ mixing ratio: } X_{\text{CH}_4} \text{ (nmol mol}^{-1}\text{)} = (\text{CH}_4 - 6.90 \text{ nmol mol}^{-1}) / 0.9967 \quad (11)$$

$$\text{Remaining standard uncertainty: } u_{\text{CH}_4} \text{ (nmol mol}^{-1}\text{)} = \text{sqrt}(0.2 \text{ nmol mol}^{-1} + 1.30\text{e-}07 * X_{\text{CH}_4}^2) \quad (12)$$

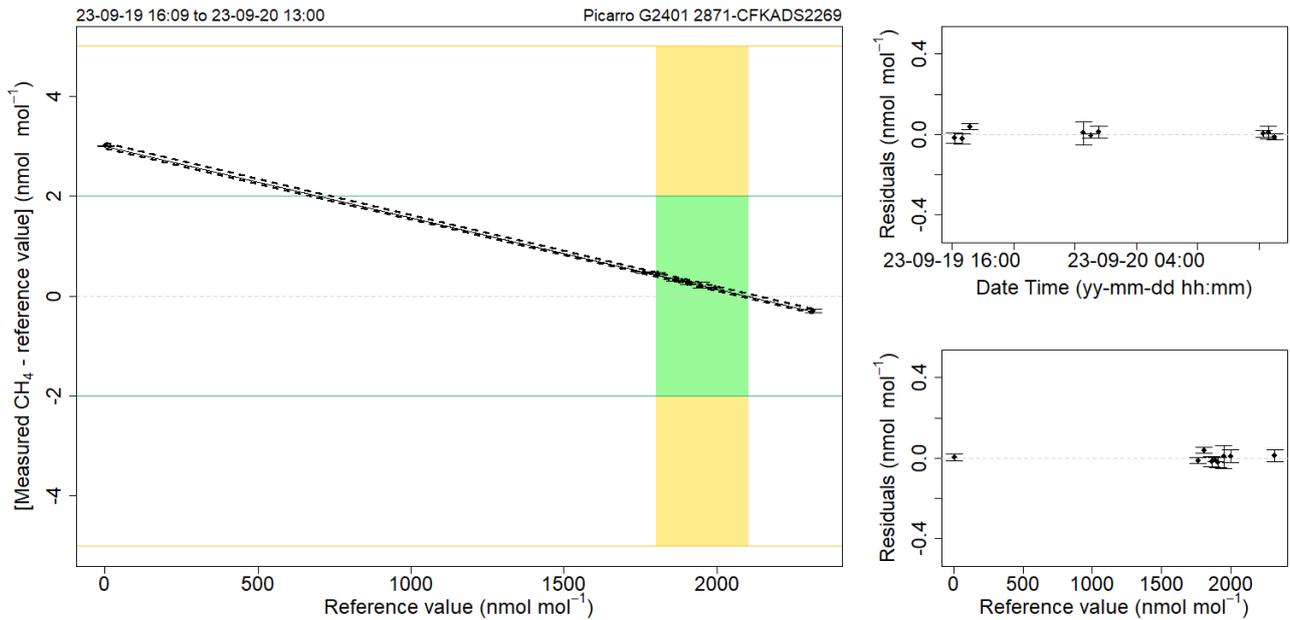


Figure 5. Left: Bias of the Picarro G2401 #2871-CFKADS2269 instrument (CNR) with respect to the WMO-X2004A CH₄ reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CMN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).

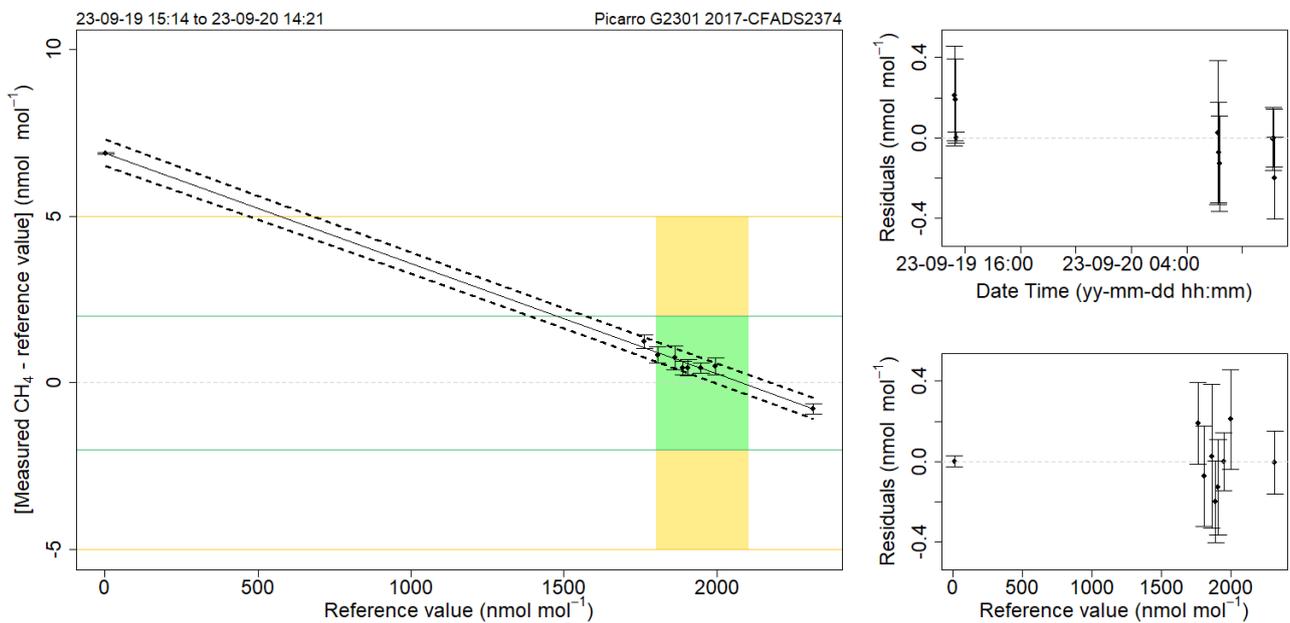


Figure 6. Left: Bias of the Picarro G2301 #2017-CFADS2374 instrument (CAMP) with respect to the WMO-X2004A CH₄ reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CMN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).

The result of the comparison can be summarised as follows:

Excellent agreement well with the WMO/GAW compatibility goal was found for both the CNR/ICOS and the CAMM instruments in the relevant range of amount fractions. A small amount fraction dependent bias was observed, which may be due to residual inconsistencies of the used calibration standards used. Part of the amount fraction dependent bias may also be due to residual inconsistencies in the WMO-X2004A CH₄ calibration scale, as a similar dependence is often observed during WCC-Empa audits. In addition to CCL standards, WCC-Empa also uses methane-free zero air to calibrate its travelling standards, which may explain the observed amount fraction dependence. However, the bias in the relevant amount fraction range is small and well within the WMO/GAW compatibility goals. The good results indicate that the whole system, including calibration procedures and standard gases, is fully adequate and no further action is required at this time.

3.4 Carbon dioxide measurements

CAMM started continuous measurements of CO₂ at CMN using NDIR technique in 1979, and continuous data series are available since then. The CMN CO₂ record is one of the longest in the world. Since 2015, measurements have been made with a CRDS instruments. In 2017, CNR also started with CO₂ measurements using CRDS technique.

Instrumentation, standards and calibration. See CH₄.

Intercomparison (performance audit). The comparison consisted of repeated challenges of the CMN instrument with randomly selected CO₂ levels from travelling standards.

The following equations characterise the instrument bias. The results are further illustrated in Figures 7 and 8 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G2401 #2871-CFKADS2269 (CNR):

$$\text{Unbiased CO}_2 \text{ mixing ratio: } X_{\text{CO}_2} (\mu\text{mol mol}^{-1}) = (\text{CO}_2 - 0.21 \mu\text{mol mol}^{-1}) / 0.99953 \quad (13)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}_2} (\mu\text{mol mol}^{-1}) = \text{sqrt} (0.00 \mu\text{mol mol}^{-1} + 3.28\text{e-}8 * X_{\text{CO}_2}^2) \quad (14)$$

Picarro G2301 #2017-CFADS2374 (CAMM):

$$\text{Unbiased CO}_2 \text{ mixing ratio: } X_{\text{CO}_2} (\mu\text{mol mol}^{-1}) = (\text{CO}_2 - 0.22 \mu\text{mol mol}^{-1}) / 0.99951 \quad (15)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}_2} (\mu\text{mol mol}^{-1}) = \text{sqrt} (0.00 \mu\text{mol mol}^{-1} + 3.28\text{e-}8 * X_{\text{CO}_2}^2) \quad (16)$$

The result of the comparison can be summarised as follows:

The result was within the WMO/GAW network compatibility goal in the relevant CO₂ range. The bias showed small dependence on the amount fraction with an offset of about 0.2 μmol mol⁻¹ at zero. This could be due to small inconsistencies in the standards available at CMN. However, due to the good results in the relevant amount fraction range, no further action is required.

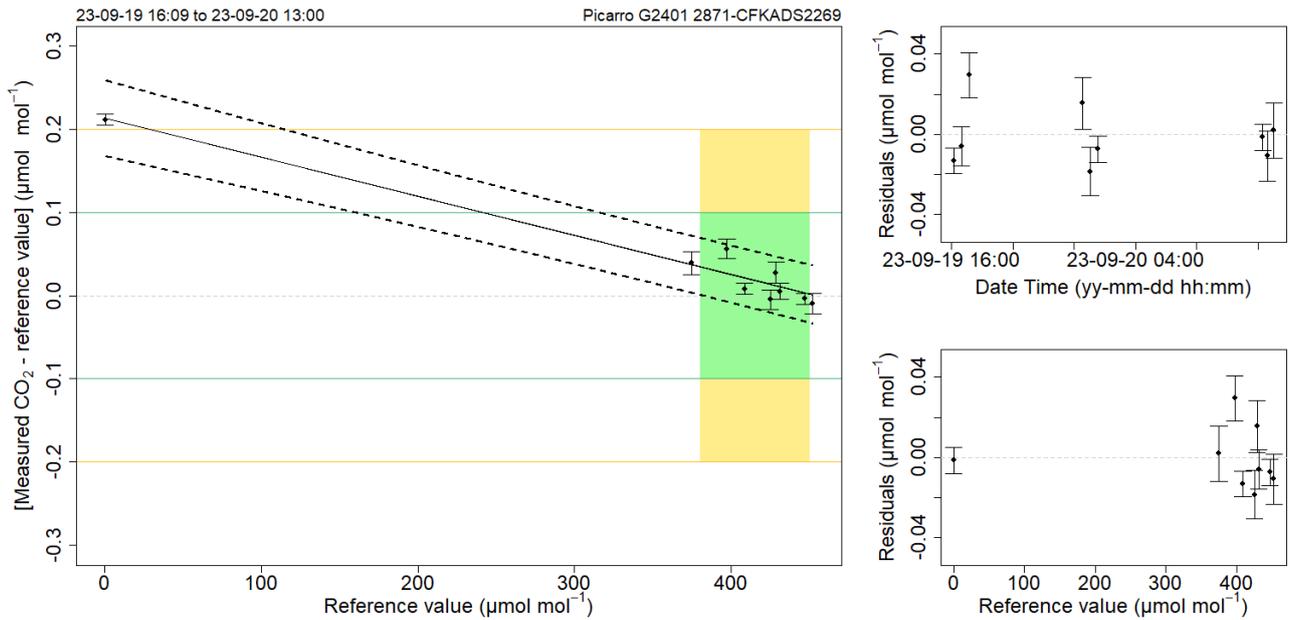


Figure 7. Left: Bias of the Picarro G2401 #2871-CFKADS2269 CO₂ instrument (CNR-ISAC/ICOS) with respect to the WMO-X2019 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CMN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).

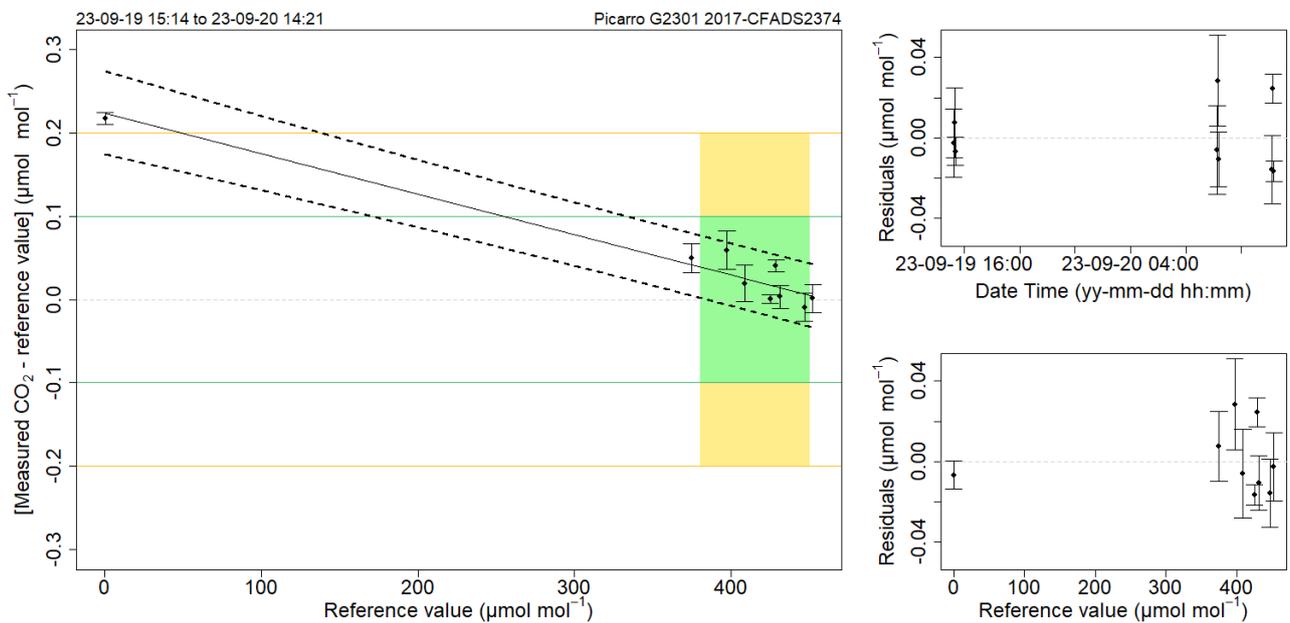


Figure 8. Left: Bias of the Picarro G2301 #2017-CFADS2374 CO₂ instrument (CAMM) with respect to the WMO-X2019 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CMN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).

4. Comparison of CMN Performance Audit Results with other Stations

This section compares the results of the CMN performance audit with other station audits conducted by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO₂ and CH₄, and Zellweger et al. (2019) for CO, but is also applicable to other compounds. Essentially, the bias in the middle of the relevant amount fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant amount fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO₂, CH₄, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone the amount fraction range of 0-100 nmol mol⁻¹ was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 9 shows the bias vs. slope of the WCC-Empa performance audits by for O₃, CO, CH₄, and CO₂. The grey dots show all comparisons made during WCC-Empa audits for the main station analysers, but exclude cases with known instrumental problems. Where an adjustment was made during an audit, only the final comparison is shown. The results of the current CMN audit are shown as coloured dots in Figure 9.

The results were within the DQOs for the main surface ozone analyser and the ozone calibrator. The backup ozone analyser did not meet the DQOs and will need to be calibrated or corrected if data from this instrument is used. The WMO/GAW network compatibility goals were also met for the main instruments for the CH₄, and CO₂ measurements carried out by CNR and CAMM, and the results were within the extended WMO/GAW network compatibility goals for CO.

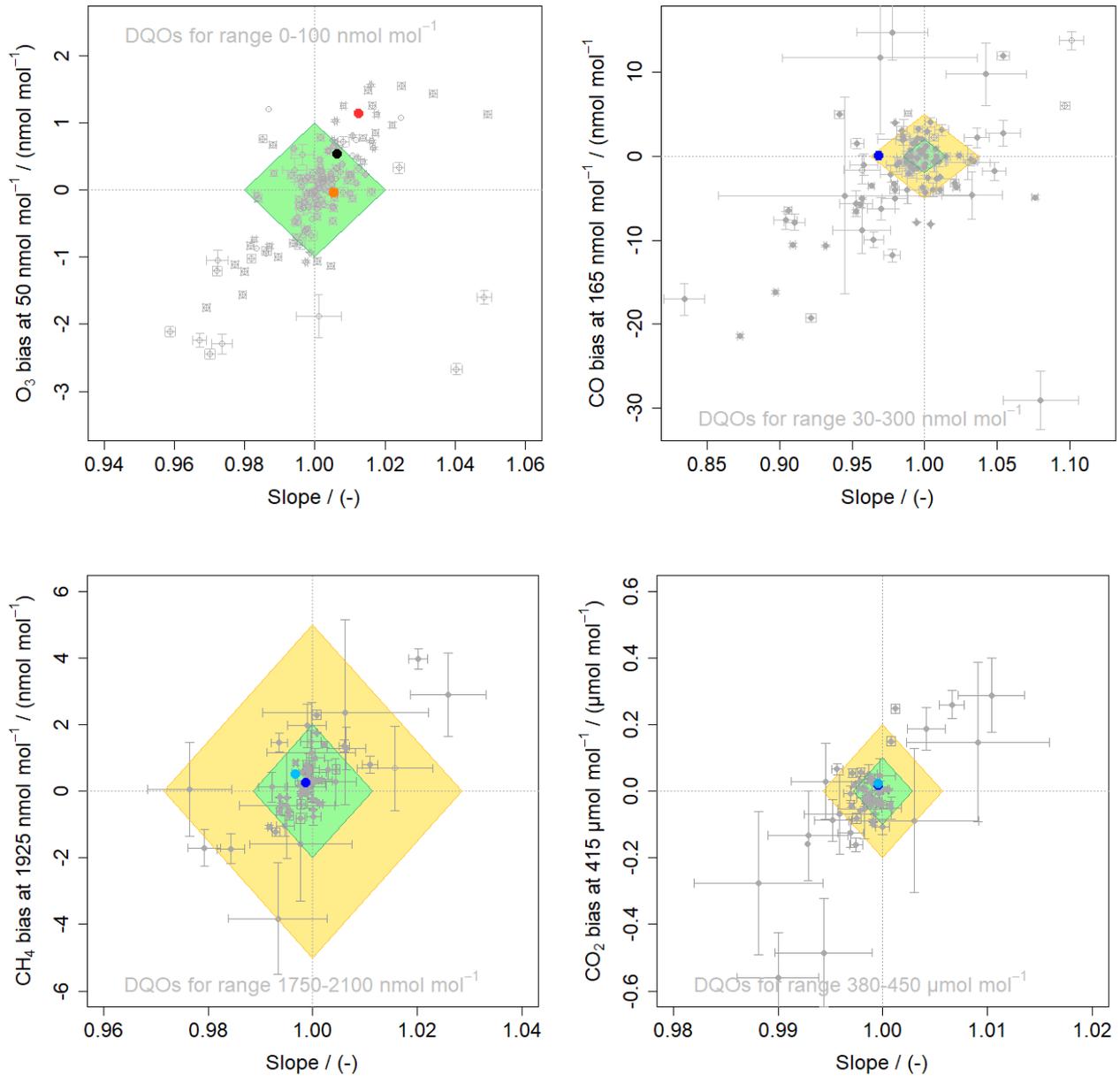


Figure 9. O₃ (upper left), CO (upper right), CH₄ (bottom left) and CO₂ (bottom right) bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show CMN results (orange: Thermo Scientific 49i # 1225011092, red: Thermo Scientific 49i # 1182780003, black: Thermo Scientific 49i-PS # 1118511036, dark blue: CNR Picarro G2401, light blue: CAMM Picarro G2301). Filled symbols refer to a comparison with the same calibration scale at the station and at the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and the extended compatibility goals (yellow).

