SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE, CARBON DIOXIDE AND NITROUS OXIDE AT THE

GLOBAL GAW STATION MT. CIMONE ITALY JUNE 2018

World Meteorological Organization

GLOBAL ATMOSPHERE WATCH

Submitted to the World Meteorological Organization by

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WCC-Empa Report 18/1

Acknowledgements

Activities of WCC-Empa and QA/SAC Switzerland are financially supported by MeteoSwiss and Empa.

WCC-Empa acknowledges logistical, scientific and technical support by CAMM, CNR and the University of Urbino.

WCC-Empa Report 18/1

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The second system and performance audit by WCC-Empa[1] at the global GAW station Mt. Cimone was conducted from 12 - 15 June 2018 in agreement with the WMO/GAW quality assurance system (WMO, 2017a). A previous audit at the Mt. Cimone GAW station was made by WCC-Empa in September 2012 (Zellweger et al., 2012b).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Lt. Col. Antonio Vocino	Director, Italian Air Force Mountain Meteorological Centre (CAMM Mt. Cimone)
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Dr Paolo Cristofanelli	CNR-ISAC, station manager, PI reactive and greenhouse gases
Dr Pamela Trisolino	CNR-ISAC, scientist
Mr Francescopiero Calzolari	CNR-ISAC, technician
Dr Jgor Arduini	University of Urbino, scientist

This report summarises the assessment of the Mt. Cimone GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide measurements in particular.

The report is distributed to the Director of the Italian Air Force Mountain Meteorological Centre (CAMM), the Institute of Atmospheric Sciences and Climate (ISAC) of the Italian National Research Council (CNR), the University of Urbino, the Italian GAW country contact, and the World Meteorological Organization in Geneva. The report will be posted on the internet (www.empa.ch/web/s503/wcc-empa).

The recommendations found in this report are graded as minor, important and critical and are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Management and Operation

The facilities at Mt. Cimone (CMN) GAW station are owned by the Mountain Air Force Centre (Centro Aeronautica Militare di Montagna, CAMM), and the station is jointly operated by CAMM, CNR-ISAC, and the University of Urbino. Until June 2018, the station was permanently staffed with CAMM personnel. Since 15 June 2018, the station is only staffed during weekdays. Scientist and technicians from CNR-ISAC and the University of Urbino are visiting the station regularly for instrument maintenance and calibrations.

Station Location and Access

CMN (44.167°N, 10.683°E, 2165m a.s.l.) is located on the highest peak of the Northern Apennine. The closest inhabited areas are small villages 15 km away at an altitude of 1100 m below the station. Further information is available from GAWSIS (https://gawsis.meteoswiss.ch) and the station web site of CNR-ISAC (http://www.isac.cnr.it/cimone/).

[1]WMO/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 the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

The location is adequate for the intended purpose. Year-round access to CMN is possible by car or snow mobile in winter and the cog railway of CAMM. Access to the site can be difficult during a few days per year.

Station Facilities

CMN station comprises extensive laboratory and office space. Kitchen and sanitary facilities are available. CAMM facilities are in the main building, and laboratories of CNR-ISAC and University of Urbino are located approximately 50 m away in the Ottavio Vittori observatory. Laboratories are air-conditioned. Internet access is only available in the CNR-ISCA and University of Urbino laboratories. CMN is an ideal platform for continuous atmospheric research as well as for extensive measurement campaigns.

> **Recommendation 1 (**, important, 2018)**
> *Internet access is important for remote control of the instrumentation. It is recommended to establish internet connectivity also in the CAMM laboratories.*

Measurement Programme

The CMN station comprises a comprehensive measurement programme that covers major focal areas of the GAW programme. The CAMM observatory was established in 1937 and comprises one of the longest continuous CO_2 series starting in 1979.

An overview on measured species is available from GAWSIS and the station web site (http://www.isac.cnr.it/cimone/). The information available from GAWSIS was reviewed and partly updated as part of the audit.

> **Recommendation 2 (***, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. Part of the reviewed information was not up to date while others (e.g. information on in-situ GHG measurements) were entirely missing. Information needs to be updated. The GAWSIS support should be contacted for updates which are not possible through the web interface (e.g. new station contacts).*

Data Submission

As of June 2018, data of the scope of the audit has been submitted to the World Data Centres by the involved organisations:

CAMM, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CO_2 (1979-2017), CH_4 (2016-2017)

CNR-ISAC, submission to WDCGG:
O_3 (1996-2013), CO GC instrument (2007-2010), CO NDIR instrument (2012-2016)

CNR-ISAC, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2015-2016)

University of Urbino, submission to WDCGG:
CO (2008-2017), CH_4 (2008-2017), N_2O (2008-2017)

Data shown in this report was accessed on 12 November 2018.

> **Recommendation 3 (***, important, ongoing)**
> *Data submission is an obligation of all GAW stations. It is recommended to submit data to the corresponding data centres at least in yearly intervals. One hourly data must be submitted for all parameters.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG and WDCRG was reviewed. Summary plots and a short description of the findings are presented in the Appendix.

Documentation

CNR-ISAC and University of Urbino:

All information is entered in electronic and hand written log books. The instrument manuals are available at the site. Standard Operating Procedures (SOPs) have been prepared for the analysers operated by CNR-ISAC. The reviewed information was comprehensive and up-to-date.

CAMM:

Hand written logbooks and notes are available. Some of the requested information, e.g. previous calibration settings of the Picarro, was not available on site, since the logbooks are stored at CAMM in Sestola.

> **Recommendation 4 (***, important, ongoing)**
> *Electronic logbooks, preferably server based, are recommended. Access to the information should be possible on-site and also from the office.*

Air Inlet System

CNR-ISAC and University of Urbino:

The design of the air inlet systems has not been changed since the last audit by WCC-Empa. The air intake is located 1.5 m above the roof of the building and consist of a glass manifold with 2.5 m total length and an inner diameter of 12 cm. The only change since the last audit was the replacement of the inlet blower, which now reaches a flow rate of 70 l/sec. This results in residence times shorter than 2 seconds. From there, the individual instruments are connected with short lines. The inlet system is adequate, and no change is required.

CAMM:

The inlet is located on a tower next to the main building. The air intake is approx. 12 m above ground, and 3-4 m above the height of the building. In total, approx. 30 m 6mm Synflex 1300 tubing is used. Air is sampled with a KNF pump, which is installed a few meters upstream the calibration unit of the instrument. Thus, air is passing through the pump prior to analysis which may alter (contaminate or deplete) the sample and is a possible source of leaks. The flow rate is 3.3 l/min, which results in a residence time of less than 10 seconds. The air is not dried for the Picarro CO_2 and CH_4 measurements. A stainless steel particulate filter is used to protect the instrument from particles.

> **Recommendation 5 (**, important, 2018)**
> *It is recommended to change the position of the air intake pump to the end of the system, after the calibration unit.*

Surface Ozone Measurements

Surface ozone measurements CMN were established in 1996 by CNR-ISAC, and continuous time series are available since then.

Instrumentation. CMN is currently equipped with two ozone analysers (Thermo Scientific 49i and Dasibi 1108). Data of the Dasibi instrument is no longer used, and replacement with a Thermo Scientific is planned. It was therefore not considered for the current audit. In addition, a Thermo Scientific 49i-PS ozone calibrator with traceability to the WCC-Empa SRP#15 (calibration at Empa in 2017) is available.

Data of the Thermo Scientific 49i is corrected based on the last calibration with the ozone calibrator. The current correction function was:

True value = 0.9906 * Thermo Scientific 49i +1.0455 (1)

This correction function was applied to the data obtained during the audit.

Data Acquisition. Custom made data acquisition system programmed in LabVIEW. 1-min time resolution is available for ozone data, and other instrument parameters are recorded every 5 min.

Intercomparison (Performance Audit). The CMN analyser and calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 90 ppb. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system (ozone calibrator) and the CMN data acquisition system. Data of the CMN analyser was corrected by the above function provided by the station manager. No further corrections were applied to the CMN ozone calibrator. The following equations characterise the bias of the instruments:

Thermo Scientific 49i #1225011092 (BKG 0.0 ppb, SPAN 1.000, corrected by calibration function (1)):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 0.76 ppb) / 0.9833 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.37 ppb^2 + 2.66e-05 * X_{O3}^2) (1b)

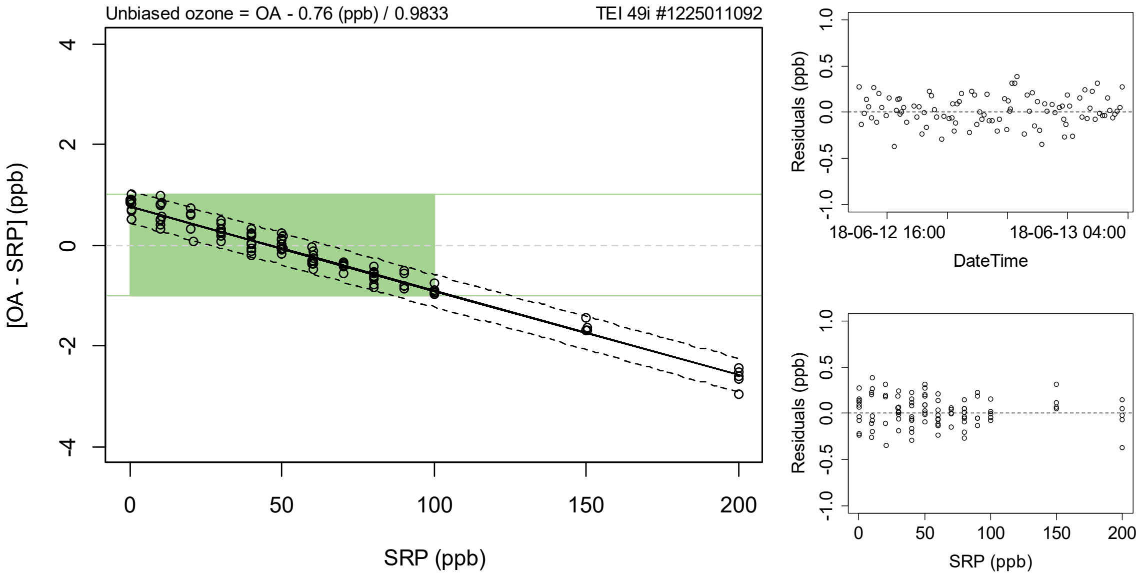

Figure 1. *Left: Bias of the CMN ozone analyser (Thermo Scientific 49i #1225011092) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

Thermo Scientific 49i-PS #111851136 (BKG -0.3 ppb, SPAN 1.013), no corrections applied:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OC] - 0.07 ppb) / 0.9994 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.31 ppb^2 + 2.55e-05 * X_{O3}^2) (1d)

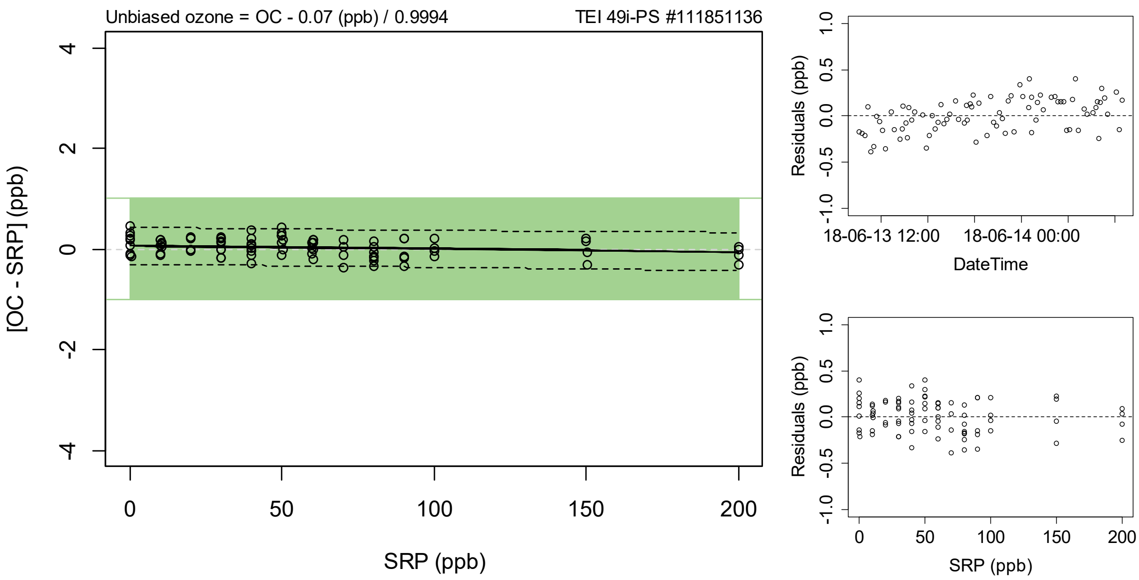

Figure 2. *Same as above for the CMN ozone calibrator (Thermo Scientific 49i-PS #111851136).*

The results of the comparisons can be summarised as follows:

Perfect agreement between the WCC-Empa travelling instrument and the CMN calibrator was found, which confirms the validity of the calibration against the WCC-Empa SRP in 2017.

Slightly larger deviations were found for the CMN analyser. These deviations are probably due to the fact that results were corrected based on a single comparison with the ozone calibrator carried out at CMN. This procedure results in small step changes due to the uncertainty of individual calibrations. Therefore, the following recommendation is made regarding the future calibration strategy:

> **Recommendation 6 (***, important, 2018)**
> *It is recommended to adjust the calibration settings of the CMN ozone analyser based on a careful comparison with the CMN ozone calibrator covering several ozone levels in the range from 0 – 200 ppb. Each level should be measured at least three times, and the average of all data should be used to determine the new calibration settings. The new settings should also be compared with the results of the current audit, which suggest that the settings should be close to BKG 0.7 ppb, COEF 1.017.*
> *After this initial calibration, no further change of the calibration settings should be made. Continuation of the 3-montly comparisons with the station calibrator is recommended, but no change or corrections should be applied if the results stay within the WMO/GAW data quality objective of 1 ppb. If the bias is larger, the comparison should be repeated. If results then are still exceeding 1 ppb, the reason should be identified by further checks of the analyser and the calibrator.*

Carbon Monoxide Measurements

Continuous measurements of CO at CMN started in 2007 using a GC/FID system (University of Urbino). A non-Dispersive Infrared (NDIR) instrument was additionally installed in 2012 by CNR-ISAC. Since 2017, CO is also measures as part of the ICOS programme with a Picarro G2401 CRDS instrument. Continuous CO time series are available since 2007.

Instrumentation. A Picarro G2401 analyser, which is part of the ICOS programme, a Thermo Environmental 48C-TL NDIR analyser, and a GC/FID with methaniser are available.

Standards. University of Urbino (GC/FID): A set of 4 NOAA reference standards and a working standard is used to calibrate the GC system. CNR-ISAC: A set of 4 calibration standards from the ICOS Central Analytical Laboratory with traceability to the latest NOAA scales and three target cylinders are available. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figures 3 to 5 with respect to the WMO GAW DQOs (WMO, 2014):

Picarro G2401 #2871-CFKADS2269 (CNR-ISAC / ICOS):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 1.79) / 0.9883 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.9 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

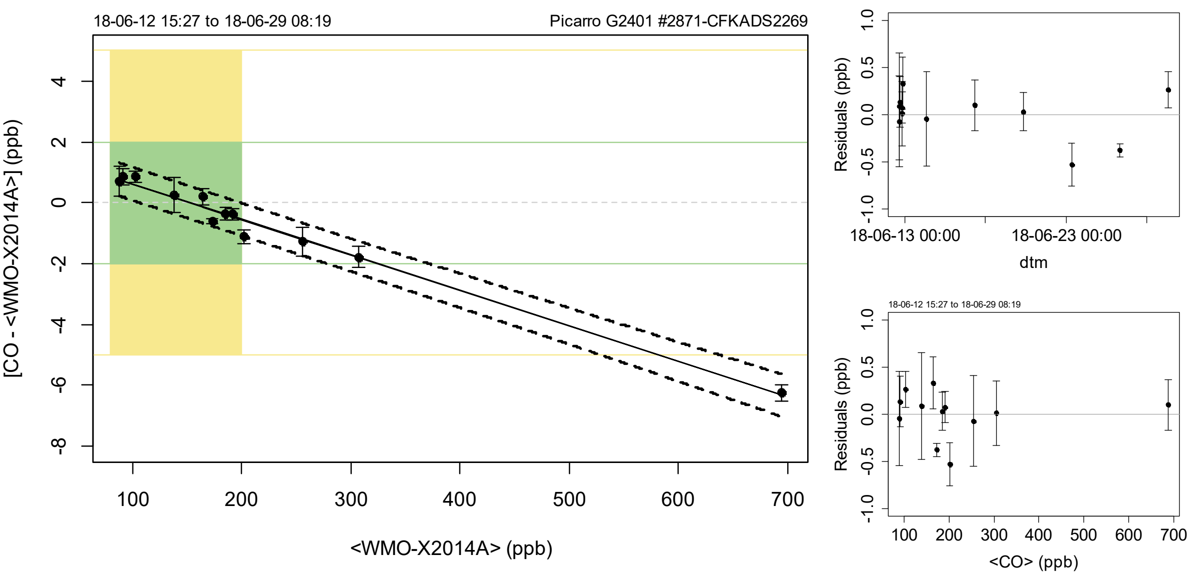

Figure 3. *Left: Bias of the CMN Picarro G2401 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole 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 mole fraction dependence).*

Thermo Environmental 48C-TL (CNR-ISAC):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 18.42) / 0.9778 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (12.3 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

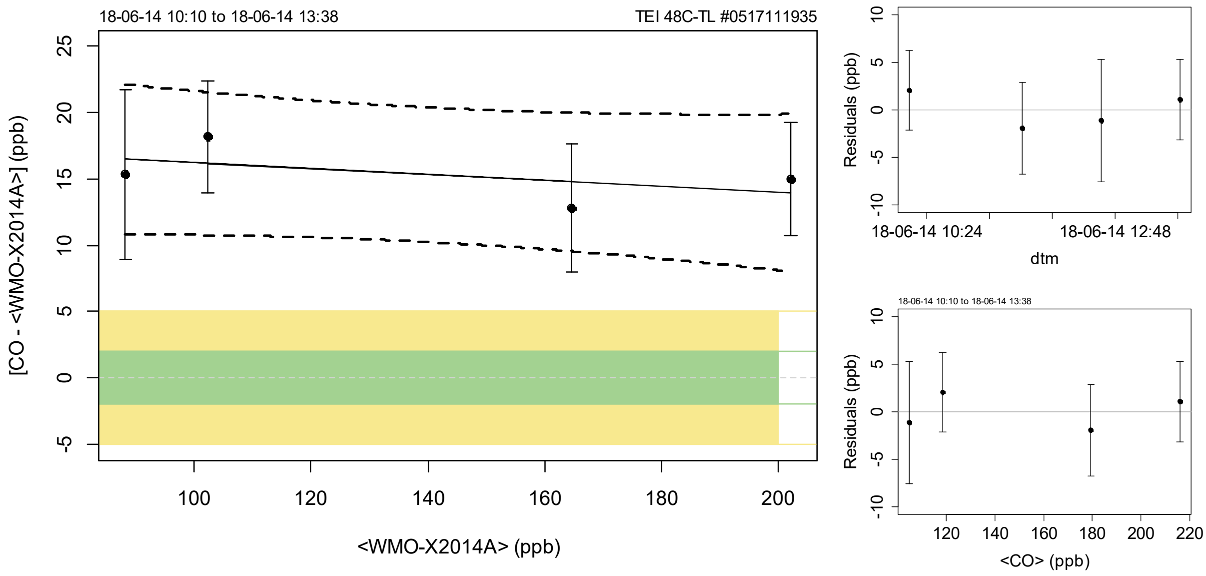

Figure 4. *Same as above, for the Thermo Environmental 48C-TL carbon monoxide analyser.*

GC/FID Agilent 6890N #US10541006 (University of Urbino):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 0.22) / 0.9921 (2e)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (1.6 ppb^2 + 1.01e-04 * X_{CO}^2) (2f)

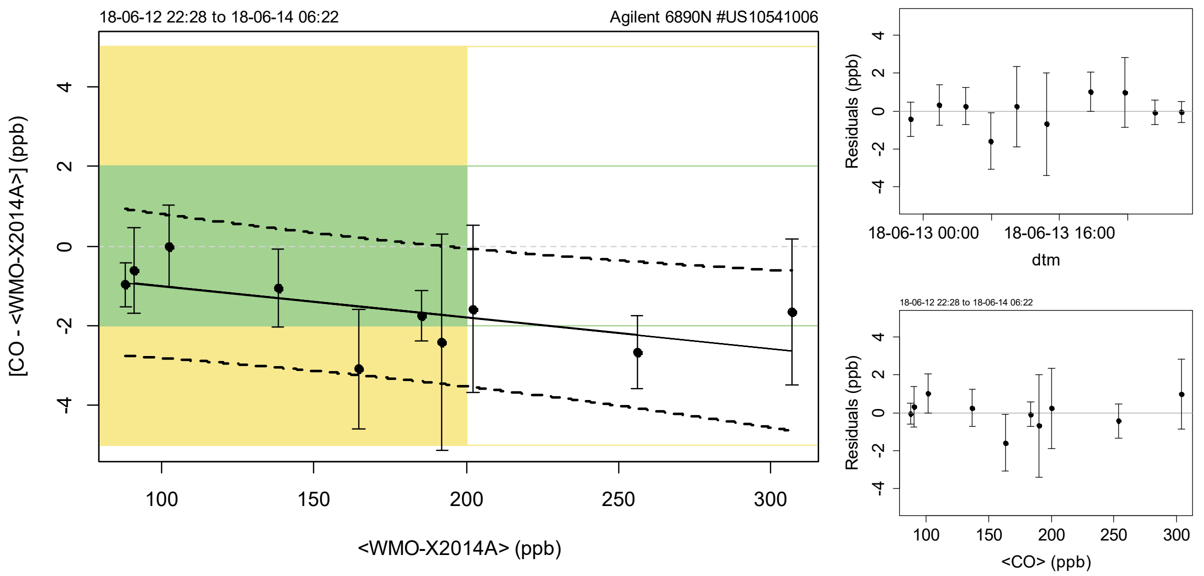

Figure 5. *Same as above, for carbon monoxide GC/FID with methaniser operated by the University of Urbino.*

The results of the comparisons can be summarised as follows:

At the relevant mole fraction, the bias is small and mostly within the network compatibility goals for the CNR-ISAC Picarro G2401 and the University of Urbino GC/FID systems. However, a mole fraction dependent bias was found between the WCC-Empa assigned values and the station measurements. This is most probably due to calibration differences and issues with the carbon monoxide scale. WCC-Empa measurements were tied to a very recent NOAA standard which potentially slightly overestimates assigned mole fraction due to an overestimation of drift at the CCL (https://www.esrl.noaa.gov/gmd/ccl/co_scale_update.html).

