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

REGIONAL GAW STATION JEJU GOSAN REPULIC OF KOREA JUNE 2022

WCC-Empa Report 22/1

Submitted to the World Meteorological Organization by

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WCC-Empa Report 22/1

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 2nd system and performance audit by WCC-Empa[1] at the regional GAW station Jeju Gosan (JGS) was conducted from 29 June - 1 July 2022 in agreement with the WMO/GAW quality assurance system (WMO, 2017). The audit report of the first audit is available from the WCC-Empa webpage (www.empa.ch/gaw).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Dr Haeyoung Lee	NIMS, scientist, measurement leader of greenhouse gases
Ms Sumin Kim	NIMS, scientist, measurement leader of reactive gases
Ms Miyoung Ko	NIMS, station operator
Ms Soojeong Lee	NIMS, scientist, central calibration laboratory and WCC for SF_6 operator

This report summarises the assessment of the Jeju Gosan 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 station manager and measurement leaders of the Jeju Gosan GAW station, the national focal point for GAW of the Republic of Korea, and the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and 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 Jeju Gosan GAW station (JGS) is operated by the National Institute of Meteorological Sciences (NIMS), which is part of the Korea Meteorological Administration (KMA). The station is visited during weekdays by approximately 5 - 10 scientists, technical and administrational staff. The operation and maintenance of the station is well organized, with clear assignments of responsibilities.

Station Location and Access

The GAW activities on Jeju Island are carried out on two stations, namely at the Jeju Gosan (JGS) (33.30005°N, 126.2057°E, 52 m a.s.l), and at the Gosan (GSN) (33.29382°N, 126.16283°E, 71 m a.s.l) GAW stations. The stations are approximately 4.1 km apart. The measurement of greenhouse gases (GHGs) and reactive gases have always been made at the GSN station. However, these measurements are reported as being made at JGS in GAWSIS, which is not correct. The current audit was made at the GSN site where all the instrumentation is installed.

Recommendation 1 (*, critical, 2023)**
Measurements are discontinued at the JGS site for all parameters, and the station should be closed in the GAWSIS metadata repository. All GHG and reactive gases measurements need to be assigned to the GSN station. All, also past GHG data, was measured at GSN. The location information given in the metadata from WDCGG is also wrong, and refers to JGS instead of GSN. This also needs to be corrected.

[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 Science and Technology (Empa). The mandate is to conduct system and performance audits at Global GAW stations based on mutual agreement.

Gosan is located on the south-western tip of Jeju Island (Republic of Korea), facing the East China Sea to the south. The station rests at the top of a cliff, about 100 km south of the Korean peninsula, 500 km northeast of Shanghai, China, and 250 km west of Kyushu, Japan. Jeju Island is regarded as one of the cleanest areas in South Korea, with low emissions of air pollutants. This unique location makes JGS one of the most important sites for monitoring the outflows from the Asian continent.

More information on JGS and GSN is available from GAWSIS (https://gawsis.meteoswiss.ch).

The location of Gosan (GSN) is fully adequate for the intended purpose. Year-round access to JGS and GSN is possible by road.

Station Facilities and Infrastructure

JGS comprises extensive laboratory space, and a 12 m measurement tower, and office, kitchen and sanitary facilities are available. Internet access is available with sufficient bandwidth. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

Furthermore, a calibration laboratory is available at NIMS (Seogwipo, Jeju Island), and it is equipped with state-of-the-art instrumentation for the calibration of GHGs and CO. A large set of laboratory standards from the CCL is available ensuring full traceability to the WMO/GAW reference. The NIMS calibration facility serves all GAW stations operated by KMA / NIMS.

> **Recommendation 2 (**, important, near future)**
> *Due to the excellent calibration infrastructure at NIMS, it should be considered to expand calibration services also to other programmes, both on the national and international level. The facilities at NIMS would be ideal for a regional calibration centre.*

Measurement Programme

The JGS regional GAW station hosts a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured species is available from GAWSIS.

The information available from GAWSIS was reviewed as part of the audit. Information in GAWSIS has been updated recently, and the information was mostly up-to-date. However, some details regarding instrumentation and station contacts needs to be re-visited and corrected.

A critical issue however is that all measurements are made at Gosan (GSN), and not Jeju Gosan (JGS). This needs to be corrected, and WMO needs to be informed.

> **Recommendation 3 (***, critical, 2023)**
> *Measurements made at Gosan / Jeju Gosan need to be affiliated to the correct location / station ID. This needs to be corrected also for data which has been submitted to the World Data Centres.*

> **Recommendation 4 (***, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. Part of the reviewed information needs to be updated. The GAWSIS support should be contacted for updates which are not possible through the web interface (e.g. deletion of station contacts).*

Data Submission

As of December 2022, the following JGS data of the scope of the audit has been submitted to the World Data Centres:

Submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2018-2021)

JGS, submission to World Data Centre for Greenhouse Gases (WDCGG):
CO_2 (2012-2019), CO (2018-2020) (measurements are made at the GSN site)

GSN, submission to World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2002-2011), CO_2 (2002-2011), N_2O (2002-2011)

Data shown in this report was accessed on 9 December 2022. Data of the scope of the audit has been partly submitted with a submission delay of two to three years. It was noted that the CH_4 and N_2O data of JGS has not yet been submitted.

Recommendation 5 (, 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.
KMA started submitting hourly data following the WCC-Empa audit in 2017 and hourly data is now available for most parameters. However, the CH_4 data series and recent N_2O data of JGS are currently missing. Submission of these data is strongly encouraged.

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCRG and WDCGG was reviewed. Time series plots are shown in the Appendix. The accessed time series look sound.

Documentation

All operation and maintenance actions are entered in electronic and hand written log books. The instrument manuals are available at the site, and weekly checklists are available. The reviewed information was only partly up to date, and the records of the calibrations settings of the ozone analyser were not available during the audit, which complicates post-correction of the ozone data.

Recommendation 6 (*, critical, ongoing)**
The station staff must be aware that documentation of all relevant information is of utmost importance for reliable data and measurements. The current practice is appropriate, but it has to be made sure that the information is archived together with the measurement data.

Air Inlet System

Ozone, CO and other reactive gases are sampled from a small tower approximately 5 m above the roof of the JGS laboratory. A 9.5 m long ½ inch outer diameter perfluoroalcoxy (PFA) tube is connected to a common glass manifold, from where instruments are connected by ¼ inch outer diameter tubing and inlet filters. The manifold is flushed at 20 l/min. The residence time is estimated to be approximately 10 seconds based on the volume and flow rate of the inlet. This inlet is adequate for the measurements of reactive gases.

A common air inlet system for GHG and CO measurements by Cavity Ringdown Spectroscopy (CRDS) is in place. Air is pumped from the 12 m tower to the laboratory building, and automatically dried to a dew point of about -50°C (trap temperature -80°C) using two cryogenic traps alternating every 24 hours. The stainless steel manifold is pressurized to approx. 2.5 bar, and instruments are directly connected to this manifold. This inlet is adequate for GHG measurements.

Surface Ozone Measurements

Surface ozone measurements at JGS commenced in 2012, and continuous data is available since then. However, data of the early period until the first ozone audit of WCC-Empa is of questionable data quality, and reliable ozone data is available from 2017 onwards.

> **Recommendation 7 (**, important, 2023)**
> *It should be explored if the data from 2000 to 2017 is of sufficiently high quality to be submitted to WDCRG. If the data can be rescued, submission is highly recommended.*

Instrumentation. JGS is currently equipped with one ozone analyser (Thermo Scientific 49i). The instrument has been calibrated during the audit in 2017 (Zellweger et al., 2017).

Standards. No ozone standard is available at JGS. The ozone instrument has been sent to the Korea Research Institute of Standards and Science (KRISS) for a function check, which was made on 12 November 2021. The function check is not a calibration, and no adjustments of the calibration settings are made during this check according to information from KRISS.

Data Acquisition. Data (1-min time resolution) is acquired on a custom made data acquisition system. The system is fully adequate.

Intercomparison (Performance Audit). The JGS ozone analyser (OA) was 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 250 nmol mol^{-1}. 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. The following equations characterise the bias of instruments and the remaining uncertainty after compensation of the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the ozone absorption cross section of 1.1476x10^{-17} cm^2 (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #1118248979 (BKG -0.5 nmol mol^{-1}, COEF 1.025):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -0.76 nmol mol^{-1}) / 1.0159 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.07e-05 * X_{O3}^2) (1b)

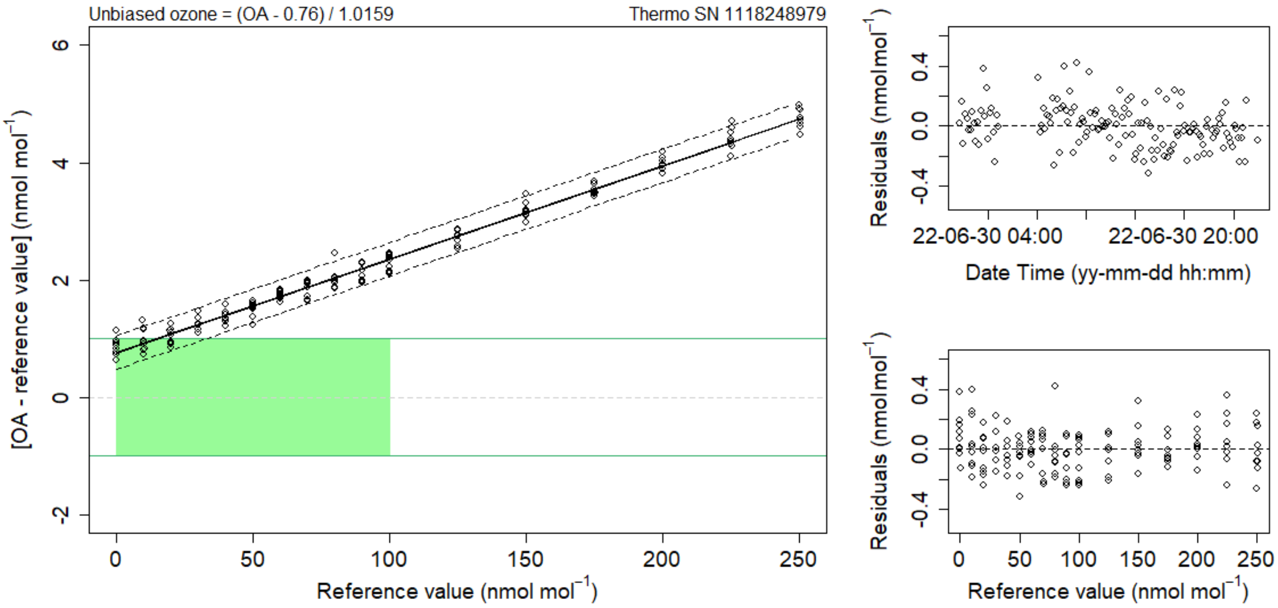

Figure 1. *Left: Bias of the main JGS ozone analyser (Thermo Scientific 49i #1118248979, BKG -0.5 nmol mol^{-1}, COEF 1.025) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant 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).*

The results of the comparisons can be summarised as follows:

The current calibration setting of the Thermo Scientific 49i #1118248979 (BKG -0.5 nmol mol^{-1}, COEF 1.025) resulted in a significant positive amount fraction dependent bias compared to the WCC-Empa reference, and is exceeding the WMO/GAW DQOs. The agreement would be likely within the WMO/GAW DQOs with the calibration settings of the last calibration by WCC-Empa in 2017. Changes in the COEF parameter do proportionally change the mole fraction readings of the instruments. At that time, it was recommended to not change the settings.

Recommendation 8 (*, critical, 2023)**
It is recommended to change the calibration settings of the instrument back to the settings of the initial calibration made by WCC-Empa (BKG -0.1 nmol mol-1, COEF 1.004) in 2017.

Recommendation 9 (*, critical, 2023)**
All data acquired since 2017 need to be recalculated to the calibration settings of 2017 (BKG -0.1 nmol mol-1, COEF 1.004).

Recommendation 10 (*, critical, 2023)**
The calibration settings (BKG -0.1 nmol mol^{-1}, COEF 1.004) of the Thermo Scientific 49i #1118248979 instrument should NOT be changed.

Carbon Monoxide Measurements

Continuous measurements of CO at JGS started in 2012 using non-dispersive infrared (NDIR) technique. Near-infrared Cavity Ringdown Spectroscopy (CRDS) measurements started in 2020.

Instrumentation. Picarro G2401 (near-IR CRDS). The air is dried to a dew point of -50°C by a cold trap.

Standards. Several working standards are available at JGS for the calibration of the instruments. The assignments of the WS values are done at the central calibration facility at NIMS, where several laboratory standards from the CCL are available. An overview of available standards at JGS and NIMS is shown in Table 5 in the Appendix.