5. Parallel Measurements of Ambient Air

The audit included parallel measurements of CO₂, CH₄ and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401 #1497-CFKADS2098). The TI was operated in the main building at CMN from 21 September to 16 October 2023. The TI was connected to an independent inlet line leading to the same inlet location as for the CAMM analyser. The TI sampled air in the following sequence: 3210 min ambient air followed by 75 min measurement of three standard gases, each for 25 min. The sample air was dried with a Nafion dryer (model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum in the purge air stream. To account for the residual effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the CO₂ and CH₄ data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The data were processed by the station staff (CAMM data) and by the ICOS Atmospheric Thematic Centre (ATC) (ICOS data).

Figures 10 to 14 show the comparison of hourly CO, CH₄, and CO₂ measurements between the WCC-Empa TI and the CMN Picarro G2401 analysers operated by CAMM and CNR/ICOS. Hourly averages were calculated based on 1 minute data with simultaneous data availability from the station analysers and the WCC-Empa TI.

The results of the ambient air comparison can be summarised as follows:

5.1 Carbon Monoxide

The CNR-ISAC/ICOS measurements were in agreement within the extended WMO/GAW compatibility goals. The measurements of the station were slightly lower on average compared to WCC-Empa. This is in contrast to the comparison of the travelling standards, where slightly higher values were found by CNR-ISAC/ICOS for the corresponding amount fractions. However, the bias of the ambient air comparison was variable with time, and short periods of better agreement with the TS comparison were also observed during the observation period.

5.2 Methane

Good agreement within the WMO/GAW network compatibility goals was found between the TI and both the CNR-ISAC/ICOS and the CAMM measurements, which is consistent with the results from the TS comparisons. However, the CNR-ISAC/ICOS site tended to be more influenced by air masses with higher CH₄ amount fractions. The CAMM and the CNR-ISAC/ICOS air intake locations are separated by about 90 m, and the ICOS inlet is at a slightly lower altitude. The differences observed between the WCC-Empa TI and CNR-ISAC/ICOS can be explained to the different inlet locations. Similar observations were made during the WCC-Empa audit in 2018.

5.3 Carbon dioxide

Good agreement within the WMO/GAW network compatibility goals was found between the TI and the CAMM measurements, while the bias of the CNR-ISAC/ICOS instrument was highly variable and within the extended WMO/GAW network compatibility goals. Again, this can be attributed to the different inlet locations and is in consistent with the results of the previous WCC-Empa audit. The recommendation made in 2018 is therefore still valid.

Recommendation 11 (, important, 2024)**

A detailed analysis of CAMM and CNR-ISAC/ICOS CO₂ and CH₄ data, focusing on the influence of the different air inlet locations, is strongly recommended. A continuous comparison of the two datasets, together with meteorological and ancillary parameters, is strongly recommended.

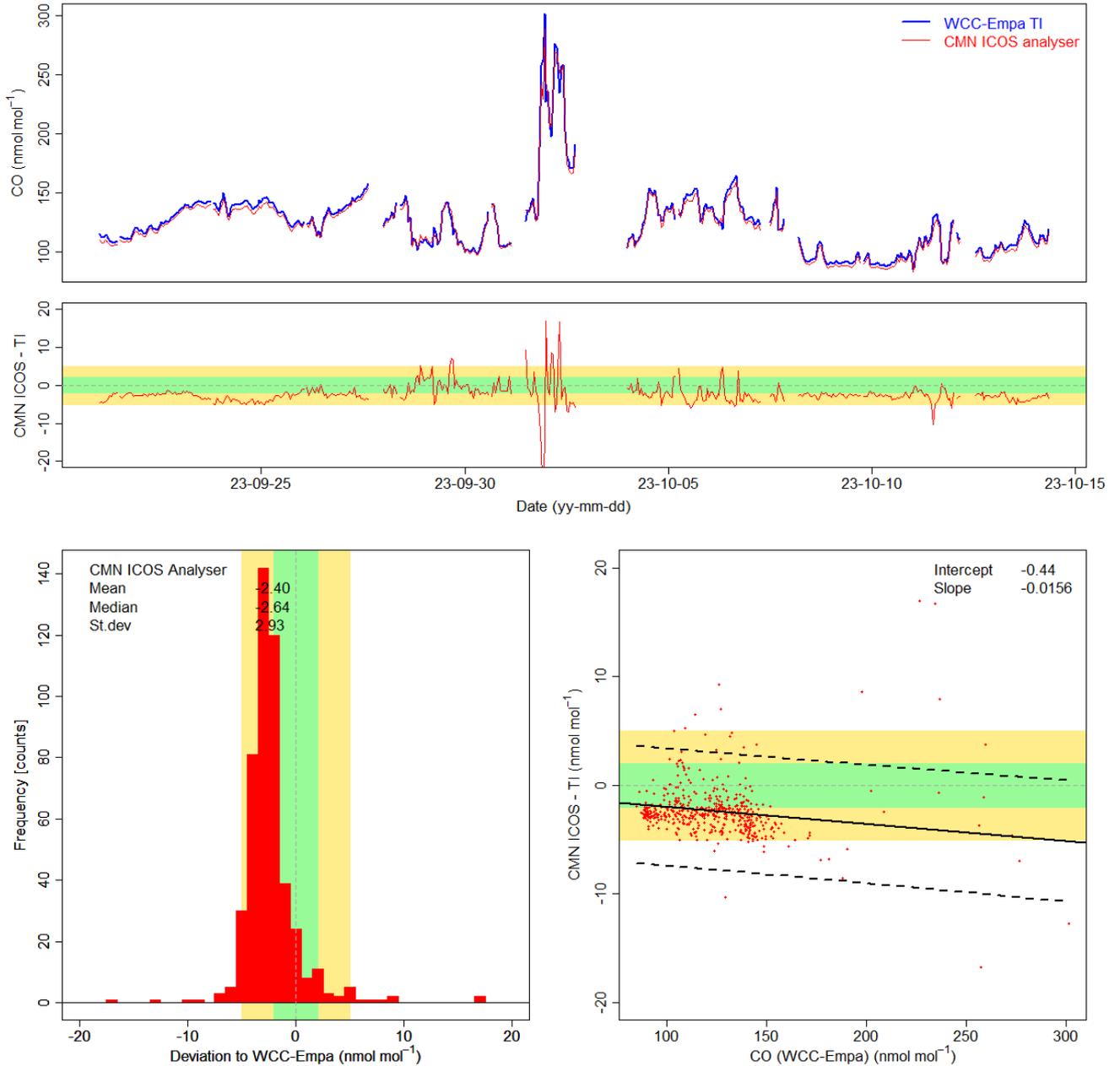


Figure 10. Top: Comparison of the Picarro G2401#2871-CFKADS2269 (CNR/ICOS instrument) with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G2401#2871-CFKADS2269 analyser compared to the WCC-Empa TI. Bottom right: CMN instrument bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

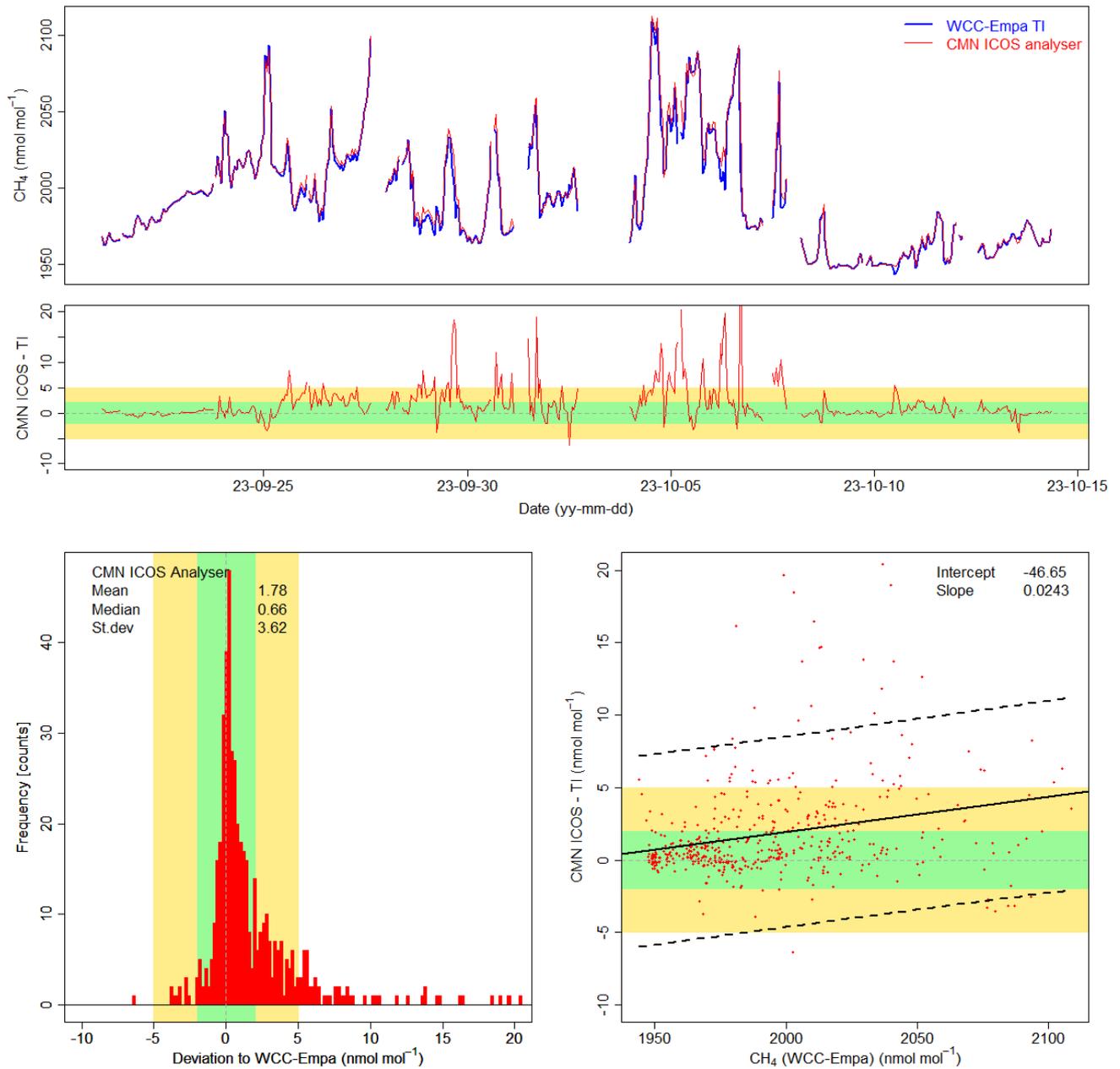


Figure 11. Top: Comparison of the Picarro G2401#2871-CFKADS2269 (CNR/ICOS analyser) with the WCC-Empa travelling instrument for CH₄. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CH₄ deviation histograms for the Picarro G2401#2871-CFKADS2269 analyser compared to the WCC-Empa TI. Bottom right: CMN instrument bias as a function of the CH₄ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

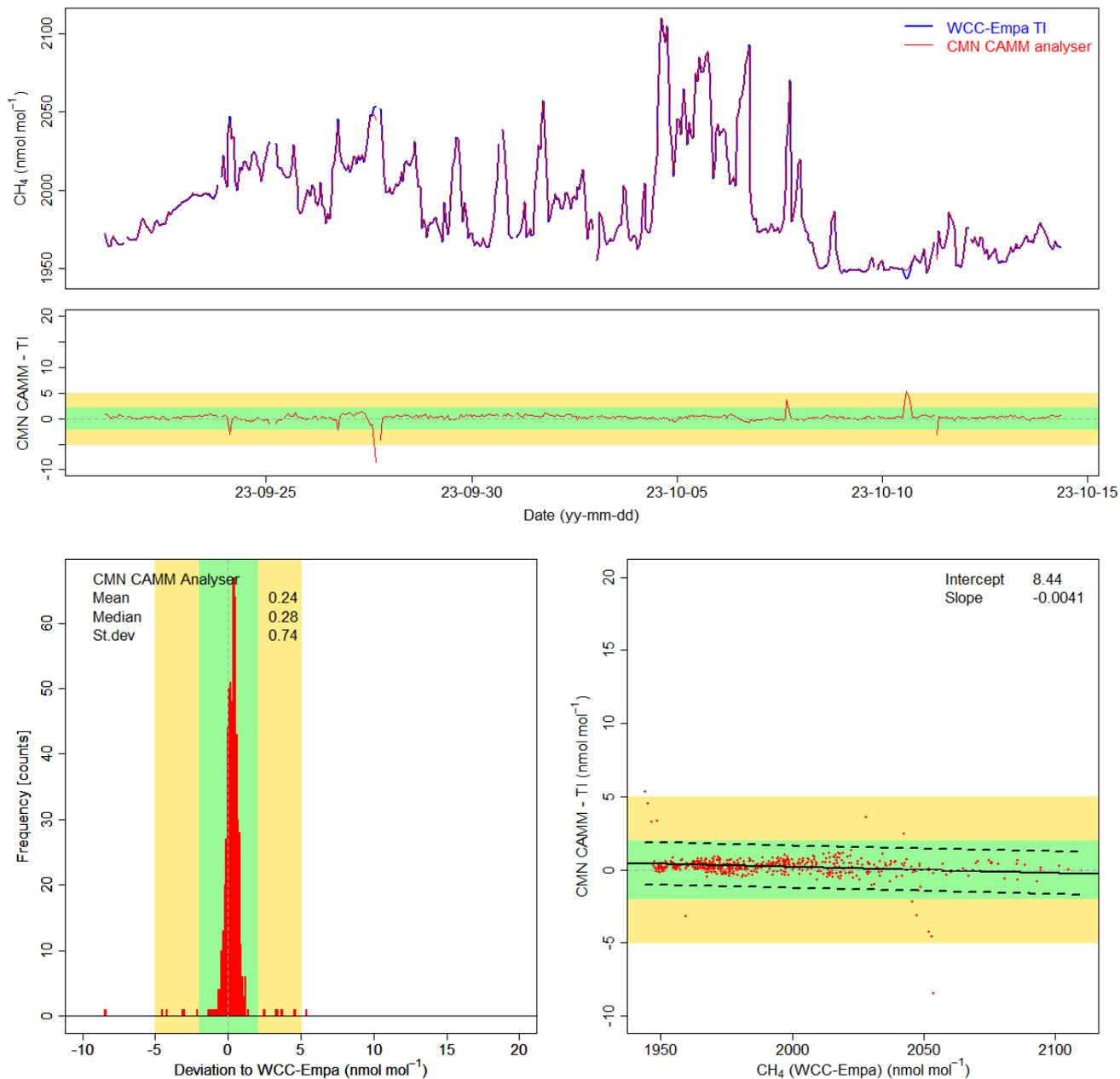


Figure 12. Top: Comparison of the Picarro G2301#2017-CFADS2374 (CMM analyser) with the WCC-Empa travelling instrument for CH₄. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CH₄ deviation histograms for the Picarro G2401#2871-CFKADS2269 analyser compared to the WCC-Empa TI. Bottom right: CMN instrument bias as a function of the CH₄ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