The results of the Thermo Environmental 48C-TL analyser were significantly worse were and showed a consistent and mole fraction independent bias larger than the extended WMO/GAW compatibility goal. This was most likely caused by small differences in the sample pressure between zeroing, calibration and measurements of WCC-Empa cylinders. Pressure stabilisation would be needed for better results.

Recommendation 7 (*, minor, 2018)
Compared to the NDIR analyser, more reliable CO instruments are available at CMN. Available resources should focus on these techniques. It is recommended to decommission the NDIR CO analyser.

Similar results were also observed during the ambient air comparison, which are shown further below.

Methane Measurements

Continuous measurements of CH_4 at CMN started in 2007 using GC/FID with a methaniser (University of Urbino). In 2015, CAMM installed a Picarro G2301 CRDS instrument, and another CRDS analyser was added in 2017 by CNR-ISAC. Continuous time series are available since 2007.

Instrumentation. Picarro G2301 (CAMM), Picarro G2401 (CNR-ISAC), GC/FID with methaniser (University of Urbino).

Standards. University of Urbino (GC/FID): A set of 4 NOAA reference standards and a working standard is used to calibrate the GC system. CNR-ISAC: A set of 4 calibration standards from the ICOS Central Calibration Laboratory with traceability to the latest NOAA scales and three target cylinders are available. CAMM: 3 NOAA standards. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN instruments with randomised CH_4 levels from travelling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The results are further illustrated in Figures 6 to 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2301 #2017-CFADS2374 (CAMM):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 11.7 ppb) / 0.9936 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.2 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

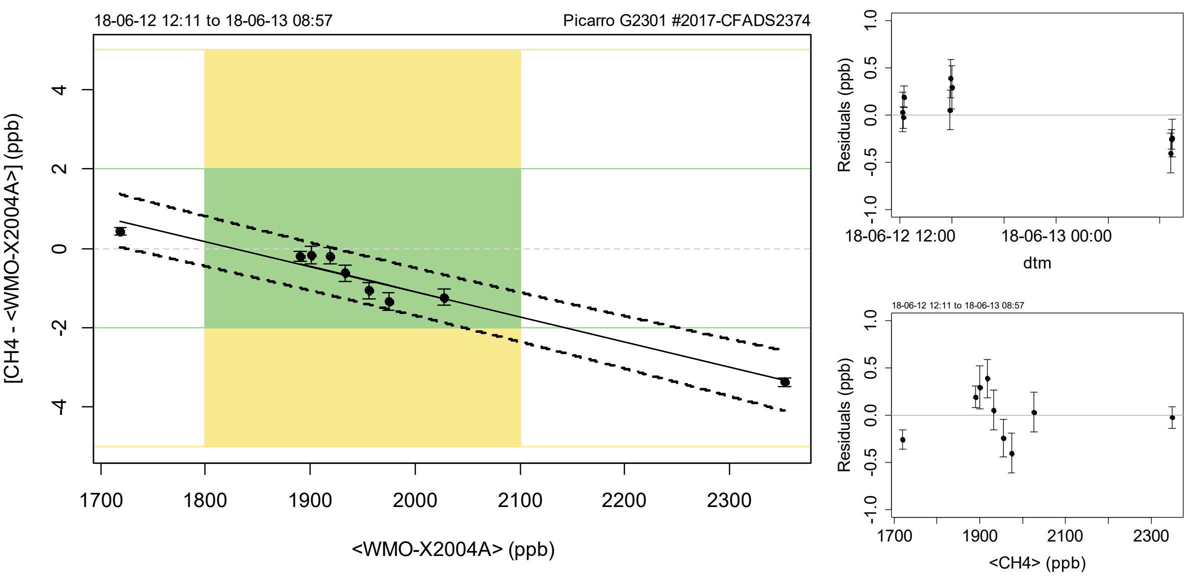

Figure 6. *Left: Bias of the Picarro G2301 methane instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole 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 mole fraction dependence).*

Picarro G2401 #2871-CFKADS2269 (CNR-ISAC / ICOS):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 2.7 ppb) / 0.9986 (3c)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.1 ppb^2 + 1.30e-07 * X_{CH4}^2) (3d)

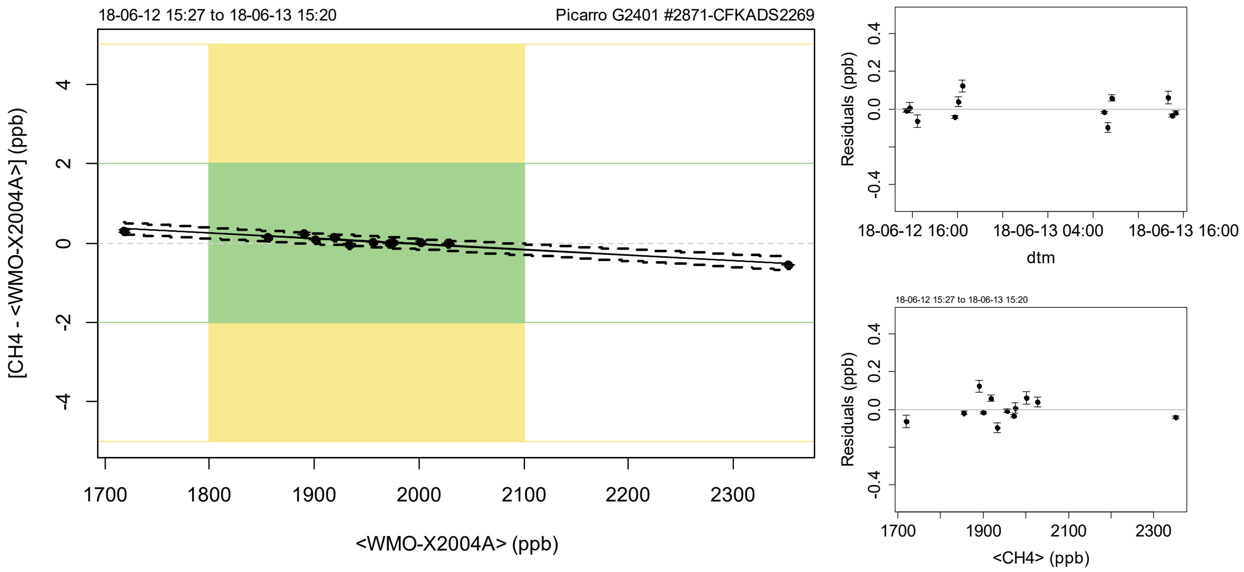

Figure 7. *Same as above, for the Picarro G2401 methane analyser (CNR-ISAC / ICOS).*

GC/FID Agilent 6890N #US10541006 (University of Urbino):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 + 1.0 ppb) / 1.0001 (3e)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.7 ppb^2 + 1.30e-07 * X_{CH4}^2) (3f)

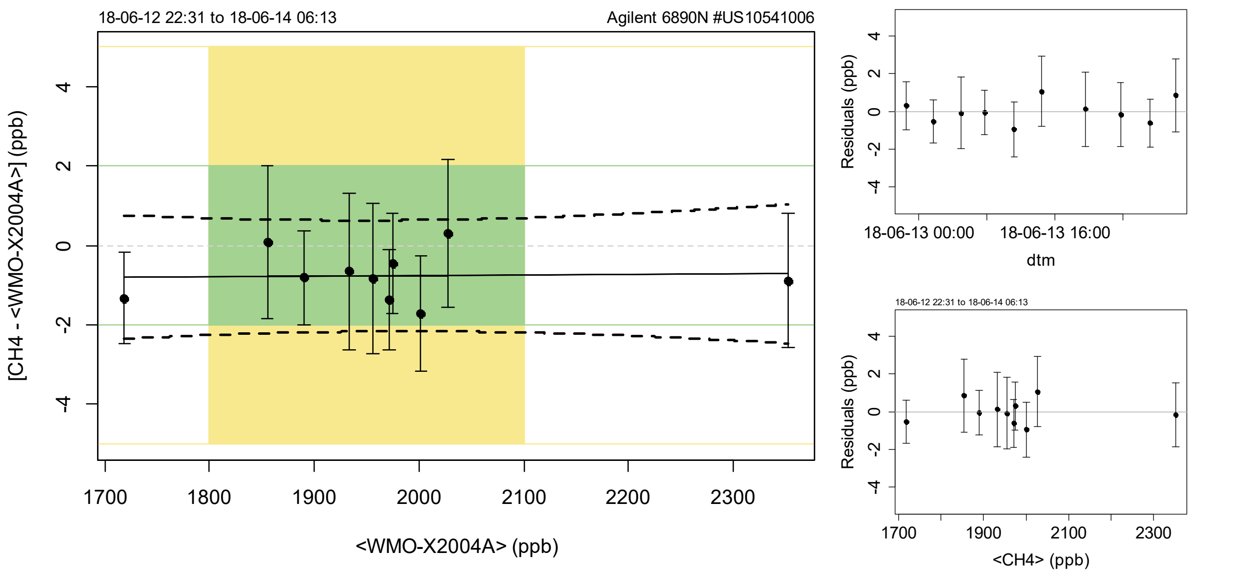

Figure 8. *Same as above, for the Agilent 6890N methane GC/FID (University of Urbino)*

The result of the comparison can be summarised as follows:

Excellent agreement well with the WMO/GAW compatibility goal was found for the Picarro G2401 operated by CNR-ISAC / ICOS, which confirms that the instrument is in good calibration. A slightly larger bias, but still within the WMO/GAW compatibility goal of 2 ppb in the relevant mole fraction range, was observed for the Picarro G2301 operated by CAMM. As for CO_2, the difference can mostly likely be explained by different standards and calibration procedures. The CNR-ISAC Picarro G2401 is further corrected by an individually obtained water vapour correction function, whereas CAMM used for the Picarro G2301 a correction function described in a Picarro whitepaper for a G1301 instrument (Rella, 2010). This function is not valid for G2301 instruments, and correction with this function leads to a significant bias in the ambient air measurements.

The GC/FID system run by the University of Urbino showed poorer repeatability compared to the CRDS instruments, which is expected. Results were within the extended WMO/GAW compatibility goal in the relevant mole fraction range.

Recommendation 8 (*, critical, 2018)**
It is strongly recommended to determine the instrument specific water vapour correction function of the Picarro G2301 operated by CAMM (already done after the audit). The correction function should be validated by repeated experiments at least once per year.

Recommendation 9 (*, critical, 2018)**
CH_4 (and CO_2) data by CAMM, which were evaluated using the wrong correction function, needs to be withdrawn and potential data users must be informed. All data must be re-analysed using the correct function obtained in the experiment carried out after the audit in August 2018.

Recommendation 10 (*, important, next purchase of NOAA standards by CAMM)**
Since the CRDS technique shows a linear response of the entire range of the instrument, the standards used for calibration should cover a range as wide as possible. The currently available standards are all lower than the present ambient CH_4 mole fraction. It is recommended to add standards with high CH_4 levels.

Recommendation 11 (*, important, next purchase of NOAA standards by University of Urbino)**
Current CH_4 standards of the University of Urbino cover only a narrow range of less than 100 ppb methane. It should be considered to add standards with high levels, since the GC/FID system is expected to be linear.

A similar bias was also observed during the ambient air comparison for the two Picarro instruments, but an issue with the GC/FID system resulted in a larger bias which is discussed further below.

Carbon Dioxide Measurements

Continuous measurements of CO_2 operated by CAMM commenced in 1979 at CMN, and continuous data is available since then. The CMN CO_2 record is one of the longest world-wide. The instrumentation was recently upgraded with two CRDS instruments, one operated by CAMM, and the other by CNR-ISAC / ICOS.

Instrumentation. Picarro G2301 (CAMM), Picarro G2401 (CNR-ISAC). The NDIR instrument, which was assessed during the last WCC-Empa audit, is still at CMN but was not working at the time of the audit.

Standards. University of Urbino (GC/FID): A set of 4 NOAA reference standards and a working standard is used to calibrate the GC system. CNR-ISAC: A set of 4 calibration standards from the ICOS Central Calibration Laboratory with traceability to the latest NOAA scales and three target cylinders are available. CAMM: 3 NOAA standards. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN instrument with randomised CO_2 levels from travelling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figures 9 and 10 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2301 #2017-CFADS2374 (CAMM):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.96 ppm) / 0.99749 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.002 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4b)

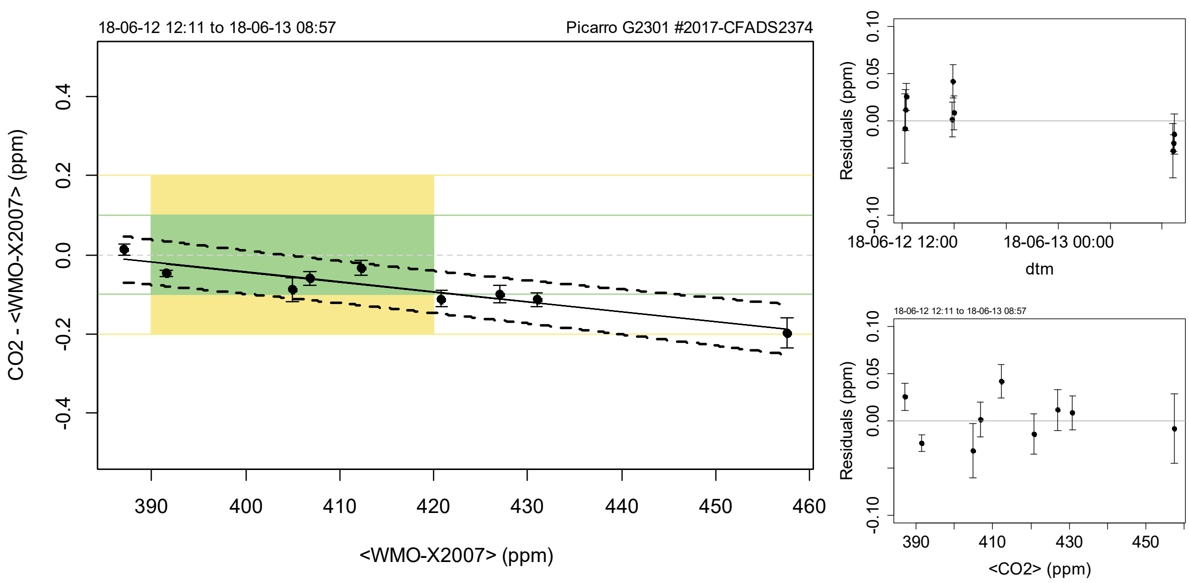

Figure 9. *Left: Bias of the Picarro G2301 CO_2 instrument (CAMM) with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole 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 mole fraction dependence).*

Picarro G2401 #2871-CFKADS2269 (CNR-ISAC / ICOS):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.43 ppm) / 0.99886 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.002 ppm^2 + 3.28e-08 * X_{CO2}^2) (4d)

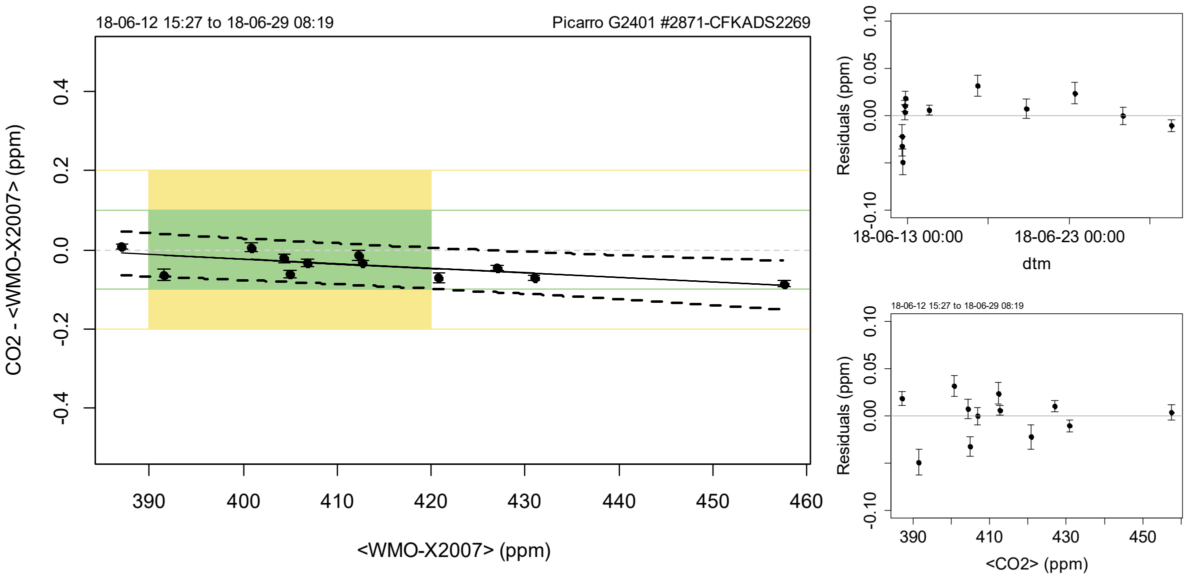

Figure 10. *Same as above for the Picarro G2401 CO_2 instrument (CNR-ISAC / ICOS).*

The result of the comparison can be summarised as follows:

Both instruments show agreement within the WMO/GAW compatibility goals in the relevant mole fraction range. The results of the Picarro G2401 operated by CR-ISAC / ICOS were slightly better compared to CAMM. Most likely this is related to calibration standards and procedures.

Recommendation 12 (*, critical, 2018)**
As for CO_2, it is strongly recommended to determine the instrument specific water vapour correction function of the Picarro G2301 operated by CAMM (already done after the audit in August 2018).

Good results were also observed during the ambient air comparison, but only after CAMM implemented the correct water vapour correction function. However, the air intake location has a larger influence on CO_2 measurements compared to other parameters, which is shown further below.

Nitrous Oxide Measurements

Continuous measurements of N_2O commenced in 2007 using GC/ECD by the University of Urbino, and continuous time series are available since then.

Instrumentation. GC/ECD Agilent 6890N (University of Urbino).