Calibrations of the instrument are carried out every two weeks

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JGS instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equation characterises the instrument bias, and the results are further illustrated in Figure 2 with respect to the WMO GAW DQOs (WMO, 2020):

Picarro G2401 #3438-CFKADS2342:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 9.23 nmol mol^{-1}) / 0.9534 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (3.3 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2b)

The results of the comparisons can be summarised as follows:

The comparison results were within the extended network compatibility goal of 5 nmol mol^{-1} for the range from 100 to 300 nmol mol^{-1}. However, a strong amount fraction dependency of the bias with a large offset at zero was observed. Most likely, this can be explained by the drift of standards gases. Therefore, a calibration strategy based on standards with high CO amount fractions and zero air should be considered as an alternative.

Recommendation 11 (*, minor, 2023)
The CRDS measurement technique shows a linear response for CO in the amount fraction range from at least 0 to 4000 nmol mol^{-1}. To minimise the influence of standard drift, WCC-Empa recommends that the calibration strategy focuses on higher CO amount fractions (>500 nmol mol^{-1}), and also includes CO free air (or N_2 6.0) to compensate for a zero offset. Before such a calibration scheme is implemented, the linearity of the analyser needs to be confirmed.

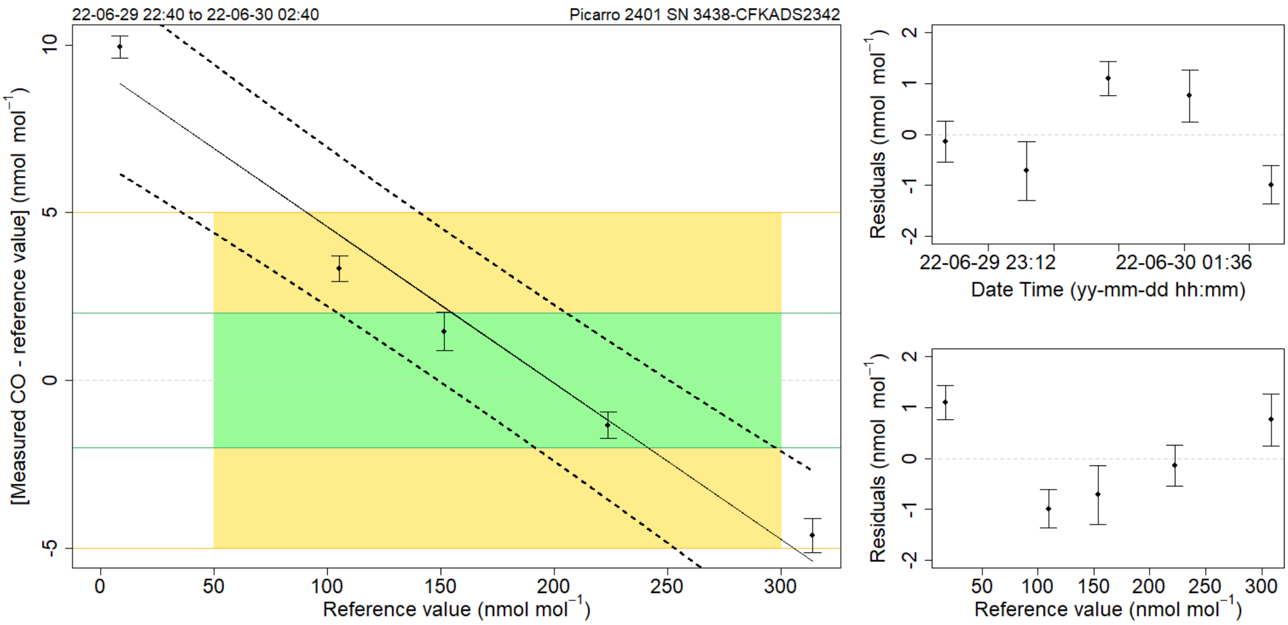

Figure 2. *Left: Bias of the JGS Picarro G2401 #3438-CFKADS2342 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for JGS. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Methane Measurements

Continuous measurements of CH_4 at JGS started in 2002 using gas chromatography (GC) coupled to flame ionization detection (FID). These measurements have been made by the National Institute Of Environmental Research (NIER). Since 2015 CH_4 measurements are made using CRDS technique, and the GC/FID system is no longer in operation.

Instrumentation. Picarro G2401 (near-IR CRDS). The air is dried to a dew point of -50°C by a cold trap.

Standards and calibration. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JGS instrument with randomised CH_4 levels from travelling standards. The result of the comparison is summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 3 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #3438-CFKADS2342):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 + 2.09 nmol mol^{-1}) / 1.0009 (3a)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.1 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (3b)

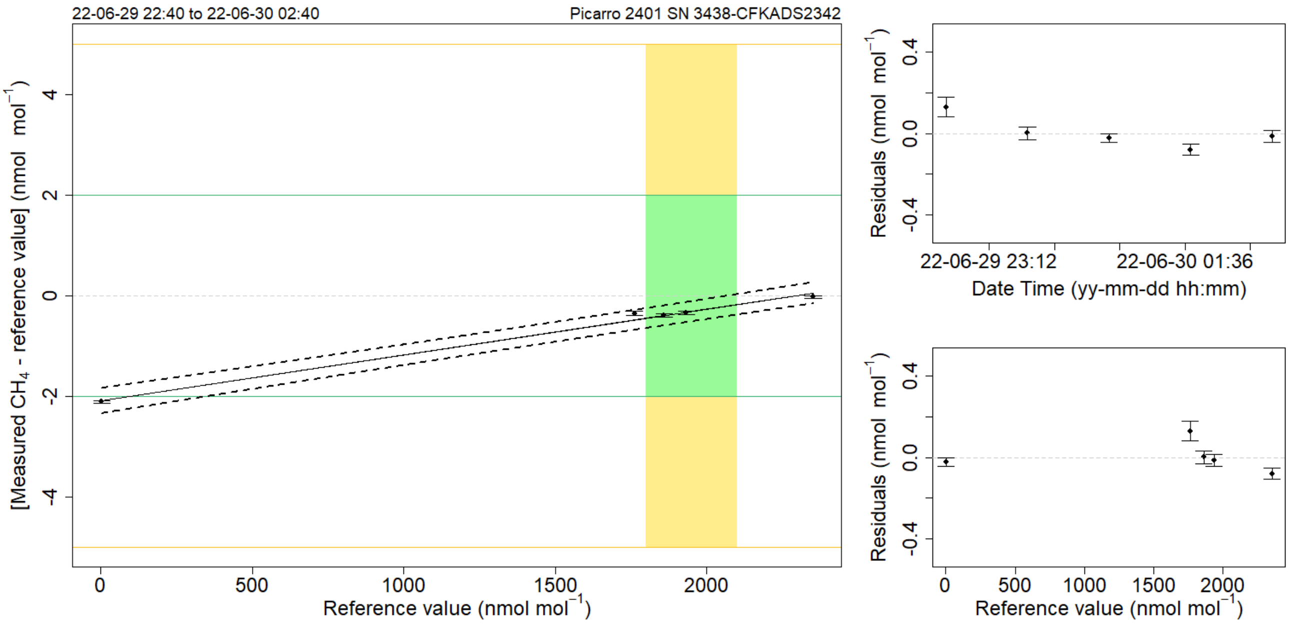

Figure 3. *Left: Bias of the Picarro G2401 #3438-CFKADS2342 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for JGS. 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:

Excellent agreement well with the WMO/GAW compatibility goal was found. A small dependency of the bias on the amount fraction was observed, which may be due to remaining inconsistencies of the used calibration standard. The amount fraction dependent bias may also be due to remaining inconsistencies in the WMO-X2004A CH_4 calibration scale, since a similar dependency is often observed during WCC-Empa audits. WCC-Empa uses in addition to CCL standards also methane free zero air to calibrate its travelling standards, which may explain the observed amount fraction dependency. However, the bias in the relevant amount fraction range is small and well within the WMO/GAW compatibility goals. The good results show that the whole system, including calibration procedures and standards gases, is fully appropriate, and no further action is required.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at JGS started in 2009 using NDIR technique. Since 2014 CO_2 measurements are made using CRDS technique, and the NDIR system is no longer in operation.

Instrumentation. Picarro G2401 (near-IR CRDS). The air is dried to a dew point of -50°C by a cold trap.

Standards and calibration. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JGS instruments with randomised CO_2 levels from travelling standards. The results of the comparisons are summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 4 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #3438-CFKADS2342:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.97 µmol mol^{-1}) / 0.99772 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.002 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4b)

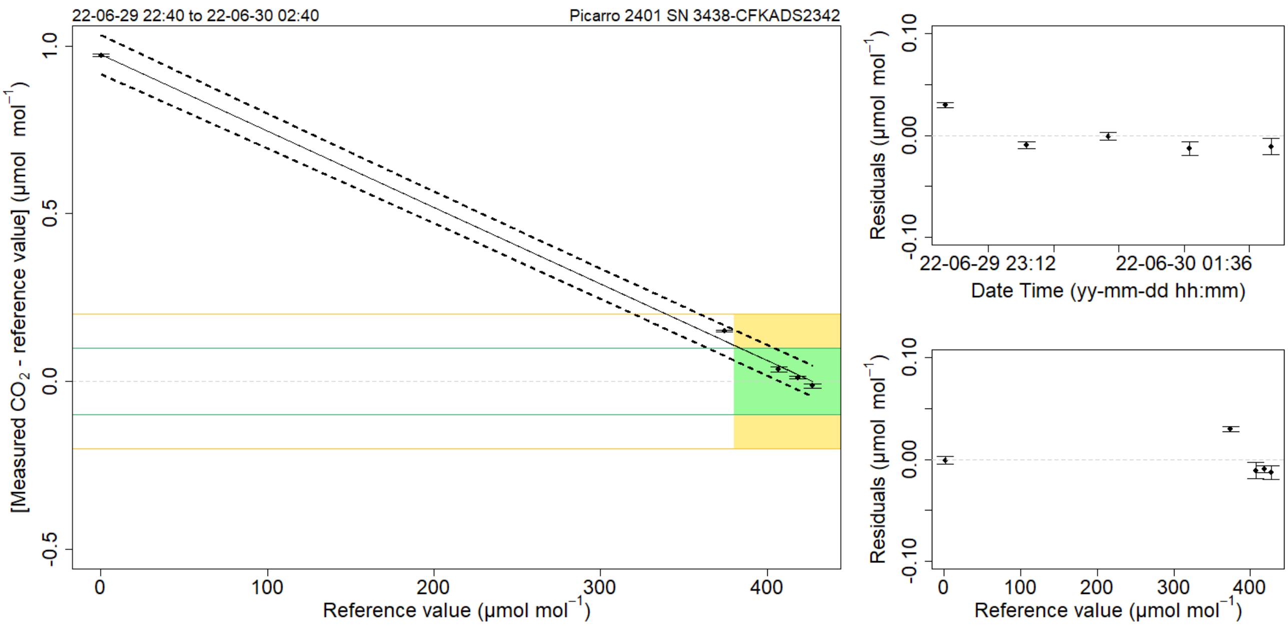

Figure 4. *Left: Bias of the Picarro G2401 #3438-CFKADS2342 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for JGS. 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 result was within the WMO/GAW network compatibility goal at the relevant CO_2 level, but the bias showed a dependency on the amount fraction with a clear offset at zero, likely due to the rather narrow range (390 – 453 µmol mol^{-1}) of CO_2 mole fractions in the reference cylinders. To further improve the measurements, additional standards covering the entire range (250 – 800 µmol mol^{-1}) of the WMO-X2019 calibration scale are needed to calibrate the instrument.

Recommendation 12 (*, minor, 2023)
The agreement of the JGS CO_2 measurements can most likely be improved using additional standards that cover the entire range of the WMO-X2019 calibration scale.

Nitrous Oxide Measurements

Continuous measurements of N_2O at JGS started in 2012 using GC / electron capture detection (ECD), and continuous time series are available since then. Earlier measurements (2002-2011) were made at GSN, and only those have been submitted so far. From 2012 to 2016, no calibration standards were available, and reliable measurements are available since 2017.

Instrumentation. Gas chromatograph (Agilent 7890N) with Electron Capture Detector (GC/ECD).

Recommendation 13 (*, minor, 2023/4)
Newer spectroscopic instruments have proofed to show better performance for N_2O measurements compared to CG/ECD. It should be considered to replace the GC/ECD system with a spectroscopic instrument.