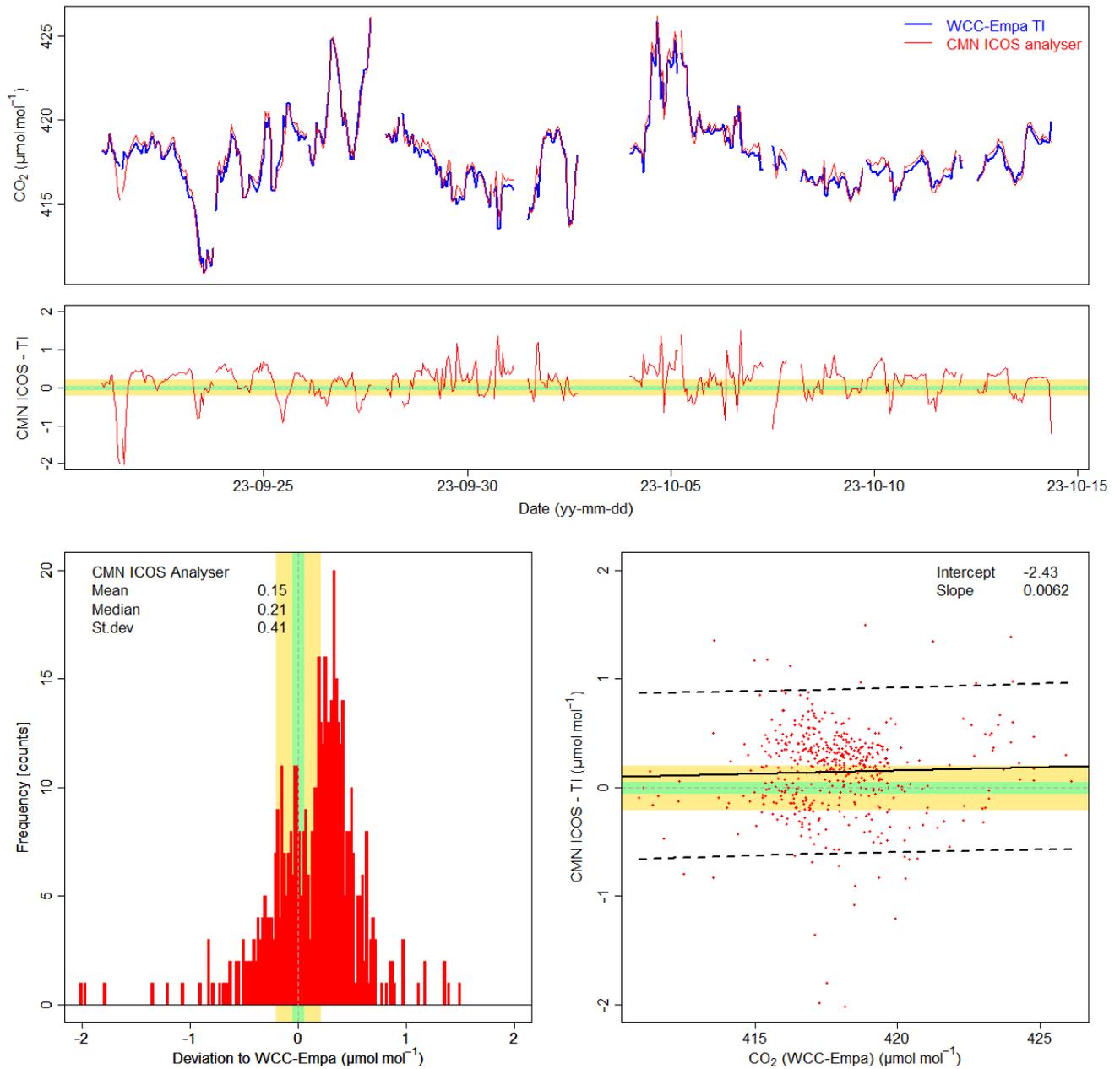


Figure 13. Top: Comparison of the Picarro G2401#2871-CFKADS2269 (CNR ICOS analyser) with the WCC-Empa travelling instrument for CO₂. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO₂ deviation histograms for the Picarro G2401#2871-CFKADS2269 analyser compared to the WCC-Empa TI. Bottom right: CMN instrument bias as a function of the CH₄ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

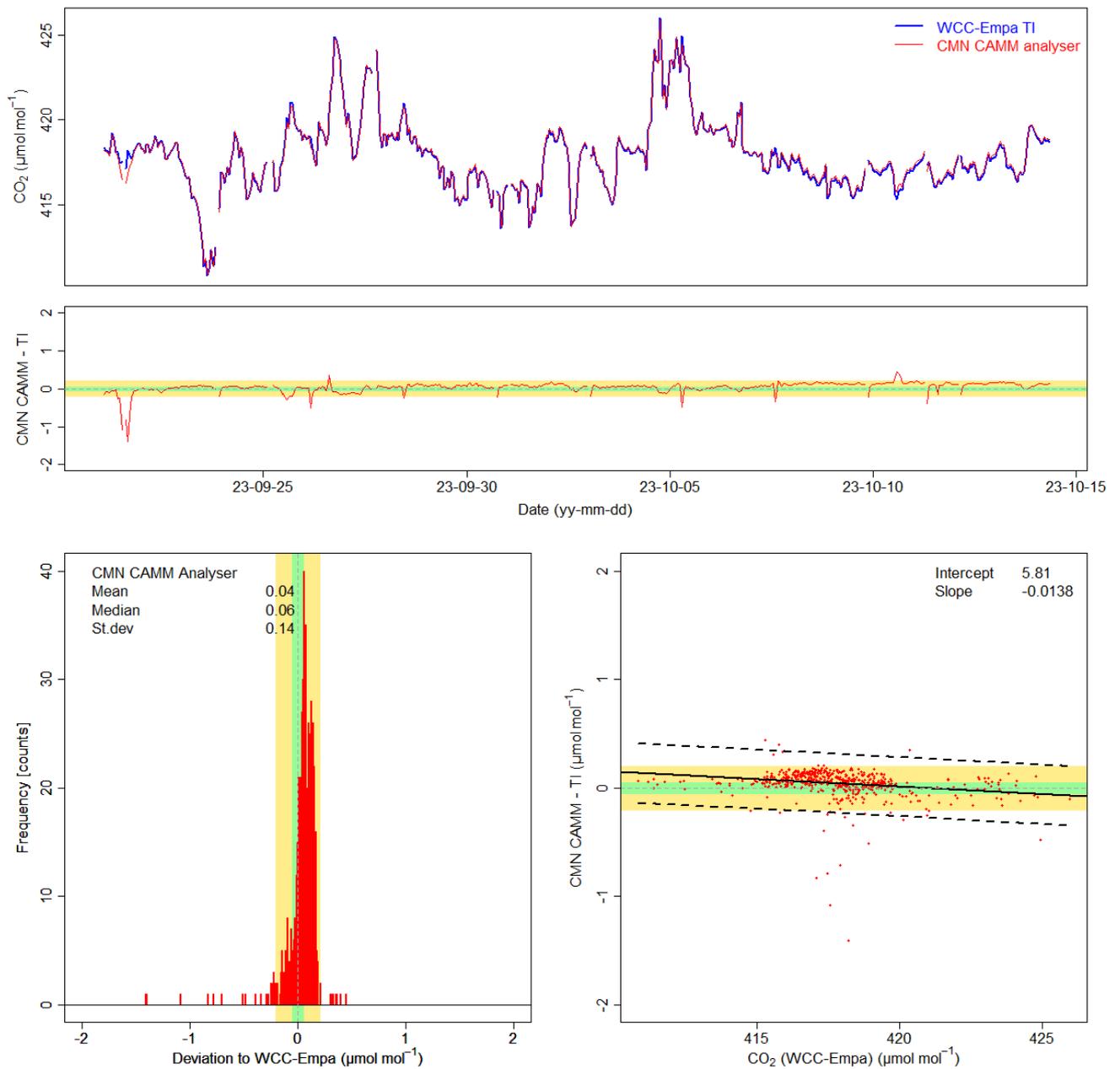


Figure 14. Top: Comparison of the Picarro G2301#2017-CFADS2374 (CAMM analyser) with the WCC-Empa travelling instrument for CO₂. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO₂ deviation histograms for the Picarro G2401#2871-CFKADS2269 analyser compared to the WCC-Empa TI. Bottom right: CMN instrument bias as a function of the CH₄ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

6. Conclusions

The facilities at the Monte Cimone Global GAW Station provide a comprehensive research platform that facilitates numerous ongoing observations across in all WMO/GAW focal areas and supports various research projects. The GAW activities at CMN are well embedded in the national and international research landscape, making it a very important contributor to the WMO/GAW programme. Therefore, the continuation of the Monte Cimone measurement series is essential for GAW. With its comprehensive monitoring of atmospheric constituents and exceptional data quality, the station enables cutting-edge research.

Most of the measurements evaluated were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant range of amount fractions. The parallel measurements performed as part of the audit showed small differences between the inlet locations of CAMM and CNR/ICOS. However, this is not unexpected and contributes to a better understanding of the local processes.

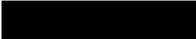
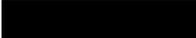
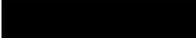
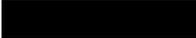
Only minor recommendations were made due to the good results of the comparisons and the well-established and fully appropriate operating procedures.

Table 1 summarises the results of the performance audit with travelling standards and the ambient air comparison in relation to the WMO/GAW compatibility goals.

Table 1. Summary of the results of the performance audit and parallel measurement at Monte Cimone. A tick mark in the table indicates that the compatibility goal (green) or the extended compatibility goal (orange) has been met on average, and **X** indicates results exceeding the compatibility goals.

Compound / Instrument	Range	Unit	ISO within DQO/eDQO
O ₃ (Thermo Scientific 49i #1225011092, main analyser)	0 -100	nmol mol ⁻¹	✓
O ₃ (Thermo Scientific 49i #1182780003, backup analyser)	0 -100	nmol mol ⁻¹	X
CO (Picarro G2401 #2871-CFKADS2269, CNR/ICOS)	30 - 300	nmol mol ⁻¹	✓
CO (Picarro G2401 #2871-CFKADS2269), parallel measurements	NA	nmol mol ⁻¹	✓
CH ₄ (Picarro G2401 #2871-CFKADS2269, CNR/ICOS)	1750 - 2100	nmol mol ⁻¹	✓
CH ₄ (Picarro G2301 #2017-CFADS2374, CAMM)	1750 - 2100	nmol mol ⁻¹	✓
CH ₄ (Picarro G2401 #2871-CFKADS2269), parallel measurements	NA	nmol mol ⁻¹	✓
CH ₄ (Picarro G2301 #2017-CFADS2374), parallel measurements	NA	nmol mol ⁻¹	✓
CO ₂ (Picarro G2401 #2871-CFKADS2269, CNR/ICOS)	380 - 450	µmol mol ⁻¹	✓
CO ₂ (Picarro G2301 #2017-CFADS2374, CAMM)	380 - 450	µmol mol ⁻¹	✓
CO ₂ (Picarro G2401 #2871-CFKADS2269), parallel measurements	NA	µmol mol ⁻¹	✓
CO ₂ (Picarro G2301 #2017-CFADS2374), parallel measurements	NA	µmol mol ⁻¹	✓

7. Summary Ranking of the Monte Cimone GAW Station

System Audit Aspect	Adequacy [#]	Comment
Measurement programme	 (5)	Comprehensive programme
Access	 (4)	Year round access, dependent on CAMM infrastructure
Facilities		
Laboratory and office space	 (5)	Adequate, with limited space for additional research campaigns
Internet access	 (5)	High-speed connection
Air Conditioning	 (5)	Air conditioned, temperature fluctuations of a few degrees (<2°C)
Power supply	 (4)	Mostly reliable and stable, UPS
General Management and Operation		
Organisation	 (5)	Well-coordinated and managed
Competence of staff	 (5)	Highly skilled staff (CNR), frequent fluctuations of staff (CAMM)
Air Inlet System	 (4)	Adequate, different locations of CAMM and ICOS inlets
Instrumentation		
Ozone	 (5)	Adequate instrumentation
CH ₄ /CO ₂ /CO Picarro G2401	 (5)	State of the art instrumentation
Standards		
O ₃	 (5)	Transfer standards with SRP traceability on site
CO, CO ₂ , CH ₄	 (5)	Full traceability to the WMO/GAW reference (CAMM: NOAA , ICOS: FCL)
Data Management		
Data acquisition	 (5)	Fully adequate systems
Data processing	 (5)	Skilled staff, appropriate procedures
Data submission WDCRG	 (5)	Ozone data is available
WDCGG submission (CNR)	 (1)	ICOS data not submitted
WDCGG submission (CAMM)	 (5)	Timely data submissions

[#]0: inadequate thru 5: adequate.

Appendix

A1. List of recommendations

The recommendations made in this report are summarised below, with an indication of their priority, significance and proposed completion date.

#	Recommendation	Priority	Significance	Date
1	<i>The operation of the CMN measurements is highly dependent on the infrastructure provided by CAMM. A long-term commitment as well as financial and logistical support is required for the sustainable operation of the CAMM/CMN GAW station.</i>	Medium	Important	Ongoing
2	<i>It is recommended that GAWSIS is updated annually or when major changes occur. Some of the reviewed information needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface (e.g. deletion of station contacts).</i>	Medium	Important	Ongoing
3	<i>Data submission to the WMO/GAW data centres is mandatory for all GAW stations. It is recommended to submit data to the respective data centres at least once a year. Hourly data are required for all parameters. The ICOS GHG and CO data must be submitted to the WDCGG.</i>	High	Critical	2024
4	<i>It is recommended that the University of Urbino submits data to WDCGG from 2018 onwards.</i>	Medium	Important	2024
5	CAMM: Electronic logbooks, preferably server based, are recommended. Access to the information should be possible both in the field and from the office.	High	Important	2024
6	<i>CAMM: It is recommended to change the position of the air intake pump to the end of the system, after the calibration unit.</i>	Low	Minor	2024
7	<i>It is recommended that the Thermo Scientific 49i #1182780003 ozone analyser be calibrated using the CMN ozone calibrator if it is to be used as the primary analyser.</i>	Low	Minor	2024
8	<i>The bias of the Thermo Scientific 49i-PS #1118511036 ozone calibrator needs to be compensated when it is used for ozone calibration.</i>	Low	Minor	Ongoing
9	<i>It is recommended to characterise the zero offset and the linearity of the CO instrument between 0 and 1000 nmol mol⁻¹ CO. High purity nitrogen (grade 6.0) can be used to characterise the instrument response at zero air.</i>	Medium	Important	2024
10	<i>For the CAMM system, it is recommended to use the measurements of the working standards to apply a drift correction. The results of the target tank measurements should be used for quality control.</i>	Medium	Important	2024

11	<i>It was noted that the CAMM data were provided in UTC+2, which corresponds to European summer time. In addition, a time difference of 9 minutes was observed with respect to synchronised clocks. The time needs to be regularly synchronised with a time server and data should be acquired in either UTC or local standard time (UTC+1) throughout the year.</i>	High	Critical	2024
12	<i>A detailed analysis of CAMM and CNR-ISAC/ICOS CO₂ and CH₄ data, focusing on the influence of the different air intake locations, is strongly recommended. Continuously comparing the two datasets, along with meteorological and additional parameters, is highly advised.</i>	Medium	Important	2024

A2. Data review

The following figures show summary plots of CMN data obtained from WDCRG and WDCGG on 28 February 2024. In addition, GHG and CO data accessed from the ICOS data portal on 19 February 2024 are shown. The plot shows the time series of hourly data, the frequency distributions and the diurnal and seasonal variations.

The main results of the data review can be summarised as follows:

Surface ozone:

The data set for the period 1996 to 2022 is shown below.

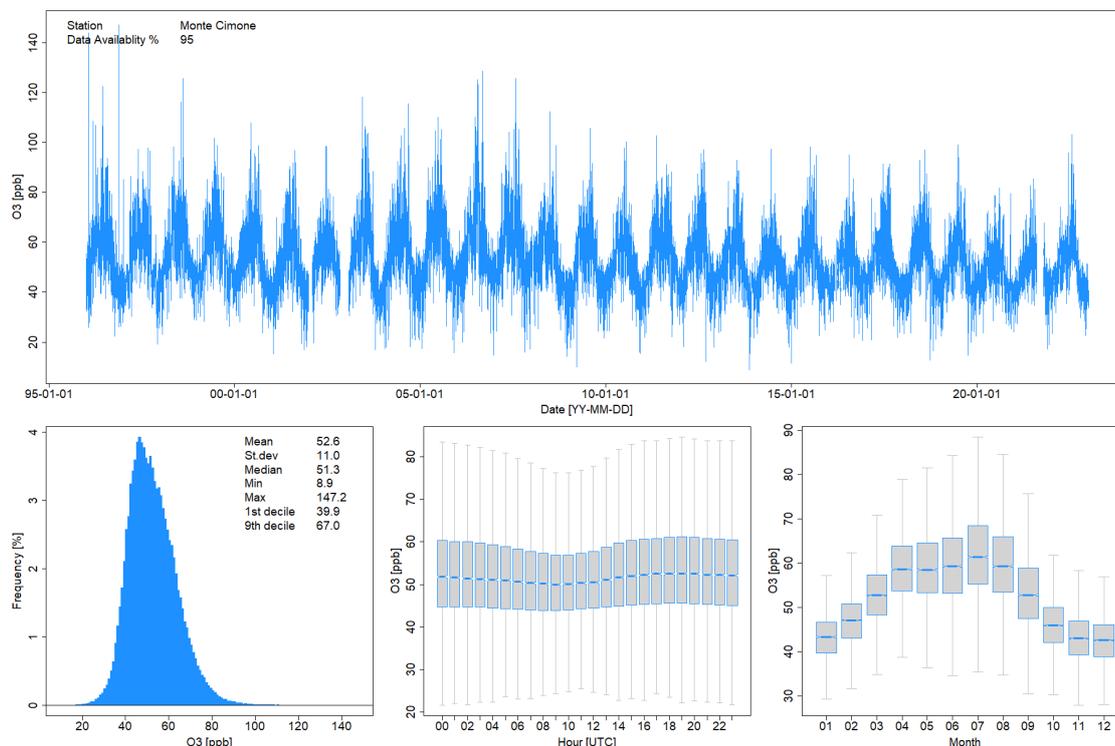


Figure 15. WDCRG O₃ data for the period 1996 to 2022. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

- The dataset looks good in terms of amount fraction, trend, seasonal and diurnal variation.

Carbon monoxide:

CO data submitted by ICOS, the University of Urbino and CNR/ISAC are shown in the figures below.