Standards. A set of 4 NOAA reference standards and a working standard is used to calibrate the GC system. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 11 with respect to the WMO GAW DQOs (WMO, 2014):

GC/ECD Agilent 6890N #US10541006 (University of Urbino):

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 4.28) / 0.98726 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.42 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

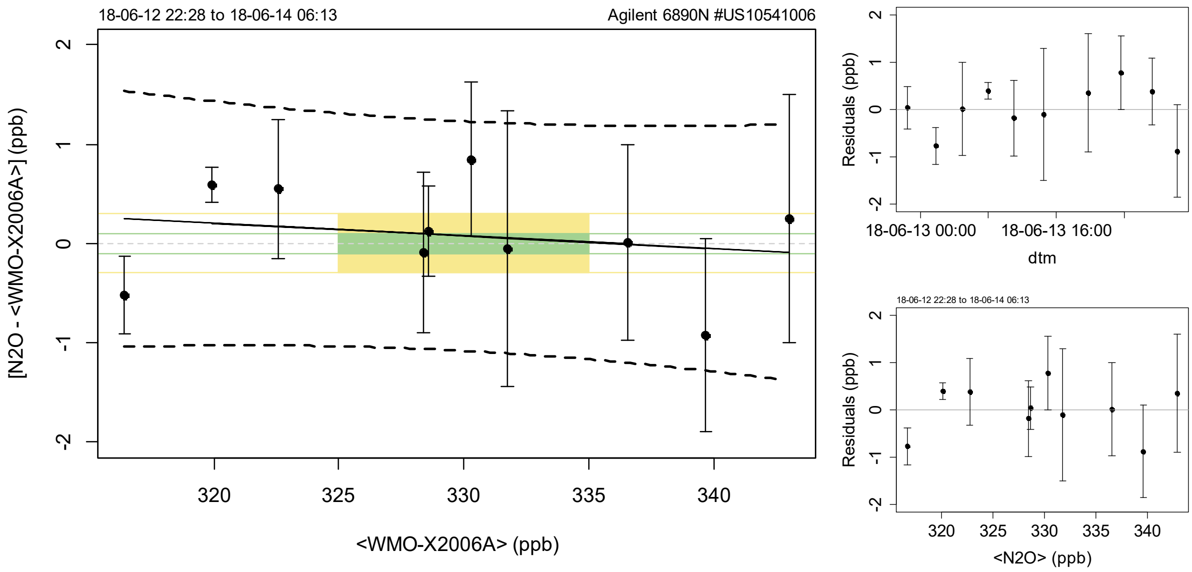

Figure 11. *Left: Bias of the Agilent 6890N nitrous oxide GC/ECD system with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole 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 mole fraction dependence).*

The result of the comparison can be summarised as follows:

The average agreement was only slightly exceeding the WMO/GAW compatibility goal of 0.1 ppb. However, individual results showed a relatively large uncertainty. It should be explored whether the GC/ECD can be optimised with regard to the repeatability of measurements. Alternatively, change to spectroscopic measurement techniques should be considered.

Recommendation 13 (*, minor, 2018/20)
It should be considered to purchase a spectroscopic instrument for N_2O measurements, since they generally show better performance and require less consumables.

Recommendation 14 (, important, 2018/19)**
It should be explored if the current GC/ECD system can be optimised with regard to repeatability and reproducibility.

CMN PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the CMN performance audit to other station audits made by WCC-Empa and WCC-N_2O. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2015 meeting (WMO, 2016) for CO_2, CH_4 and CO and refer to conditions usually found in unpolluted air masses. Using a fixed mole fraction range however might not be appropriate in the case of N_2O due to the significant upward trend in the atmosphere over the past decades. The range currently representing the unpolluted troposphere has been recently defined as 325-335 nmol/mol (WMO, 2016), which corresponds well to the mean global atmospheric N_2O amount fraction of 328.9 ± 0.1 nmol/mol observed in 2016 (WMO, 2017b). A trend analysis made by Blunden and Arndt (2017) showed an annual increase of about 0.8 nmol/mol per year over the last decade, which is in agreement with a fairly constant annual growth rate of 0.81 nmol/mol per year from 1977 until today determined by the National Oceanic and Atmospheric Administration (NOAA, 2018). Based on this, the analysis of N_2O audit results was made using a variable amount fraction range covering 10 nmol/mol with the centre being representative for the unpolluted troposphere for the year of the audit. For surface ozone the mole fraction range of 0 -100 ppb was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility goals in a certain mole fraction range. Figure 12 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, while the results for CO, CH_4, CO_2 and N_2O are shown in Figure 13. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If 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 12 and 13, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

The results were within the DQOs for ozone and CH_4 (all instruments) and CO_2 (CNR Picarro). CO_2 (CAMM Picarro), CO (CNR Picarro and GC/FID) and N_2O were within the eDQOs. The NDIR CO instrument however did not pass. Overall, this result is very good in the context of other comparisons.

Table 1. *CMN performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5-7th columns show the percentage of all WCC-Empa and WCC-N_2O audits within these criteria since 1996 (O_3), 2002 (N_2O), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound	Range	Unit	CMN within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]	% of audits outside eDQOs
O_3 (CNR)	0 -100	ppb	✓	65	NA	35
CO (CNR/NDIR)	30 - 300	ppb	✗	22	46	54
CO (CNR/CRDS)	30 - 300	ppb	✓	22	46	54
CO (Urbino)	30 - 300	ppb	✓	22	46	54
CH_4 (CAMM)	1750 - 2100	ppb	✓	67	92	8
CH_4 (CNR)	1750 - 2100	ppb	✓	67	92	8
CH_4 (Urbino)	1750 - 2100	ppb	✓	67	92	8
CO_2 (CAMM)	380 - 450	ppm	✓	34	56	44
CO_2 (CNR)	380 - 450	ppm	✓	34	56	44
N_2O (Urbino)	325 - 335	ppb	✓	0	34	66

[1] Percentage of stations within the eDQO and DQO

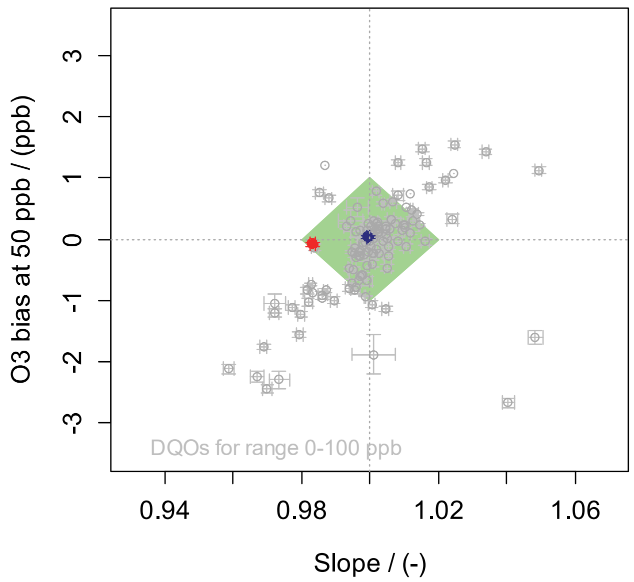

Figure 12. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the CMN calibrator (blue) and analyser (red) results. The green area corresponds to the WMO/GAW DQO for surface ozone.*

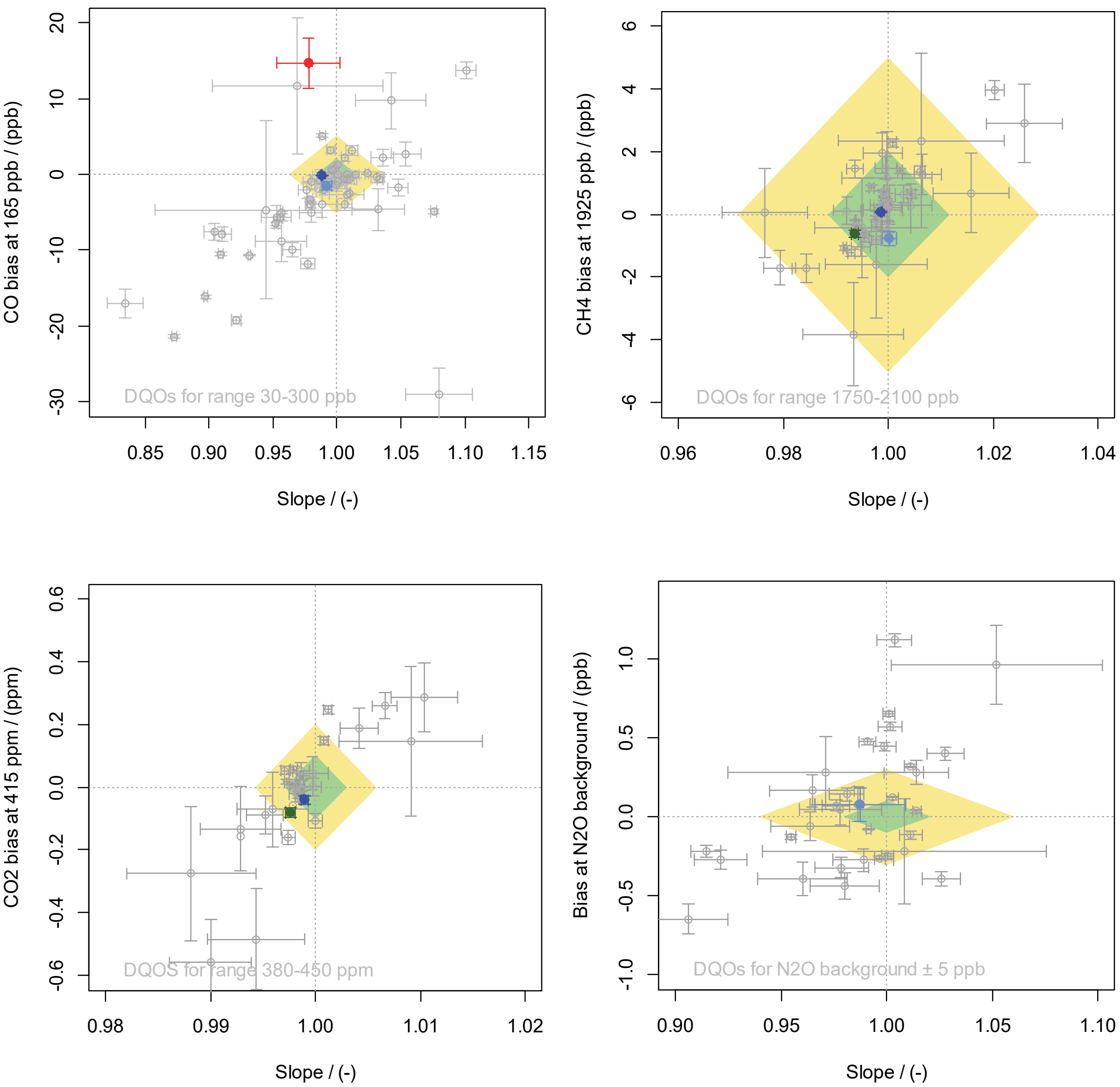

Figure 13. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show CMN results (blue: CNR Picarro G2410, dark green: CAMM Picarro G2301, light blue: Urbino GC system, red: TEI48C). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

PARALLEL MEASUREMENTS OF AMBIENT AIR

The audit included parallel measurements of CO_2, CH_4 and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401). The TI was running from 13 June through 24 July 2018. The TI was connected to a separate independent inlet line sampling from the same location as the CAMM analyser, with is approximately 50 m away from the CMR inlet and at a slightly higher altitude. The TI was sampling air using the following sequence: 1809 min ambient air followed by 60 min measurement of three standard gases (20 min each). The sample air was reduced to approximately 70 ml/min with a needle valve and dried by a Nafion dryer (Model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum in the purge air. To account for the remaining effect of water vapour a correction function (Zellweger et al., 2012a; Rella et al., 2013) was applied to the TI data. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below.

Carbon monoxide

Figure 14 shows the comparison of hourly CO between the WCC-Empa TS and the CNR Picarro G2401 and the GC/FID system of the University of Urbino. The corresponding deviation histograms are shown in Figure 15.

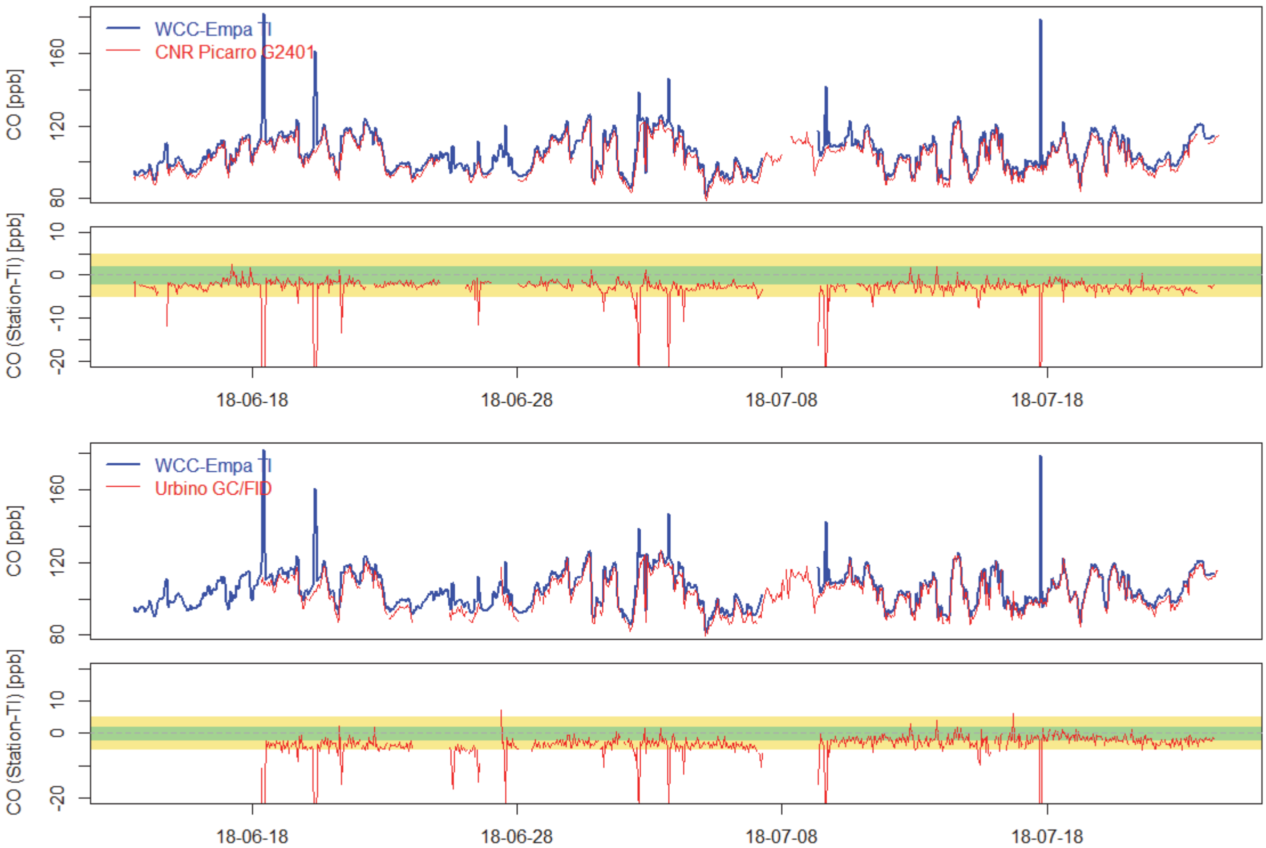

Figure 14. *Comparison of the CNR Picarro G2401 analyser (top) and the Urbino GC/FID system (bottom) with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

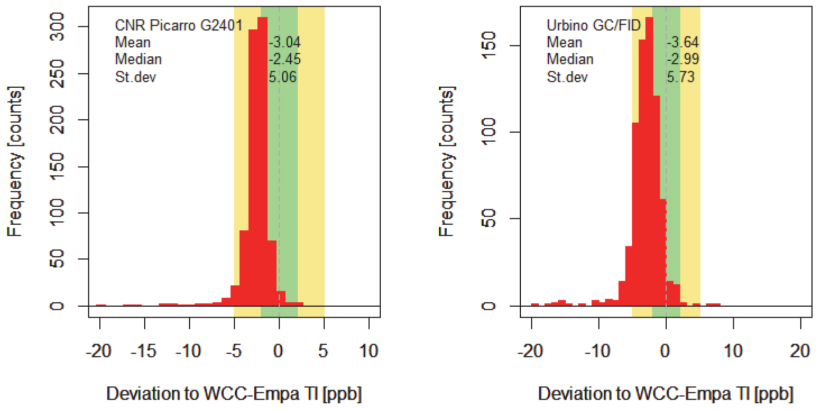

Figure 15. *Carbon monoxide deviation histograms for the CMN Picarro G2401 analyser (left) and the Urbino GC/FID system (right).*

The temporal variation was well captured by both station instruments. In both cases, lower values were observed by CMN, which is partly explainable by the findings of the TS comparison. However, the deviation is larger than expected for the CNR Picarro G2401. A potential reason could be issues with the water compensation of this instrument.

Recommendation 15 (, important, 2018)**
It should be regularly checked if the internal water vapour correction function of the Picarro G2401 instrument is adequate. Alternatively, drying of the sample air should be considered.

It further was noticed that the WCC-Empa TI showed periods with high CO mole fractions which were not present in data of the CMN instruments. These are potential contaminations by local pollution episodes at the CAMM site, which needs further investigation. The pollution events were only observed during day time between 07:30 and 18:30 UTC.

Recommendation 16 (, important, 2018)**
Local pollution might be an issue at the CAMM site. Potential pollution sources need to be identified and eliminated if possible.

Methane

Figure 16 shows the comparison of hourly CH_4 between the WCC-Empa TS and the CAMM and CNR Picarros and the GC/FID system of the University of Urbino. The corresponding deviation histograms are shown in Figure 17.