Standards and calibration. A working standards is available at JGS for the calibration of the instruments. The assignments of the WS value is done at the central calibration facility at NIMS, where several laboratory standards from the CCL are available. An overview of available standards at JGS and NIMS is shown in Table 5 in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JGS instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equation characterises the instrument bias, and the result is further illustrated in Figure 5 with respect to the WMO GAW DQOs (WMO, 2020):

Agilent 7890N GC/ECD:

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O - 28.07) / 0.9163 (5a)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.01 + 1.01e-07 * X_{N2O}^2) (5b)

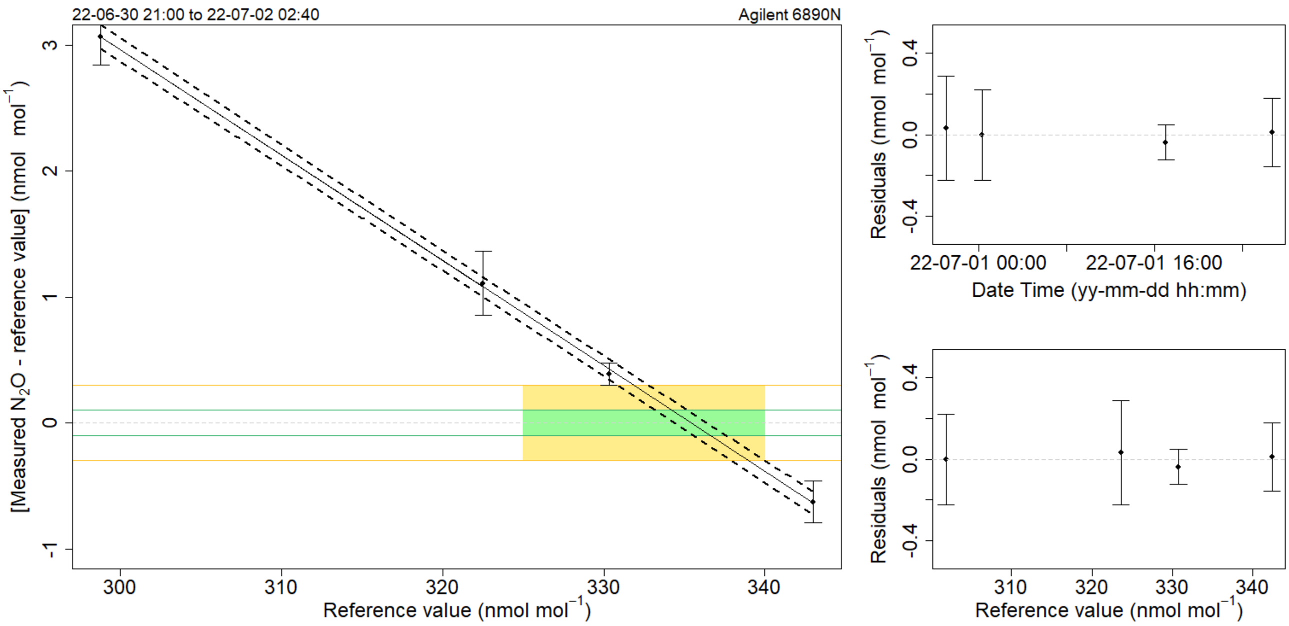

Figure 5. *Left: Bias of the Agilent 7890N nitrous oxide GC with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for JGS. 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:

Agreement within the WMO/GAW network compatibility goal was only found for the current N_2O background levels. The bias of the JGS measurements showed a strong amount fraction dependency, which most likely was caused by an insufficient characterization of the non-linearity of the GC/ECD system. Currently, only a one point calibration using a working standard slightly above the current background level is made. Measurements of N_2O could be improved by a characterization of the non-linearity of the ECD detector.

> **Recommendation 14 (**, important, 2023)**
> *It is recommended to characterize the non-linearity of the GC/ECD system using a set of standards covering at least the range from 320 to 350 nmol mol^{-1}.*

JGS PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the JGS performance audit to other station audits made by WCC-Empa. 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, and Zellweger et al. (2019) for CO and N_2O, 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-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions usually found in unpolluted air masses. For N_2O, the mole fraction range covers 10 nmol mol^{-1} and depends on the time of the comparison due to the large annual increase combined with low variability (see Zellweger et al. (2019) for details). For surface ozone the mole fraction range of 0-100 nmol mol^{-1} 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 network goals in a certain mole fraction range. Figure 6 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 7. 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 JGS audit are shown as coloured dots in Figure 6 and 7, 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 CH_4, and within the extended DQOs for CO_2. CO, N_2O and O_3 were not meeting the DQOs; however, data of the ozone instrument can be corrected if the history of the calibration settings is known.

Table 1. *JGS 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 5th and 6th columns show the percentage of all WCC-Empa and WCC-N_2O audits until September 2020 within these criteria since 1996 (O_3), 2002 (N_2O), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound / Instrument	**Range**	**Unit**	**JGS within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**
O_3 (Thermo 49i #1118248979)	0 -100	nmol mol^{-1}	✗	65	NA
CO (Picarro G2401 3438-CFKADS2342)	30 - 300	nmol mol^{-1}	✗	18	49
CH_4 (Picarro G2401 3438-CFKADS2342)	1750 - 2100	nmol mol^{-1}	✓	76	94
CO_2 (Picarro G2401 3438-CFKADS2342)	380 - 450	µmol mol^{-1}	✓	48	74
N_2O (Agilent 7890N GC/ECD)	325 - 335	nmol mol^{-1}	✗	4	44

[1] Percentage of stations within the eDQO and DQO

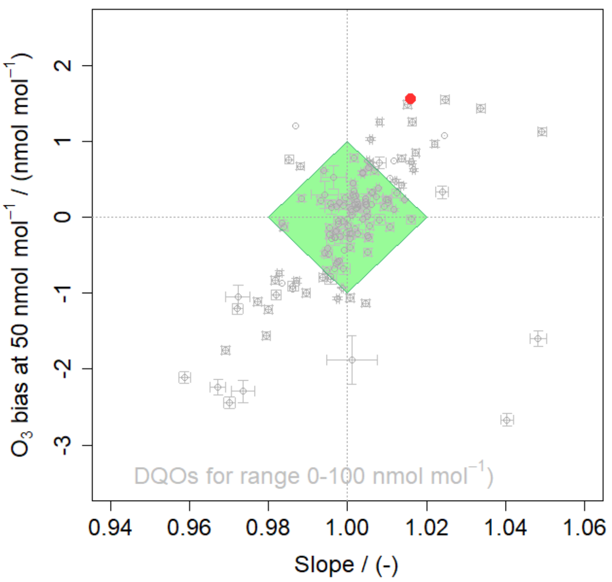

Figure 6. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the red dots shows the results of the JGS instrument. The uncertainty bars refer to the standard uncertainty, and the green area corresponds to the WMO/GAW DQO for surface ozone.*

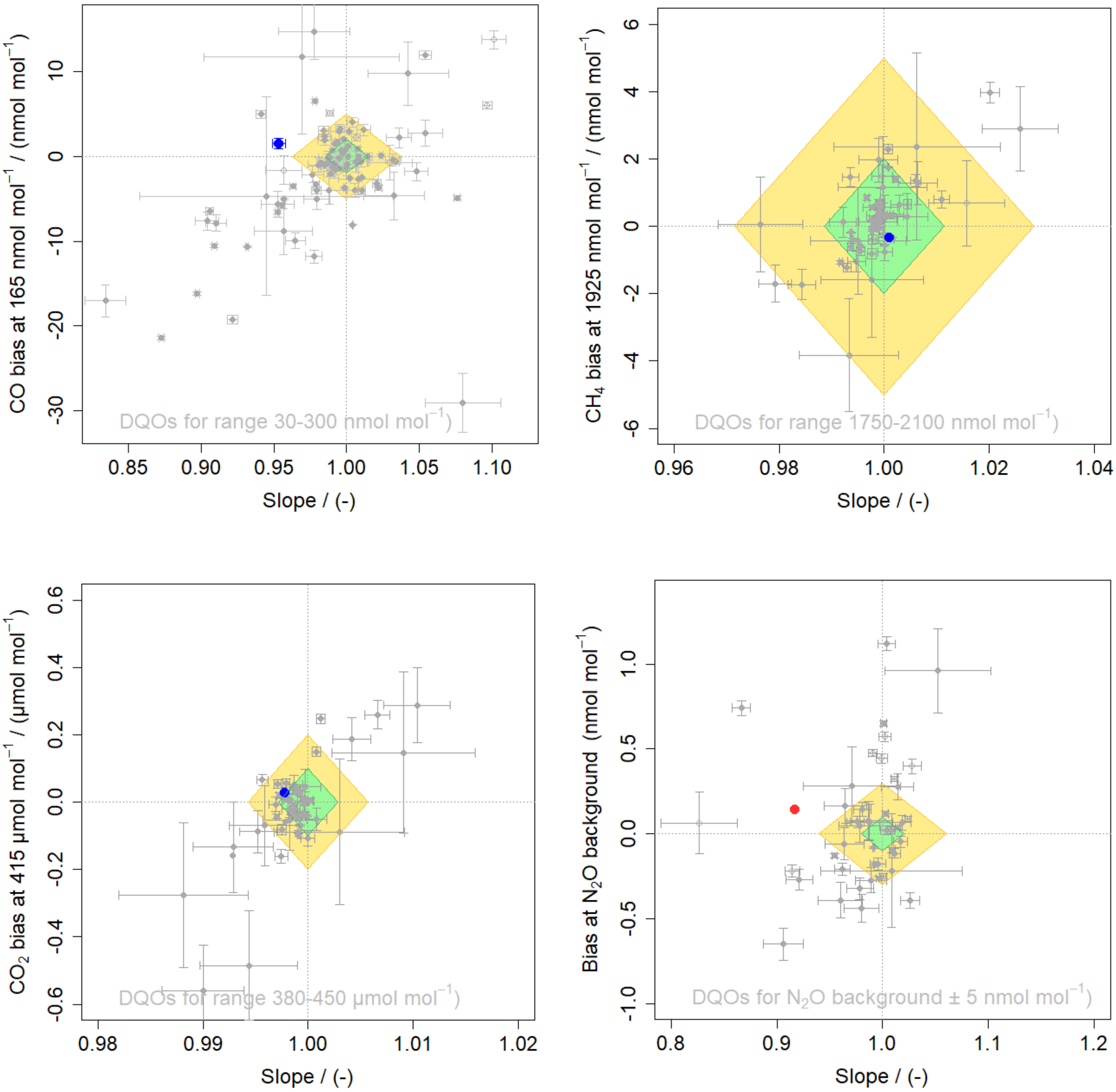

Figure 7. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show JGS results (blue: Picarro G2401, red: Agilent 7890N). Filled symbols refer to a comparison with the same calibration scale at the station and the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and 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 29 June through 30 July 2022 at JGS. The TI was connected to the JGS inlet system. The TI was sampling air using the following sequence: 1775 min ambient air followed by 30 min measurement of three standard gases, each 10 min. The sample air was dried by a Nafion dryer (Model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum in the purge air flow. To account for the remaining effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below.

Figures 8 to 10 show the comparison of hourly CO, CH_4, and CO_2 measurements between the WCC-Empa TI and the JGS Picarro G2401 analyser. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers and the WCC-Empa TI.

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

Carbon Monoxide

The observed bias of the JGS analyser compared to the WCC-Empa TI strongly correlates with the CO amount fraction, which is in line with the results of the travelling standard comparison. The observed slope is comparable to the TS comparison, but an absolute difference of about 5 nmol mol^{-1} was observed between the TS and the ambient air comparison.

Methane

On average, excellent agreement within the WMO/GAW network compatibility goals was found between the TI and the JGS instrument, which confirms the results of the performance audit using traveling standards. The temporal variation was well captured by both instruments; larger deviations were only observed during periods with fast changes of the amount fraction. Slightly different residence times in the inlet and periphery leading to slightly different response times of the measurements system can then result in short but rather large deviations. No significant dependency of the bias on the amount fraction was observed.

Carbon dioxide

The temporal variability was well captured by both instruments, and only a small dependency of the bias on the amount fraction was observed. On average, the agreement was within the extended WMO/GAW network compatibility goal. The observed bias during the ambient air comparison was slightly larger compared to the travelling standard comparison.