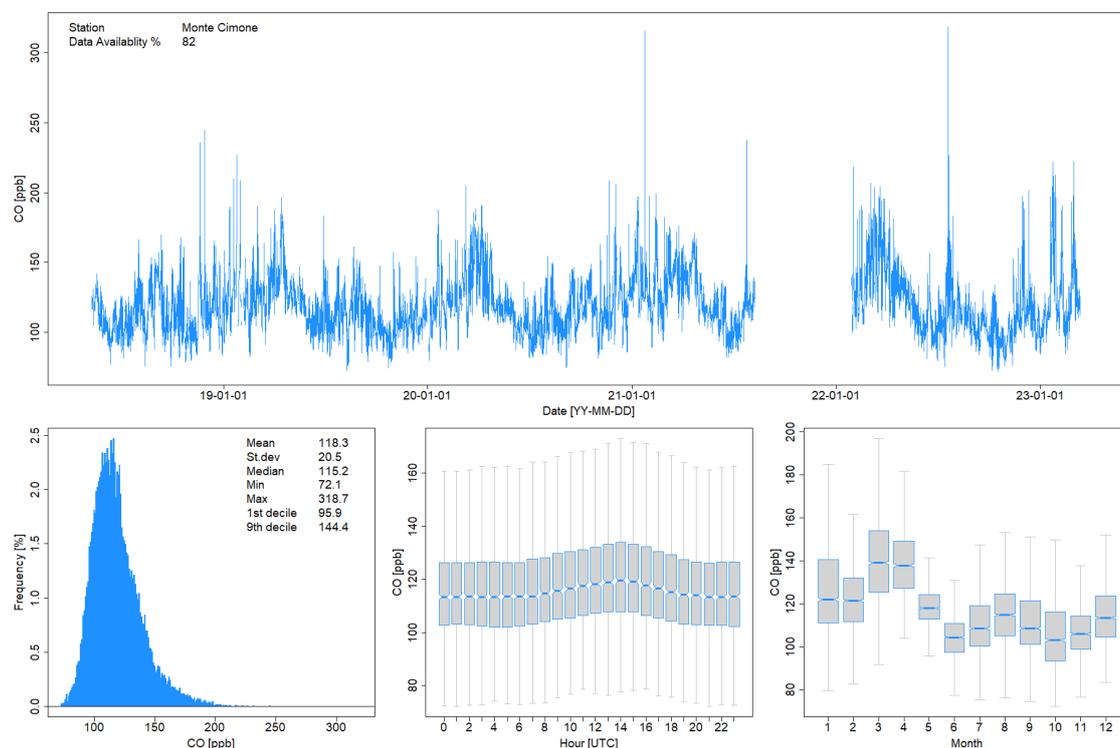


Figure 16. CMN CO data (2018-2023) submitted to WDCGG by ICOS. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

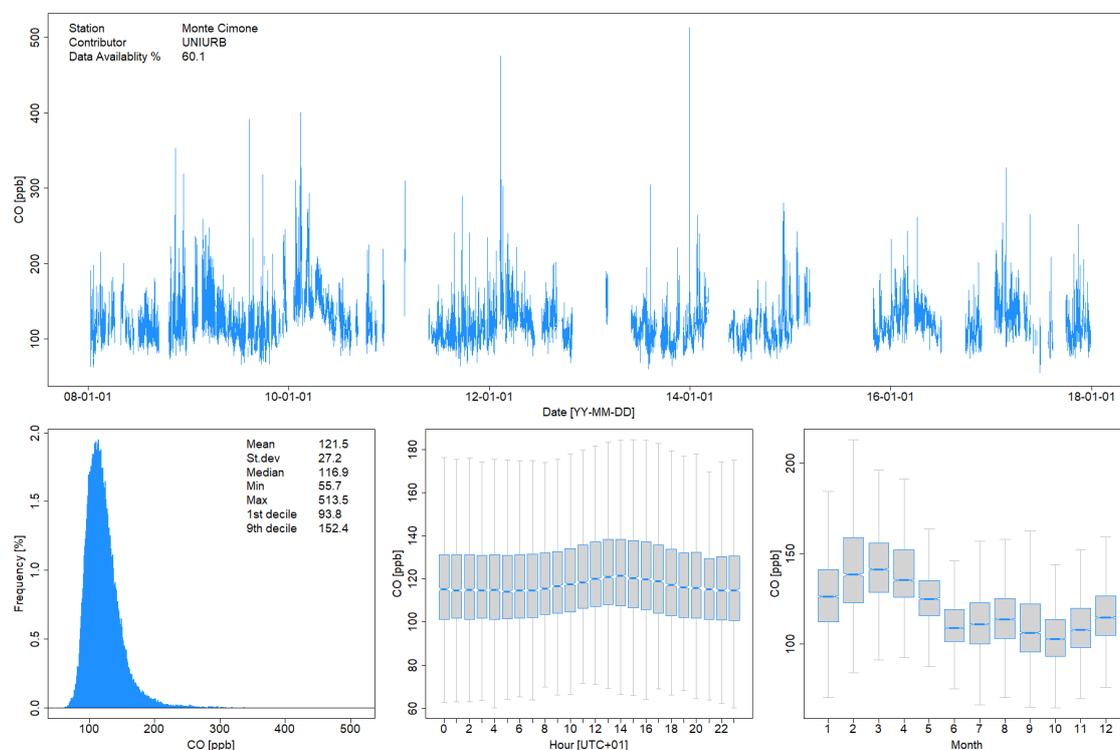


Figure 17. CMN CO data (2008-2017) submitted to WDCGG by the University of Urbino. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

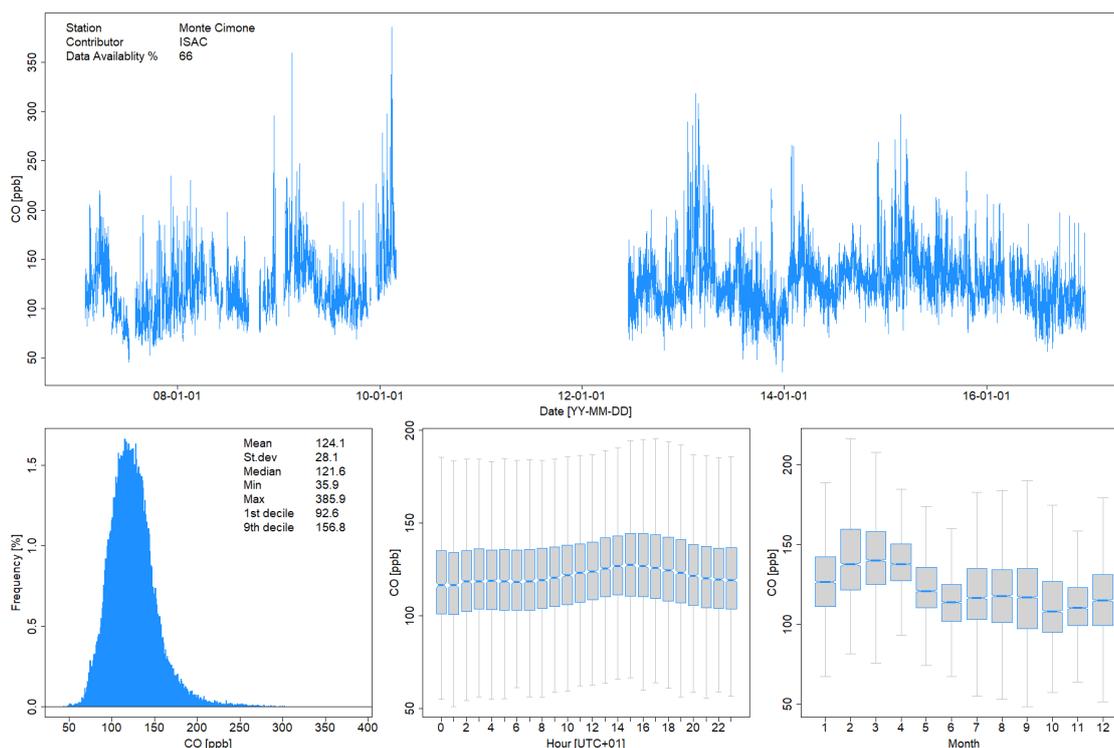


Figure 18. CMN CO data (2007-2016) submitted to WDCGG by CNR/ISAC. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

- All CO data sets looks sound in terms of amount fraction, trend, seasonal and diurnal variation.
- ICOS data has not been submitted to WDCGG.
- CNR/ISAC and University of Urbino data sets were probably only partly submitted. In case more data is available, submission is strongly recommended.

Methane:

The CH₄ data submitted by ICOS, the University of Urbino and CNR/ISAC are shown in the figures below.

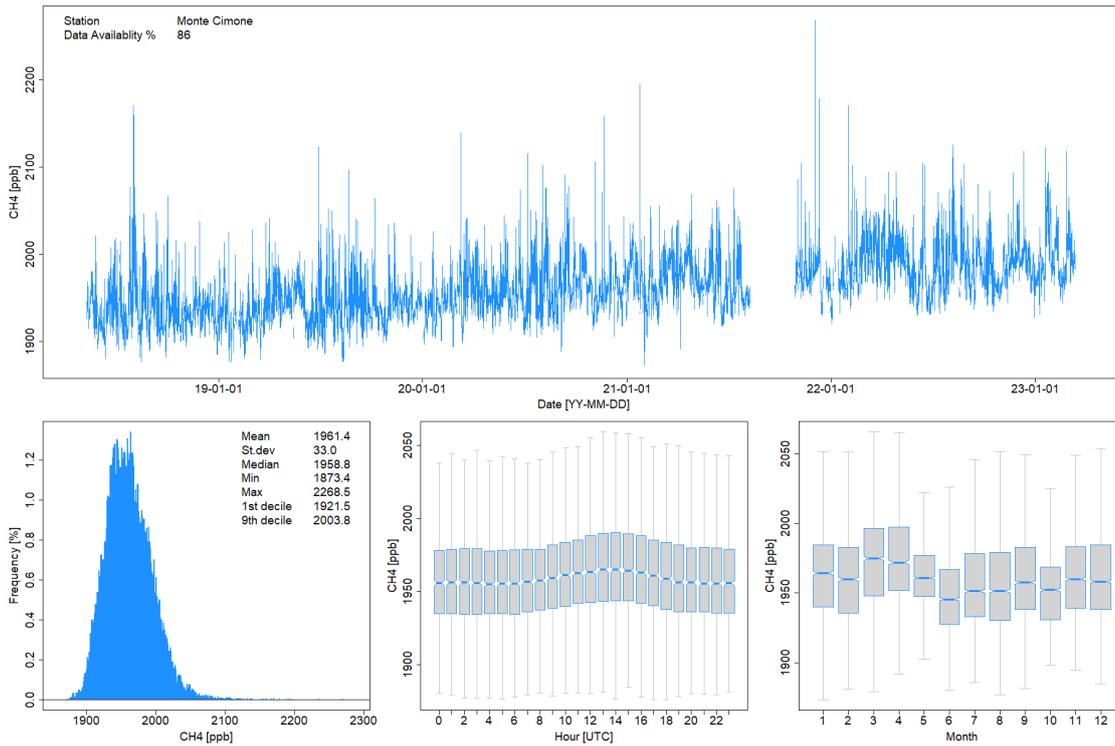


Figure 19. CMN in-situ CH₄ data (2018-2023) provided by ICOS. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

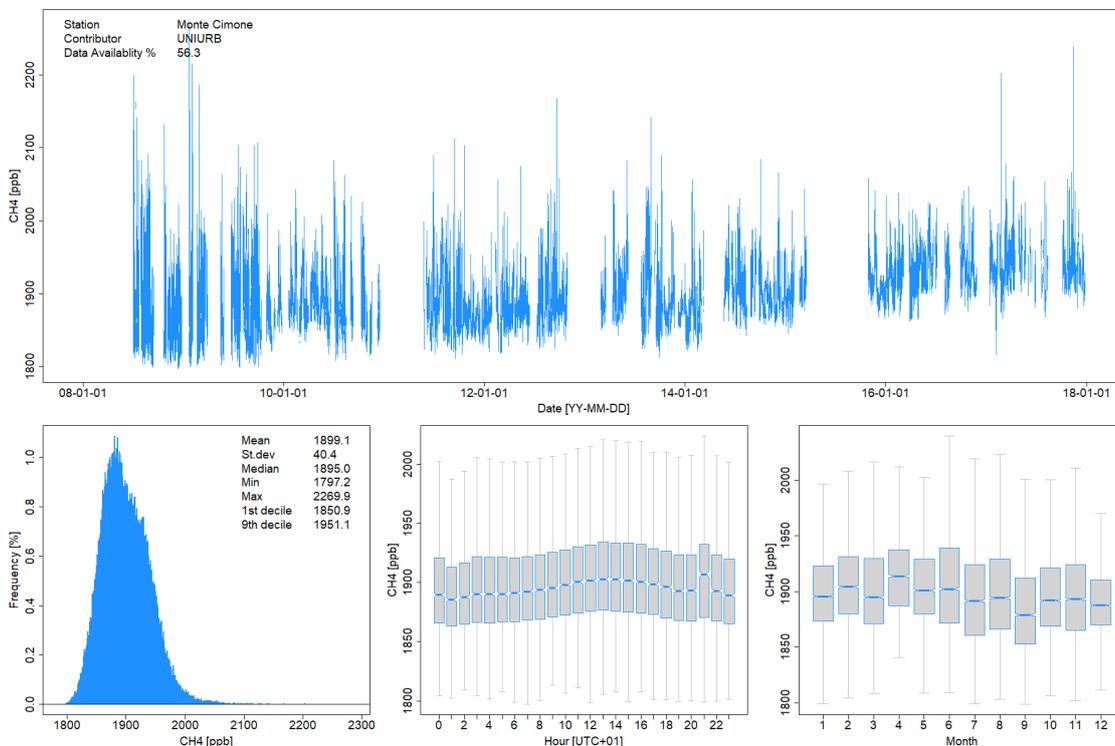


Figure 20. CMN in-situ CH₄ data (2008-2017) provided by the University of Urbino. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

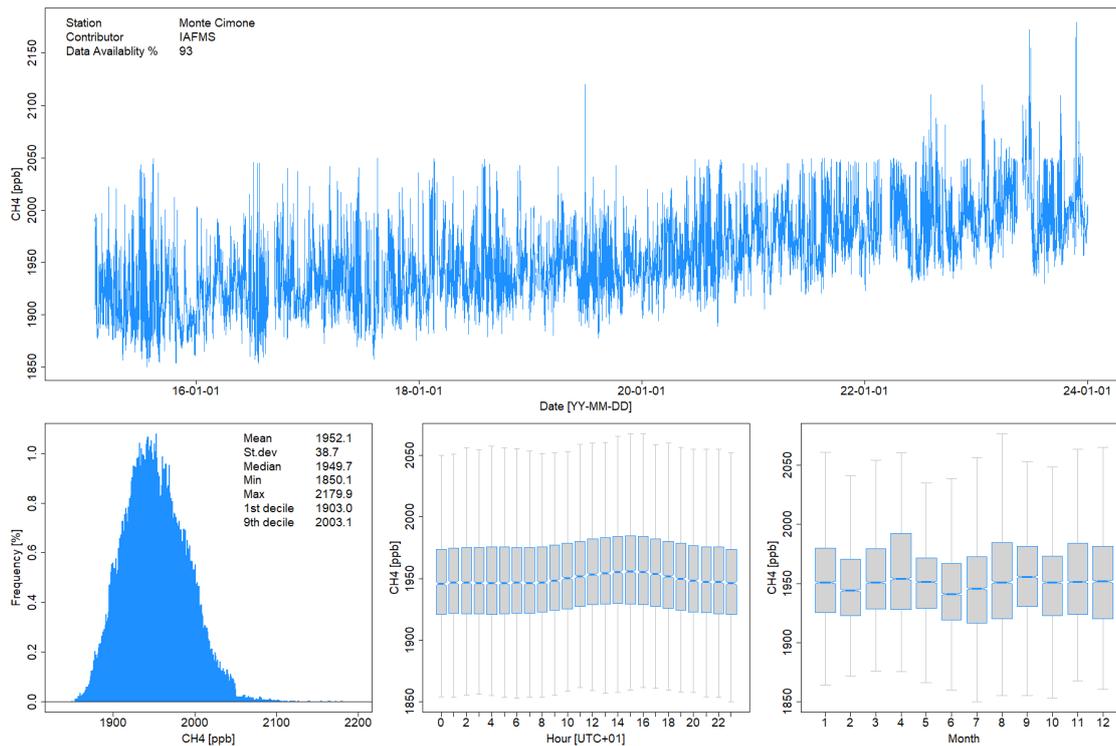


Figure 21. CMN in-situ CH₄ data (2015-2023) provided by CAMM. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

- All CH₄ data sets looks sound in terms of amount fraction, trend, seasonal and diurnal variation.
- ICOS data has not been submitted to WDCGG.
- CNR/ISAC and University of Urbino data sets were probably only partly submitted. In case more data is available, submission is strongly recommended.