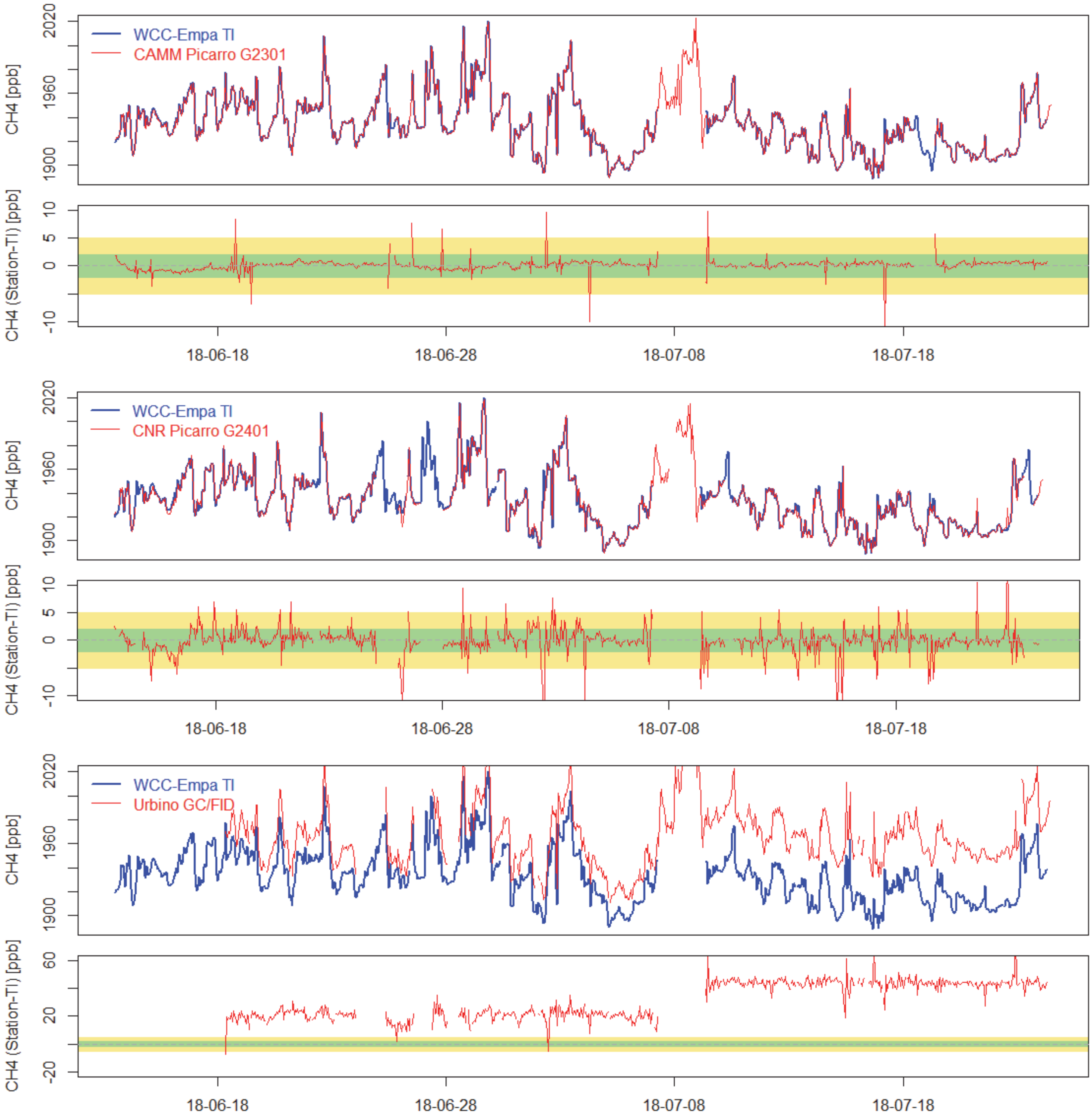

Figure 16. *Comparison of the CAMM Picarro G2301 (top), the CNR Picarro G2401 (middle) and the Urbino GC/FID system (bottom) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

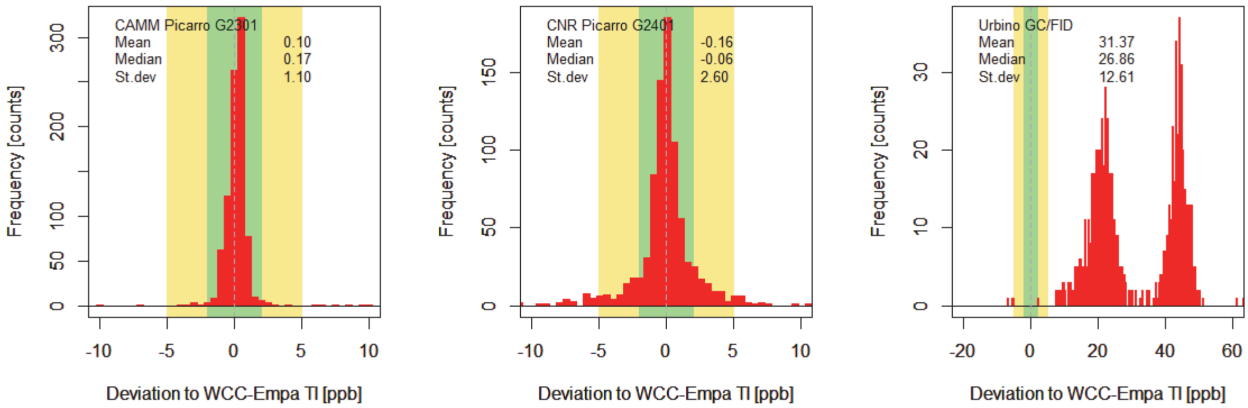

Figure 17. *Methane deviation histograms for the CAMM Picarro G2301 (left), the CMN Picarro G2401 (middle) and the Urbino GC/FID system (right).*

The temporal variation was well captured by all instruments, and excellent agreement within the DQOs were observed for the Picarro systems of CAMM and CNR. The scatter is larger for the comparison between CNR and WCC-Empa compared to CAMM, but this is most likely due to the fact that the CNR inlet is located 50 m away from the CAMM and WCC-Empa inlet, which results in slightly different air masses and a time lag between the two locations. The ambient air comparison confirms the good results of the TS comparison for CNR and CAMM.

The University of Urbino GC/FID system however showed a large positive bias compared to the TI, with two distinctly different periods. Problems with the ambient air measurements of the GC/FID system were already identified by comparison with CNR before the WCC-Empa audit, but the reason was unknown. After the comparison campaign, a faulty membrane in the air inlet pump was identified as the reason, and the problem was fixed in August 2018. As a consequence, data needs to be carefully re-evaluated.

Recommendation 17 (*, critical, 2018)**

A leak in the air inlet pump caused a strong positive bias in the ambient air measurement of the GC/FID system for methane. Data needs to be re-analysed and compared to CNR to identify the time period with invalid data. If such data has already been used or submitted, the corresponding users need to be informed and data needs to be withdrawn. It further must be carefully checked if CO and N_2O data of the GC system was also affected by the faulty pump.

Carbon dioxide

Figure 18 shows the comparison of hourly CO_2 between the WCC-Empa TS and the CAMM and CNR Picarros. The corresponding deviation histograms are shown in Figure 19.

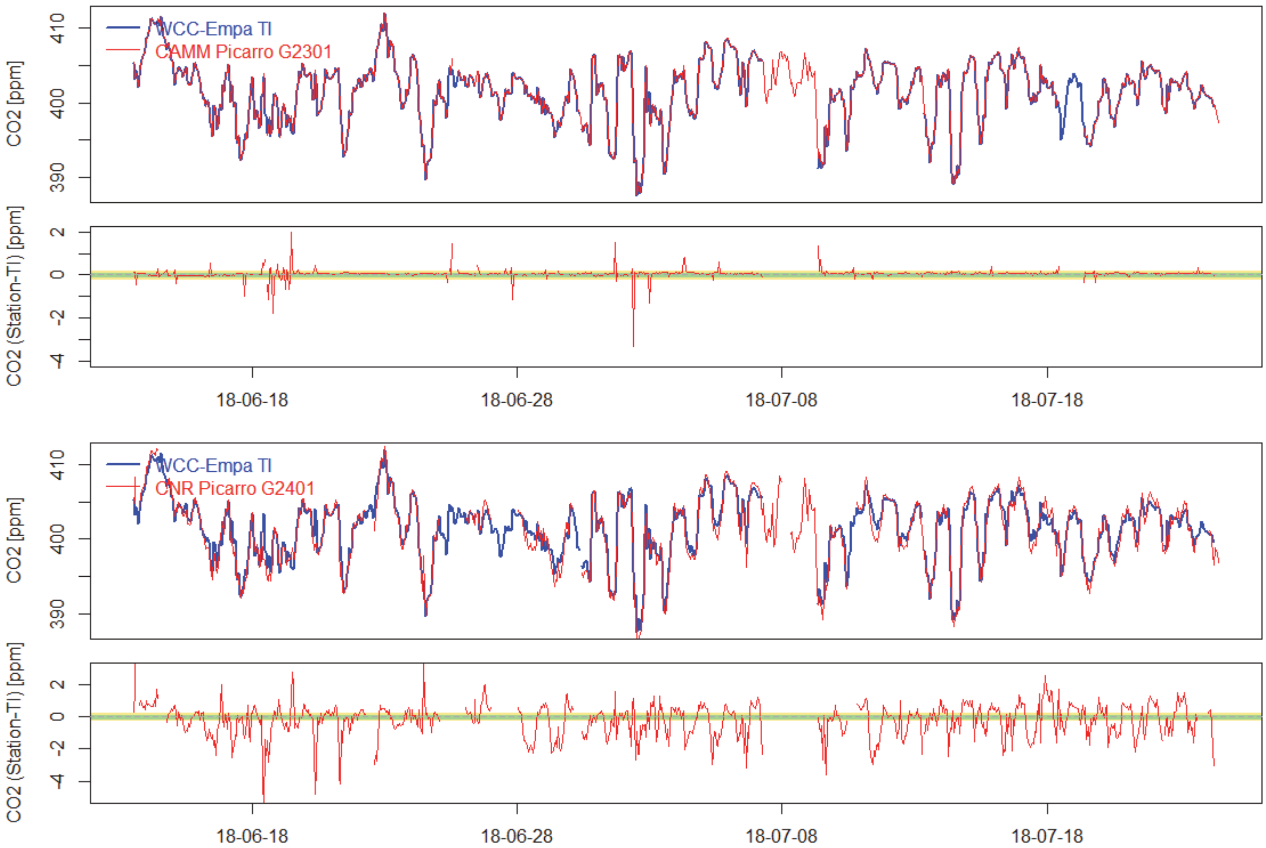

Figure 18. *Comparison of the CAMM Picarro G2301 (top) and the CNR Picarro G2401 (bottom) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

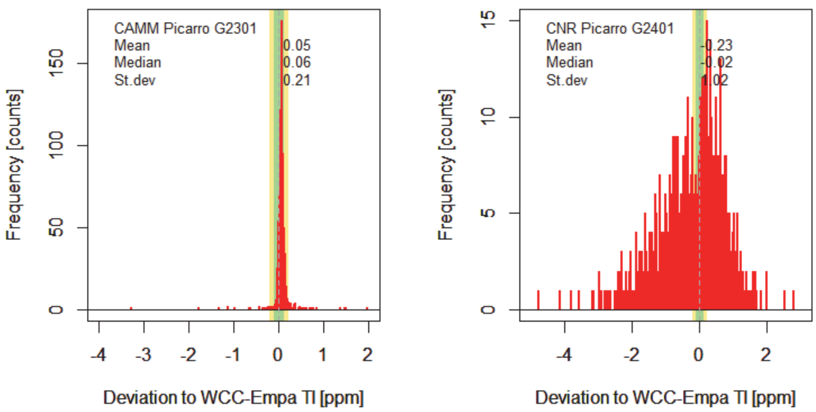

Figure 19. *Carbon dioxide deviation histograms for the CAMM Picarro G2301 (left) and the CMN Picarro G2401 (right).*

The temporal variation was well captured by both the CAMM and the CMR instruments, and excellent agreement within the DQOs was observed for the Picarro system of CAMM. On average, the Picarro G2401 of CNR was also in good agreement with the WCC-Empa TI with median bias of -0.02 ppm. However, the scatter of the bias for hourly data was significantly larger compared to CAMM, and a distinct diurnal cycle of the bias was found (Figure 20).

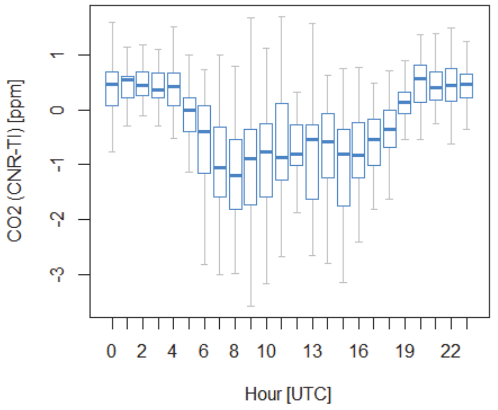

Figure 20. *Box plot of the diurnal variation of the difference between the CNR Picarro G2041 and the WCC-Empa TI.*

The difference between the CAMM and the CNR inlet can partly be explained as follows:

- The inlet location of CAMM and WCC-Empa were almost identical, but the CMR inlet is located 50 m away at slightly lower elevation. This results in sampling of slightly different air masses at the two sites, which likely explains the observed scatter.
- It seems that the CNR inlet is more affected by CO_2 uptake than the CAMM inlet, which could be due to the lower elevation of the CNR air intake. This could be the case especially at calm days with low wind speed.
- At night, CO_2 levels at the CNR location are slightly higher compared to CAMM, which needs further investigation.

Recommendation 18 (*, important, ongoing)**
It is recommended to further analyse CAMM and CNR CO_2 data with respect to the difference between the two air intake locations. Ongoing comparisons of the two time series including meteorological and other parameters are strongly encouraged.

CONCLUSIONS

The global GAW station Mt. Cimone provides extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects, which makes it a very significant contribution to the GAW programme. CMN has one of the longest continuous CO_2 time series worldwide. Many parameters are independently measured by different groups, which allow internal comparison and strengthens the quality of the measurements.

Most assessed measurements were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant mole fraction range. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Please note that Table 2 refers only to the mole fractions relevant to CMN, whereas Table 1 further above covers a wider mole fraction range.

Table 2. *Synthesis of the performance audit and ambient air comparison results. A tick mark indicates that the compatibility goal (green) or extended compatibility goal (orange) was met on average. Tick marks in parenthesis mean that the goal was only partly reached in the relevant mole fraction range (performance audit only), and ✗ indicates results outside the compatibility goals.*

Comparison type	O_3 CNR	CO CNR NDIR	CO CNR CRDS	CO GC/FID Urbino	CH_4 CAMM CRDS	CH_4 CNR CRDS	CO_2 CAMM CRDS	CO_2 CNR CRDS	N_2O GC/ECD
Audit with TS	✓	✗	✓	✓	✓	✓	✓	✓	✓
Ambient air comparison	NA	NA	✓	✓	✓	✓	✓	✓	NA

NA no ambient air comparison was made for ozone and nitrous oxide

The continuation of the Mt. Cimone measurement series is highly important for GAW. The large number of measured atmospheric constituents in combination with the high data quality enables state of the art research.

SUMMARY RANKING OF THE MT. CIMONE GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(4)	Year round access, difficult in spring and autumn. No weekend access.
Facilities		
Laboratory and office space	(5)	Adequate, with space for additional research campaigns.
Internet access	(3)	Only in CNR-ISAC laboratory
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable, UPS
General Management and Operation		
Organisation	(5)	Well-coordinated
Competence of staff	(4)	Skilled staff (CNR-ISAC, Urbino), training needed (CAMM)
Air Inlet System	(4)	Mostly adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2 (CAMM)	(5)	State of the art instrumentation
CO/CH_4/CO_2 (CNR-ISAC)	(5)	State of the art instrumentation
CO (CNR-ISAC NDIR)	(2)	Calibration issues, not adequate
CO/CH_4/N_2O (Urbino)	(4)	Adequate, higher noise compared to spectroscopic systems
Standards		
O_3, CO, CO_2, CH_4, N_2O	(5)	NIST (O_3) and NOAA traceable standards available
Data Management		
Data acquisition	(5)	Fully adequate system except for ozone with manual data download
Data processing	(4)	Skilled staff (CNR-ISAC, Urbino), training needed (CAMM)
Data submission	(4)	All data submitted, partly with more than 2 years delay.

#0: inadequate thru 5: adequate.

Dübendorf, November 2018

Dr. C. Zellweger WCC-Empa	Dr. M. Steinbacher QA/SAC Switzerland	Dr. B. Buchmann Head of Department

APPENDIX

Data Review

The following figures show summary plots of CMN data accessed on 12 November 2018 from WDCGG and WDCRG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

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

CAMM:

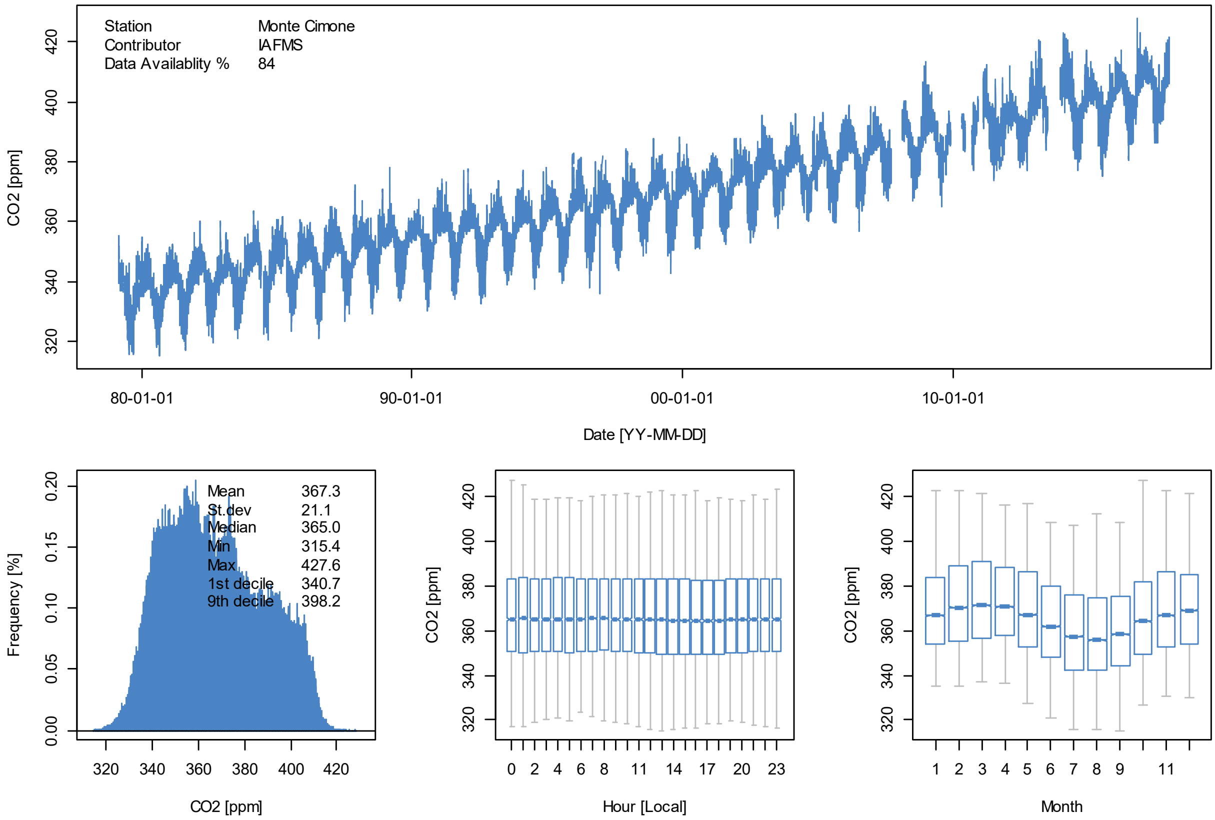

Figure 21. *CAMM CO_2 data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

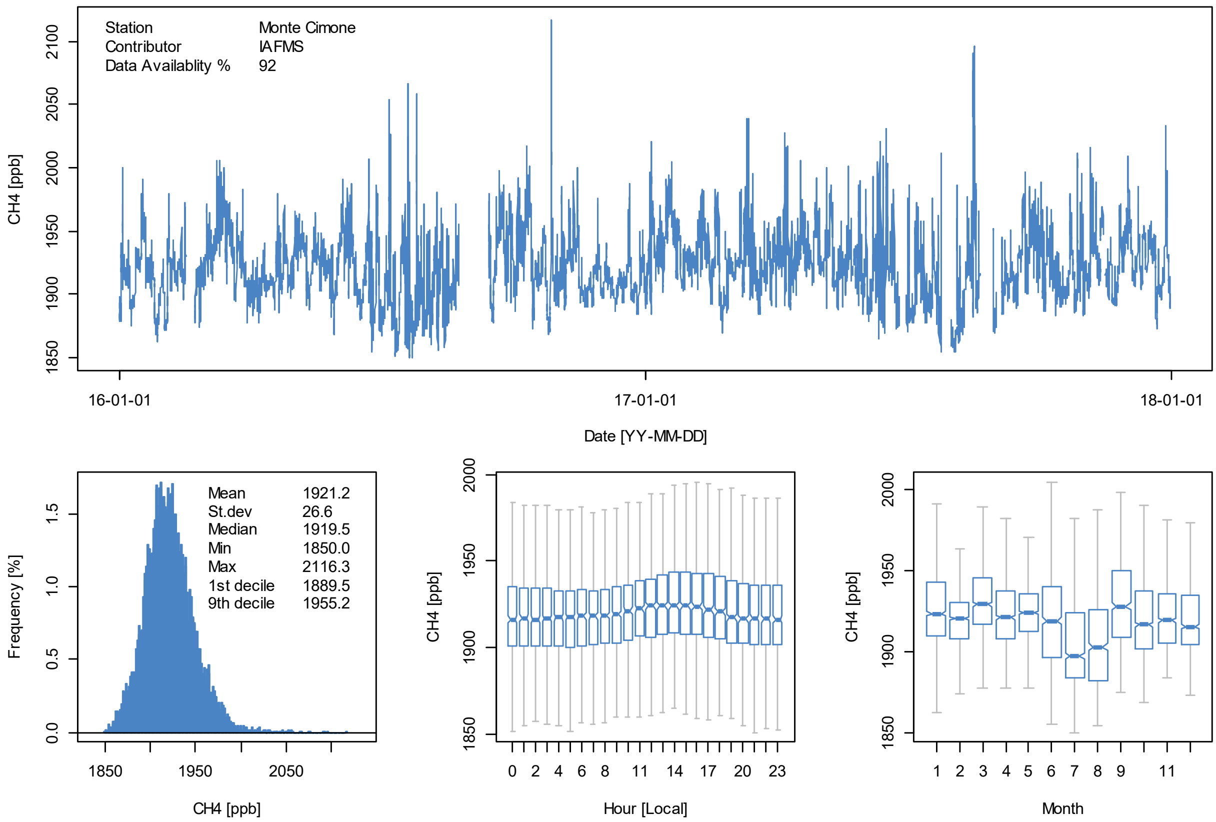

Figure 22. *Same as above for CH_4.*

CAMM carbon dioxide:

- Data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

CAMM methane:

- Data set looks sound.
- Only two years available from the CAMM instrument.