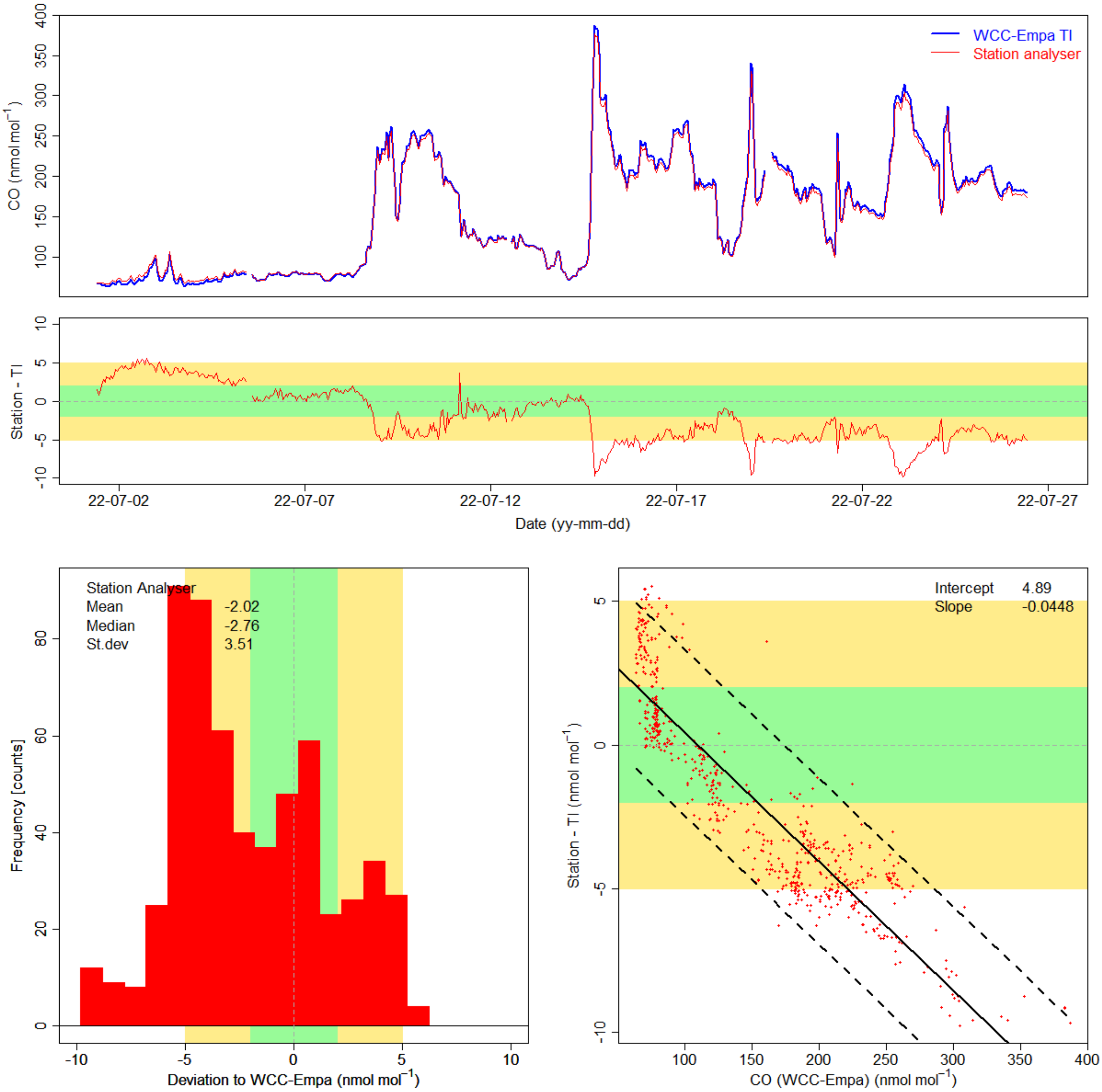

Figure 8. *Top: Comparison of the Picarro G2401#3438-CFKADS2342 with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. Lower left: CO deviation histograms for the Picarro G2401#3438-CFKADS2342 analyser compared to the WCC-Empa TI. Lower right: Bias of the JGS instrument as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

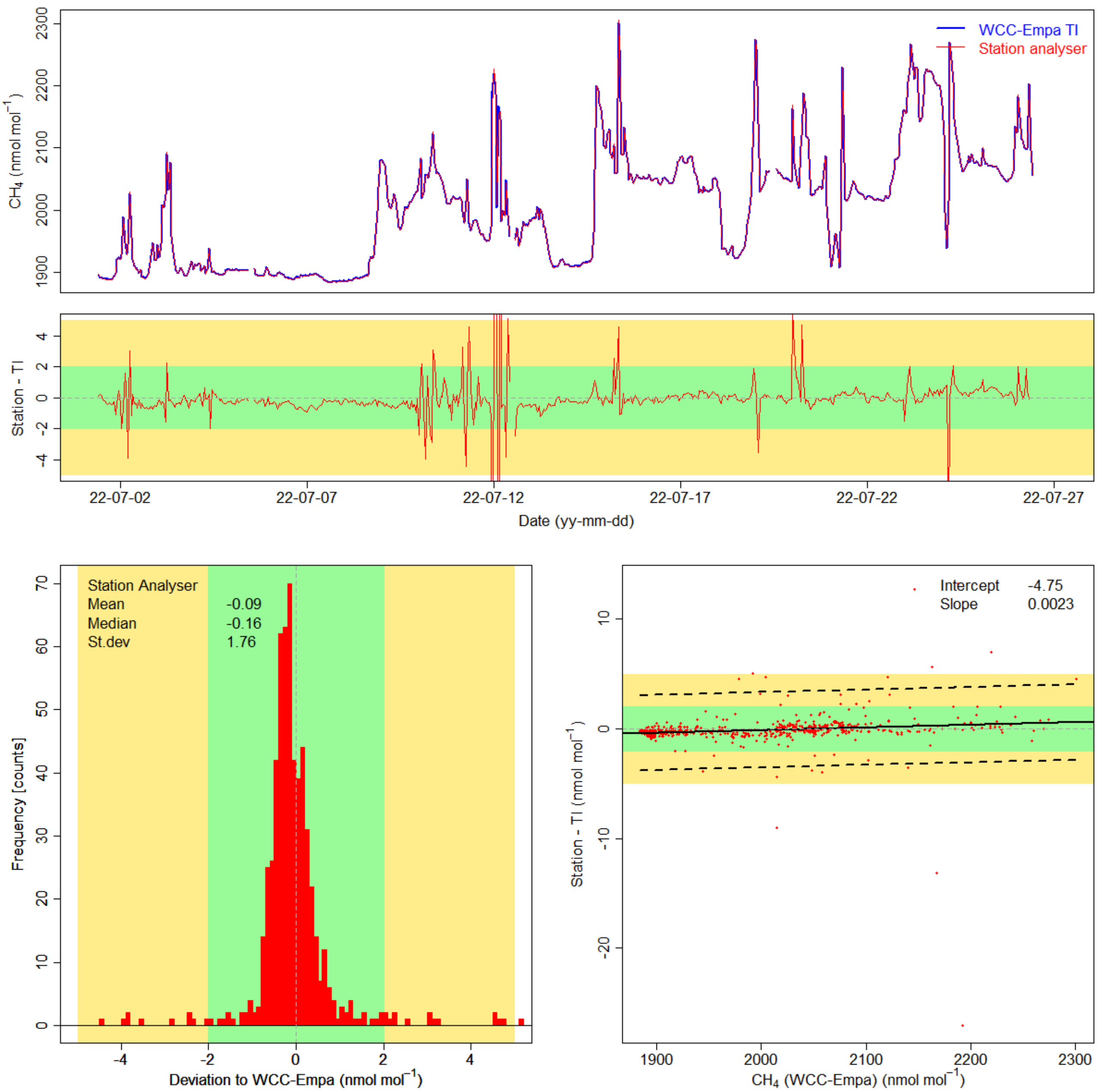

Figure 9. *Top: Comparison of the Picarro G2401#3438-CFKADS2342 with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. Lower left: CH_4 deviation histograms for the Picarro G2401#3438-CFKADS2342 analyser compared to the WCC-Empa TI. Lower right: Bias of the JGS instrument as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

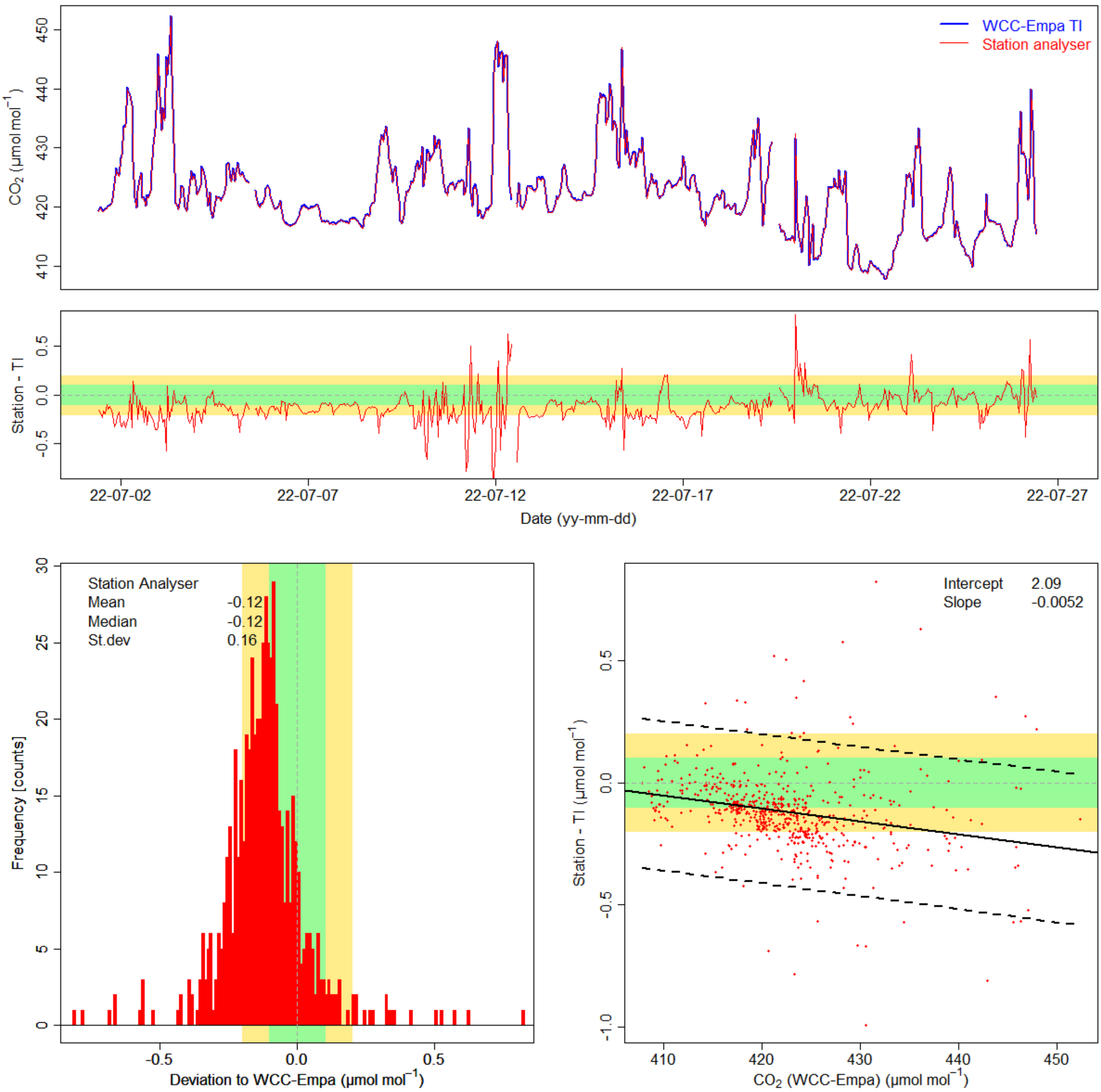

Figure 10. *Top: Comparison of the Picarro G2401#3438-CFKADS2342 with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. Lower left: CO_2 deviation histograms for the Picarro G2401#3438-CFKADS2342 analyser compared to the WCC-Empa TI. Lower right: Bias of the JGS instrument as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

CONCLUSIONS

The regional GAW station Jeju Gosan comprises an extensive research infrastructure, and hosts a large number of long-term continuous observations in all WMO/GAW focal areas. In combination with the central calibration facilities at NIMS, the JGS GAW station and the NIMS laboratory could serve as a regional calibration centre both on the national and international level, and expanding the services of NIMS are encouraged.

The large number of measured atmospheric constituents at JGS in combination with the high data quality enables state of the art research. Furthermore, the geographical location of JGS is strategically very important for the GAW programme, because it enables the source attributions of pollutants in combination with transport models (Park et al., 2021). Thus, the continuation of the Jeju Gosan measurement series is highly important for GAW.

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. However, improvements are possible for the surface ozone measurements due to calibration issues, and for nitrous oxide due to a measurement technique which is no longer state-of-the-art. Furthermore, the geographical location assignments of the JGS and GSN measurements needs to be controlled and corrected in GAWSIS.

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 JGS, whereas Table 1 further above covers a wider mole fraction range.

Table 2. *Synthesis of the performance audit results for the TS and ambient air comparisons. 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 Thermo 49i	CO Picarro G2401	CH_4 Picarro G2401 Empa analysis	CO_2 Picarro G2401	N_2O Picarro G5310
TS	✗	(✓)	✓	✓	(✓)
Air	NA	✓	✓	✓	NA

NA: no comparison was made

SUMMARY RANKING OF THE JEJU GOSAN GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access
Facilities		
Laboratory and office space	(5)	Fully adequate, with space for additional research campaigns
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate
Power supply	(5)	Reliable and stable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(4)	Skilled staff, further training with respect to surface ozone needed
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2 Picarro G2401	(5)	State of the art instrumentation
CO Picarro G2401	(3)	Adequate instrument
N_2O Agilent GC/ECD	(4)	Adequate, replacement with spectroscopic technique recommended
Standards		
O_3	(0)	No standard available, calibration strategy needs to be revised
CO, CO_2, CH_4, N_2O	(5)	Full traceability to the GAW reference through central calibration facility at NIMS
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(4)	Skilled staff and appropriate procedures
Data submission	(3)	Mostly timely submission, methane data is missing

#0: inadequate thru 5: adequate.