Carbon dioxide:

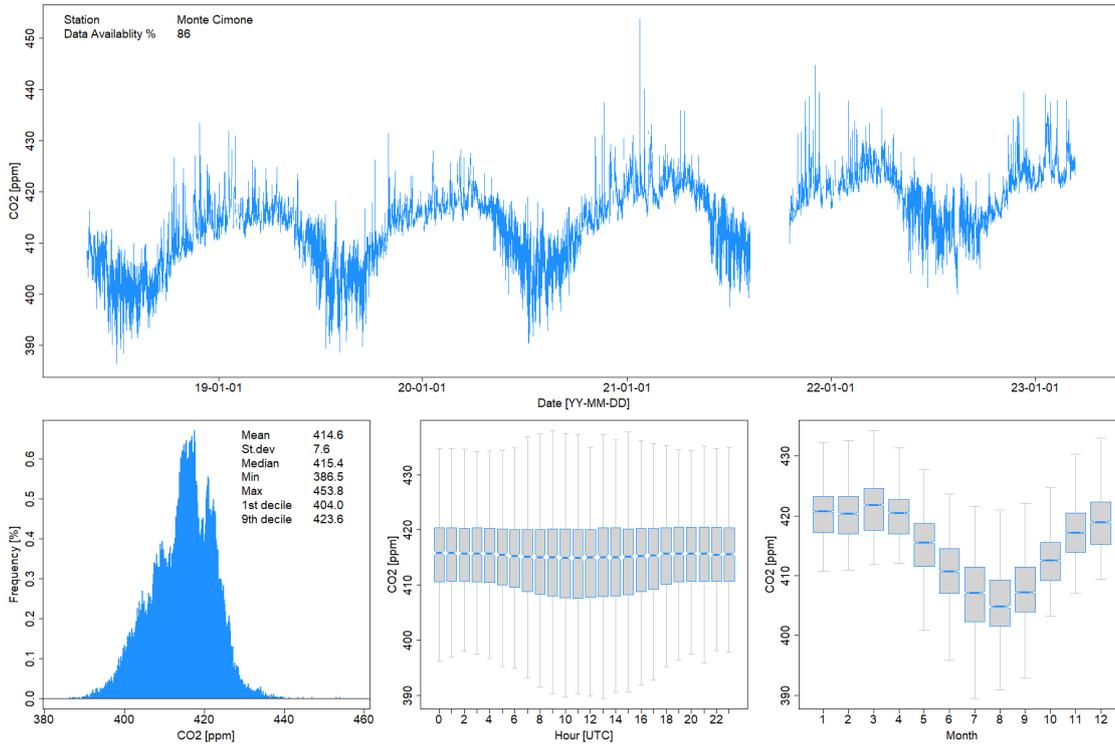


Figure 22. CMN in-situ CO₂ data (2018-2023) submitted by ICOS. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

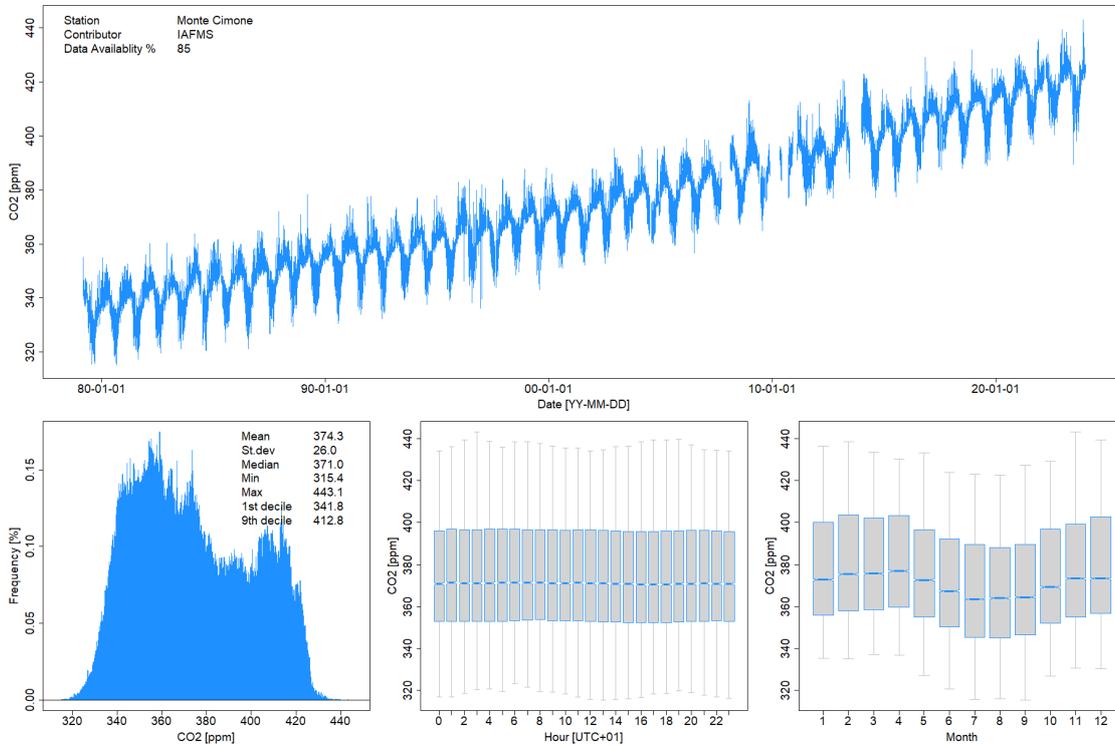


Figure 23. CMN in-situ CO₂ data (1979-2023) submitted by CAMM. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution, middle: Diurnal variation, right: Seasonal variation; the horizontal blue line shows the median and the blue boxes the interquartile range.

- Both ICOS and CAMM CO₂ data sets look good in terms of amount fraction, trend, seasonal and diurnal variation. CAMM has one of the longest time series of Europe.

A3. Performance audit results for surface ozone

All procedures were carried out according to the standard operating procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the standard reference photometer at Empa before and after the analyser comparison. The internal ozone generator of the WCC-Empa transfer standard was used to generate a randomised sequence of ozone levels ranging from 0 to 250 nmol mol⁻¹. Zero air was generated using a custom built zero air generator (Nafion dryer, Purafil, activated charcoal) for the comparison of the CMN ozone calibrator and analysers. The TS was connected to the station analyser using approximately 1.5 m of PFA tubing. Table 2 details the experimental setup for the travelling standard and the station analyser comparisons. The data used for the evaluation were recorded by the WCC-Empa and CMN data acquisition systems.

Table 2. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG +0.0 COEF 0.991
Pressure readings (hPa)	Ambient 789.6; TS 789.8 (no adjustment was made)
Main CMN ozone analyser (OA)	
Model, S/N	Thermo Scientific 49i #1225011092
Principle	UV absorption
Settings	BKG 0.0 nmol mol ⁻¹ , COEF 1.001
Pressure readings (hPa)	Ambient 789.7; OA 787.5 (no adjustment was made)
Backup CMN ozone analyser (OA)	
Model, S/N	Thermo Scientific 49i #1182780003
Principle	UV absorption
Settings	BKG 0.0 nmol mol ⁻¹ , COEF 1.012
Pressure readings (hPa)	Ambient 789.7; OA 789.1 (no adjustment was made)
CMN ozone calibrator (OC)	
Model, S/N	Thermo Scientific 49i-PS #1182780003
Principle	UV absorption
Settings	BKG -0.3 nmol mol ⁻¹ , COEF 1.013
Pressure readings (hPa)	Ambient 790.6; OC 789.7 (no adjustment was made)

Results

Each ozone level was measured for approximately ten minutes, and the last ten 40 s averages (comparison of the CMN analysers) or the last five 1 min averages (comparison of the CMN calibrator) were aggregated. These aggregates were used to evaluate the comparison. All results are valid for the calibration factors as given in Table 2 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment was applied as for the ambient air analysis.

The results of the assessment are shown in the following table (individual measurement points) and are also presented in the Executive Summary.

Table 3. Comparison of the main CMN ozone analyser (OA) Thermo Scientific 49i #1182780003 (BKG 0.0 nmol mol⁻¹, COEF 1.012) with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)	OA (nmol mol ⁻¹)	sdOA (nmol mol ⁻¹)	OA-TS (nmol mol ⁻¹)	OA-TS (%)
2023-09-19 15:55	199.95	0.18	202.92	0.58	2.97	1.49
2023-09-19 16:04	125.00	0.08	127.28	0.50	2.28	1.82
2023-09-19 16:13	224.94	0.14	228.48	0.47	3.54	1.57
2023-09-19 16:22	150.03	0.12	152.28	0.59	2.25	1.50
2023-09-19 16:30	75.04	0.14	76.52	0.64	1.48	1.97
2023-09-19 16:39	100.07	0.09	101.86	0.54	1.79	1.79
2023-09-19 16:51	0.18	0.17	0.83	0.34	0.65	NA
2023-09-19 16:59	25.06	0.15	26.07	0.22	1.01	4.03
2023-09-19 17:08	50.11	0.12	51.53	0.58	1.42	2.83
2023-09-19 17:17	174.98	0.18	178.00	0.53	3.02	1.73
2023-09-19 17:25	249.96	0.08	253.46	0.63	3.50	1.40
2023-09-19 17:34	174.96	0.16	177.35	0.58	2.39	1.37
2023-09-19 17:43	224.96	0.12	228.32	0.52	3.36	1.49
2023-09-19 17:55	0.24	0.15	0.84	0.44	0.60	NA
2023-09-19 18:03	74.99	0.12	76.50	0.67	1.51	2.01
2023-09-19 18:12	124.96	0.13	126.94	0.48	1.98	1.58
2023-09-19 18:21	149.96	0.17	152.37	0.51	2.41	1.61
2023-09-19 18:29	199.92	0.07	203.01	0.41	3.09	1.55
2023-09-19 18:38	50.05	0.20	51.14	0.59	1.09	2.18
2023-09-19 18:47	249.94	0.18	253.43	0.56	3.49	1.40
2023-09-19 18:55	25.13	0.17	26.02	0.31	0.89	3.54
2023-09-19 19:04	99.99	0.11	101.72	0.48	1.73	1.73
2023-09-19 19:13	75.09	0.20	76.59	0.39	1.50	2.00
2023-09-19 19:22	224.98	0.09	227.97	0.36	2.99	1.33
2023-09-19 19:30	175.02	0.15	177.31	0.54	2.29	1.31
2023-09-19 19:39	150.05	0.08	151.88	0.52	1.83	1.22
2023-09-19 19:48	249.92	0.11	253.41	0.67	3.49	1.40
2023-09-19 19:56	199.91	0.10	202.81	0.59	2.90	1.45
2023-09-19 20:05	50.01	0.14	51.24	0.51	1.23	2.46
2023-09-19 20:17	0.01	0.11	0.80	0.38	0.79	NA
2023-09-19 20:25	100.06	0.10	101.63	0.65	1.57	1.57
2023-09-19 20:34	25.16	0.10	25.99	0.36	0.83	3.30
2023-09-19 20:43	125.04	0.11	127.14	0.50	2.10	1.68
2023-09-19 20:52	149.97	0.15	152.23	0.55	2.26	1.51
2023-09-19 21:03	0.23	0.12	0.58	0.46	0.35	NA
2023-09-19 21:12	75.08	0.13	76.72	0.62	1.64	2.18
2023-09-19 21:21	174.99	0.09	177.65	0.56	2.66	1.52
2023-09-19 21:29	25.11	0.11	26.02	0.50	0.91	3.62
2023-09-19 21:38	224.92	0.13	228.03	0.41	3.11	1.38
2023-09-19 21:47	125.01	0.17	126.88	0.45	1.87	1.50
2023-09-19 21:55	50.10	0.13	51.10	0.49	1.00	2.00
2023-09-19 22:04	249.98	0.10	253.73	0.51	3.75	1.50
2023-09-19 22:13	100.10	0.28	102.10	0.96	2.00	2.00
2023-09-19 22:21	200.04	0.11	203.23	0.57	3.19	1.59
2023-09-20 00:12	100.01	0.11	101.94	0.51	1.93	1.93
2023-09-20 00:24	0.05	0.16	0.51	0.47	0.46	NA

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
2023-09-20 00:32	150.03	0.10	152.45	0.52	2.42	1.61
2023-09-20 00:41	125.06	0.11	127.08	0.56	2.02	1.62
2023-09-20 00:50	75.06	0.11	76.53	0.62	1.47	1.96
2023-09-20 00:58	50.10	0.14	51.47	0.51	1.37	2.73
2023-09-20 01:07	200.02	0.12	202.83	0.62	2.81	1.40
2023-09-20 01:16	224.99	0.12	228.39	0.52	3.40	1.51
2023-09-20 01:24	175.04	0.12	177.62	0.45	2.58	1.47
2023-09-20 01:33	25.15	0.11	25.85	0.40	0.70	2.78
2023-09-20 01:42	249.93	0.12	253.70	0.64	3.77	1.51
2023-09-20 01:50	249.98	0.14	253.51	0.51	3.53	1.41
2023-09-20 01:59	174.97	0.13	177.86	0.47	2.89	1.65
2023-09-20 02:08	225.03	0.14	228.21	0.47	3.18	1.41
2023-09-20 02:16	50.10	0.12	51.41	0.55	1.31	2.61
2023-09-20 02:25	75.05	0.13	76.43	0.38	1.38	1.84
2023-09-20 02:34	25.30	0.63	26.22	0.58	0.92	3.64
2023-09-20 02:43	199.98	0.16	202.70	0.46	2.72	1.36
2023-09-20 02:51	100.11	0.07	102.00	0.48	1.89	1.89
2023-09-20 03:00	125.04	0.11	127.02	0.54	1.98	1.58
2023-09-20 03:12	0.15	0.21	0.78	0.25	0.63	NA
2023-09-20 03:20	150.00	0.15	152.31	0.50	2.31	1.54
2023-09-20 03:29	125.00	0.14	127.10	0.59	2.10	1.68
2023-09-20 03:38	100.01	0.13	101.78	0.67	1.77	1.77
2023-09-20 03:50	0.20	0.14	0.86	0.39	0.66	NA
2023-09-20 03:58	174.95	0.08	177.63	0.67	2.68	1.53
2023-09-20 04:16	25.11	0.18	26.13	0.37	1.02	4.06
2023-09-20 04:25	199.93	0.15	202.79	0.42	2.86	1.43
2023-09-20 04:34	249.95	0.15	253.58	0.68	3.63	1.45
2023-09-20 04:42	75.10	0.09	76.30	0.27	1.20	1.60
2023-09-20 04:51	50.13	0.12	51.06	0.34	0.93	1.86
2023-09-20 05:00	225.00	0.12	228.51	0.51	3.51	1.56
2023-09-20 05:08	150.05	0.13	152.54	0.28	2.49	1.66
2023-09-20 05:17	199.92	0.11	202.85	0.45	2.93	1.47
2023-09-20 05:26	224.94	0.09	228.14	0.61	3.20	1.42
2023-09-20 05:34	100.06	0.16	101.75	0.53	1.69	1.69
2023-09-20 05:43	249.90	0.24	253.39	0.43	3.49	1.40
2023-09-20 05:52	50.10	0.09	50.94	0.27	0.84	1.68
2023-09-20 06:00	75.07	0.13	76.35	0.55	1.28	1.71
2023-09-20 06:12	25.10	0.16	25.92	0.25	0.82	3.27
2023-09-20 06:21	175.02	0.14	177.72	0.69	2.70	1.54
2023-09-20 06:29	149.96	0.12	152.20	0.43	2.24	1.49
2023-09-20 06:41	0.22	0.12	0.80	0.50	0.58	NA
2023-09-20 06:50	125.00	0.18	126.83	0.44	1.83	1.46
2023-09-20 08:37	100.04	0.09	101.61	0.56	1.57	1.57
2023-09-20 08:46	75.05	0.11	76.36	0.45	1.31	1.75
2023-09-20 08:55	25.11	0.16	26.06	0.33	0.95	3.78
2023-09-20 09:03	50.08	0.09	51.40	0.39	1.32	2.64
2023-09-20 09:12	200.00	0.14	203.52	0.40	3.52	1.76
2023-09-20 09:21	249.94	0.14	253.91	0.21	3.97	1.59

Date – Time	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)	OA (nmol mol ⁻¹)	sdOA (nmol mol ⁻¹)	OA-TS (nmol mol ⁻¹)	OA-TS (%)
2023-09-20 09:32	0.16	0.19	0.46	0.53	0.30	NA
2023-09-20 09:41	150.01	0.17	152.28	0.58	2.27	1.51
2023-09-20 09:50	224.93	0.11	228.25	0.56	3.32	1.48
2023-09-20 09:58	174.99	0.09	177.77	0.58	2.78	1.59
2023-09-20 10:07	125.02	0.12	127.25	0.50	2.23	1.78

Table 4. Comparison of the CMN ozone analyser (OA) Thermo Scientific 49i #1225011092 (BKG 0.0 nmol mol⁻¹, COEF 1.001) with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)	OA (nmol mol ⁻¹)	sdOA (nmol mol ⁻¹)	OA-TS (nmol mol ⁻¹)	OA-TS (%)
2023-09-19 15:55	199.95	0.18	200.67	1.03	0.72	0.36
2023-09-19 16:04	125.00	0.08	125.24	0.58	0.24	0.19
2023-09-19 16:13	224.94	0.14	225.75	0.99	0.81	0.36
2023-09-19 16:22	150.03	0.12	150.57	0.70	0.54	0.36
2023-09-19 16:30	75.04	0.14	75.42	0.82	0.38	0.51
2023-09-19 16:39	100.07	0.09	100.25	0.51	0.18	0.18
2023-09-19 16:51	0.18	0.17	0.12	0.65	-0.06	NA
2023-09-19 16:59	25.06	0.15	25.21	0.63	0.15	0.60
2023-09-19 17:08	50.11	0.12	50.14	0.94	0.03	0.06
2023-09-19 17:17	174.98	0.18	175.66	1.12	0.68	0.39
2023-09-19 17:25	249.96	0.08	251.01	0.97	1.05	0.42
2023-09-19 17:34	174.96	0.16	175.82	1.49	0.86	0.49
2023-09-19 17:43	224.96	0.12	225.94	1.20	0.98	0.44
2023-09-19 17:55	0.24	0.15	0.30	0.95	0.06	NA
2023-09-19 18:03	74.99	0.12	75.28	1.08	0.29	0.39
2023-09-19 18:12	124.96	0.13	125.62	0.65	0.66	0.53
2023-09-19 18:21	149.96	0.17	150.77	1.04	0.81	0.54
2023-09-19 18:29	199.92	0.07	200.86	1.08	0.94	0.47
2023-09-19 18:38	50.05	0.20	50.01	0.54	-0.04	-0.08
2023-09-19 18:47	249.94	0.18	250.77	0.93	0.83	0.33
2023-09-19 18:55	25.13	0.17	25.50	0.83	0.37	1.47
2023-09-19 19:04	99.99	0.11	100.33	0.49	0.34	0.34
2023-09-19 19:13	75.09	0.20	75.24	0.67	0.15	0.20
2023-09-19 19:22	224.98	0.09	225.79	1.18	0.81	0.36
2023-09-19 19:30	175.02	0.15	175.96	1.57	0.94	0.54
2023-09-19 19:39	150.05	0.08	150.36	0.62	0.31	0.21
2023-09-19 19:48	249.92	0.11	251.15	0.69	1.23	0.49
2023-09-19 19:56	199.91	0.10	200.99	0.93	1.08	0.54
2023-09-19 20:05	50.01	0.14	49.61	0.66	-0.40	-0.80
2023-09-19 20:17	0.01	0.11	0.40	0.92	0.39	NA
2023-09-19 20:25	100.06	0.10	99.76	0.55	-0.30	-0.30
2023-09-19 20:34	25.16	0.10	24.82	0.91	-0.34	-1.35
2023-09-19 20:43	125.04	0.11	125.42	0.36	0.38	0.30
2023-09-19 20:52	149.97	0.15	150.43	0.74	0.46	0.31
2023-09-19 21:03	0.23	0.12	0.02	0.92	-0.21	NA
2023-09-19 21:12	75.08	0.13	74.74	0.61	-0.34	-0.45
2023-09-19 21:21	174.99	0.09	175.76	0.54	0.77	0.44