CNR-ISAC:

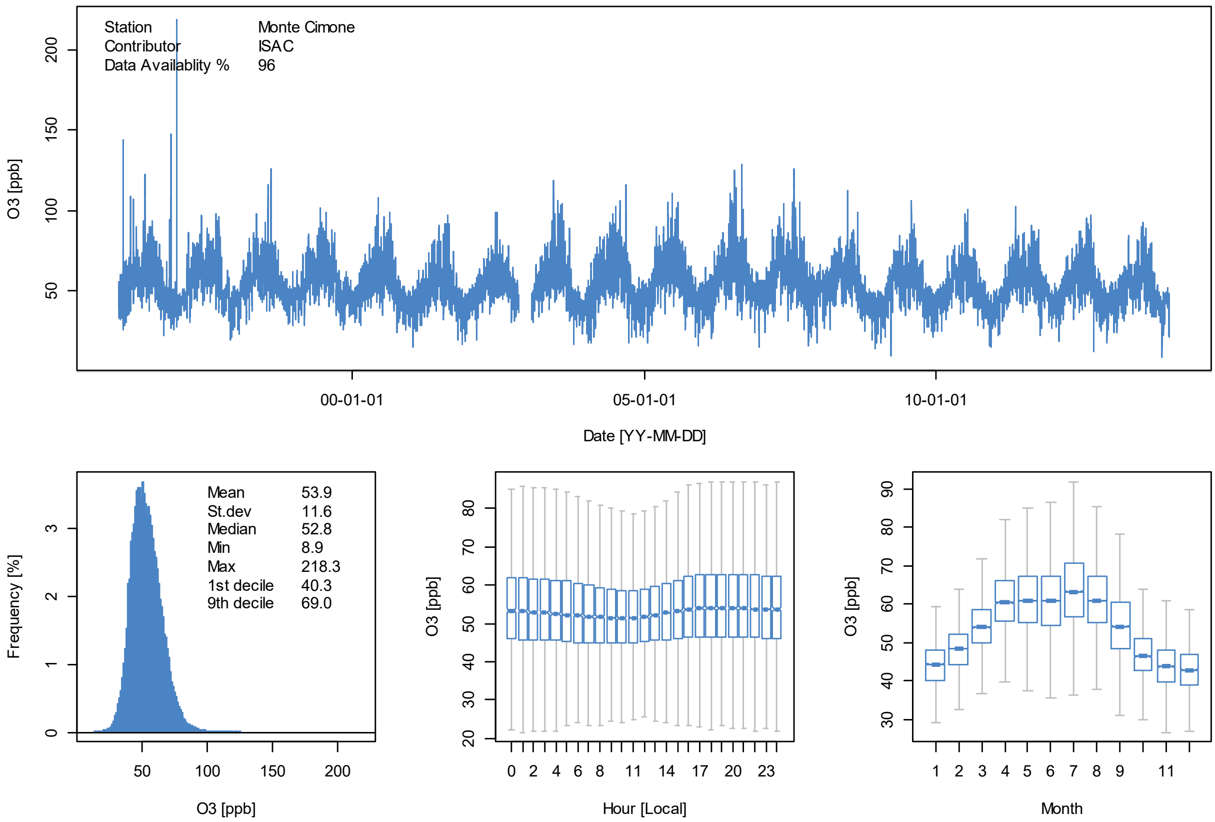

Figure 23. *CNR-ISAC O_3 data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

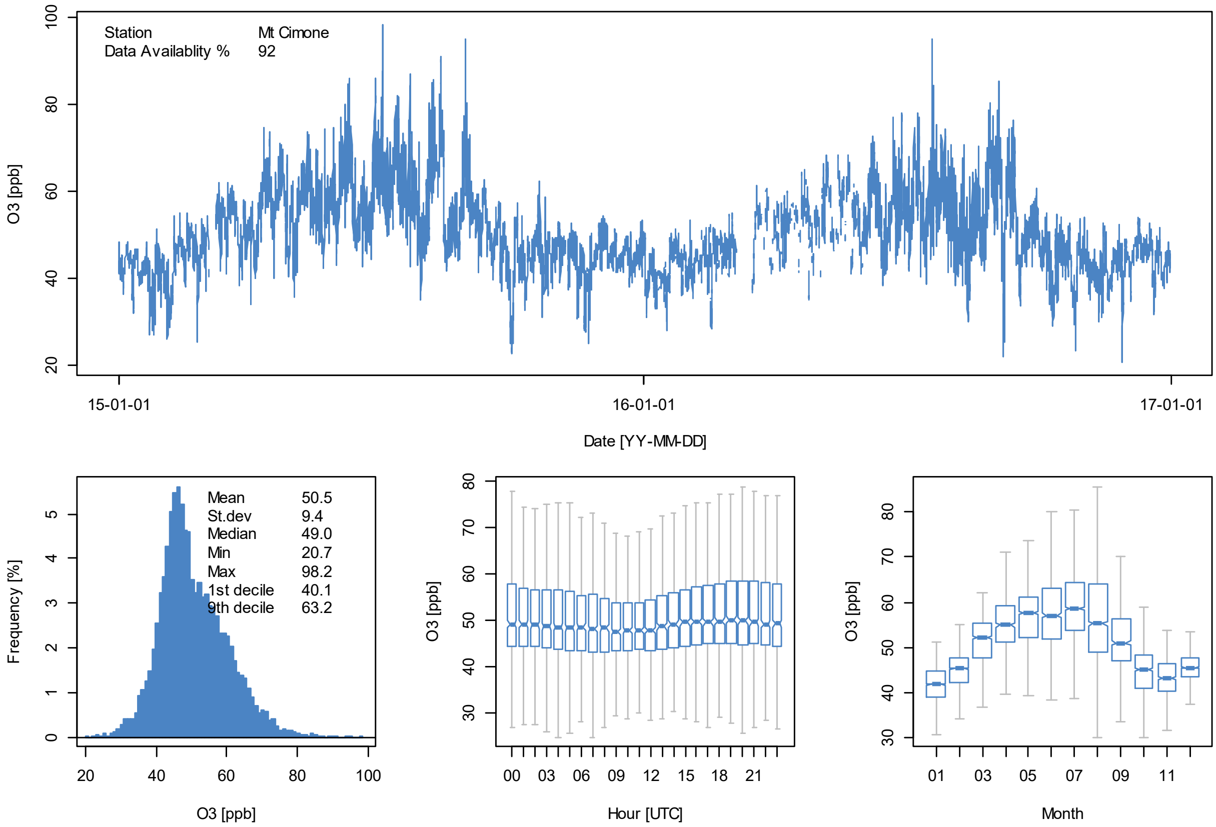

Figure 24. *Same as above for data downloaded from WDCRG.*

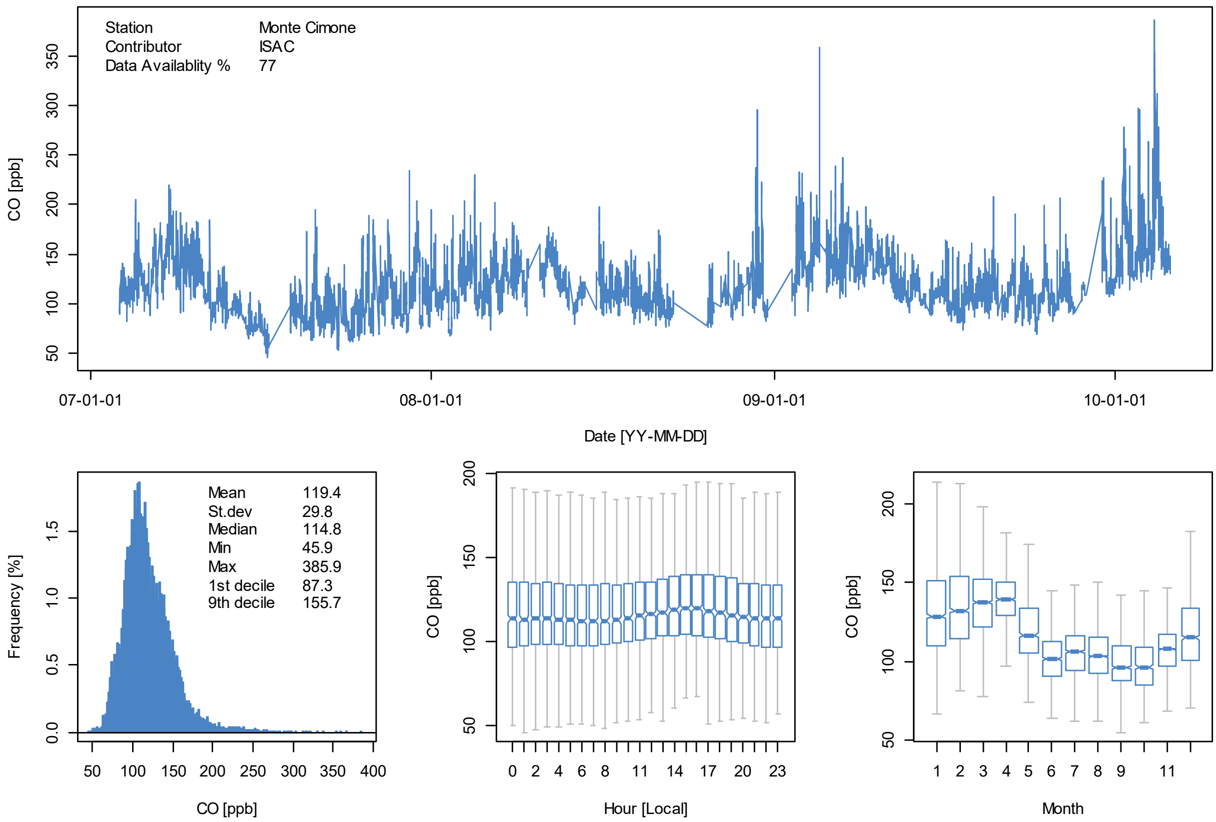

Figure 25. *CNR-ISAC CO data (GC/RGD instrument) accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

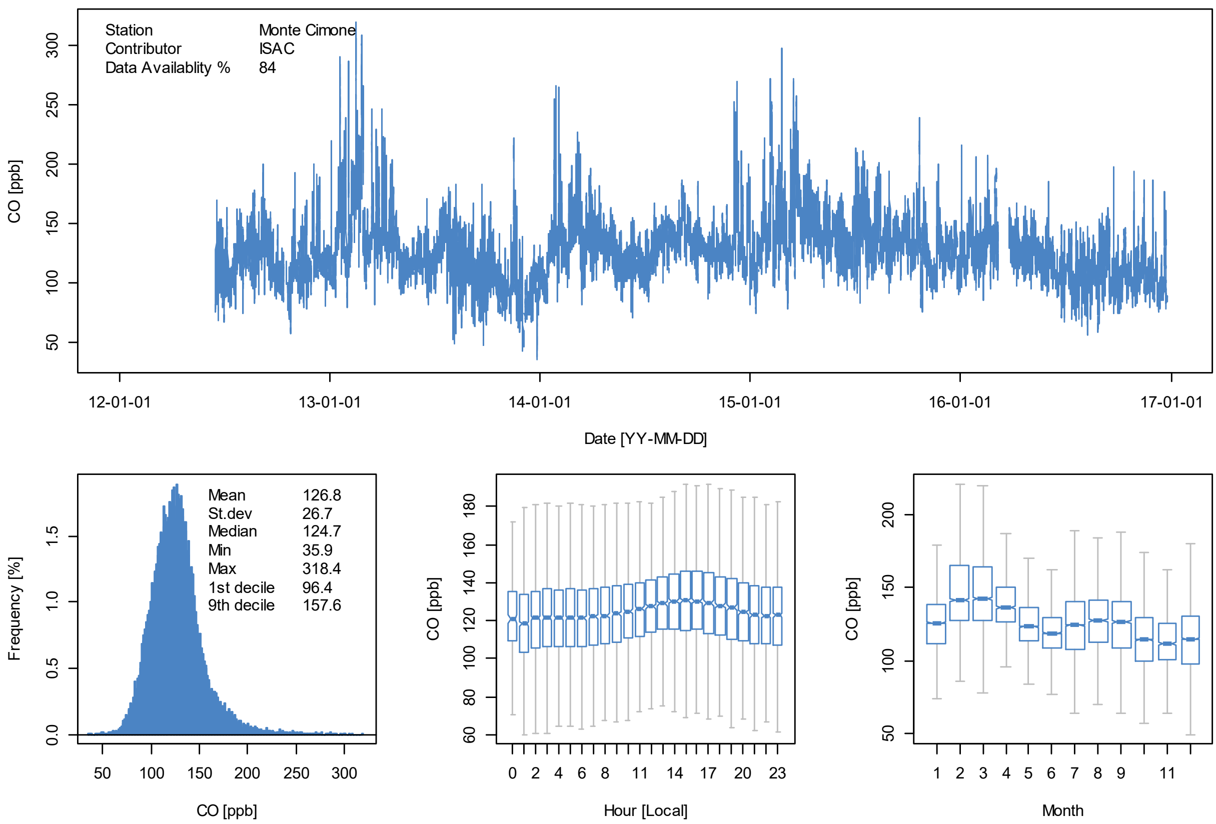

Figure 26. *Same as above for the time series of the NDIR instrument.*

CNR-ISAC ozone:

- Two data sets are available, from WDCGG (until 2010) and WDCRG (starting 2012).
- Both data sets look sound with respect to mole fraction, trend, seasonal and diurnal variation.

CNR-ISAC carbon monoxide:

- Two data sets are available, from the GC/RGD instrument (in operation 2007 – 2010) and the NDIR analyser (in operation since 2012)
- Both data sets look sound with respect to mole fraction, trend, seasonal and diurnal variation.
- CO (and CO_2, CH_4) from the Picarro instrument has not yet been submitted due to the short deployment period (since Dec 2017).

University of Urbino:

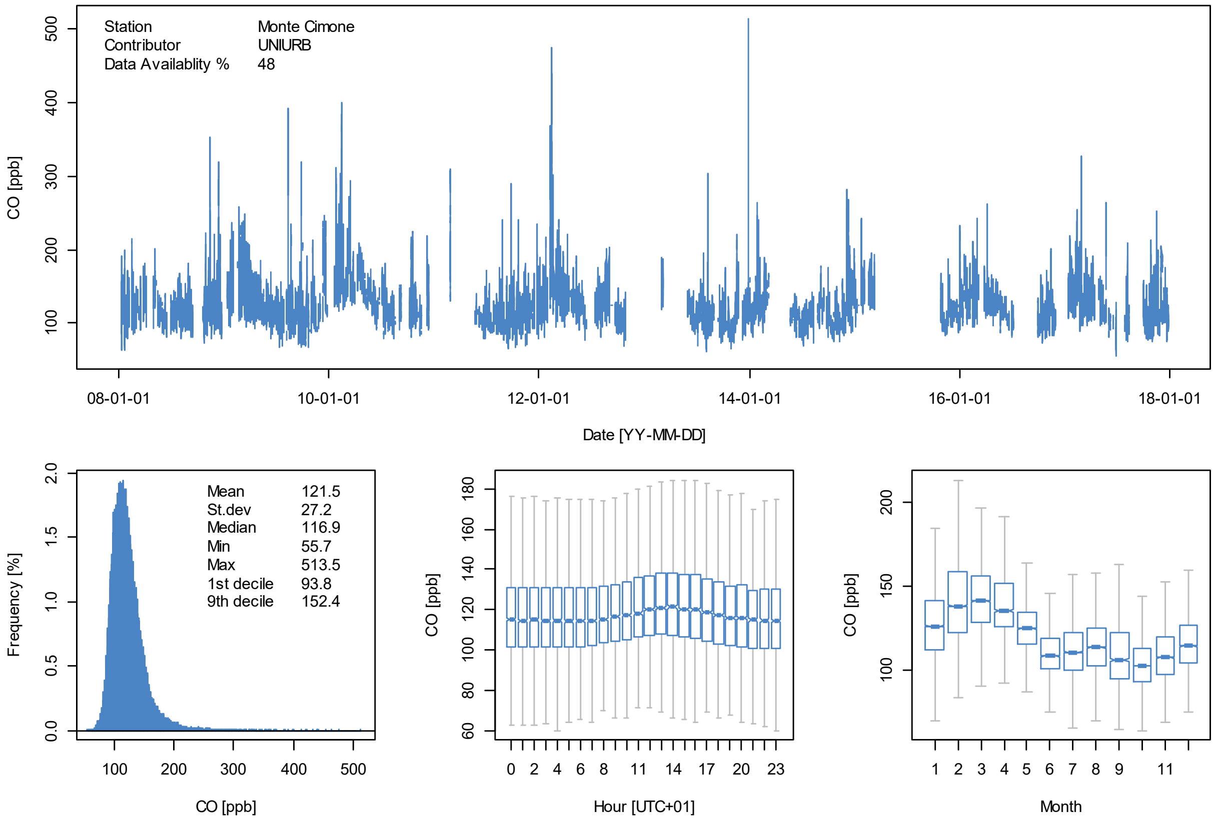

Figure 27. *University of Urbino CO data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

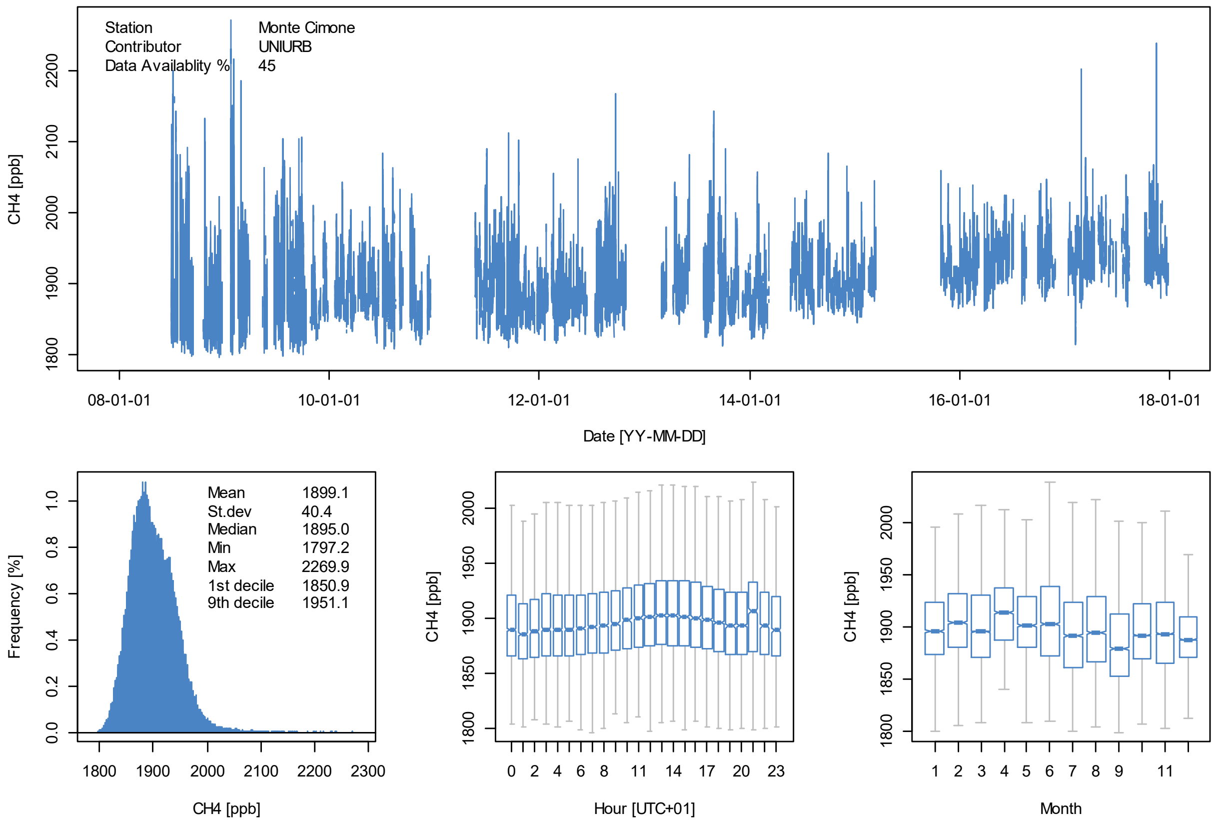

Figure 28. *Same as above for CH_4.*

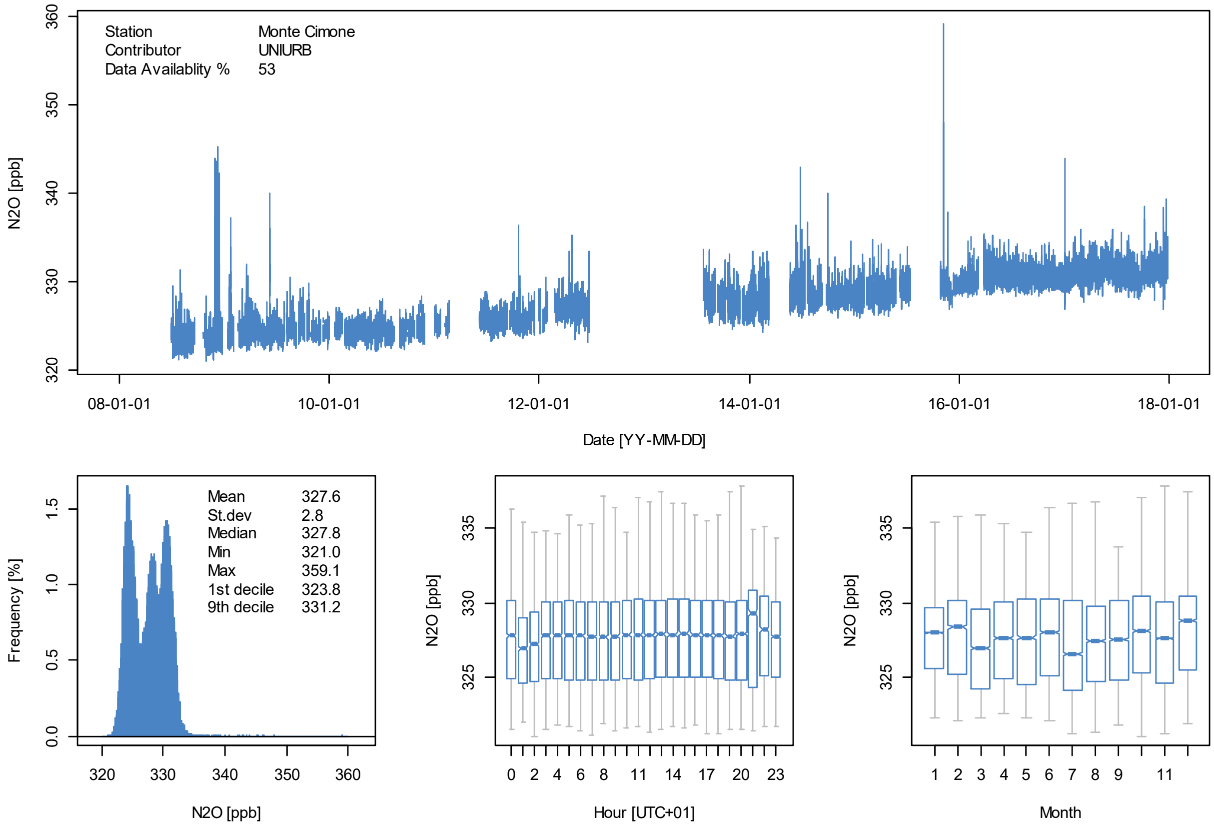

Figure 29. *Same as above for N_2O.*

University of Urbino carbon monoxide:

- Data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

University of Urbino methane:

- Variation at the start of the measurement period seems larger than towards the end.
- Otherwise, time series looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

University of Urbino nitrous oxide:

- Large noise probably due to the uncertainty of the GC/ECD system.
- A few outliers / invalid data points are probably still present in the current data set.
- Otherwise, time series looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

Surface Ozone Comparisons

All procedures were conducted 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 comparison of the analyser.

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa and CMN data acquisition systems.

Table 3. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #0810-153 (WCC-Empa)
Settings	BKG 0.0, COEF 1.004
Pressure readings (hPa)	Ambient 748.0 TS 785.4, (no adjustment was made)
CMN Station analyser (OA)	
Model, S/N	Thermo Scientific 49i #1225011092
Principle	UV absorption
Range	0-1 ppm
Settings	BKG 0.0 ppb, COEF 1.000 A correction based on the last calibration with the calibrator was applied: True value = 0.9906 * Thermo Scientific 49i +1.0455
Pressure readings (hPa)	Ambient 784.1; OA 783.9 (no adjustment was made)
CMN Station calibrator (OC)	
Model, S/N	Thermo Scientific 49i-PS #111851136
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.3 ppb, COEF 1.013
Pressure readings (hPa)	Ambient 784.1; OC 783.5 (no adjustment was made)

Results

Each ozone level was applied for 10 (analyser) and 15 (calibrator) minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser values.
The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary.

Table 4. *Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CMN ozone analyser (OA) Thermo Scientific 49i #1225011092 with the WCC-Empa travelling standard (TS).*

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2018-06-12 14:08	1	0	0.31	1.32	0.27	0.16	1.01	325.8
2018-06-12 14:18	1	90	89.91	89.09	0.09	0.48	-0.82	-0.9
2018-06-12 14:28	1	30	30.01	30.27	0.14	0.10	0.26	0.9
2018-06-12 14:38	1	60	60.00	59.93	0.11	0.34	-0.07	-0.1
2018-06-12 14:48	1	70	70.02	69.71	0.11	0.27	-0.31	-0.4
2018-06-12 14:58	1	40	40.03	40.08	0.07	0.43	0.05	0.1
2018-06-12 15:08	1	10	10.48	11.33	0.98	0.78	0.85	8.1
2018-06-12 15:18	1	20	20.04	20.36	0.35	0.32	0.32	1.6
2018-06-12 15:28	1	50	49.99	50.14	0.12	0.26	0.15	0.3
2018-06-12 15:38	1	80	80.02	79.54	0.17	0.45	-0.48	-0.6
2018-06-12 15:58	2	40	40.00	40.08	0.23	0.39	0.08	0.2
2018-06-12 16:08	2	100	100.01	99.31	0.11	0.24	-0.70	-0.7
2018-06-12 16:28	2	200	200.07	197.24	0.11	0.33	-2.83	-1.4
2018-06-12 16:38	2	30	30.00	30.29	0.16	0.26	0.29	1.0
2018-06-12 16:43	2	0	0.39	1.27	0.27	0.30	0.88	NA
2018-06-12 16:48	2	80	79.94	79.56	0.15	0.32	-0.38	-0.5
2018-06-12 16:53	2	60	60.01	59.78	0.09	0.30	-0.23	-0.4
2018-06-12 16:58	2	50	50.07	50.02	0.16	0.29	-0.05	-0.1
2018-06-12 17:08	2	150	149.94	148.35	0.12	0.47	-1.59	-1.1
2018-06-12 17:18	2	10	9.91	10.40	0.24	0.38	0.49	4.9
2018-06-12 17:48	3	0	0.42	1.22	0.21	0.13	0.80	NA
2018-06-12 17:58	3	90	90.05	89.31	0.10	0.42	-0.74	-0.8
2018-06-12 18:08	3	30	29.94	30.27	0.22	0.38	0.33	1.1
2018-06-12 18:18	3	60	60.02	59.57	0.09	0.13	-0.45	-0.7
2018-06-12 18:28	3	70	69.99	69.62	0.13	0.45	-0.37	-0.5
2018-06-12 18:38	3	40	40.05	40.00	0.09	0.40	-0.05	-0.1
2018-06-12 18:48	3	10	10.00	10.81	0.24	0.18	0.81	8.1
2018-06-12 18:58	3	20	20.03	20.64	0.09	0.35	0.61	3.0
2018-06-12 19:08	3	50	50.02	50.00	0.06	0.31	-0.02	0.0
2018-06-12 19:18	3	80	80.04	79.46	0.09	0.47	-0.58	-0.7
2018-06-12 19:38	4	40	40.06	39.88	0.11	0.14	-0.18	-0.4
2018-06-12 19:48	4	100	99.96	99.08	0.06	0.46	-0.88	-0.9
2018-06-12 20:08	4	200	200.03	197.52	0.03	0.43	-2.51	-1.3
2018-06-12 20:18	4	30	30.00	30.21	0.32	0.32	0.21	0.7
2018-06-12 20:23	4	0	0.28	1.11	0.26	0.11	0.83	NA
2018-06-12 20:28	4	80	80.10	79.36	0.10	0.49	-0.74	-0.9
2018-06-12 20:33	4	60	60.02	59.69	0.14	0.31	-0.33	-0.5
2018-06-12 20:38	4	50	50.02	50.06	0.23	0.32	0.04	0.1
2018-06-12 20:48	4	150	150.02	148.49	0.15	0.56	-1.53	-1.0
2018-06-12 20:58	4	10	9.98	10.77	0.16	0.19	0.79	7.9
2018-06-12 21:28	5	0	0.53	1.05	0.05	0.14	0.52	NA
2018-06-12 21:38	5	90	89.99	89.53	0.06	0.27	-0.46	-0.5
2018-06-12 21:48	5	30	29.91	30.37	0.20	0.31	0.46	1.5
2018-06-12 21:58	5	60	59.99	59.65	0.09	0.39	-0.34	-0.6
2018-06-12 22:08	5	70	69.98	69.61	0.15	0.08	-0.37	-0.5

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2018-06-12 22:18	5	40	40.02	40.06	0.10	0.29	0.04	0.1
2018-06-12 22:28	5	10	10.24	10.79	0.44	0.50	0.55	5.4
2018-06-12 22:38	5	20	20.02	20.64	0.10	0.20	0.62	3.1
2018-06-12 22:48	5	50	50.03	49.88	0.14	0.29	-0.15	-0.3
2018-06-12 22:58	5	80	80.00	79.38	0.10	0.25	-0.62	-0.8
2018-06-12 23:18	6	40	40.03	39.94	0.17	0.11	-0.09	-0.2
2018-06-12 23:28	6	100	100.02	99.10	0.11	0.47	-0.92	-0.9
2018-06-12 23:48	6	200	199.98	197.68	0.14	0.51	-2.30	-1.2
2018-06-12 23:58	6	30	30.03	30.11	0.12	0.42	0.08	0.3
2018-06-13 00:03	6	0	0.20	1.08	0.25	0.11	0.88	NA
2018-06-13 00:08	6	80	80.02	79.50	0.12	0.10	-0.52	-0.6
2018-06-13 00:13	6	60	60.03	59.86	0.13	0.38	-0.17	-0.3
2018-06-13 00:18	6	50	49.95	50.22	0.25	0.40	0.27	0.5
2018-06-13 00:28	6	150	150.00	148.66	0.05	0.55	-1.34	-0.9
2018-06-13 00:38	6	10	10.18	11.15	0.48	0.38	0.97	9.5
2018-06-13 01:08	7	0	0.52	1.03	0.25	0.19	0.51	NA
2018-06-13 01:18	7	90	90.03	89.53	0.16	0.23	-0.50	-0.6
2018-06-13 01:28	7	30	30.00	30.29	0.21	0.45	0.29	1.0
2018-06-13 01:38	7	60	59.98	59.99	0.17	0.19	0.01	0.0
2018-06-13 01:48	7	70	69.98	69.46	0.12	0.24	-0.52	-0.7
2018-06-13 01:58	7	40	40.03	40.25	0.20	0.43	0.22	0.5
2018-06-13 02:08	7	10	10.02	10.42	0.29	0.15	0.40	4.0
2018-06-13 02:18	7	20	20.73	20.80	0.97	0.84	0.07	0.3
2018-06-13 02:28	7	50	50.00	50.04	0.13	0.29	0.04	0.1
2018-06-13 02:38	7	80	80.02	79.50	0.11	0.21	-0.52	-0.6
2018-06-13 02:58	8	40	40.02	40.21	0.22	0.35	0.19	0.5
2018-06-13 03:08	8	100	100.05	99.19	0.16	0.23	-0.86	-0.9
2018-06-13 03:28	8	200	200.02	197.62	0.11	0.21	-2.40	-1.2
2018-06-13 03:38	8	30	30.05	30.39	0.12	0.42	0.34	1.1
2018-06-13 03:43	8	0	0.34	1.01	0.37	0.11	0.67	NA
2018-06-13 03:48	8	80	80.02	79.22	0.12	0.47	-0.80	-1.0
2018-06-13 03:53	8	60	60.05	59.71	0.15	0.42	-0.34	-0.6
2018-06-13 03:58	8	50	49.98	50.12	0.09	0.33	0.14	0.3
2018-06-13 04:08	8	150	150.03	148.45	0.16	0.41	-1.58	-1.1
2018-06-13 04:18	8	10	9.95	10.28	0.18	0.15	0.33	3.3
2018-06-13 04:48	9	0	0.12	1.03	0.23	0.19	0.91	NA
2018-06-13 04:58	9	90	89.99	89.25	0.11	0.31	-0.74	-0.8
2018-06-13 05:08	9	30	30.00	30.51	0.12	0.29	0.51	1.7
2018-06-13 05:18	9	60	59.98	59.71	0.16	0.18	-0.27	-0.5
2018-06-13 05:28	9	70	70.04	69.71	0.07	0.52	-0.33	-0.5
2018-06-13 05:38	9	40	40.00	40.33	0.11	0.21	0.33	0.8
2018-06-13 05:48	9	10	10.10	10.61	0.24	0.18	0.51	5.0
2018-06-13 05:58	9	20	20.00	20.74	0.14	0.18	0.74	3.7
2018-06-13 06:08	9	50	50.00	49.94	0.03	0.23	-0.06	-0.1
2018-06-13 06:18	9	80	79.98	79.42	0.12	0.52	-0.56	-0.7
2018-06-13 06:28	10	0	0.32	1.03	0.21	0.04	0.71	NA
2018-06-13 06:38	10	40	40.00	40.27	0.13	0.23	0.27	0.7
2018-06-13 06:48	10	100	100.04	99.21	0.11	0.16	-0.83	-0.8

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2018-06-13 06:58	10	60	60.04	59.77	0.08	0.35	-0.27	-0.4
2018-06-13 07:08	10	200	200.03	197.56	0.08	0.40	-2.47	-1.2
2018-06-13 07:18	10	30	29.98	30.27	0.03	0.16	0.29	1.0
2018-06-13 07:28	10	80	80.04	79.56	0.05	0.41	-0.48	-0.6
2018-06-13 07:38	10	50	50.06	50.28	0.13	0.34	0.22	0.4

Table 5. *Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CMN ozone calibrator (OC) Thermo Scientific 49i-PS #111851136 with the WCC-Empa travelling standard (TS).*

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2018-06-13 10:08	1	0	0.08	-0.04	0.26	0.07	-0.12	-150.0
2018-06-13 10:23	1	90	90.01	89.89	0.11	0.31	-0.12	-0.1
2018-06-13 10:38	1	30	30.02	29.86	0.09	0.15	-0.16	-0.5
2018-06-13 10:53	1	60	60.03	60.20	0.08	0.25	0.17	0.3
2018-06-13 11:08	1	70	70.04	69.71	0.13	0.16	-0.33	-0.5
2018-06-13 11:23	1	40	39.97	39.70	0.14	0.28	-0.27	-0.7
2018-06-13 11:38	1	10	10.55	10.61	0.53	0.69	0.06	0.6
2018-06-13 11:53	1	20	19.94	19.94	0.25	0.18	0.00	0.0
2018-06-13 12:08	1	50	49.97	49.88	0.07	0.05	-0.09	-0.2
2018-06-13 12:23	1	80	80.05	79.75	0.13	0.15	-0.30	-0.4
2018-06-13 12:53	2	40	40.04	40.15	0.19	0.18	0.11	0.3
2018-06-13 13:08	2	100	99.99	99.91	0.16	0.28	-0.08	-0.1
2018-06-13 13:38	2	200	200.06	199.90	0.07	0.30	-0.16	-0.1
2018-06-13 13:51	2	0	0.23	0.14	0.22	0.09	-0.09	NA
2018-06-13 13:53	2	30	29.98	30.15	0.22	0.27	0.17	0.6
2018-06-13 14:08	2	80	80.05	80.04	0.17	0.33	-0.01	0.0
2018-06-13 14:15	2	60	60.02	59.84	0.11	0.33	-0.18	-0.3
2018-06-13 14:23	2	50	50.03	50.19	0.09	0.14	0.16	0.3
2018-06-13 14:38	2	150	150.05	150.08	0.11	0.52	0.03	0.0
2018-06-13 14:53	2	10	10.38	10.48	0.41	0.27	0.10	1.0
2018-06-13 15:35	3	0	0.26	0.32	0.25	0.11	0.06	NA
2018-06-13 15:53	3	90	90.02	89.73	0.16	0.28	-0.29	-0.3
2018-06-13 16:08	3	30	30.01	29.85	0.29	0.31	-0.16	-0.5
2018-06-13 16:23	3	60	59.96	60.03	0.14	0.24	0.07	0.1
2018-06-13 16:38	3	70	70.06	69.99	0.10	0.27	-0.07	-0.1
2018-06-13 16:53	3	40	40.02	40.01	0.20	0.42	-0.01	0.0
2018-06-13 17:08	3	10	10.17	10.35	0.39	0.30	0.18	1.8
2018-06-13 17:23	3	20	19.96	19.94	0.03	0.09	-0.02	-0.1
2018-06-13 17:38	3	50	50.05	50.07	0.09	0.27	0.02	0.0
2018-06-13 17:53	3	80	80.00	80.09	0.12	0.24	0.09	0.1
2018-06-13 18:23	4	40	40.05	40.27	0.17	0.19	0.22	0.5
2018-06-13 18:38	4	100	99.98	100.01	0.03	0.24	0.03	0.0
2018-06-13 19:08	4	200	200.01	200.01	0.06	0.14	0.00	0.0
2018-06-13 19:21	4	0	0.16	0.33	0.18	0.10	0.17	NA
2018-06-13 19:23	4	30	30.02	30.04	0.22	0.19	0.02	0.1

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2018-06-13 19:38	4	80	80.00	80.19	0.10	0.17	0.19	0.2
2018-06-13 19:45	4	60	59.99	60.15	0.10	0.18	0.16	0.3
2018-06-13 19:53	4	50	49.89	50.18	0.15	0.33	0.29	0.6
2018-06-13 20:08	4	150	150.03	149.82	0.08	0.20	-0.21	-0.1
2018-06-13 20:23	4	10	10.20	10.39	0.22	0.31	0.19	1.9
2018-06-13 21:05	5	0	0.54	0.37	0.39	0.06	-0.17	NA
2018-06-13 21:23	5	90	89.99	90.26	0.09	0.27	0.27	0.3
2018-06-13 21:38	5	30	29.99	29.99	0.12	0.07	0.00	0.0
2018-06-13 21:53	5	60	59.97	59.92	0.14	0.41	-0.05	-0.1
2018-06-13 22:08	5	70	70.00	70.10	0.10	0.33	0.10	0.1
2018-06-13 22:23	5	40	40.00	40.03	0.15	0.29	0.03	0.1
2018-06-13 22:38	5	10	10.19	10.06	0.27	0.32	-0.13	-1.3
2018-06-13 22:53	5	20	20.04	20.26	0.30	0.23	0.22	1.1
2018-06-13 23:08	5	50	50.00	50.28	0.09	0.32	0.28	0.6
2018-06-13 23:22	5	80	80.00	79.90	0.10	0.16	-0.10	-0.1
2018-06-13 23:53	6	40	39.98	40.38	0.09	0.25	0.40	1.0
2018-06-14 00:08	6	100	99.91	100.18	0.19	0.38	0.27	0.3
2018-06-14 00:38	6	200	199.99	200.17	0.12	0.21	0.18	0.1
2018-06-14 00:39	6	0	-0.14	0.31	0.15	0.12	0.45	NA
2018-06-14 00:50	6	80	79.97	79.85	0.09	0.29	-0.12	-0.2
2018-06-14 00:53	6	30	30.04	30.30	0.13	0.26	0.26	0.9
2018-06-14 01:15	6	60	60.02	60.04	0.16	0.22	0.02	0.0
2018-06-14 01:23	6	50	50.07	50.28	0.22	0.40	0.21	0.4
2018-06-14 01:38	6	150	149.99	150.29	0.04	0.09	0.30	0.2
2018-06-14 01:53	6	10	10.47	10.60	0.51	0.36	0.13	1.2
2018-06-14 02:34	7	0	0.05	0.31	0.33	0.08	0.26	NA
2018-06-14 02:53	7	90	89.99	90.27	0.11	0.33	0.28	0.3
2018-06-14 03:08	7	30	30.01	30.23	0.13	0.17	0.22	0.7
2018-06-14 03:23	7	60	60.04	60.26	0.08	0.15	0.22	0.4
2018-06-14 03:38	7	70	69.96	70.19	0.08	0.18	0.23	0.3
2018-06-14 03:53	7	40	40.02	39.92	0.16	0.25	-0.10	-0.2
2018-06-14 04:08	7	10	10.06	9.97	0.39	0.25	-0.09	-0.9
2018-06-14 04:23	7	20	19.98	20.21	0.21	0.20	0.23	1.2
2018-06-14 04:38	7	50	49.98	50.45	0.04	0.19	0.47	0.9
2018-06-14 04:53	7	80	80.02	79.93	0.13	0.16	-0.09	-0.1
2018-06-14 05:23	8	40	39.98	40.11	0.10	0.21	0.13	0.3
2018-06-14 05:38	8	100	99.97	100.06	0.18	0.49	0.09	0.1
2018-06-14 06:08	8	200	200.00	200.12	0.08	0.15	0.12	0.1
2018-06-14 06:23	8	30	29.97	30.11	0.14	0.25	0.14	0.5
2018-06-14 06:30	8	0	0.09	0.30	0.20	0.11	0.21	NA
2018-06-14 06:38	8	80	79.93	79.76	0.14	0.31	-0.17	-0.2
2018-06-14 06:45	8	60	60.02	60.23	0.10	0.19	0.21	0.3
2018-06-14 06:53	8	50	49.95	50.31	0.17	0.42	0.36	0.7
2018-06-14 07:08	8	150	149.95	150.21	0.16	0.30	0.26	0.2
2018-06-14 07:23	8	10	10.09	10.17	0.11	0.12	0.08	0.8
2018-06-14 08:08	9	0	0.01	0.32	0.31	0.06	0.31	NA
2018-06-14 08:23	9	90	89.95	89.86	0.19	0.13	-0.09	-0.1
2018-06-14 08:38	9	30	30.02	30.26	0.15	0.34	0.24	0.8

Carbon Monoxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix.