Dübendorf, July 2023

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 JGS data accessed on 9 December 2022 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations. Historical data from GSN are not shown since they have already been discussed in the previous audit (Zellweger et al., 2017).

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

Surface ozone:

The JGS ozone time series submitted to WDCRG is shown in the following figure.

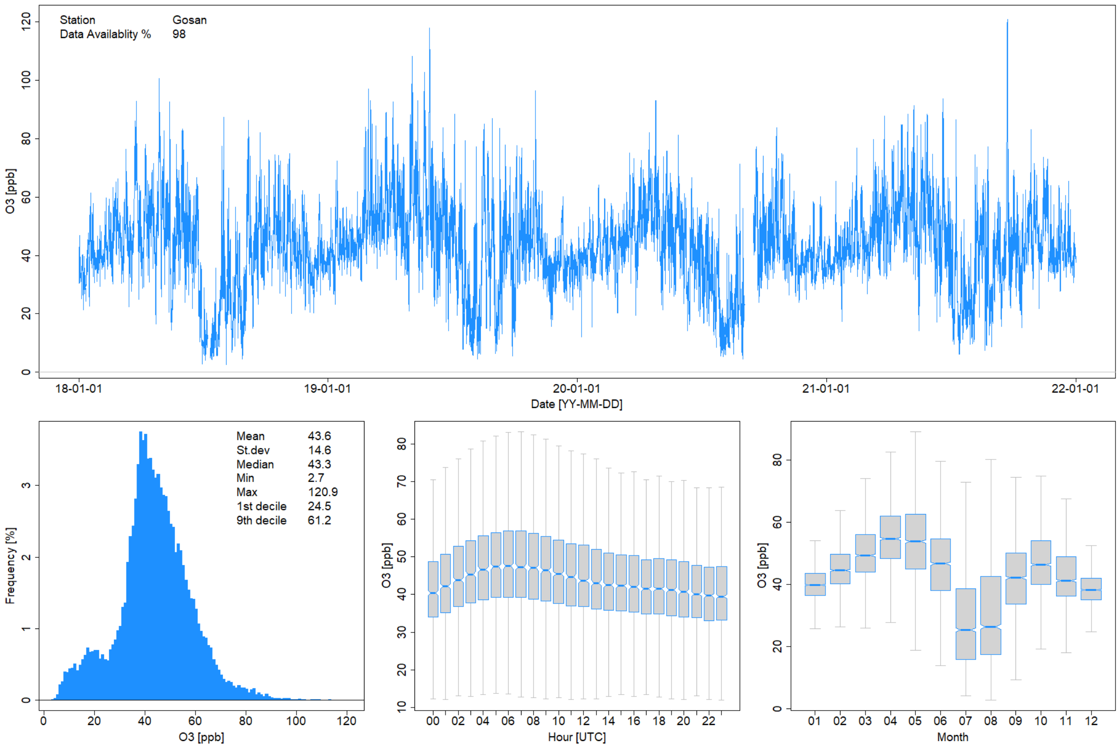

Figure 11. *O_3 data for the period from 2018 to 2021 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data sets looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

Carbon monoxide and Carbon dioxide:

The JGS CO and CO_2 time series submitted to WDCGG is shown in the following figures.

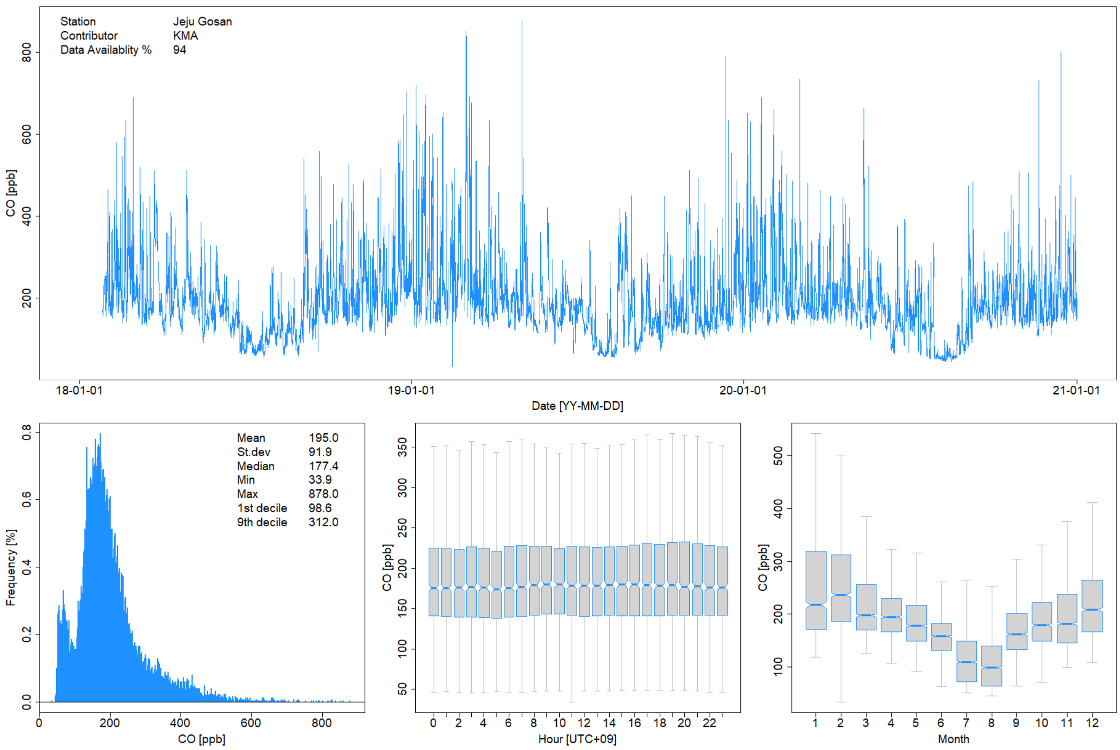

Figure 12. *JGS CO in-situ data (2018-2020) submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

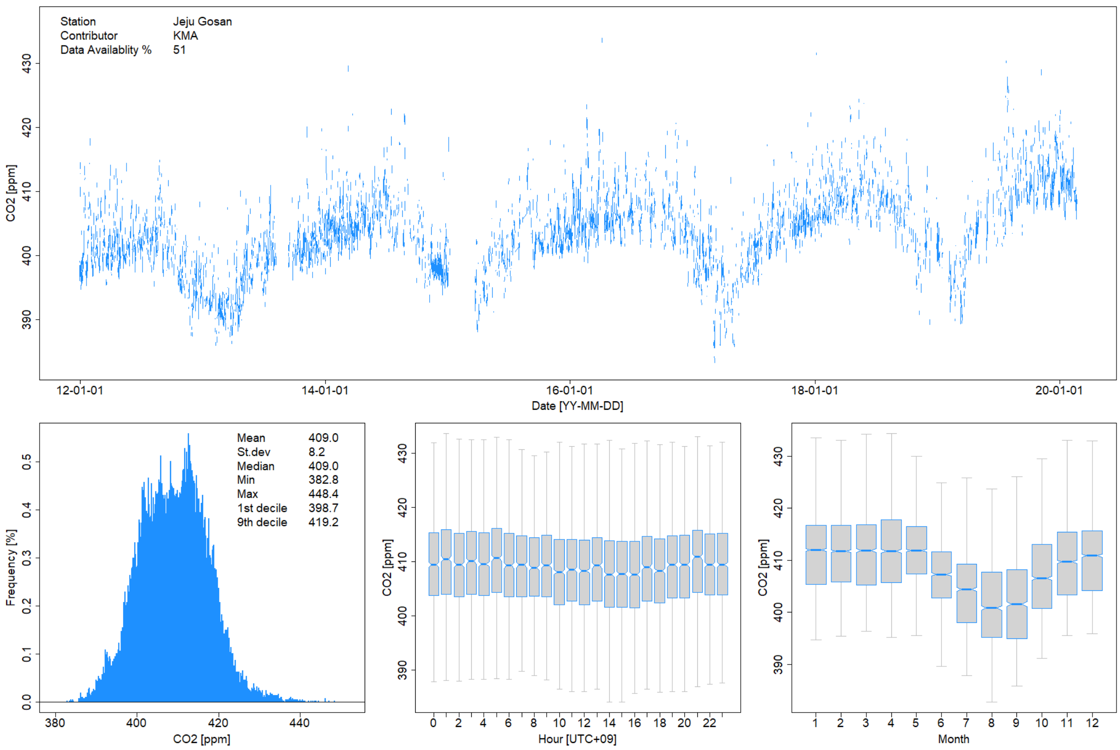

Figure 13. *Same as above, for JGS CO_2 in-situ data (2012-2019) submitted to WDCGG.*

- The JGS CO and CO_2 data set 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 nmol mol^{-1}. 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 JGS 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 1.007
Pressure readings (hPa)	Ambient 1001.3;TS 1000.5 (adjusted to 1001.3 before the comparison)
JGS analyser (OA) (main instrument)	
Model, S/N	Thermo Scientific 49i #1118248979
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.5 nmol mol^{-1}, COEF 1.025
Pressure readings (hPa)	Ambient 1001.3; OA 1000.5 (no adjustment was made)

Results

Each ozone level was measures for approximately ten minutes, and the last ten 40 s 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 same treatment as for ambient air analysis was applied.
The results of the assessment is shown in the following Table (individual measurement points) and further presented in the Executive Summary.

Table 4. Comparison of the JGS ozone analyser (OA) Thermo Scientific 49i #1118248979 (*BKG -0.5 nmol mol^{-1}, COEF 1.025) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-06-30 01:41	80.13	0.18	82.19	0.28	2.06	2.57
2022-06-30 01:51	0.06	0.20	0.99	0.14	0.93	NA
2022-06-30 01:59	175.17	0.21	178.60	0.31	3.43	1.96
2022-06-30 02:08	19.98	0.23	21.14	0.15	1.16	5.81
2022-06-30 02:16	150.11	0.23	153.31	0.26	3.20	2.13
2022-06-30 02:25	90.09	0.15	92.26	0.33	2.17	2.41
2022-06-30 02:33	250.26	0.24	254.98	0.26	4.72	1.89
2022-06-30 02:42	100.08	0.12	102.53	0.30	2.45	2.45

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-06-30 02:50	200.17	0.14	204.14	0.22	3.97	1.98
2022-06-30 02:59	60.00	0.15	61.61	0.26	1.61	2.68
2022-06-30 03:07	150.05	0.13	153.23	0.31	3.18	2.12
2022-06-30 03:16	250.29	0.17	254.91	0.29	4.62	1.85
2022-06-30 03:24	69.99	0.17	71.96	0.40	1.97	2.81
2022-06-30 03:34	-0.08	0.25	1.06	0.11	1.14	NA
2022-06-30 03:42	100.09	0.17	102.51	0.29	2.42	2.42
2022-06-30 03:51	9.98	0.29	11.15	0.36	1.17	11.72
2022-06-30 03:59	80.08	0.12	82.02	0.26	1.94	2.42
2022-06-30 04:08	49.97	0.17	51.61	0.42	1.64	3.28
2022-06-30 04:16	60.05	0.12	61.88	0.37	1.83	3.05
2022-06-30 04:25	175.10	0.11	178.60	0.18	3.50	2.00
2022-06-30 04:33	225.14	0.16	229.24	0.32	4.10	1.82
2022-06-30 04:42	19.84	0.21	20.99	0.54	1.15	5.80
2022-06-30 04:50	125.09	0.17	127.84	0.21	2.75	2.20
2022-06-30 08:05	150.04	0.18	153.51	0.30	3.47	2.31
2022-06-30 08:14	80.03	0.18	82.02	0.31	1.99	2.49
2022-06-30 08:22	200.17	0.18	204.12	0.27	3.95	1.97
2022-06-30 08:31	30.00	0.15	31.36	0.22	1.36	4.53
2022-06-30 08:39	100.04	0.16	102.38	0.32	2.34	2.34
2022-06-30 08:49	0.07	0.11	0.90	0.11	0.83	NA
2022-06-30 08:57	69.98	0.11	71.92	0.19	1.94	2.77
2022-06-30 09:06	225.18	0.20	229.54	0.23	4.36	1.94
2022-06-30 09:14	40.01	0.22	41.59	0.25	1.58	3.95
2022-06-30 09:23	250.24	0.20	254.72	0.39	4.48	1.79
2022-06-30 09:31	90.01	0.17	92.30	0.28	2.29	2.54
2022-06-30 09:40	19.94	0.17	21.19	0.37	1.25	6.27
2022-06-30 09:48	49.98	0.18	51.36	0.43	1.38	2.76
2022-06-30 09:57	125.12	0.19	127.99	0.38	2.87	2.29
2022-06-30 10:05	175.14	0.15	178.82	0.17	3.68	2.10
2022-06-30 10:14	9.83	0.37	11.14	0.29	1.31	13.33
2022-06-30 10:22	60.05	0.24	61.87	0.33	1.82	3.03
2022-06-30 10:31	150.14	0.27	153.32	0.33	3.18	2.12
2022-06-30 10:40	200.18	0.20	204.36	0.25	4.18	2.09
2022-06-30 10:48	175.11	0.20	178.74	0.36	3.63	2.07
2022-06-30 10:57	40.02	0.18	41.24	0.37	1.22	3.05
2022-06-30 11:05	70.05	0.15	72.05	0.22	2.00	2.86
2022-06-30 11:14	80.05	0.15	82.50	0.34	2.45	3.06
2022-06-30 11:22	10.05	0.34	10.86	0.14	0.81	8.06
2022-06-30 11:32	0.08	0.21	0.85	0.10	0.77	NA
2022-06-30 11:40	60.12	0.13	61.88	0.24	1.76	2.93
2022-06-30 11:49	250.25	0.16	255.02	0.21	4.77	1.91
2022-06-30 11:57	30.03	0.19	31.20	0.24	1.17	3.90
2022-06-30 12:06	49.99	0.17	51.51	0.23	1.52	3.04
2022-06-30 12:14	225.22	0.25	229.92	0.42	4.70	2.09
2022-06-30 12:23	90.04	0.19	92.32	0.24	2.28	2.53
2022-06-30 12:31	19.95	0.15	21.01	0.23	1.06	5.31
2022-06-30 12:40	100.11	0.16	102.54	0.36	2.43	2.43