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
2023-09-19 21:29	25.11	0.11	24.74	0.62	-0.37	-1.47
2023-09-19 21:38	224.92	0.13	225.94	1.05	1.02	0.45
2023-09-19 21:47	125.01	0.17	125.19	0.76	0.18	0.14
2023-09-19 21:55	50.10	0.13	50.20	0.72	0.10	0.20
2023-09-19 22:04	249.98	0.10	251.25	0.74	1.27	0.51
2023-09-19 22:13	100.10	0.28	101.00	0.90	0.90	0.90
2023-09-19 22:21	200.04	0.11	200.80	0.86	0.76	0.38
2023-09-20 00:12	100.01	0.11	100.38	0.69	0.37	0.37
2023-09-20 00:24	0.05	0.16	0.02	0.51	-0.03	NA
2023-09-20 00:32	150.03	0.10	150.38	0.85	0.35	0.23
2023-09-20 00:41	125.06	0.11	125.02	0.80	-0.04	-0.03
2023-09-20 00:50	75.06	0.11	75.19	0.52	0.13	0.17
2023-09-20 00:58	50.10	0.14	50.14	0.47	0.04	0.08
2023-09-20 01:07	200.02	0.12	200.71	0.60	0.69	0.34
2023-09-20 01:16	224.99	0.12	225.96	0.60	0.97	0.43
2023-09-20 01:24	175.04	0.12	175.17	0.63	0.13	0.07
2023-09-20 01:33	25.15	0.11	25.07	0.39	-0.08	-0.32
2023-09-20 01:42	249.93	0.12	250.98	0.48	1.05	0.42
2023-09-20 01:50	249.98	0.14	251.36	0.53	1.38	0.55
2023-09-20 01:59	174.97	0.13	175.98	0.38	1.01	0.58
2023-09-20 02:08	225.03	0.14	226.13	0.84	1.10	0.49
2023-09-20 02:16	50.10	0.12	49.99	0.57	-0.11	-0.22
2023-09-20 02:25	75.05	0.13	75.09	0.70	0.04	0.05
2023-09-20 02:34	25.30	0.63	24.89	0.85	-0.41	-1.62
2023-09-20 02:43	199.98	0.16	200.71	0.62	0.73	0.37
2023-09-20 02:51	100.11	0.07	100.18	0.77	0.07	0.07
2023-09-20 03:00	125.04	0.11	125.48	0.55	0.44	0.35
2023-09-20 03:12	0.15	0.21	0.19	0.53	0.04	NA
2023-09-20 03:20	150.00	0.15	150.15	0.72	0.15	0.10
2023-09-20 03:29	125.00	0.14	125.26	0.72	0.26	0.21
2023-09-20 03:38	100.01	0.13	100.43	0.69	0.42	0.42
2023-09-20 03:50	0.20	0.14	-0.13	0.53	-0.33	NA
2023-09-20 03:58	174.95	0.08	175.60	0.60	0.65	0.37
2023-09-20 04:16	25.11	0.18	24.82	0.63	-0.29	-1.15
2023-09-20 04:25	199.93	0.15	200.23	0.89	0.30	0.15
2023-09-20 04:34	249.95	0.15	251.28	0.59	1.33	0.53
2023-09-20 04:42	75.10	0.09	74.80	0.38	-0.30	-0.40
2023-09-20 04:51	50.13	0.12	50.03	0.63	-0.10	-0.20
2023-09-20 05:00	225.00	0.12	226.01	0.89	1.01	0.45
2023-09-20 05:08	150.05	0.13	150.49	0.69	0.44	0.29
2023-09-20 05:17	199.92	0.11	200.29	0.49	0.37	0.19
2023-09-20 05:26	224.94	0.09	225.98	0.52	1.04	0.46
2023-09-20 05:34	100.06	0.16	99.95	0.79	-0.11	-0.11
2023-09-20 05:43	249.90	0.24	251.02	0.58	1.12	0.45
2023-09-20 05:52	50.10	0.09	50.09	0.60	-0.01	-0.02
2023-09-20 06:00	75.07	0.13	75.30	0.73	0.23	0.31
2023-09-20 06:12	25.10	0.16	25.19	0.53	0.09	0.36
2023-09-20 06:21	175.02	0.14	175.59	0.57	0.57	0.33

Date – Time	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)	OA (nmol mol ⁻¹)	sdOA (nmol mol ⁻¹)	OA-TS (nmol mol ⁻¹)	OA-TS (%)
2023-09-20 06:29	149.96	0.12	150.30	0.54	0.34	0.23
2023-09-20 06:41	0.22	0.12	-0.19	0.76	-0.41	NA
2023-09-20 06:50	125.00	0.18	125.02	0.57	0.02	0.02
2023-09-20 08:37	100.04	0.09	100.17	0.80	0.13	0.13
2023-09-20 08:46	75.05	0.11	75.04	0.72	-0.01	-0.01
2023-09-20 08:55	25.11	0.16	24.96	1.02	-0.15	-0.60
2023-09-20 09:03	50.08	0.09	49.95	0.94	-0.13	-0.26
2023-09-20 09:12	200.00	0.14	200.52	0.39	0.52	0.26
2023-09-20 09:21	249.94	0.14	251.43	0.81	1.49	0.60
2023-09-20 09:32	0.16	0.19	-0.29	0.66	-0.45	NA
2023-09-20 09:41	150.01	0.17	150.46	0.74	0.45	0.30
2023-09-20 09:50	224.93	0.11	225.98	0.66	1.05	0.47
2023-09-20 09:58	174.99	0.09	175.50	0.77	0.51	0.29
2023-09-20 10:07	125.02	0.12	125.39	0.65	0.37	0.30

Table 5. Comparison of the CMN ozone calibrator (OC) Thermo Scientific 49i-PS # 1118511036 (BKG -0.3 nmol mol⁻¹, COEF 1.013) with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)	OC (nmol mol ⁻¹)	sdOC (nmol mol ⁻¹)	OC-TS (nmol mol ⁻¹)	OC-TS (%)
2023-09-20 15:56	0.24	0.05	0.53	0.13	0.29	NA
2023-09-20 16:06	75.05	0.10	75.68	0.14	0.63	0.84
2023-09-20 16:16	149.99	0.05	150.68	0.29	0.69	0.46
2023-09-20 16:26	50.04	0.05	50.55	0.12	0.51	1.02
2023-09-20 16:36	249.91	0.14	251.73	0.16	1.82	0.73
2023-09-20 16:46	199.94	0.09	201.68	0.22	1.74	0.87
2023-09-20 16:56	100.01	0.08	101.15	0.15	1.14	1.14
2023-09-20 17:06	25.10	0.08	25.50	0.28	0.40	1.59
2023-09-20 17:16	175.00	0.08	176.52	0.23	1.52	0.87
2023-09-20 17:26	224.91	0.09	226.75	0.39	1.84	0.82
2023-09-20 17:36	125.06	0.03	126.12	0.16	1.06	0.85
2023-09-20 17:46	0.11	0.09	0.36	0.24	0.25	NA
2023-09-20 17:56	149.99	0.09	151.15	0.32	1.16	0.77
2023-09-20 18:08	25.13	0.12	25.38	0.15	0.25	0.99
2023-09-20 18:16	175.01	0.07	176.25	0.33	1.24	0.71
2023-09-20 18:26	199.97	0.03	201.28	0.11	1.31	0.66
2023-09-20 18:36	50.03	0.04	50.63	0.11	0.60	1.20
2023-09-20 18:46	75.08	0.09	75.94	0.21	0.86	1.15
2023-09-20 18:56	224.96	0.12	226.48	0.29	1.52	0.68
2023-09-20 19:06	100.10	0.08	101.06	0.24	0.96	0.96
2023-09-20 19:16	125.03	0.09	125.96	0.10	0.93	0.74
2023-09-20 19:26	249.98	0.06	251.79	0.15	1.81	0.72
2023-09-20 19:36	0.24	0.08	0.41	0.15	0.17	NA
2023-09-20 19:46	50.07	0.12	50.81	0.14	0.74	1.48
2023-09-20 19:56	200.02	0.06	201.59	0.08	1.57	0.78
2023-09-20 20:06	149.97	0.17	151.52	0.26	1.55	1.03
2023-09-20 20:16	100.04	0.03	100.96	0.24	0.92	0.92
2023-09-20 20:26	250.00	0.03	251.87	0.17	1.87	0.75

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OC (nmol mol⁻¹)	sdOC (nmol mol⁻¹)	OC-TS (nmol mol⁻¹)	OC-TS (%)
2023-09-20 20:36	75.03	0.05	75.87	0.15	0.84	1.12
2023-09-20 20:47	15.31	0.12	15.68	0.30	0.37	2.42
2023-09-20 20:56	175.01	0.08	176.40	0.22	1.39	0.79
2023-09-20 21:06	125.02	0.05	125.99	0.13	0.97	0.78
2023-09-20 21:16	224.96	0.11	226.78	0.20	1.82	0.81
2023-09-20 21:26	0.19	0.19	0.43	0.12	0.24	NA
2023-09-20 21:36	75.04	0.09	75.61	0.21	0.57	0.76
2023-09-20 21:46	150.02	0.06	151.07	0.19	1.05	0.70
2023-09-20 21:56	50.09	0.08	50.49	0.18	0.40	0.80
2023-09-20 22:06	249.92	0.14	251.39	0.19	1.47	0.59
2023-09-20 22:16	199.97	0.11	201.22	0.27	1.25	0.63
2023-09-20 22:26	100.07	0.09	100.95	0.30	0.88	0.88
2023-09-20 22:36	25.11	0.12	25.48	0.14	0.37	1.47
2023-09-20 22:46	175.01	0.05	176.45	0.10	1.44	0.82
2023-09-20 22:56	225.01	0.09	226.80	0.15	1.79	0.80
2023-09-20 23:06	125.03	0.07	126.02	0.27	0.99	0.79
2023-09-20 23:16	0.26	0.08	0.19	0.08	-0.07	NA
2023-09-20 23:26	149.96	0.13	151.16	0.21	1.20	0.80
2023-09-20 23:36	25.13	0.12	25.66	0.17	0.53	2.11
2023-09-20 23:46	175.00	0.13	176.21	0.19	1.21	0.69
2023-09-20 23:56	200.06	0.07	201.48	0.30	1.42	0.71
2023-09-21 00:06	50.10	0.06	50.58	0.02	0.48	0.96
2023-09-21 00:16	75.07	0.06	75.99	0.22	0.92	1.23
2023-09-21 00:26	224.95	0.08	226.53	0.19	1.58	0.70
2023-09-21 00:36	100.01	0.08	100.95	0.08	0.94	0.94
2023-09-21 00:46	125.05	0.09	126.09	0.24	1.04	0.83
2023-09-21 00:56	249.97	0.10	251.56	0.15	1.59	0.64
2023-09-21 01:06	0.17	0.11	0.52	0.13	0.35	NA
2023-09-21 01:16	50.12	0.00	50.76	0.15	0.64	1.28
2023-09-21 01:26	200.02	0.02	201.31	0.16	1.29	0.64
2023-09-21 01:36	150.04	0.10	151.11	0.16	1.07	0.71
2023-09-21 01:46	100.09	0.09	100.75	0.29	0.66	0.66
2023-09-21 01:56	249.92	0.14	251.44	0.27	1.52	0.61
2023-09-21 02:06	75.07	0.07	75.80	0.07	0.73	0.97
2023-09-21 02:16	15.17	0.08	15.45	0.09	0.28	1.85
2023-09-21 02:26	175.04	0.07	176.25	0.09	1.21	0.69
2023-09-21 02:36	125.05	0.03	125.93	0.18	0.88	0.70
2023-09-21 02:46	224.93	0.02	226.58	0.24	1.65	0.73
2023-09-21 02:56	0.18	0.10	0.28	0.04	0.10	NA
2023-09-21 03:06	75.03	0.07	75.74	0.09	0.71	0.95
2023-09-21 03:16	150.00	0.06	151.11	0.17	1.11	0.74
2023-09-21 03:26	50.06	0.07	50.84	0.21	0.78	1.56
2023-09-21 03:36	249.94	0.04	251.58	0.15	1.64	0.66
2023-09-21 03:46	200.00	0.08	201.37	0.38	1.37	0.69
2023-09-21 03:56	100.05	0.07	100.94	0.15	0.89	0.89
2023-09-21 04:06	25.11	0.12	25.55	0.19	0.44	1.75
2023-09-21 04:16	174.95	0.08	176.40	0.16	1.45	0.83
2023-09-21 04:26	224.92	0.06	226.47	0.09	1.55	0.69

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OC (nmol mol⁻¹)	sdOC (nmol mol⁻¹)	OC-TS (nmol mol⁻¹)	OC-TS (%)
2023-09-21 04:36	125.03	0.05	126.06	0.23	1.03	0.82
2023-09-21 04:46	0.31	0.14	0.41	0.12	0.10	NA
2023-09-21 04:56	149.97	0.07	151.23	0.14	1.26	0.84
2023-09-21 05:06	25.15	0.08	25.48	0.12	0.33	1.31
2023-09-21 05:16	174.97	0.07	176.36	0.21	1.39	0.79
2023-09-21 05:26	199.96	0.10	201.22	0.26	1.26	0.63
2023-09-21 05:36	50.09	0.08	50.66	0.16	0.57	1.14
2023-09-21 05:46	75.09	0.15	75.91	0.24	0.82	1.09
2023-09-21 05:56	224.90	0.06	226.32	0.13	1.42	0.63
2023-09-21 06:06	100.08	0.11	101.13	0.20	1.05	1.05
2023-09-21 06:16	125.03	0.07	126.15	0.19	1.12	0.90
2023-09-21 06:26	249.94	0.12	251.56	0.21	1.62	0.65
2023-09-21 06:36	0.18	0.05	0.45	0.27	0.27	NA
2023-09-21 06:46	50.16	0.08	50.75	0.11	0.59	1.18
2023-09-21 06:56	199.95	0.07	201.32	0.24	1.37	0.69
2023-09-21 07:06	150.00	0.08	150.94	0.29	0.94	0.63
2023-09-21 07:16	100.04	0.06	100.88	0.19	0.84	0.84
2023-09-21 07:26	249.89	0.03	251.84	0.31	1.95	0.78
2023-09-21 07:36	75.09	0.03	75.89	0.28	0.80	1.07
2023-09-21 07:46	15.13	0.13	15.40	0.08	0.27	1.78
2023-09-21 07:56	174.96	0.07	176.37	0.20	1.41	0.81
2023-09-21 08:06	125.03	0.05	126.26	0.16	1.23	0.98
2023-09-21 08:16	224.98	0.04	226.84	0.20	1.86	0.83

A4. Performance audit results for carbon monoxide

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before and after the audit. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA are given further below.

Table 6 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation were recorded by the CMN data acquisition system.

Table 6. Experimental details of the CMN comparison.

<i>Travelling standard (TS)</i>	
WCC-Empa travelling standards (6 l aluminium cylinders containing a mixture of natural and synthetic air). The assigned values and standard uncertainties are given in Table 16.	
<i>Station analyser (CO, CH₄, CO₂) (CNR)</i>	
Model, S/N	Picarro G2401 #2871-CFKADS2269
Principle	Near-IR CRDS
Drying system	Nafion dryer (MD-070-144S-4)
<i>Comparison procedure</i>	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

The result of the evaluation is shown in the Executive Summary, and the individual measurements of the TS is shown in the following table.

Table 7. CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2871-CFKADS2269 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (nmol mol ⁻¹)		AL (nmol mol ⁻¹)		N	AL-TS (nmol mol ⁻¹)		AL-TS (%)
		TS	sdTS	AL	sdAL		AL-TS	AL-TS	
(23-09-19 16:39:00)	150601_FA02482	1339.7	0.3	1303.1	1.4	4	-36.7	-2.7	
(23-09-19 17:09:00)	171124_FA01467	146.3	0.6	146.2	0.9	4	-0.1	-0.1	
(23-09-19 16:09:00)	171128_FA01477	117.8	0.6	118.2	0.4	4	0.4	0.3	
(23-09-20 12:35:24)	220927_FA02789	124.2	0.4	124.5	0.5	5	0.2	0.2	
(23-09-20 11:50:00)	230127_FB03377	8.3	0.4	18.1	1.3	2	9.9	119.5	
(23-09-20 01:03:00)	230426_FB03870	76.2	0.7	78.7	0.5	4	2.5	3.2	
(23-09-20 01:33:00)	230424_FB03912	492.3	0.5	481.1	0.8	4	-11.2	-2.3	
(23-09-20 13:00:30)	180318_FF21167	226.8	0.3	224.9	0.8	4	-2.0	-0.9	
(23-09-20 00:33:00)	171204_FF31496	161.1	0.7	160.5	0.8	4	-0.7	-0.4	

A5. Performance audit results for methane

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the WCC-Empa travelling standards before and after the audit. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA are given below.

Table 6 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation was recorded by the CMN data acquisition system. The standards used for the calibration of the CMN instruments are listed in Table 13.

Table 8. *Experimental details of the CMN comparison.*

<i>Travelling standard (TS)</i>	
WCC-Empa travelling standards (6 l aluminium cylinders containing a mixture of natural and synthetic air). The assigned values and standard uncertainties are given in Table 16.	
<i>Station analyser (CO, CH₄, CO₂) (CNR)</i>	
Model, S/N	Picarro G2401 #2871-CFKADS2269
Principle	Near-IR CRDS
Drying system	Nafion dryer (MD-070-144S-4)
<i>Station analyser (CO, CH₄, CO₂) (CAMM)</i>	
Model, S/N	Picarro G2301 #2017-CFADS2374
Principle	Near-IR CRDS
Drying system	Nafion dryer (MD-070-72S-4)
<i>Comparison procedure</i>	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

The result of the assessment is shown in the Executive Summary, and the individual measurements of the TS are presented in the following tables.