Table 6 shows details of the experimental setup during the comparison of the transfer 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 shown in Table 7.

Table 6. Experimental details of CMN CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 22.	
Station Analyser CNR-ISAC	
Model, S/N	Picarro G2401 #2871-CFKADS2269.
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference
Backup Station Analyser CNR-ISAC	
Model, S/N	TEI 48C-TL #0517111935 (COEF 1.044, BKG automatically changing due to pressure compensation)
Principle	NDIR, gas filter correlation, zeroing every 15 min for 15 min.
Drying system	PERMAPURE MD-110144F4 Nafion drier in sample line
Station Analyser University of Urbino	
Model, S/N	Agilent 6890N (G1540N) #US10541006.
Principle	GC/FID with methaniser
Comparison procedures	
Connection	TEI48C-TL: WCC-Empa TS were measured using the sample inlet, including the Nafion drier with excess flow GC/FID and Picarro: WCC-Empa TS were connected to spare calibration gas ports.

Table 7 *Reference standards available at CMN. Calibration scales:* CH_4*-WMOX2004A,* N_2O*-WMOX2006A, CO-WMOX2014A,* CO_2*-WMOX2007.*

Cylinder ID	CH_4 (ppb)		N_2O (ppb)		CO (ppb)		CO_2 (ppb)		Type
CB09909	1886.42	0.10	326.1	0.11	130.19	0.82	NA	NA	LS Urbino
CB10047	1957.97	0.07	329.98	0.13	183.82	0.82	NA	NA	LS Urbino
CB10081	1926.93	0.33	327.17	0.12	163.06	0.80	NA	NA	LS Urbino
CB09706	1975.49	0.08	332.89	0.12	226.69	0.85	NA	NA	LS Urbino
JU-015	1930.64	0.15	328.40	0.28	135.62	2.60	NA	NA	WS Urbino
D550030	1799.67	0.16	324.61	0.02	62.01	0.01	379.40	0.01	LS ICOS
D550031	1899.32	0.11	328.47	0.03	100.38	0.02	399.68	0.01	LS ICOS
D550032	1998.16	0.14	334.74	0.03	175.02	0.02	419.59	0.01	LS ICOS

D550033	2096.13	0.16	339.89	0.03	250.09	0.03	454.70	0.01	LS ICOS
D550034	2098.94	0.18	339.93	0.03	250.38	0.03	453.99	0.01	Target ICOS
D550035	1899.71	0.13	329.07	0.03	99.23	0.02	399.55	0.01	Target ICOS
D550036	1899.81	0.14	329.20	0.03	99.79	0.02	403.70	0.01	Target ICOS
CB08939	NA	NA	NA	NA	NA	NA	392.13	0.00	LS CAMM
CB09045	NA	NA	NA	NA	NA	NA	399.50	0.01	LS CAMM
CC339491	NA	NA	NA	NA	NA	NA	409.33	0.01	LS CAMM
CC327204	1681.15	0.03	NA	NA	NA	NA	NA	NA	LS CAMM
CC339483	1824.92	0.20	NA	NA	NA	NA	NA	NA	LS CAMM
CC339501	1897.76	0.11	NA	NA	NA	NA	NA	NA	LS CAMM

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 8. *CO aggregates computed from single analysis (mean and standard deviation of 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 (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-12 15:27:00)	171204_FA02769	138.2	0.9	138.4	0.6	2	0.3	0.2
(18-06-12 15:47:00)	140514_FB03899	256.0	0.8	254.7	0.5	3	-1.3	-0.5
(18-06-12 16:27:00)	171123_FA02789	91.0	1.1	91.8	0.3	3	0.9	1.0
(18-06-12 19:45:00)	160622_FB03911	306.9	0.8	305.1	0.3	2	-1.8	-0.6
(18-06-12 20:05:00)	160825_FB03887	192.0	0.9	191.7	0.2	3	-0.4	-0.2
(18-06-12 20:25:00)	130819_FB03865	164.7	0.9	164.9	0.3	2	0.2	0.1
(18-06-14 08:19:00)	160926_FB03367	88.3	1.2	89.0	0.5	3	0.7	0.8
(18-06-17 08:19:00)	150601_FA02466	694.7	0.4	688.5	0.3	3	-6.2	-0.9
(18-06-20 08:19:00)	140514_FB03918	185.3	0.7	184.9	0.2	3	-0.4	-0.2
(18-06-23 08:19:00)	140514_FB03910	202.1	0.6	201.0	0.2	3	-1.1	-0.6
(18-06-26 08:19:00)	160825_FB03382	173.0	0.9	172.4	0.1	3	-0.6	-0.4
(18-06-29 08:19:00)	171204_FA01469	102.4	0.7	103.2	0.2	3	0.9	0.8

Table 9. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the TEI 48C-TL #0517111935instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-14 10:10:15)	171204_FA01469	102.4	0.7	120.6	4.2	24	18.2	17.8
(18-06-14 11:37:14)	130819_FB03865	164.7	0.9	177.5	4.8	25	12.8	7.8
(18-06-14 12:37:35)	160926_FB03367	88.3	1.2	103.6	6.4	24	15.3	17.4
(18-06-14 13:38:00)	140514_FB03910	202.1	0.6	217.1	4.3	26	15.0	7.4

Table 10. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Agilent 6890N #US10541006 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	**TS Cylinder**	**TS (ppb)**	**sdTS (ppb)**	**AL (ppb)**	**sdAL (ppb)**	**N**	**AL-TS (ppb)**	**AL-TS (%)**
(18-06-12 22:28:00)	140514_FB03899	256.0	0.8	253.3	0.9	6	-2.7	-1.0
(18-06-13 01:53:00)	171123_FA02789	91.0	1.1	90.4	1.1	6	-0.6	-0.7
(18-06-13 04:58:00)	171204_FA02769	138.2	0.9	137.1	1.0	6	-1.0	-0.8
(18-06-13 07:58:00)	130819_FB03865	164.7	0.9	161.6	1.5	6	-3.1	-1.9
(18-06-13 10:58:00)	140514_FB03910	202.1	0.6	200.6	2.1	6	-1.6	-0.8
(18-06-13 14:28:00)	160825_FB03887	192.0	0.9	189.6	2.7	8	-2.4	-1.3
(18-06-13 19:40:51)	171204_FA01469	102.4	0.7	102.4	1.0	7	0.0	0.0
(18-06-13 23:43:00)	160622_FB03911	306.9	0.8	305.2	1.8	8	-1.6	-0.5
(18-06-14 03:13:00)	140514_FB03918	185.3	0.7	183.6	0.6	6	-1.7	-0.9
(18-06-14 06:22:00)	160926_FB03367	88.3	1.2	87.3	0.6	5	-1.0	-1.1

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 7, and Table 11 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 11. *Experimental details of CMN CH_4 comparison.*

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 22.	
Station Analyser CNR-ISAC	
Model, S/N	Picarro G2401 #2871-CFKADS2269.
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference using a individual and instrument specific correction function.
Station Analyser CAMM	
Model, S/N	Picarro G2301 #2017-CFADS2374.
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference with Picarro built in correction function.
Station Analyser University of Urbino	
Model, S/N	Agilent 6890N (G1540N) #US10541006.
Principle	GC/FID with methaniser
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

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 12. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CAMM Picarro G2301 #2017-CFADS2374 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-12 12:11:20)	160825_FB03887	2027.27	0.04	2026.03	0.21	3	-1.24	-0.06
(18-06-12 12:14:40)	160622_FB03911	2352.60	0.11	2349.23	0.12	3	-3.37	-0.14
(18-06-12 12:18:20)	130819_FB03865	1890.47	0.11	1890.27	0.12	3	-0.20	-0.01
(18-06-12 15:51:40)	171204_FA01469	1933.25	0.07	1932.63	0.21	3	-0.62	-0.03
(18-06-12 15:55:00)	160825_FB03382	1918.59	0.04	1918.40	0.20	3	-0.19	-0.01
(18-06-12 15:58:20)	150601_FA02466	1900.50	0.08	1900.33	0.23	3	-0.17	-0.01
(18-06-13 08:50:40)	140514_FB03899	1974.67	0.07	1973.33	0.21	3	-1.34	-0.07
(18-06-13 08:54:00)	171123_FA02789	1718.76	0.10	1719.20	0.10	3	0.44	0.03
(18-06-13 08:57:20)	171204_FA02769	1956.06	0.03	1955.00	0.20	3	-1.06	-0.05

Table 13. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CNR Picarro G2401 #2871-CFKADS2269 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-12 20:25:00)	130819_FB03865	1890.47	0.11	1890.72	0.03	2	0.25	0.01
(18-06-12 15:47:00)	140514_FB03899	1974.67	0.07	1974.69	0.03	3	0.02	0.00
(18-06-12 19:45:00)	160622_FB03911	2352.60	0.11	2352.05	0.01	2	-0.55	-0.02
(18-06-12 20:05:00)	160825_FB03887	2027.27	0.04	2027.25	0.03	3	-0.02	0.00
(18-06-12 16:27:00)	171123_FA02789	1718.76	0.10	1719.06	0.03	3	0.30	0.02
(18-06-12 15:27:00)	171204_FA02769	1956.06	0.03	1956.09	0.01	2	0.03	0.00
(18-06-13 09:39:00)	160825_FB03382	1918.59	0.04	1918.74	0.02	3	0.15	0.01
(18-06-13 15:00:00)	140514_FB03918	1971.43	0.03	1971.41	0.01	3	-0.02	0.00
(18-06-13 14:40:00)	140514_FB03910	2001.80	0.05	2001.83	0.03	3	0.03	0.00
(18-06-13 08:59:00)	150601_FA02466	1900.50	0.08	1900.60	0.01	3	0.10	0.01
(18-06-13 15:20:00)	160926_FB03367	1855.15	0.07	1855.31	0.01	3	0.16	0.01
(18-06-13 09:19:00)	171204_FA01469	1933.25	0.07	1933.22	0.03	3	-0.03	0.00

Table 14. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the University of Urbino Agilent 6890N #US10541006 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-12 22:31:00)	140514_FB03899	1974.67	0.07	1974.21	1.27	5	-0.46	-0.02
(18-06-13 01:43:00)	171123_FA02789	1718.76	0.10	1717.43	1.15	7	-1.33	-0.08
(18-06-13 04:58:00)	171204_FA02769	1956.06	0.03	1955.23	1.90	6	-0.83	-0.04
(18-06-13 07:43:00)	130819_FB03865	1890.47	0.11	1889.66	1.18	5	-0.81	-0.04
(18-06-13 11:13:00)	140514_FB03910	2001.80	0.05	2000.10	1.46	5	-1.70	-0.08

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-13 14:28:00)	160825_FB03887	2027.27	0.04	2027.58	1.86	8	0.31	0.02
(18-06-13 19:36:34)	171204_FA01469	1933.25	0.07	1932.61	1.98	7	-0.64	-0.03
(18-06-13 23:43:00)	160622_FB03911	2352.60	0.11	2351.71	1.69	8	-0.89	-0.04
(18-06-14 03:13:00)	140514_FB03918	1971.43	0.03	1970.06	1.27	6	-1.37	-0.07
(18-06-14 06:13:00)	160926_FB03367	1855.15	0.07	1855.23	1.92	6	0.08	0.00

Carbon Dioxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 7, and Table 15 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 15. *Experimental details of CMN CO_2 comparison.*

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 22.	
Station Analyser CNR-ISAC	
Model, S/N	Picarro G2401 #2871-CFKADS2269.
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference using a individual and instrument specific correction function.
Station Analyser CAMM	
Model, S/N	Picarro G2301 #2017-CFADS2374.
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference with Picarro built in correction function.
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 16. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the CAMM Picarro G2301 #2017-CFADS2374 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(18-06-12 12:11:20)	160825_FB03887	457.62	0.03	457.42	0.04	3	-0.20	-0.04
(18-06-12 12:14:40)	160622_FB03911	427.06	0.02	426.96	0.02	3	-0.10	-0.02
(18-06-12 12:18:20)	130819_FB03865	387.09	0.03	387.10	0.01	3	0.01	0.00
(18-06-12 15:51:40)	171204_FA01469	406.84	0.03	406.78	0.02	3	-0.06	-0.01
(18-06-12 15:55:00)	160825_FB03382	412.29	0.01	412.26	0.02	3	-0.03	-0.01
(18-06-12 15:58:20)	150601_FA02466	430.97	0.02	430.86	0.02	3	-0.11	-0.03
(18-06-13 08:50:40)	140514_FB03899	404.96	0.02	404.87	0.03	3	-0.09	-0.02
(18-06-13 08:54:00)	171123_FA02789	391.57	0.05	391.52	0.01	3	-0.05	-0.01
(18-06-13 08:57:20)	171204_FA02769	420.83	0.02	420.72	0.02	3	-0.11	-0.03

Table 17. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CNR Picarro G2401 #2871-CFKADS2269 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).*

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(18-06-12 15:27:00)	171204_FA02769	420.83	0.02	420.76	0.01	2	-0.07	-0.02
(18-06-12 15:47:00)	140514_FB03899	404.96	0.02	404.90	0.01	3	-0.06	-0.01
(18-06-12 16:27:00)	171123_FA02789	391.57	0.05	391.51	0.01	3	-0.06	-0.02
(18-06-12 19:45:00)	160622_FB03911	427.06	0.02	427.02	0.01	2	-0.04	-0.01
(18-06-12 20:05:00)	160825_FB03887	457.62	0.03	457.53	0.01	3	-0.09	-0.02
(18-06-12 20:25:00)	130819_FB03865	387.09	0.03	387.10	0.01	2	0.01	0.00
(18-06-14 08:19:00)	160926_FB03367	412.70	0.01	412.67	0.01	3	-0.03	-0.01
(18-06-17 08:19:00)	140514_FB03918	400.83	0.03	400.84	0.01	3	0.01	0.00
(18-06-20 08:19:00)	140514_FB03910	404.36	0.02	404.34	0.01	3	-0.02	0.00
(18-06-23 08:19:00)	160825_FB03382	412.29	0.01	412.28	0.01	3	-0.01	0.00
(18-06-26 08:19:00)	171204_FA01469	406.84	0.03	406.81	0.01	3	-0.03	-0.01
(18-06-29 08:19:00)	150601_FA02466	430.97	0.02	430.90	0.01	3	-0.07	-0.02

Nitrous Oxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 7, and Table 15 shows details of the experimental setup during the comparison of the transfer standards and the station analyser.

Table 18. *Experimental details of CMN N_2O comparison.*

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 22.	
Station Analyser University of Urbino	
Model, S/N	Agilent 6890N (G1540N) #US10541006.
Principle	GC/ECD
Comparison procedures	
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 Table.

Table 19. *N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the GC/ECD instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(18-06-12 22:28:00)	140514_FB03899	328.57	0.04	328.69	0.45	6	0.12	0.04
(18-06-13 01:48:00)	171123_FA02789	316.44	0.06	315.92	0.39	6	-0.52	-0.16
(18-06-13 04:58:00)	171204_FA02769	336.55	0.06	336.56	0.99	6	0.01	0.00
(18-06-13 07:58:00)	130819_FB03865	319.92	0.03	320.51	0.18	6	0.59	0.18
(18-06-13 10:58:00)	140514_FB03910	328.37	0.05	328.28	0.81	6	-0.09	-0.03
(18-06-13 14:28:00)	160825_FB03887	331.74	0.04	331.68	1.39	8	-0.06	-0.02
(18-06-13 19:43:00)	171204_FA01469	343.01	0.06	343.26	1.25	8	0.25	0.07
(18-06-13 23:36:34)	160622_FB03911	330.28	0.02	331.13	0.78	7	0.85	0.26
(18-06-14 03:13:00)	140514_FB03918	322.59	0.05	323.14	0.70	6	0.55	0.17
(18-06-14 06:13:00)	160926_FB03367	339.67	0.06	338.74	0.97	6	-0.93	-0.27

WCC-Empa Traveling Standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the Standard Reference Photometer before and after the audit. The following instruments were used:

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

WCC-Empa TS: Thermo Scientific 49C-PS #0810-153, BKG 0.0, COEF 1.004

Zero air source: Pressurized air - Dryer – Breitfuss zero air generator – Purafil – charcoal – outlet filter

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 20. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 30). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (ppb)} = ([TS] - 0.01 \text{ ppb}) / 0.9993 \quad (6a)$$

$$u_{TS} \text{ (ppb)} = \text{sqrt}((0.43 \text{ ppb})^2 + (0.0034 * X)^2) \quad (6b)$$