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-06-30 12:48	125.09	0.21	127.94	0.23	2.85	2.28
2022-06-30 12:57	150.09	0.20	153.22	0.37	3.13	2.09
2022-06-30 13:05	60.06	0.11	61.75	0.34	1.69	2.81
2022-06-30 13:14	10.08	0.22	11.03	0.19	0.95	9.42
2022-06-30 13:22	175.19	0.23	178.73	0.20	3.54	2.02
2022-06-30 13:31	80.05	0.21	82.08	0.43	2.03	2.54
2022-06-30 13:39	50.09	0.20	51.66	0.35	1.57	3.13
2022-06-30 13:48	100.07	0.17	102.45	0.26	2.38	2.38
2022-06-30 13:56	125.15	0.14	127.82	0.22	2.67	2.13
2022-06-30 14:06	0.07	0.15	0.95	0.11	0.88	NA
2022-06-30 14:14	70.10	0.14	71.77	0.23	1.67	2.38
2022-06-30 14:23	200.17	0.21	204.20	0.39	4.03	2.01
2022-06-30 14:31	19.94	0.18	21.03	0.29	1.09	5.47
2022-06-30 14:40	90.08	0.27	92.14	0.33	2.06	2.29
2022-06-30 14:48	250.14	0.13	255.12	0.24	4.98	1.99
2022-06-30 14:57	39.93	0.18	41.39	0.30	1.46	3.66
2022-06-30 15:05	29.93	0.19	31.28	0.17	1.35	4.51
2022-06-30 15:14	225.25	0.24	229.53	0.35	4.28	1.90
2022-06-30 15:23	225.17	0.32	229.68	0.44	4.51	2.00
2022-06-30 15:31	60.00	0.22	61.79	0.20	1.79	2.98
2022-06-30 15:40	0.01	0.21	0.97	0.14	0.96	NA
2022-06-30 15:49	175.23	0.19	178.72	0.35	3.49	1.99
2022-06-30 15:57	100.05	0.11	102.18	0.27	2.13	2.13
2022-06-30 16:06	80.05	0.28	81.90	0.33	1.85	2.31
2022-06-30 16:14	9.97	0.12	10.91	0.10	0.94	9.43
2022-06-30 16:23	30.02	0.15	31.11	0.15	1.09	3.63
2022-06-30 16:31	39.98	0.22	41.40	0.31	1.42	3.55
2022-06-30 16:40	20.03	0.24	20.87	0.33	0.84	4.19
2022-06-30 16:48	250.29	0.23	255.19	0.21	4.90	1.96
2022-06-30 16:57	200.21	0.27	204.19	0.35	3.98	1.99
2022-06-30 17:06	49.98	0.17	51.22	0.31	1.24	2.48
2022-06-30 17:14	150.17	0.30	153.32	0.33	3.15	2.10
2022-06-30 17:23	70.02	0.24	71.74	0.33	1.72	2.46
2022-06-30 17:31	90.12	0.16	92.09	0.31	1.97	2.19
2022-06-30 17:40	125.12	0.19	127.79	0.33	2.67	2.13
2022-06-30 17:48	80.04	0.24	81.91	0.25	1.87	2.34
2022-06-30 17:57	10.08	0.25	11.23	0.13	1.15	11.41
2022-06-30 18:05	50.09	0.20	51.63	0.32	1.54	3.07
2022-06-30 18:15	0.16	0.16	0.80	0.08	0.64	NA
2022-06-30 18:23	90.11	0.19	92.11	0.28	2.00	2.22
2022-06-30 18:32	250.19	0.16	255.11	0.34	4.92	1.97
2022-06-30 18:40	125.02	0.18	127.56	0.25	2.54	2.03
2022-06-30 18:49	150.16	0.26	153.15	0.26	2.99	1.99
2022-06-30 18:57	20.01	0.18	20.91	0.18	0.90	4.50
2022-06-30 19:06	100.07	0.13	102.30	0.22	2.23	2.23
2022-06-30 19:14	225.27	0.23	229.85	0.28	4.58	2.03
2022-06-30 19:23	39.98	0.18	41.34	0.32	1.36	3.40
2022-06-30 19:31	175.12	0.14	178.60	0.31	3.48	1.99

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-06-30 19:40	200.17	0.26	204.25	0.41	4.08	2.04
2022-06-30 19:48	30.01	0.26	31.47	0.29	1.46	4.87
2022-06-30 19:57	60.00	0.25	61.68	0.35	1.68	2.80
2022-06-30 20:05	70.09	0.24	71.98	0.32	1.89	2.70
2022-06-30 20:14	70.11	0.17	71.75	0.36	1.64	2.34
2022-06-30 20:23	150.12	0.16	153.23	0.37	3.11	2.07
2022-06-30 20:31	80.02	0.21	82.01	0.37	1.99	2.49
2022-06-30 20:40	225.19	0.24	229.51	0.29	4.32	1.92
2022-06-30 20:48	29.98	0.15	31.23	0.28	1.25	4.17
2022-06-30 20:57	90.04	0.24	92.20	0.30	2.16	2.40
2022-06-30 21:05	100.06	0.12	102.21	0.43	2.15	2.15
2022-06-30 21:14	175.13	0.15	178.62	0.23	3.49	1.99
2022-06-30 21:22	40.03	0.16	41.36	0.19	1.33	3.32
2022-06-30 21:31	19.98	0.14	20.93	0.20	0.95	4.75
2022-06-30 21:39	125.13	0.18	127.70	0.35	2.57	2.05
2022-06-30 21:48	60.06	0.15	61.78	0.16	1.72	2.86
2022-06-30 21:56	50.01	0.13	51.60	0.23	1.59	3.18
2022-06-30 22:05	10.18	0.20	10.91	0.32	0.73	7.17
2022-06-30 22:14	0.09	0.17	0.83	0.19	0.74	NA
2022-06-30 22:23	250.25	0.24	254.91	0.25	4.66	1.86
2022-06-30 22:31	200.14	0.13	204.04	0.33	3.90	1.95
2022-06-30 22:40	59.99	0.16	61.67	0.33	1.68	2.80
2022-06-30 22:48	225.14	0.15	229.53	0.31	4.39	1.95
2022-06-30 22:57	125.10	0.13	127.86	0.25	2.76	2.21
2022-06-30 23:05	70.03	0.19	71.99	0.29	1.96	2.80
2022-06-30 23:14	19.97	0.20	20.91	0.20	0.94	4.71
2022-06-30 23:22	150.23	0.15	153.54	0.29	3.31	2.20
2022-06-30 23:31	50.01	0.17	51.52	0.21	1.51	3.02
2022-06-30 23:39	250.22	0.25	254.88	0.18	4.66	1.86
2022-06-30 23:48	39.95	0.15	41.23	0.17	1.28	3.20
2022-06-30 23:56	200.21	0.14	204.02	0.26	3.81	1.90
2022-07-01 00:06	0.02	0.16	0.78	0.10	0.76	NA
2022-07-01 00:14	10.05	0.22	10.95	0.17	0.90	8.96
2022-07-01 00:23	80.04	0.18	81.99	0.24	1.95	2.44
2022-07-01 00:31	90.13	0.14	92.08	0.25	1.95	2.16
2022-07-01 00:40	175.19	0.16	178.66	0.34	3.47	1.98
2022-07-01 00:48	29.93	0.25	31.16	0.24	1.23	4.11
2022-07-01 00:57	100.14	0.22	102.26	0.33	2.12	2.12

Calibration Standards for CO, CH_4, CO_2 and N_2O

Table 5 shows an overview of available working standards for the calibration of the CO, CH_4, CO_2 and N_2O at JGS. The reference standards from the CCL that were used for the assignments of the values at the central calibration facility at NIMS are also listed.

Table 5 *Calibration standards at JGS and NIMS as of June 2022.*

Cylinder ID	N_2O (X2006A) (nmol mol^{-1})	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2 (X2019) (µmol mol^{-1})	Usage
CA06497	NA	NA	1888.19	389.41	NIMS Laboratory Standard (NOAA)
CA06366	NA	NA	2005.52	420.47	NIMS Laboratory Standard (NOAA)
CC702840	NA	NA	2237.98	457.37	NIMS Laboratory Standard (NOAA)
CB10980	NA	NA	2440.36	493.75	NIMS Laboratory Standard (NOAA)
CC703122	326.28	92.65	NA	NA	NIMS Laboratory Standard (NOAA)
CC703073	329.74	245.93	NA	NA	NIMS Laboratory Standard (NOAA)
CC702758	334.66	341.61	NA	NA	NIMS Laboratory Standard (NOAA)
CB10990	351.09	NA	NA	NA	NIMS Laboratory Standard (NOAA)
D339621	NA	331.26	1786.16	390.49	JGS Working Standard
D600653	NA	157.82	1839.91	407.42	JGS Working Standard
D339606	NA	271.60	1987.90	429.87	JGS Working Standard
D603601	NA	546.70	2182.46	452.56	JGS Working Standard
D603600	336.17	NA	NA	NA	JGS Working Standard

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 and after the audit. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA are given further below.

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

Table 6. Experimental details of the JGS 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 Tables 13 and 14.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #3438-CFKADS2342
Principle	Near-IR CRDS
Drying system	*Cryogenic trap (-50°C)*

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 7. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3438-CFKADS2342 instrument (AL) (Empa analysis) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-06-29 22:40:00)	180318_FF21167	223.7	0.6	222.4	0.4	3	-1.3	-0.6
(22-06-29 23:40:00)	171128_FA02476	151.5	0.6	153.0	0.6	3	1.5	1.0
(22-06-30 00:40:00)	210412_FB03377	8.4	0.4	18.3	0.3	3	9.9	118.3
(22-06-30 01:40:00)	160622_FB03911	313.9	0.7	309.3	0.5	3	-4.6	-1.5
(22-06-30 02:40:00)	171204_FA01469	105.4	0.8	108.7	0.4	3	3.3	3.2

Methane Comparisons

Procedure: same as for CO, see above.

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. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3438-CFKADS2342 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-06-29 22:40:00)	180318_FF21167	1762.25	0.06	1761.89	0.05	3	-0.36	-0.02
(22-06-29 23:40:00)	171128_FA02476	1860.16	0.02	1859.76	0.03	3	-0.40	-0.02
(22-06-30 00:40:00)	210412_FB03377	2.73	0.07	0.61	0.02	3	-2.12	-77.66
(22-06-30 01:40:00)	160622_FB03911	2352.44	0.02	2352.41	0.03	3	-0.03	0.00
(22-06-30 02:40:00)	171204_FA01469	1933.27	0.03	1932.92	0.03	3	-0.35	-0.02

Carbon Dioxide Comparisons

Procedure: same as for CO, see above.

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 9. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2401 #3438-CFKADS2342 instrument (AL) with the WCC-Empa TS (WMO-X2019 CO_2 scale).

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(22-06-29 22:40:00)	180318_FF21167	374.48	0.02	374.63	0.00	3	0.15	0.04
(22-06-29 23:40:00)	171128_FA02476	418.50	0.01	418.51	0.00	3	0.01	0.00
(22-06-30 00:40:00)	210412_FB03377	0.24	0.01	1.21	0.00	3	0.97	404.17
(22-06-30 01:40:00)	160622_FB03911	427.35	0.01	427.34	0.01	3	-0.01	0.00
(22-06-30 02:40:00)	171204_FA01469	407.02	0.01	407.06	0.01	3	0.04	0.01

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 and after the audit. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA are given further below.