Table 9. CH₄ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2871-CFKADS2269 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS (nmol mol ⁻¹)		AL (nmol mol ⁻¹)		N	AL-TS (nmol mol ⁻¹)		AL-TS (%)
		TS	sdTS	AL	sdAL		AL-TS	AL-TS	
(23-09-19 16:39:00)	150601_FA02482	1906.04	0.04	1906.29	0.03	4	0.25	0.01	
(23-09-19 17:09:00)	171124_FA01467	1805.80	0.04	1806.26	0.01	4	0.46	0.03	
(23-09-19 16:09:00)	171128_FA01477	1862.04	0.03	1862.36	0.03	4	0.32	0.02	
(23-09-20 00:33:00)	171204_FF31496	1947.43	0.07	1947.65	0.06	4	0.22	0.01	
(23-09-20 13:00:30)	180318_FF21167	1762.44	0.04	1762.91	0.01	4	0.47	0.03	
(23-09-20 12:35:24)	220927_FA02789	1996.12	0.03	1996.28	0.03	5	0.16	0.01	
(23-09-20 12:17:00)	230127_FB03377	2.83	0.05	5.83	0.02	3	3.00	106.01	
(23-09-20 01:33:00)	230424_FB03912	2315.70	0.05	2315.40	0.03	4	-0.30	-0.01	
(23-09-20 01:03:00)	230426_FB03870	1889.31	0.02	1889.60	0.01	4	0.29	0.02	

Table 10. CH₄ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2301 #2017-CFADS2374 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS (nmol mol ⁻¹)		AL (nmol mol ⁻¹)		N	AL-TS (nmol mol ⁻¹)		AL-TS (%)
		TS	sdTS	AL	sdAL		AL-TS	AL-TS	
(23-09-19 15:21:00)	230127_FB03377	2.83	0.05	9.72	0.03	2	6.89	243.46	
(23-09-19 15:17:40)	180318_FF21167	1762.44	0.04	1763.69	0.20	3	1.25	0.07	
(23-09-20 10:18:40)	171124_FA01467	1805.80	0.04	1806.64	0.25	3	0.84	0.05	
(23-09-20 10:15:20)	171128_FA01477	1862.04	0.03	1862.79	0.36	3	0.75	0.04	
(23-09-20 14:21:00)	230426_FB03870	1889.31	0.02	1889.75	0.20	3	0.44	0.02	
(23-09-20 10:22:00)	150601_FA02482	1906.04	0.04	1906.49	0.24	3	0.45	0.02	
(23-09-20 14:17:40)	171204_FF31496	1947.43	0.07	1947.87	0.14	3	0.44	0.02	
(23-09-19 15:14:20)	220927_FA02789	1996.12	0.03	1996.61	0.25	3	0.49	0.02	
(23-09-20 14:14:20)	230424_FB03912	2315.70	0.05	2314.92	0.16	3	-0.78	-0.03	

A6. Performance audit results for carbon dioxide

Procedures: see CH₄.

Results

The results of the assessment are shown in the Executive Summary, and the individual measurements of the TS are presented in the following Tables.

Table 11. CO₂ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2871-CFKADS2269 instrument (AL) with the WCC-Empa TS (WMO-X2019 CO₂ scale).

Date / Time	TS Cylinder	TS		AL		N	AL-TS	AL-TS (%)
		($\mu\text{mol mol}^{-1}$)	sdTS ($\mu\text{mol mol}^{-1}$)	($\mu\text{mol mol}^{-1}$)	sdAL ($\mu\text{mol mol}^{-1}$)			
(23-09-19 16:39:00)	150601_FA02482	431.29	0.02	431.29	0.01	4	0.00	0.00
(23-09-19 17:09:00)	171124_FA01467	397.19	0.03	397.25	0.01	4	0.06	0.02
(23-09-19 16:09:00)	171128_FA01477	408.57	0.01	408.58	0.01	4	0.01	0.00
(23-09-20 12:35:24)	220927_FA02789	452.20	0.01	452.19	0.01	5	-0.01	0.00
(23-09-20 12:17:00)	230127_FB03377	0.09	0.02	0.30	0.01	3	0.21	NA
(23-09-20 01:03:00)	230426_FB03870	425.06	0.00	425.06	0.01	4	0.00	0.00
(23-09-20 01:33:00)	230424_FB03912	446.92	0.01	446.92	0.01	4	0.00	0.00
(23-09-20 13:00:30)	180318_FF21167	374.50	0.00	374.54	0.01	4	0.04	0.01
(23-09-20 00:33:00)	171204_FF31496	428.51	0.02	428.54	0.01	4	0.03	0.01

Table 12. CO₂ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2301 #2017-CFADS2374 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS		AL		N	AL-TS	AL-TS (%)
		($\mu\text{mol mol}^{-1}$)	sdTS ($\mu\text{mol mol}^{-1}$)	($\mu\text{mol mol}^{-1}$)	sdAL ($\mu\text{mol mol}^{-1}$)			
(23-09-19 15:21:00)	230127_FB03377	0.09	0.02	0.31	0.01	2	0.22	NA
(23-09-19 15:17:40)	180318_FF21167	374.50	0.00	374.55	0.02	3	0.05	0.01
(23-09-20 10:18:40)	171124_FA01467	397.19	0.03	397.25	0.02	3	0.06	0.02
(23-09-20 10:15:20)	171128_FA01477	408.57	0.01	408.59	0.02	3	0.02	0.00
(23-09-20 14:21:00)	230426_FB03870	425.06	0.00	425.06	0.01	3	0.00	0.00
(23-09-20 14:17:40)	150601_FA02482	428.51	0.02	428.55	0.01	3	0.04	0.01
(23-09-20 10:22:00)	171204_FF31496	431.29	0.02	431.29	0.01	3	0.00	0.00
(23-09-20 14:14:20)	220927_FA02789	446.92	0.01	446.91	0.02	3	-0.01	0.00
(23-09-19 15:14:20)	230424_FB03912	452.20	0.01	452.20	0.02	3	0.00	0.00

A7. Calibration Standards for CO, CH₄ and CO₂

Table 13 provides an overview the CCL (NOAA) and the ICOS Flask and Calibration Laboratory standard gases available for calibration of the CO, CH₄ and CO₂ instruments.

Table 13 CMN calibration standards as of June 2023 (CNR and CAMM).

Cylinder ID	CO (X2014A) (nmol mol ⁻¹)	CH ₄ (X2004A) (nmol mol ⁻¹)	CO ₂ (X2019) (μmol mol ⁻¹)	Usage
CB08924	NA	NA	373.64	NOAA standard, CAMM, Picarro G2301
CB09045	NA	NA	399.68	NOAA standard, CAMM, Picarro G2301
CC715924	NA	2090.51	429.68	NOAA standard, CAMM, Picarro G2301
CC339501	NA	1897.76	396.90	NOAA standard, CAMM, Picarro G2301
CC327204	NA	1681.15	NA	NOAA standard, CAMM, Picarro G2301
D550030	69.65	1799.89	379.63	ICOS standard, Picarro G2401
D550031	107.37	1899.47	399.94	ICOS standard, Picarro G2401
D550032	180.87	1998.30	419.88	ICOS standard, Picarro G2401
D550033	254.68	296.27	455.02	ICOS standard, Picarro G2401
D550034	NA	NA	NA	ICOS long-term target tank, Picarro G2401
D550036	NA	NA	NA	ICOS short-term target tank, Picarro G2401

A8. WCC-Empa ozone traveling standard

The WCC-Empa Travelling Standard (TS) was compared with the standard reference photometer before and after the audit. The instruments used were

WCC-Empa Ozone Reference: NIST Standard Reference Photometer SRP #15 (Master)

WCC-Empa TS: Thermo Scientific 49i-PS #1171430027, BKG 0.0, COEF 0.991

Zero air source: Compressed air - Dryer - Breifuss zero air generator – Purafil – Charcoal –Filter

The results of the TS calibration before and after the audit are shown in Table 14. The TS passed the pre-audit evaluation criteria defined for maximum acceptable bias (Klausen et al., 2003) (see Figure 24). The data were pooled and evaluated by linear regression analysis, taking into account the uncertainties of both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be calculated (equation 6a). The uncertainty of the TS (Equation 6b) was previously estimated (see equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (nmol mol}^{-1}\text{)} = ([TS] + 0.13 \text{ nmol mol}^{-1}) / 1.0008 \quad (17)$$

$$u_{TS} \text{ (nmol mol}^{-1}\text{)} = \text{sqrt} ((0.43 \text{ nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (18)$$

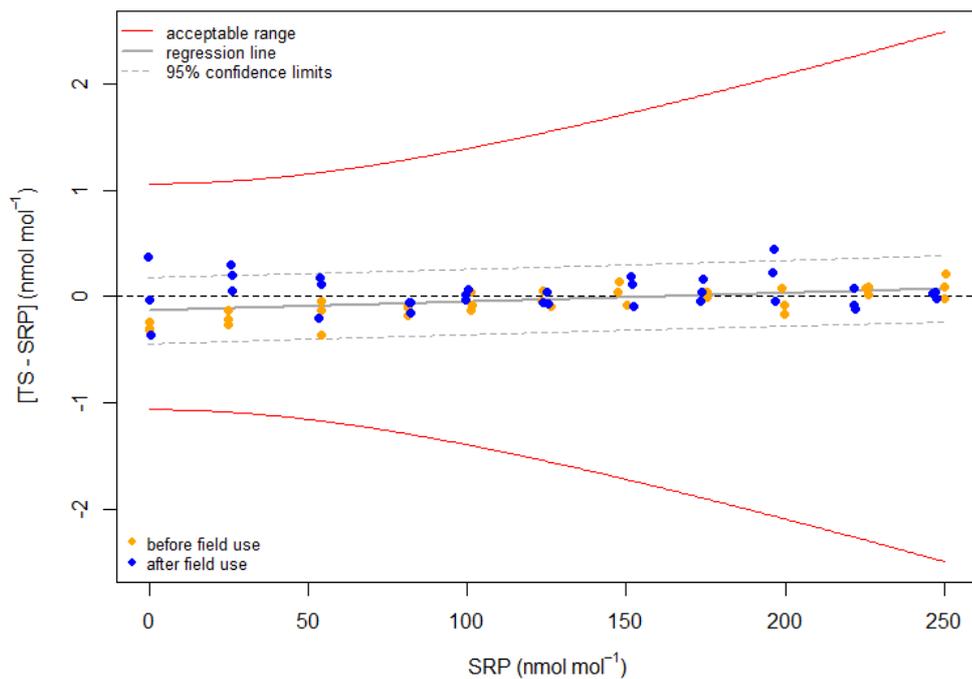


Figure 24. Deviations between Traveling Standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS in the field.

Table 14. Mean values calculated over at least five minutes for the comparison of the WCC-Empa Traveling Standard (TS) with the Standard Reference Photometer (SRP).

Date	Run	Level#	SRP (nmol mol ⁻¹)	sdSRP (nmol mol ⁻¹)	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)
2023-08-09	1	125	126.11	0.19	126.02	0.15
2023-08-09	1	0	0.02	0.17	-0.21	0.14
2023-08-09	1	55	54.21	0.28	54.17	0.12
2023-08-09	1	200	199.66	0.12	199.49	0.14
2023-08-09	1	100	101.24	0.11	101.28	0.08
2023-08-09	1	250	250.06	0.25	250.15	0.14
2023-08-09	1	150	150.36	0.14	150.27	0.13
2023-08-09	1	225	226.21	0.21	226.23	0.22
2023-08-09	1	175	175.49	0.24	175.48	0.15
2023-08-09	1	80	81.18	0.33	81.10	0.21
2023-08-09	1	25	24.67	0.15	24.55	0.09
2023-08-09	2	145	147.20	0.27	147.24	0.25
2023-08-09	2	100	101.07	0.16	100.94	0.12
2023-08-09	2	25	24.80	0.34	24.54	0.12
2023-08-09	2	250	250.19	0.36	250.17	0.19
2023-08-09	2	225	226.14	0.22	226.23	0.15
2023-08-09	2	175	175.45	0.30	175.50	0.14
2023-08-09	2	0	0.06	0.33	-0.23	0.12
2023-08-09	2	125	123.24	0.22	123.20	0.09
2023-08-09	2	200	198.83	0.29	198.91	0.14
2023-08-09	2	80	81.24	0.19	81.13	0.26
2023-08-09	2	55	54.17	0.06	53.81	0.10
2023-08-09	3	200	199.75	0.17	199.67	0.12
2023-08-09	3	250	250.54	0.19	250.75	0.12
2023-08-09	3	80	81.22	0.41	81.05	0.35
2023-08-09	3	25	24.76	0.21	24.55	0.22
2023-08-09	3	125	123.62	0.18	123.68	0.08
2023-08-09	3	0	0.11	0.33	-0.19	0.09
2023-08-09	3	150	147.77	0.14	147.92	0.14
2023-08-09	3	55	54.08	0.36	53.95	0.23
2023-08-09	3	175	174.73	0.15	174.77	0.16
2023-08-09	3	225	225.34	0.20	225.41	0.21
2023-08-09	3	100	101.32	0.24	101.24	0.11
2023-10-25	4	55	53.34	0.42	53.14	0.43
2023-10-25	4	150	151.77	0.40	151.88	0.34
2023-10-25	4	0	-0.05	0.11	-0.08	0.09
2023-10-25	4	245	246.37	0.23	246.40	0.34
2023-10-25	4	195	196.13	0.37	196.36	0.19
2023-10-25	4	80	81.82	0.40	81.77	0.24
2023-10-25	4	25	25.77	0.41	25.97	0.11
2023-10-25	4	100	99.53	0.30	99.55	0.16
2023-10-25	4	125	125.03	0.41	125.07	0.17
2023-10-25	4	175	173.62	0.33	173.67	0.25
2023-10-25	4	220	221.73	0.32	221.65	0.16

Date	Run	Level#	SRP (nmol mol ⁻¹)	sdSRP (nmol mol ⁻¹)	TS (nmol mol ⁻¹)	sdTS (nmol mol ⁻¹)
2023-10-25	5	80	82.16	0.39	82.01	0.24
2023-10-25	5	150	152.22	0.38	152.13	0.26
2023-10-25	5	25	25.89	0.22	25.94	0.14
2023-10-25	5	245	247.32	0.26	247.37	0.29
2023-10-25	5	195	196.43	0.32	196.88	0.15
2023-10-25	5	0	0.37	0.24	0.01	0.16
2023-10-25	5	125	123.89	0.31	123.83	0.21
2023-10-25	5	175	173.97	0.24	174.13	0.24
2023-10-25	5	220	222.22	0.25	222.10	0.18
2023-10-25	5	55	53.72	0.36	53.90	0.21
2023-10-25	5	100	100.45	0.22	100.52	0.13
2023-10-25	6	250	247.66	0.37	247.64	0.30
2023-10-25	6	195	196.95	0.35	196.91	0.19
2023-10-25	6	25	25.54	0.18	25.85	0.14
2023-10-25	6	125	125.62	0.51	125.55	0.14
2023-10-25	6	0	-0.29	0.34	0.09	0.08
2023-10-25	6	100	99.57	0.48	99.54	0.14
2023-10-25	6	55	54.09	0.35	54.20	0.18
2023-10-25	6	220	221.55	0.68	221.63	0.30
2023-10-25	6	175	173.48	0.49	173.44	0.20
2023-10-25	6	150	151.34	0.25	151.53	0.17
2023-10-25	6	80	81.98	0.26	81.93	0.25

#the level is only indicative.

A9. WCC-Empa GHG and CO traveling standards

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) of the WMO/GAW programme for Carbon Monoxide, Carbon Dioxide and Methane. NOAA was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL through travelling standards and by addition of new laboratory standards from the CCL. For the assignment of the amount fractions to the TS, the following calibration scales were used:

CO: WMO-X2014A scale (https://gml.noaa.gov/ccl/co_scale.html)

CO₂: WMO-X2019 scale (Hall et al., 2021)

CH₄: WMO-X2004A scale (Dlugokencky et al., 2005)

N₂O: WMO-X2006A scale (https://gml.noaa.gov/ccl/n2o_scale.html)

More information about the NOAA calibration scales can be found on the [NOAA website](#). The scales were transferred to the TS using the following instruments:

CO, CO₂ and CH₄: Picarro G2401 (Cavity Ring-Down Spectroscopy).

CO and N₂O: Los Gatos 23-r (Mid-IR Spectroscopy).

For CO, only data of the Picarro G2401 instrument was used. This instrument is calibrated using a high working standard (3244 nmol mol⁻¹) and CO-free air. The use of a high CO standard reduces the potential bias due to standard drift, which is a common issue of CO in air mixtures.

Table 15 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including the standard deviations of the WCC-Empa TS are given in Table 16, and Figure 25 shows the analysis of the TS over time.

Table 15. CCL laboratory standards and working standards at WCC-Empa.

Cylinder	CO (nmol mol ⁻¹)	CH ₄ (nmol mol ⁻¹)	N ₂ O (nmol mol ⁻¹)	CO ₂ (μmol mol ⁻¹)
CC339478 [#]	463.76	2485.25	357.19	484.63
CB11499 [#]	141.03	1933.77	329.15	407.53
CB11485 [#]	110.88	1844.78	328.46	394.49
CA02789 [*]	448.67	2097.48	342.18	496.15
190618_CC703041 [§]	3244.00	2258.07	NA	419.82

[#] used for calibrations of CO₂, CH₄ and N₂O

^{*} used for calibrations of CO

[§] used for calibrations of CO (Picarro G2401)

Table 16. Calibration summary of the WCC-Empa travelling standards for CH₄, CO₂, N₂O and CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (L) Los Gatos.

