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

AT THE

GLOBAL GAW STATION PALLAS FINLAND

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WCC-Empa Report 21/1

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 5th system and performance audit by WCC-Empa[1] at the global GAW station Pallas (PAL) was conducted from 5 - 7 July 2021 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at PAL, as well as the corresponding audit reports, 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
Mr Juha Hatakka	FMI, station manager, head of the observatory
Dr Tuomas Laurila	FMI, leader greenhouse gases research group
Mr Timo Anttila	FMI, technician, reactive gases
Dr Hermanni Aaltonen	FMI, ICOS mobile laboratory, ICOS observations

This report summarises the assessment of the Pallas 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 of Pallas, the national focal point for GAW in Finland, 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

PAL is operated by the Finnish Meteorological Institute (FMI), but the station itself is managed by Metsähallitus (https://www.metsa.fi). The station is routinely visited once a week by a local station operator from Metsähallitus. FMI scientists visit the site at least five times per year for routine checks and calibrations, or more often in case of measurement issues. PAL is also a class 1 station of the Integrated Carbon Observation System (ICOS; https://www.icos-ri.eu) and a sampling site of NOAA's cooperative air sampling network (https://gml.noaa.gov/ccgg/flask.html). ICOS is a contributing network to GAW and focusses on the observation of greenhouse gas concentrations in the atmosphere as well as carbon fluxes between the atmosphere, the land surface and the oceans in Europe. The ICOS atmosphere network is highly standardized in term of instrumentation, periphery, calibration gases, and calibration strategies. All ICOS data are centrally processed at the ICOS Atmospheric Thematic Centre in Gif-sur-Yvette, France. More information about the PAL-site can be found on the station website (https://en.ilmatieteenlaitos.fi/pallas-atmosphere-ecosystem-supersite).

Station Location and Access

PAL (67.9736°N, 24.1158°E, 560 m a.s.l.) is located within the Pallas-Yllästunturi National Park. The main monitoring station, where most of the GAW and ICOS atmospheric measurements are made, is located on top of a fjeld (a subarctic hill), ca. 300 m above the surrounding area and 100 m above the tree line. The vegetation on the fjeld top consists mainly of low vascular plants, moss, and lichen. The region is hilly with the highest elevations of 600-800 m within 3-6 km from the station. The sectors 180°-330° and 100-130° are very open. The location is free of significant local and regional pollution sources with the nearest town, Muonio with approx. 2500 inhabitants, being 19 km to the west. The second-nearest

[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 based on mutual agreement.

town, Kittilä, with 6000 inhabitants, is 46 km to the south-east. More information is available from GAWSIS (https://gawsis.meteoswiss.ch) and the station web site (https://en.ilmatieteenlaitos.fi/pallas-atmosphere-ecosystem-supersite).

The location is adequate for the intended purpose. Year-round access to PAL is possible by snow mobile during winter and with ATV (All-Terrain Vehicle) during the snow free period. Access can be difficult during autumn and spring when the snow cover is too thin for the snow mobile.

Station Facilities

The PAL facilities have not significantly changed since the last WCC-Empa audit in 2012. The station consists of a 120 m^2 building with a large room for the analytical equipment, and separate rooms for pumps, storage and office. The infrastructure is ideally supporting research projects and long-term atmospheric observations.

Measurement Programme

The PAL supersite hosts a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured species is available from GAWSIS and the station web site (https://en.ilmatieteenlaitos.fi/pallas-atmosphere-ecosystem-supersite).

The information available from GAWSIS was reviewed as part of the audit. The last update was made in June 2020, and the information was mostly up-to-date. However, more details (e.g. instrument characteristics) should be added.