Table 6 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the JGS data acquisition system. The standards used for the calibration of the JGS instruments are shown in Table 5.

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 10. *N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015 instrument (AL)) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-06-30 21:00:00)	171128_FA02476	322.52	0.03	323.63	0.26	3	1.11	0.34
(22-07-01 00:20:00)	180318_FF21167	298.78	0.10	301.84	0.22	3	3.06	1.02
(22-07-01 17:00:00)	160622_FB03911	330.32	0.05	330.71	0.09	3	0.39	0.12
(22-07-02 02:40:00)	171204_FA01469	343.01	0.07	342.38	0.17	3	-0.63	-0.18

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 49i-PS #0810-153, BKG 0.0, COEF 1.007

Zero air source: Pressurised 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 11. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 14). 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)).

$$X_{TS} \text{ (nmol mol}^{-1}\text{)} = ([TS] - 0.02 \text{ nmol mol}^{-1}) / 0.9990 \quad (6a)$$

$$u_{TS} \text{ (nmol mol}^{-1}\text{)} = \text{sqrt}((0.43 \text{ nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (6b)$$

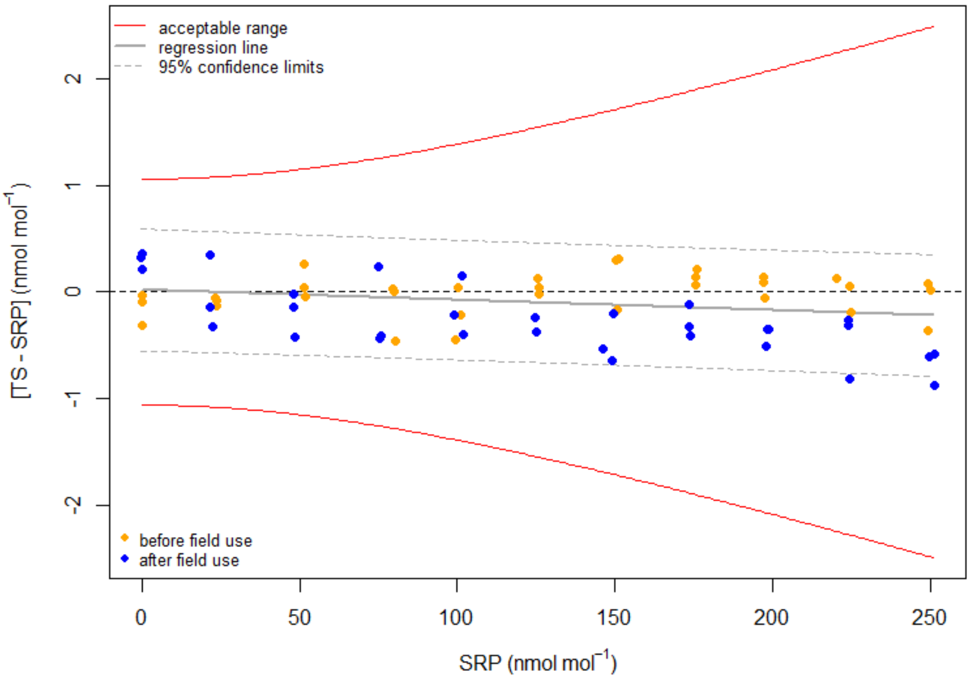

Figure 14. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 11. Mean values computed over at least five minutes for the comparison of the WCC-Empa traveling standard (TS) with the Standard Reference Photometer (SRP).

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-05-20	1	25	23.69	0.50	23.61	0.28
2022-05-20	1	50	51.44	0.48	51.71	0.19
2022-05-20	1	175	175.50	0.49	175.64	0.26
2022-05-20	1	80	80.14	0.59	79.68	0.31
2022-05-20	1	0	0.03	0.52	-0.06	0.20
2022-05-20	1	100	99.33	0.29	98.89	0.24
2022-05-20	1	195	197.21	0.29	197.31	0.17
2022-05-20	1	150	150.99	0.56	151.31	0.29
2022-05-20	1	250	249.57	0.46	249.20	0.21
2022-05-20	1	225	225.01	0.29	224.82	0.33
2022-05-20	1	125	126.02	0.39	126.07	0.19
2022-05-20	2	150	150.29	0.26	150.59	0.22
2022-05-20	2	195	196.97	0.19	197.11	0.18
2022-05-20	2	100	100.31	0.18	100.36	0.26
2022-05-20	2	125	125.82	0.34	125.80	0.33
2022-05-20	2	225	224.56	0.17	224.62	0.37
2022-05-20	2	25	23.22	0.20	23.17	0.22
2022-05-20	2	250	250.04	0.21	250.06	0.33
2022-05-20	2	80	79.53	0.28	79.56	0.21
2022-05-20	2	0	0.09	0.25	-0.22	0.17
2022-05-20	2	50	51.59	0.27	51.55	0.19
2022-05-20	2	175	175.61	0.21	175.67	0.19
2022-05-20	3	80	80.02	0.29	80.03	0.22
2022-05-20	3	125	125.29	0.19	125.42	0.18
2022-05-20	3	25	23.59	0.19	23.47	0.18
2022-05-20	3	200	197.70	0.32	197.64	0.10
2022-05-20	3	50	51.23	0.40	51.27	0.36
2022-05-20	3	175	175.96	0.35	176.18	0.15
2022-05-20	3	220	220.27	0.24	220.40	0.24
2022-05-20	3	150	150.92	0.31	150.75	0.31
2022-05-20	3	250	249.44	0.25	249.52	0.24
2022-05-20	3	100	100.94	0.25	100.73	0.28
2022-05-20	3	0	-0.13	0.24	-0.16	0.28
2022-09-16	4	25	22.36	0.34	22.04	0.33
2022-09-16	4	150	146.30	0.35	145.77	0.21
2022-09-16	4	225	224.33	0.29	223.51	0.31
2022-09-16	4	175	173.77	0.25	173.36	0.28
2022-09-16	4	75	75.04	0.18	75.28	0.21
2022-09-16	4	50	48.23	0.39	48.08	0.32
2022-09-16	4	200	198.28	0.36	197.94	0.31
2022-09-16	4	250	251.47	0.32	250.59	0.28
2022-09-16	4	0	-0.11	0.22	0.25	0.17
2022-09-16	4	100	98.85	0.22	98.64	0.23
2022-09-16	4	125	125.21	0.41	124.83	0.23
2022-09-16	5	225	223.99	0.27	223.67	0.33

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-09-16	5	250	251.24	0.46	250.66	0.32
2022-09-16	5	125	124.68	0.26	124.44	0.29
2022-09-16	5	50	48.33	0.33	47.91	0.18
2022-09-16	5	150	148.97	0.24	148.33	0.30
2022-09-16	5	175	173.43	0.20	173.31	0.24
2022-09-16	5	25	21.47	0.24	21.82	0.27
2022-09-16	5	75	75.93	0.31	75.53	0.20
2022-09-16	5	200	198.11	0.37	197.60	0.39
2022-09-16	5	100	101.82	0.27	101.42	0.30
2022-09-16	5	0	-0.29	0.38	0.04	0.32
2022-09-16	6	175	173.52	0.48	173.20	0.20
2022-09-16	6	25	21.72	0.24	21.58	0.37
2022-09-16	6	250	249.75	0.40	249.15	0.19
2022-09-16	6	150	149.47	0.21	149.27	0.23
2022-09-16	6	225	224.08	0.23	223.82	0.19
2022-09-16	6	200	198.90	0.30	198.55	0.28
2022-09-16	6	0	-0.16	0.18	0.05	0.17
2022-09-16	6	125	124.85	0.39	124.61	0.50
2022-09-16	6	75	75.48	0.47	75.05	0.17
2022-09-16	6	100	101.57	0.35	101.72	0.29
2022-09-16	6	50	47.89	0.29	47.87	0.32

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

CO: WMO-X2014A scale (Novelli et al., 2003)
CO_2: WMO-X2019 scale (Hall et al., 2021)
CH_4: WMO-X2004A scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (https://gml.noaa.gov/ccl/n2o_scale.html)

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

CO and N_2O:	Aerodyne mini-cw	(Mid-IR Spectroscopy).
CO and N_2O:	LGR 913-0015	(Mid-IR Spectroscopy).
CO, CO_2 and CH_4:	Picarro G2401	(Cavity Ring-Down Spectroscopy).

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

For N_2O, data of the LGR 913-0015 was used, because this instrument shows less cross-sensitivity to CO compared to the Aerodyne mini-cw.

Table 12 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including standard deviations of the WCC-Empa TS are listed in Table 13 and 14, and Figures 15 and 16 show the analysis of the TS over time.

Table 12. *CCL laboratory standards and working standards at WCC-Empa.*

Cylinder	CO (nmol mol^{-1})	CH_4 (nmol mol^{-1})	N_2O (nmol mol^{-1})	CO_2 (µmol mol^{-1})
CC339478#	463.76	2485.25	357.19	484.63
CB11499#	141.03	1933.77	329.15	407.53
CB11485#	110.88	1844.78	328.46	394.49
CA02789*	448.67	2097.48	342.18	496.15
190618_CC703041§	3244.00	2258.07	NA	419.82

used for calibrations of CO_2, CH_4 and N_2O
* used for calibrations of CO
§ used for calibrations of CO (Picarro G2401)

Table 13. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, and N_2O. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, and (L) LGR.*

TS	**Press. (psi)**	**CH_4 (P) (nmol mol^{-1})**	**sd**	**CO_2(P) (µmol mol^{-1})**	**sd**	**N_2O (A) (nmol mol^{-1})**	**sd**	**N_2O (L) (nmol mol^{-1})**	**sd**
160622_FB03911	320	2352.44	0.02	427.35	0.01	330.32	0.05	330.29	0.02
171128_FA02476	1360	1860.16	0.02	418.5	0.01	322.52	0.03	322.52	0.02
171204_FA01469	480	1933.27	0.03	407.02	0.01	343.01	0.07	343.05	0.01
180318_FF21167	1540	1762.25	0.06	374.48	0.02	298.78	0.1	298.89	0.03
210412_FB03377	1100	2.73	0.07	0.24	0.01	10.38	0.08	15.16	0.33

Table 14. *Calibration summary of the WCC-Empa travelling standards for CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, and (L) LGR.*

TS	**Press. (psi)**	**CO (P) (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**	**CO (L) (nmol mol^{-1})**	**sd**
160622_FB03911	320	313.92	0.68	311.04	0.31	309.67	0.27
171128_FA02476	1360	151.52	0.59	149.15	0.18	147.88	0.27
171204_FA01469	480	105.35	0.8	103.22	0.14	102.63	0.21
180318_FF21167	1540	223.70	0.57	221.12	0.13	219.47	0.16
210412_FB03377	1100	8.40	0.43	7.16	0.40	7.64	0.40