TS	Press. (psi)	CH ₄ (P) (nmol mol ⁻¹)	sd	CO ₂ (P) (μmol mol ⁻¹)	sd	N ₂ O (L) (nmol mol ⁻¹)	sd	CO (P) (nmol mol ⁻¹)	sd
150601_FA02482	550	1906.04	0.04	431.29	0.02	326.54	0.04	1339.73	0.37
171124_FA01467	590	1805.80	0.04	397.19	0.03	325.74	0.03	146.26	0.55
171128_FA01477	1120	1862.04	0.03	408.57	0.01	337.43	0.02	117.80	0.63
171204_FF31496	1510	1947.43	0.07	428.51	0.02	335.85	0.03	161.13	0.68
180318_FF21167	1380	1762.44	0.04	374.50	0.00	298.92	0.06	226.83	0.31
220815_FF61508	1910	1921.93	0.02	417.73	0.01	338.57	0.01	120.98	0.58
220927_FA02789	1800	1996.12	0.03	452.20	0.01	341.03	0.02	124.24	0.40
230127_FB03377	1500	2.83	0.05	0.09	0.02	11.57	0.48	8.25	0.39
230424_FB03912	1780	2315.70	0.05	446.92	0.01	352.44	0.03	492.28	0.51
230426_FB03870	1800	1889.31	0.02	425.06	0.00	338.65	0.02	76.21	0.67

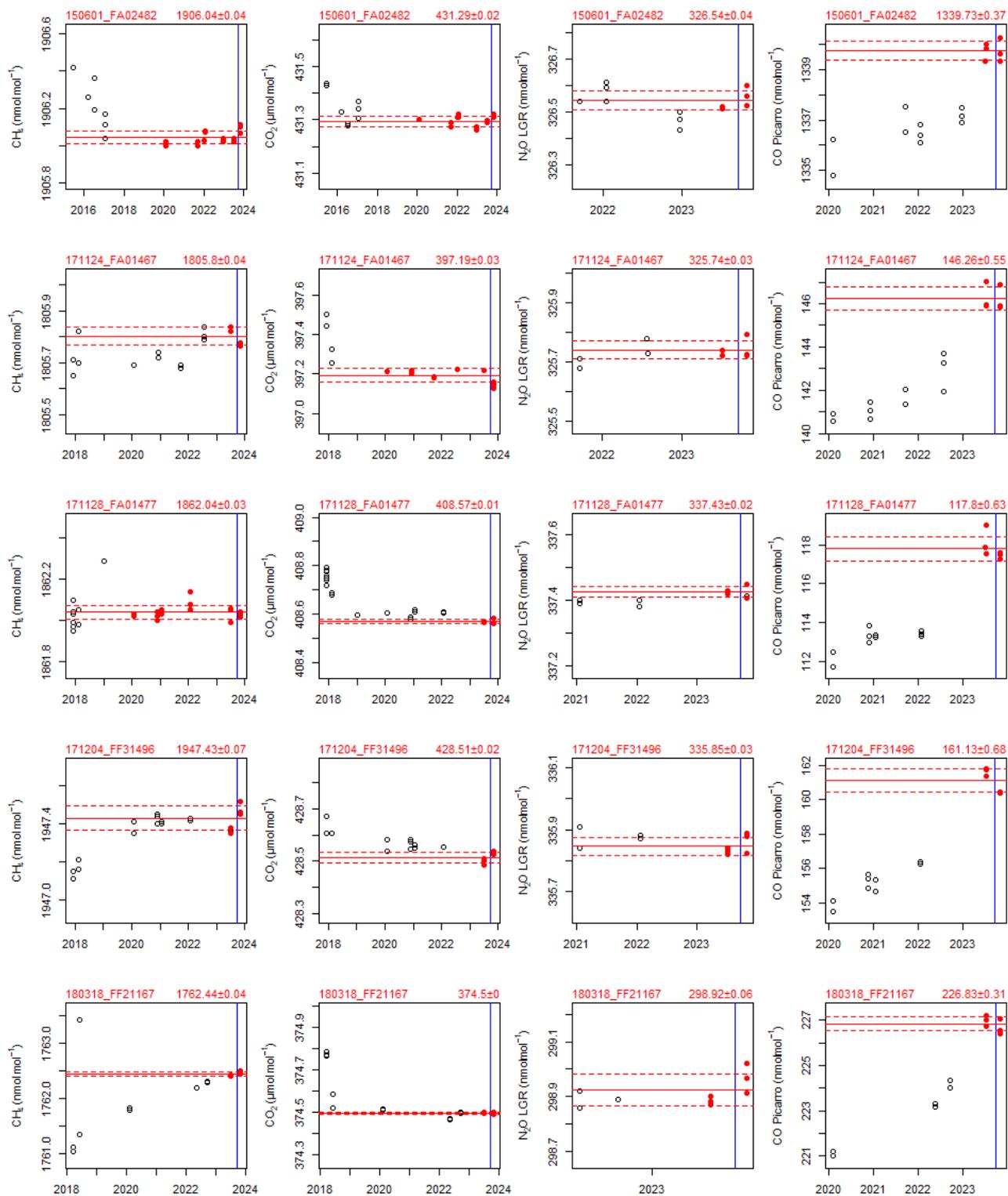


Figure 25. Results of the WCC-Empa TS calibrations for CH₄, CO₂, N₂O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.

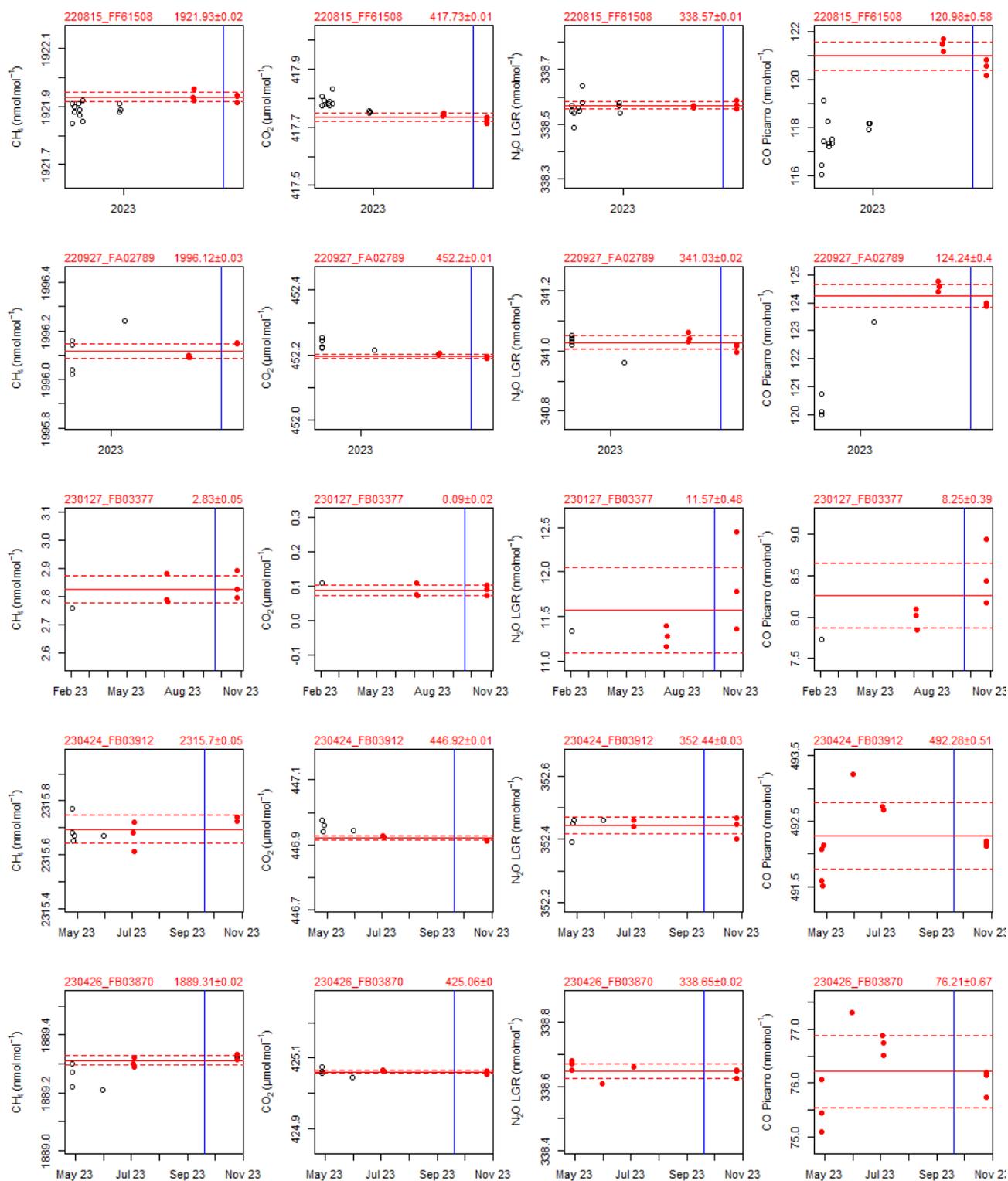


Figure 26. Results of the WCC-Empa TS calibrations for CH_4 , CO_2 , N_2O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.

A10. Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH₄ and CO₂, the Picarro G2401 #1497-CFKADS2098 was calibrated every 3210 min using one WCC-Empa TS as a working standard, and two TS as target tanks. Based on the working standard measurements, a loess fit drift correction was applied to the data as shown in the figure below. The maximum drift between two WS measurements was approximately 1.1 nmol mol⁻¹ for CH₄ and 0.1 μmol mol⁻¹ for CO₂. All target cylinder measurements were within half of the WMO GAW compatibility goals.

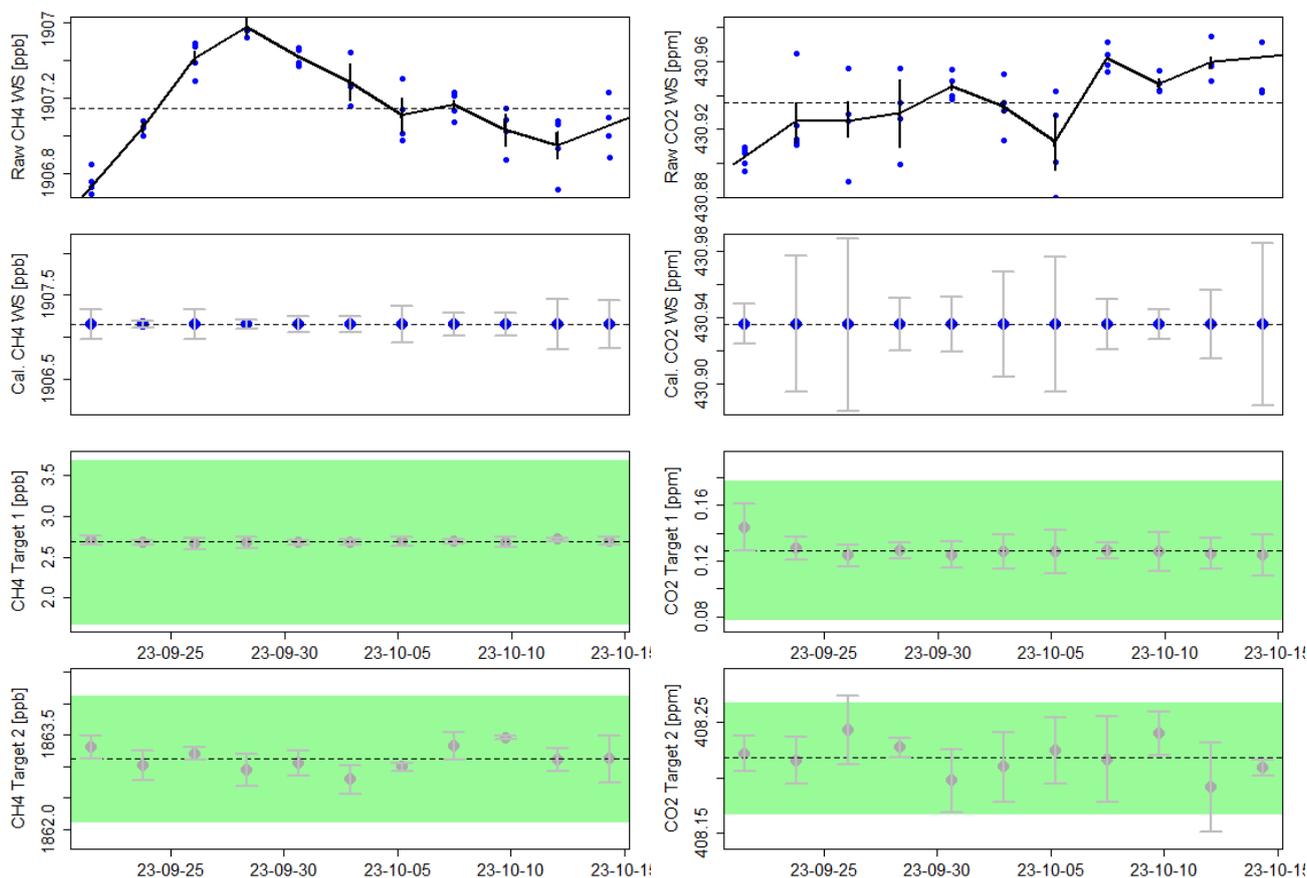


Figure 27. CH₄ (left panel) and CO₂ (right panel) calibrations of the WCC-Empa-TI. The top panel shows the raw 1 min values of the working standard and the loess fit (black line) used to account for the drift. The second panel shows the variation of the WS after application of the drift correction. The bottom panel shows the results from the two target cylinders. Individual points in the three lower panels are 5 minute averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

For CO, the Picarro G2401 was calibrated every 3210 minutes using three WCC-Empa TS as a working standards. Based on the working standard measurements, a loess fit drift correction using was first applied to the data, as shown in the figure below.

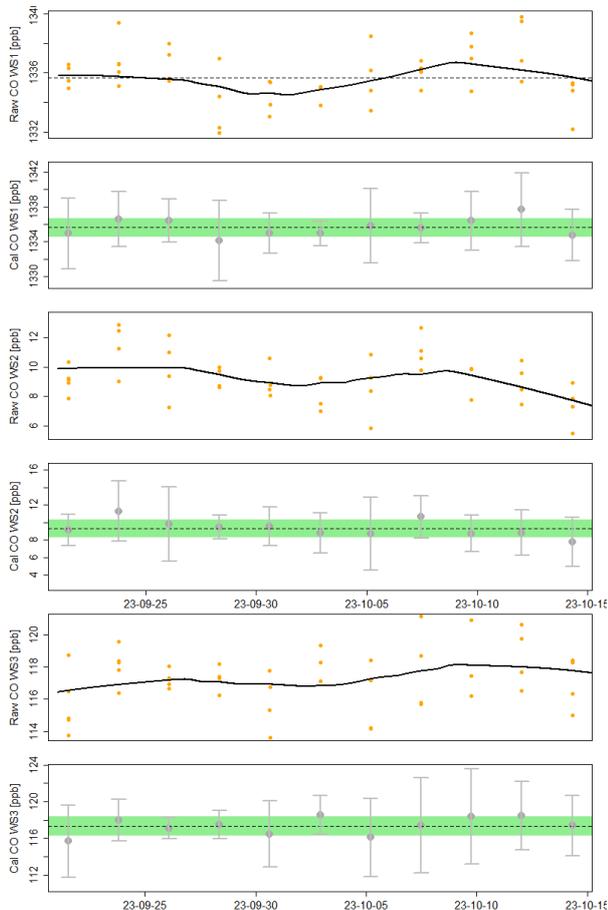


Figure 28. CO calibrations of the WCC-Empa-TI. The panels with the orange dots show the raw 1 min values of the working standards and the loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in these panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

A linear function of the drift-corrected working standard data of then was then used to calculate calibrated CO data, which is shown in the figure below.

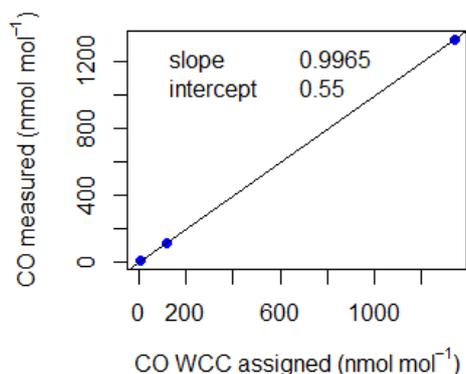


Figure 29. CO calibration function based on the average values of the drift corrected working standard measurements.

References

- Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH₄ mole fractions to a gravimetrically prepared standard scale, *Journal Of Geophysical Research-Atmospheres*, 110, Article D18306, 2005.
- Empa: Standard Operating Procedure (SOP), Measurement uncertainty of ozone measuring instruments and standards, 7th Edition from 13 February 2014 (available in German), Empa, Laboratory for Air Pollution / Environmental Technology, 2014.
- Hall, B. D., Crotwell, A. M., Kitzis, D. R., Mefford, T., Miller, B. R., Schibig, M. F., and Tans, P. P.: Revision of the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) CO₂ calibration scale, *Atmos. Meas. Tech.*, 14, 3015-3032, 2021.
- Hearn, A. G.: ABSORPTION OF OZONE IN ULTRA-VIOLET AND VISIBLE REGIONS OF SPECTRUM, *Proceedings of the Physical Society of London*, 78, 932-&, 1961.
- Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *Journal of Geophysical Research-Atmospheres*, 108, 4622, doi:4610.1029/2003JD003710, 2003.
- Naitza, L., Cristofanelli, P., Marinoni, A., Calzolari, F., Roccatò, F., Busetto, M., Sferlazzo, D., Aruffo, E., Di Carlo, P., Bencardino, M., D'Amore, F., Sprovieri, F., Pirrone, N., Dallo, F., Gabrieli, J., Vardè, M., Resci, G., Barbante, C., Bonasoni, P., and Putero, D.: Increasing the maturity of measurements of essential climate variables (ECVs) at Italian atmospheric WMO/GAW observatories by implementing automated data elaboration chains, *Computers & Geosciences*, 137, 104432, 2020.
- Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.*, 6, 837-860, 2013.
- WMO: 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019), Jeju Island, South Korea, 2-5 September 2019, GAW Report No. 255, World Meteorological Organization, Geneva, Switzerland, 2020.
- WMO: Guidelines for Continuous Measurements of Ozone in the Troposphere, WMO TD No. 1110, GAW Report No. 209, World Meteorological Organization, Geneva, Switzerland, 2013.
- WMO: Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland, 2007.
- WMO: WMO Global Atmosphere Watch (GAW) Implementation Plan: 2016-2023, GAW report no. 228, World Meteorological Organization, Geneva, Switzerland, 2017.
- Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M., Kozlova, E., Spain, T. G., Steinbacher, M., van der Schoot, M. V., and Buchmann, B.: Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, *Atmos. Meas. Tech.*, 9, 4737-4757, 2016.
- Zellweger, C., Steinbacher, M., and Buchmann, B.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, *Atmos. Meas. Tech.*, 5, 2555-2567, 2012.
- Zellweger, C., Steinbrecher, R., Laurent, O., Lee, H., Kim, S., Emmenegger, L., Steinbacher, M., and Buchmann, B.: Recent advances in measurement techniques for atmospheric carbon monoxide and nitrous oxide observations, *Atmos. Meas. Tech.*, 12, 5863-5878, 2019.

List of abbreviations

ACTRIS	Aerosol, Clouds and Trace Gases Research Infrastructure
ATC	Atmosphere Thematic Centre
BKG	Background
CAMM	Centro Aeronautica Militare di Montagna (Italian Air Force Mountain Meteorological Centre)
CCL	Central Calibration Laboratory
COEF	Coefficient
CMN	Monte Cimone GAW Station
CNR	Consiglio Nazionale delle Ricerche (National Research Council of Italy)
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
eDQO	Extended Data Quality Objective
EMEP	European Monitoring and Evaluation Programme
FCL	Flask and Calibration Laboratory
FID	Flame Ionisation Detection
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
IR	Infrared
ISAC	Institute of Atmospheric Sciences and Climate
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PI	Principle Investigator
QA/SAC	Quality Assurance/Scientific Activity Centre
SOP	Standard Operating Procedure
SN	Serial Number
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization
WS	Working Standard