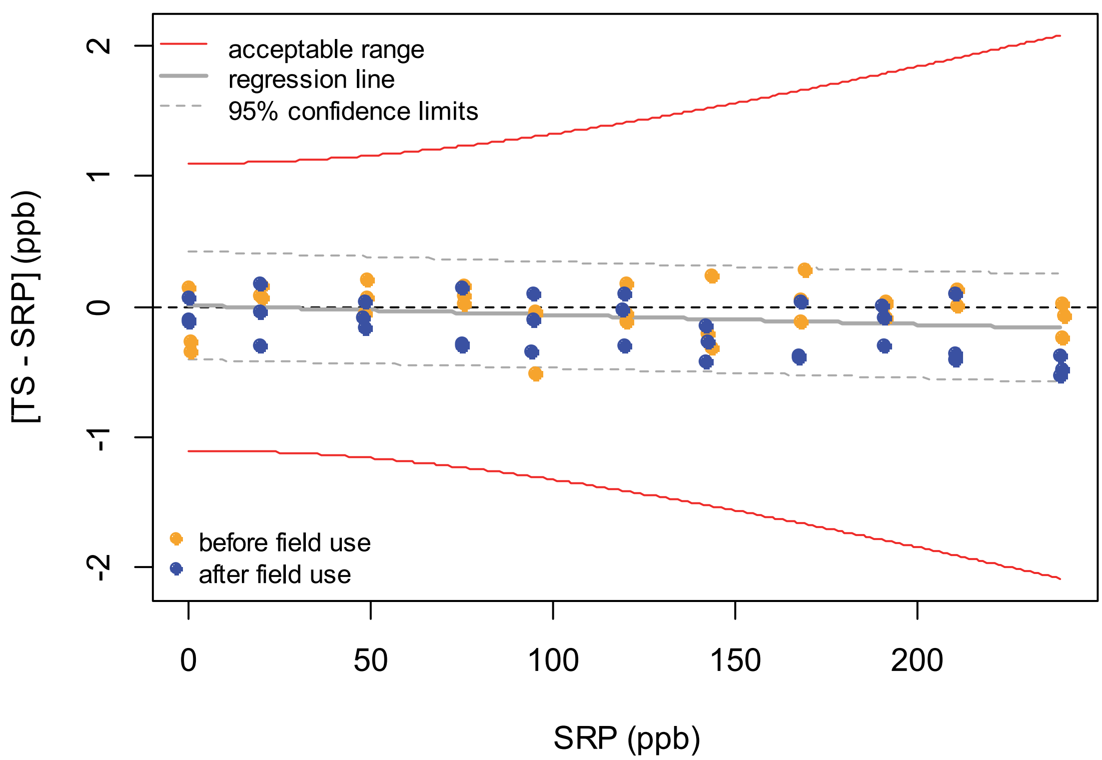

Figure 30. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 20. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2018-03-29	1	20	19.67	0.25	19.75	0.15
2018-03-29	1	170	167.79	0.36	167.69	0.25
2018-03-29	1	120	119.84	0.30	119.73	0.23
2018-03-29	1	0	0.20	0.16	-0.14	0.14
2018-03-29	1	145	143.46	0.36	143.15	0.18
2018-03-29	1	75	75.17	0.18	75.19	0.26
2018-03-29	1	210	210.74	0.22	210.87	0.25
2018-03-29	1	95	95.23	0.19	94.72	0.58
2018-03-29	1	190	191.34	0.19	191.27	0.24
2018-03-29	1	50	48.48	0.20	48.43	0.28
2018-03-29	1	240	239.86	0.23	239.62	0.30
2018-03-29	2	170	167.83	0.25	167.89	0.23
2018-03-29	2	0	0.17	0.35	-0.10	0.12
2018-03-29	2	145	143.36	0.34	143.60	0.18
2018-03-29	2	50	48.52	0.20	48.72	0.31
2018-03-29	2	95	95.01	0.23	94.95	0.26
2018-03-29	2	20	19.88	0.17	19.95	0.22
2018-03-29	2	210	210.73	0.22	210.74	0.20
2018-03-29	2	120	119.80	0.30	119.98	0.16
2018-03-29	2	190	191.29	0.31	191.32	0.20
2018-03-29	2	75	75.15	0.21	75.24	0.30
2018-03-29	2	240	239.78	0.19	239.81	0.26
2018-03-29	3	95	95.11	0.27	95.08	0.18
2018-03-29	3	75	75.39	0.23	75.56	0.18
2018-03-29	3	210	210.64	0.20	210.77	0.23
2018-03-29	3	0	0.00	0.17	0.15	0.10
2018-03-29	3	170	168.81	0.51	169.11	0.45
2018-03-29	3	120	120.20	0.24	120.14	0.27
2018-03-29	3	20	19.77	0.10	19.94	0.10
2018-03-29	3	50	48.50	0.27	48.58	0.33
2018-03-29	3	190	191.12	0.12	191.15	0.30
2018-03-29	3	140	142.50	0.33	142.30	0.13
2018-03-29	3	240	239.97	0.24	239.91	0.34
2018-09-05	4	165	167.24	0.26	166.87	0.38
2018-09-05	4	0	-0.23	0.20	-0.33	0.22
2018-09-05	4	140	142.21	0.29	141.94	0.25
2018-09-05	4	50	47.99	0.16	48.03	0.20
2018-09-05	4	95	94.14	0.21	93.79	0.26
2018-09-05	4	20	19.45	0.21	19.63	0.36
2018-09-05	4	210	210.04	0.27	209.68	0.38
2018-09-05	4	120	119.31	0.28	119.02	0.13
2018-09-05	4	190	190.56	0.17	190.27	0.17
2018-09-05	4	75	74.68	0.21	74.40	0.19
2018-09-05	4	240	239.21	0.18	238.84	0.31
2018-09-05	5	95	94.51	0.32	94.41	0.11
2018-09-05	5	75	74.81	0.26	74.52	0.19
2018-09-05	5	210	210.04	0.17	210.14	0.26
2018-09-05	5	0	-0.03	0.24	0.04	0.18
2018-09-05	5	170	167.97	0.31	168.02	0.41
2018-09-05	5	120	119.14	0.19	119.13	0.20

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2018-09-05	5	20	19.63	0.17	19.32	0.28
2018-09-05	5	50	48.03	0.27	47.88	0.22
2018-09-05	5	190	189.87	0.14	189.88	0.30
2018-09-05	5	140	141.93	0.23	141.51	0.38
2018-09-05	5	240	239.37	0.20	238.89	0.19
2018-09-05	6	75	74.64	0.21	74.79	0.24
2018-09-05	6	0	-0.04	0.23	-0.16	0.16
2018-09-05	6	210	210.16	0.23	209.75	0.28
2018-09-05	6	120	119.27	0.34	119.37	0.18
2018-09-05	6	165	167.27	0.19	166.89	0.24
2018-09-05	6	190	190.57	0.22	190.49	0.24
2018-09-05	6	20	19.49	0.21	19.46	0.13
2018-09-05	6	50	47.91	0.24	47.83	0.17
2018-09-05	6	95	94.31	0.21	94.41	0.17
2018-09-05	6	140	141.94	0.14	141.79	0.19
2018-09-05	6	240	239.29	0.36	238.77	0.21

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide and Methane. NOAA/ESRL 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 by way of traveling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-X2014A scale (Novelli et al., 2003)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004A scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

More information about the NOAA/ESRL calibration scales can be found on the GMD website (www.esrl.noaa.gov/gmd/ccl). The scales were transferred to the TS using the following instruments:

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser). CO_2 and CH_4: Picarro G1301 (Cavity Ring Down Spectroscopy).

Table 21 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 22, and Figures 31 and 32shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS.

Table 21. *NOAA/ESRL laboratory standards at WCC-Empa.*

Cylinder	CO (ppb)	CH_4 (ppb)	N_2O (ppb)	CO_2 (ppm)
CC339478[#]	463.76	2485.25	357.19	484.39
CB11499[#]	141.03	1933.77	329.15	407.33
CB11485[#]	110.88	1844.78	328.46	394.30
CA02789*	448.67	2097.48	342.18	495.85

[#] used for calibrations of CO_2, CH_4 and N_2O
* used for calibrations of CO

Table 22. *Calibration summary of the WCC-Empa travelling standards.*

TS	Pressure (psi)	CH_4 (ppb)	sdCH_4 (ppb)	CO_2 (ppm)	sdCO_2 (ppm)	N_2O (ppb)	sdN_2O (ppb)	CO (ppb)	sdCO (ppb)
130819_FB03865	600	1890.47	0.11	387.09	0.03	319.92	0.03	164.66	0.94
140514_FB03899	900	1974.67	0.07	404.96	0.02	328.57	0.04	255.99	0.80
140514_FB03910	1700	2001.80	0.05	404.36	0.02	328.37	0.05	202.13	0.64
140514_FB03918	1500	1971.43	0.03	400.83	0.03	322.59	0.05	185.29	0.74
150601_FA02466	820	1900.50	0.08	430.97	0.02	326.50	0.13	694.69	0.35
160622_FB03911	1210	2352.60	0.11	427.06	0.02	330.28	0.02	306.87	0.84
160825_FB03382	1300	1918.59	0.04	412.29	0.01	318.23	0.04	173.02	0.88
160825_FB03887	730	2027.27	0.04	457.62	0.03	331.74	0.04	192.03	0.91
160926_FB03367	700	1855.15	0.07	412.70	0.01	339.67	0.06	88.28	1.22
171123_FA02789	1600	1718.76	0.10	391.57	0.05	316.44	0.06	90.97	1.11
171204_FA01469	1710	1933.25	0.07	406.84	0.03	343.01	0.06	102.36	0.70
171204_FA02769	1610	1956.06	0.03	420.83	0.02	336.55	0.06	138.16	0.86

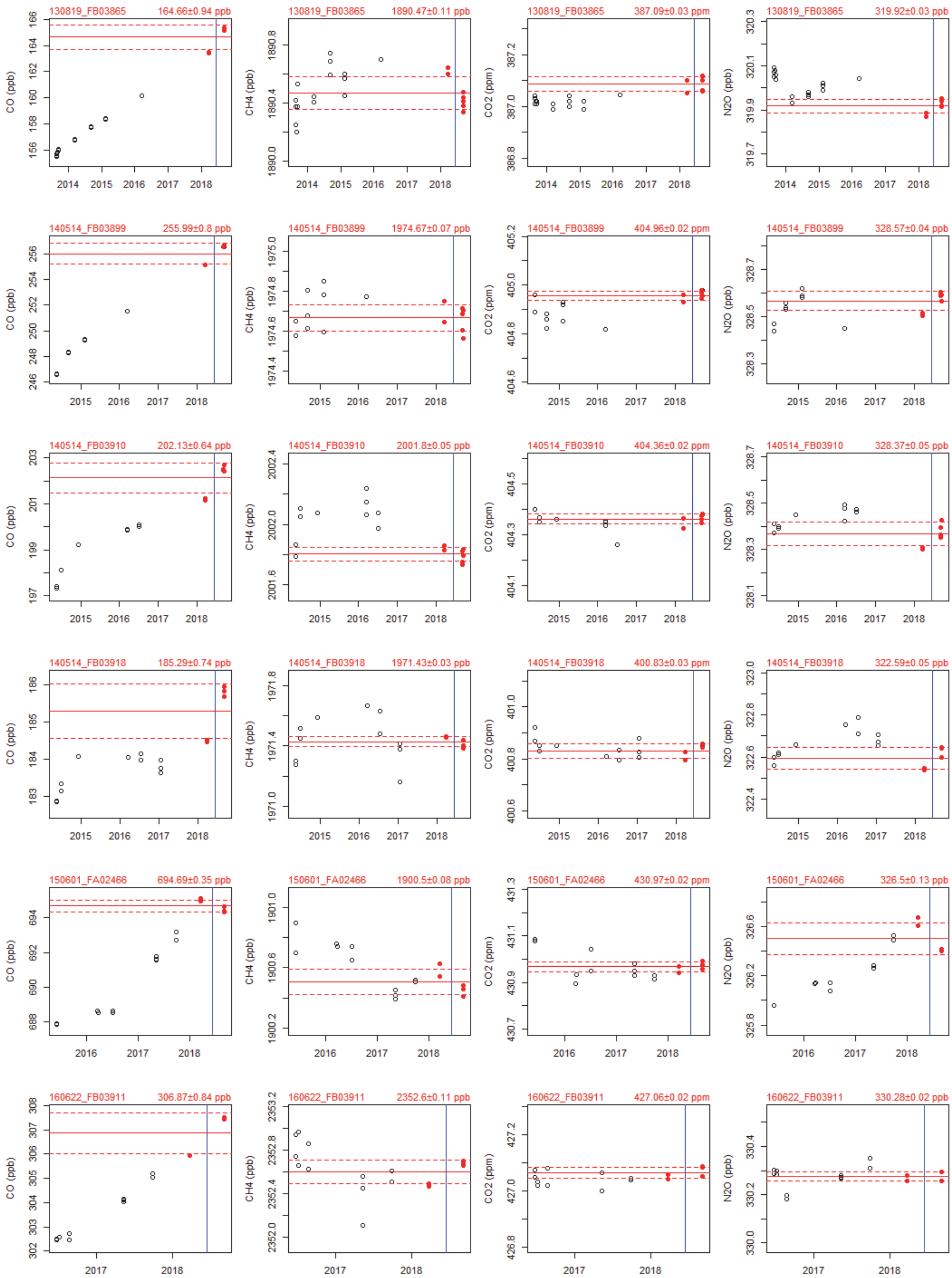

Figure 31. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

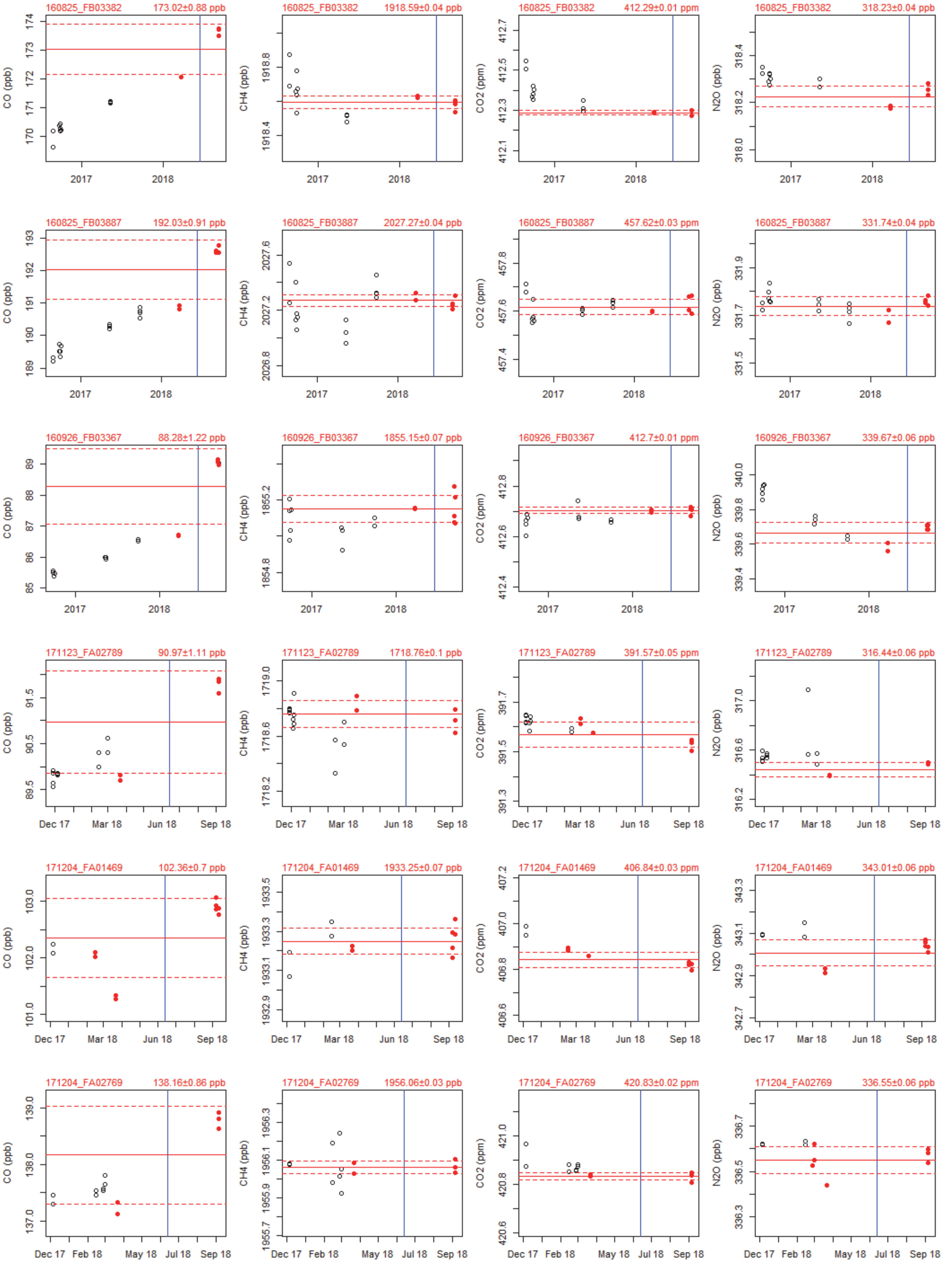

Figure 32. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH_4 and CO_2, the Picarro G2401 SN #617-CFKADS2001 was calibrated every 1809 min using one WCC-Empa TS as a working standard, and two TS were used as targets. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 2 ppb for CH_4 and 0.1 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

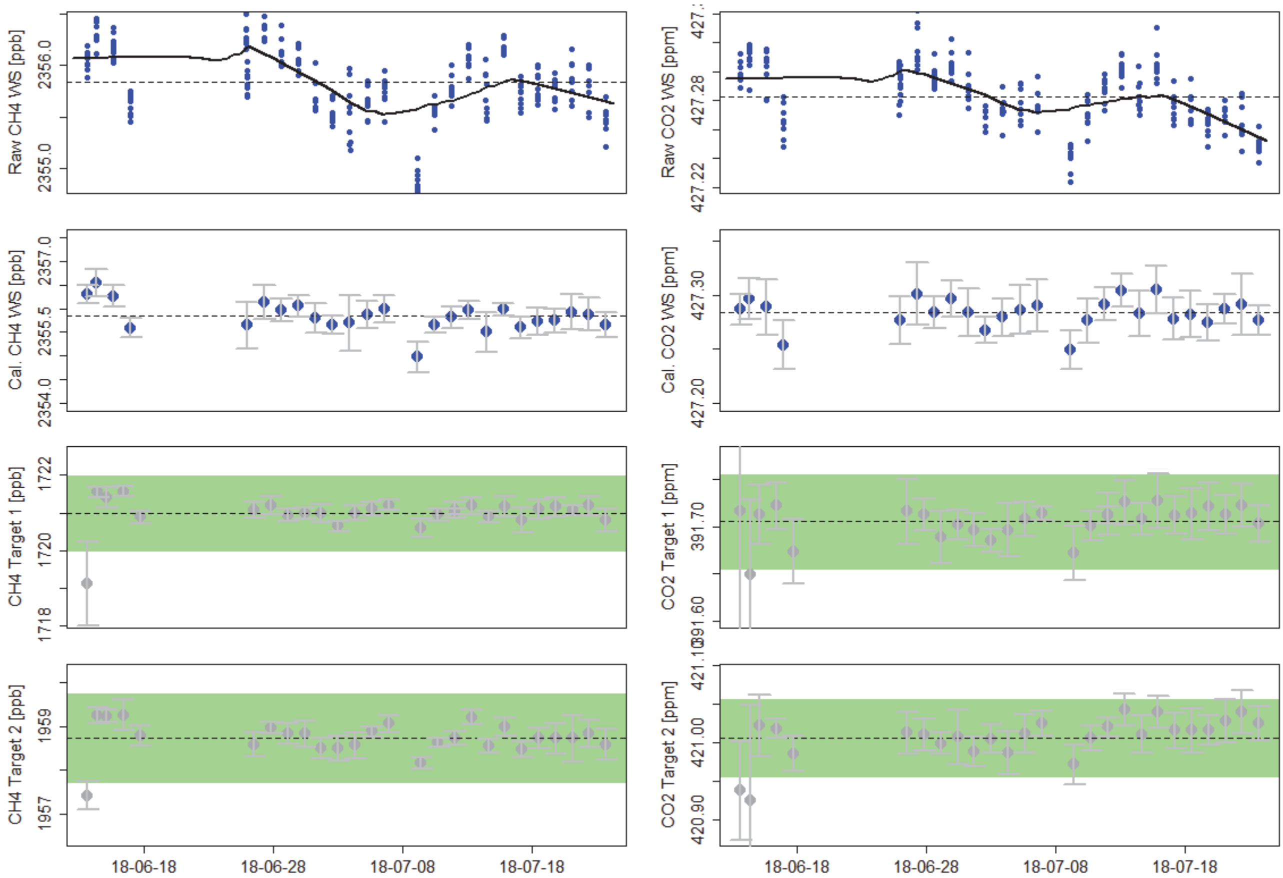

Figure 33. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 1805 min three WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

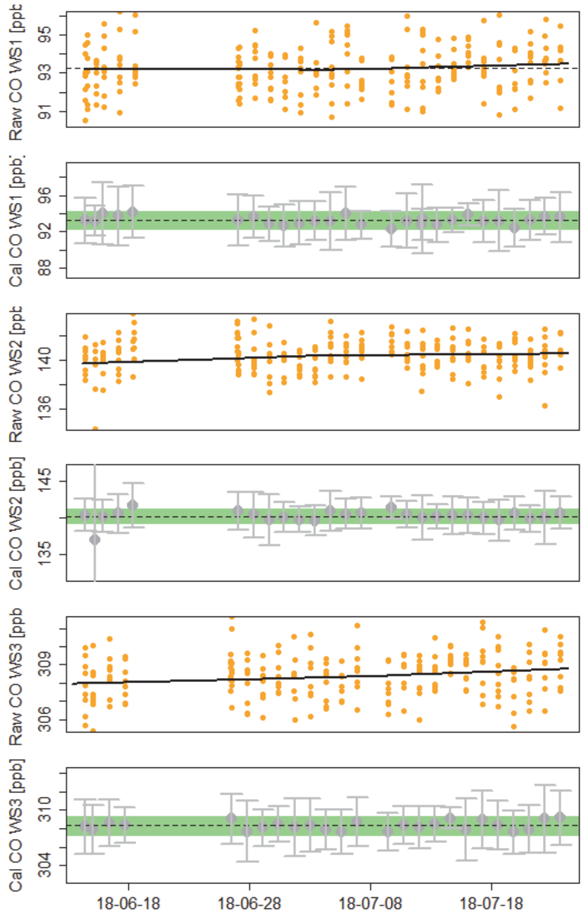

Figure 34. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

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LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
CAMM	Centro Aeronautica Militare di Montagna
COEF	Coefficient
CMN	Mt. Cimone GAW Station
CNR	Italian National Research Council (CNR)
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
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
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
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