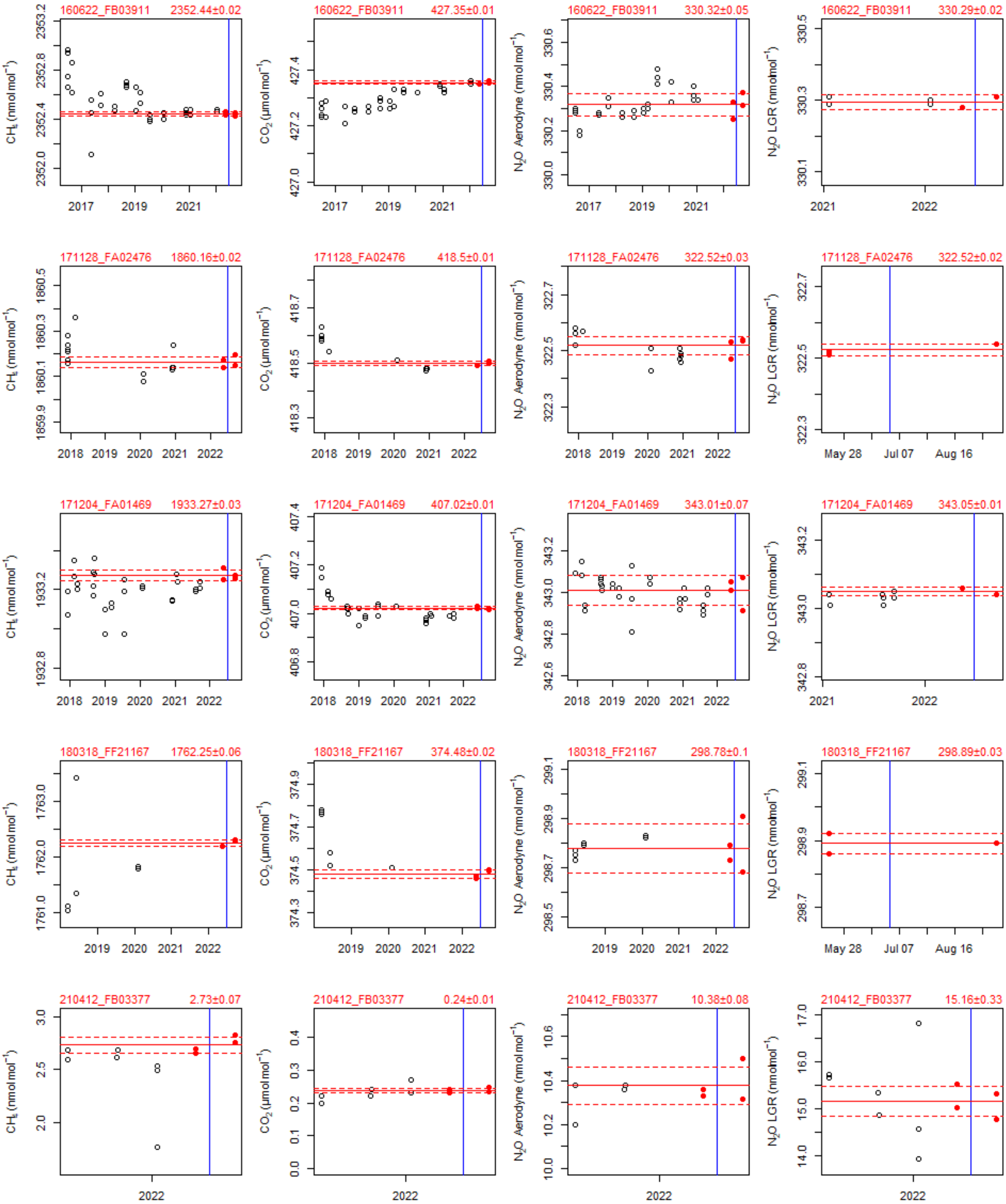

Figure 15. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

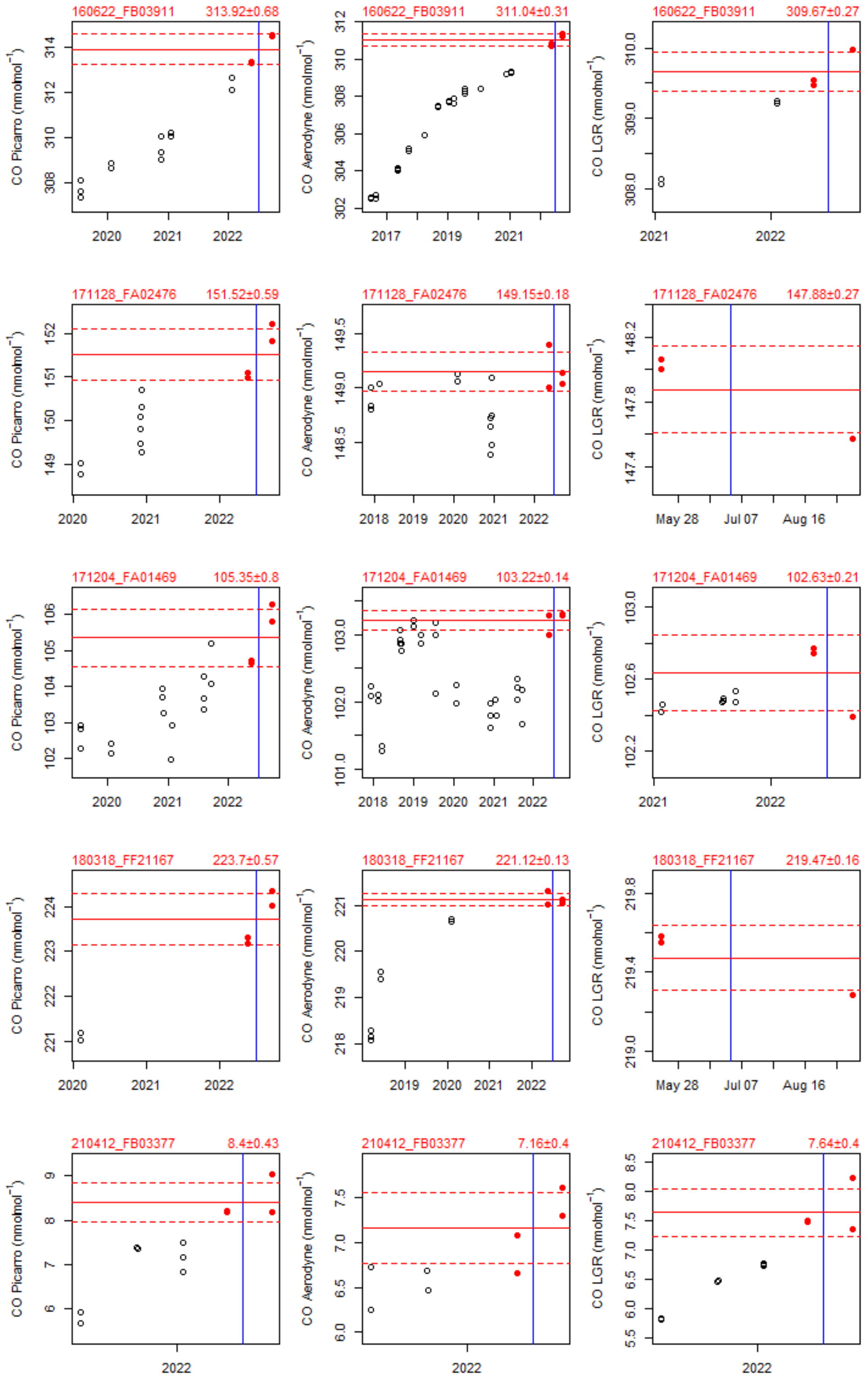

Figure 16. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

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 #1497-CFKADS2098 was calibrated every 1775 min using one WCC-Empa TS as a working standard, and two TS as target tanks. 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. 0.2 nmol mol^{-1} for CH_4 and 0.04 µmol mol^{-1} for CO_2. All target cylinders measurements were within half of the WMO GAW compatibility goals.

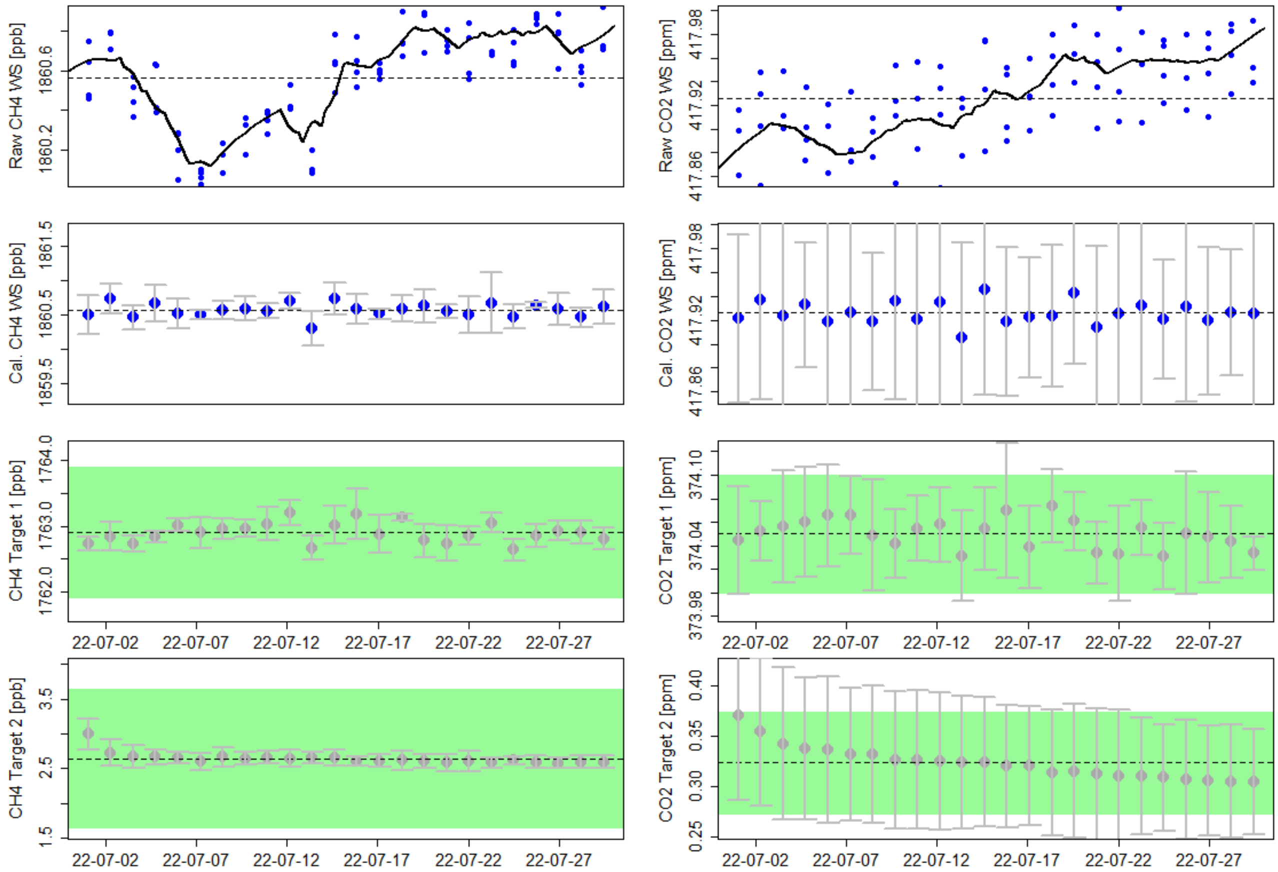

Figure 17. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 1775 min with 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.

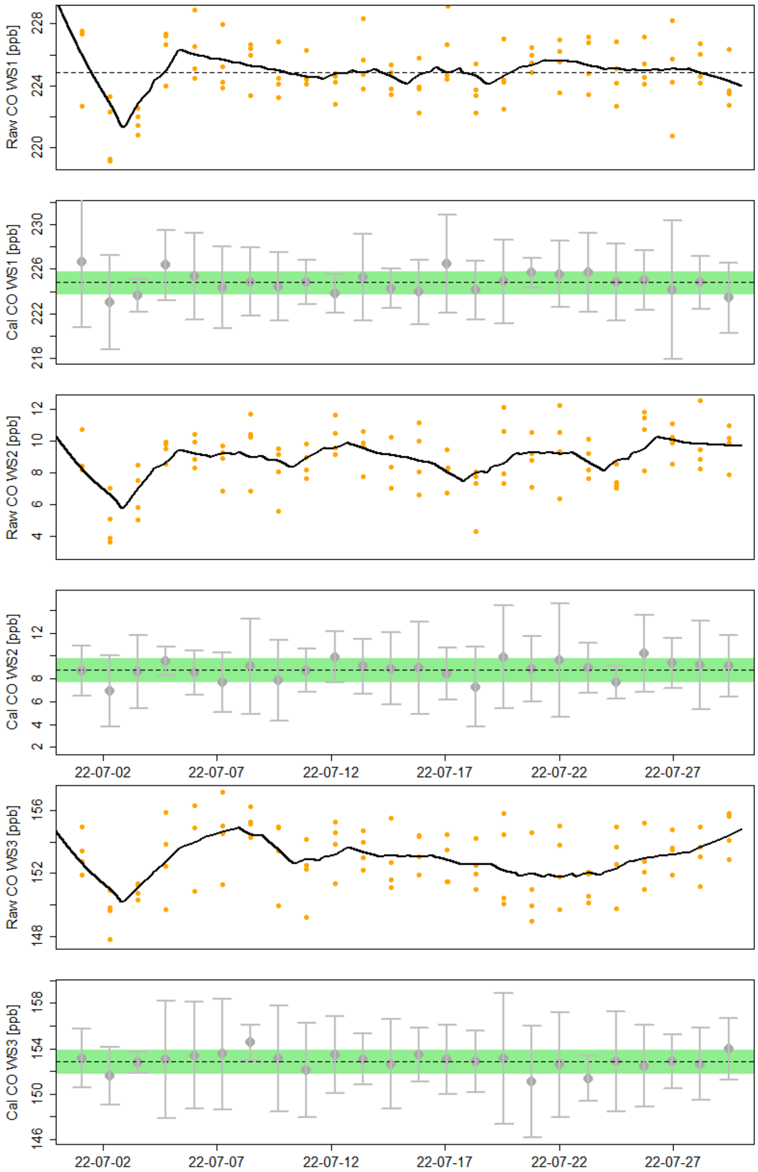

Figure 18. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the uncertainty 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
CCL	Central Calibration Laboratory
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
FID	Flame Ionization Detection
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
JGS	Jeju Gosan GAW Station
KRISS	Korea Research Institute of Standards and Science
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NIER	National Institute Of Environmental Research
NIMS	National Institute of Meteorological Sciences
NOAA	National Oceanic and Atmospheric Administration
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SN	Serial Number
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization
WS	Working Standard