> **Recommendation 1 (***, 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 October 2021, the following PAL data of the scope of the audit has been submitted to the World Data Centres:

FMI, Submission to the World Data Centre for Reactive Gases (WDCRG; https://www.gaw-wdcrg.org):
O_3 (two data sets, 1995-2013, and 2014-2020)

FMI, submission to World Data Centre for Greenhouse Gases (WDCGG; https://gaw.kishou.go.jp):
CH_4 (2004-2020), CO_2 (1998-2020)

National Oceanic and Atmospheric Administration (NOAA), submission to WDCGG:
CO_2 (2001-2020), CH_4 (2001-2020), CO (2001-2020), N_2O (2001-2020) (all flask observations)

Data shown in this report was accessed on 15 July 2021.

> **Recommendation 2 (***, important, ongoing)**
> *Data has been partly submitted for the parameters of the scope of the audit. The submission delay varies depending on the parameter, but most available data was timely submitted with a delay of one to two years. However, in-situ data of CO and N_2O has not yet been submitted. 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. Missing CO and N_2O data should also be submitted after a final quality check.*

Data Review

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

Documentation

All information is entered in electronic log books. Log books are available for all instruments as well as for the station. The log book entries are automatically transferred to a server, and can be accessed on a web application. The instrument manuals are available at the site. The reviewed information was comprehensive and up-to-date.

Air Inlet System

GAW measurements: The design of the air inlet system (O_3, CO and greenhouse gases (GHG, i.e. CO_2, CH_4, N_2O) has not been changed since the last audit by WCC-Empa. The station has a state-of-the art inlet system; the main inlet manifold is made of stainless steel with an outer diameter of 60 mm, and is continuously flushed with a nominal flow rate of 150 m^3h^{-1}. All GAW instruments (O_3, CO and GHG) are connected to this manifold with stainless steel (CO and GHG) or PFA (O_3) tubing. The air intake is located on top of the PAL building, approximately 3 m above the laboratory building roof and 7 m above round. The inlet is heated to avoid freezing and condensation of water vapour.

ICOS measurements: A separate inlet was installed for the ICOS measurements. Sampling is made from a 12 m high mast next to the PAL building. Five ¼ inch Synflex 1300 are used for direct sampling of the air. The Synflex lines are also heated to avoid freezing, and are protected with a filter unit at the air intake.

The inlet systems, both for the GAW and the ICOS measurements, are adequate regarding material and residence times, and no change is required.

Surface Ozone Measurements

Surface ozone measurements at PAL were established in 1994, and continuous time series are available since then.

Instrumentation. PAL is currently equipped with one ozone analysers (Thermo Scientific 49i).

> **Recommendation 3 (*, minor, already done)**
> *A large difference in the intensities of cell A (40630 Hz) and B (149650 Hz) was noticed. It is recommended to exchange or service the analyser; exchange was done on 4 September 2021.*

Standards. No standard is available at the site. However, a transfer standard (Thermo Scientific 49i-PS) is available at FMI, and is used approximately four times per year to verify the calibration of the PAL instrument. The FMI transfer standard has traceability to FMI's Standard Reference Photometer (SRP) #37. If the results of the check is within 5%, no further corrections are made. The calibration settings of the analyser are also not changed based on the checks if the results are within 5%.

> **Recommendation 4 (*, minor, 2022)**
> *The 5% criteria is compliant with EN 14625 (2012) but allows large deviations. It is very likely that there are instrumental problems if this limit is exceeded. It should be considered to lower the limit to 1 nmol mol^{-1} or 1% (whichever is larger).*

Data Acquisition. Envidas version 1.2.27 (Envitech Ltd) is used. One minute averages are acquired and automatically transferred to an FMI server. The data acquisition system is appropriate, and no further action is required.

Recommendation 5 (*, critical, 2022)**
It was noticed that the data acquisition was set to the time zone UTC+3, which corresponds to day light saving time. The time setting needs to be checked / verified, and it must be made sure that submitted data refers to only one time zone (either UTC or local standard time, UTC+2).

Intercomparison (Performance Audit). The PAL analyser 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 200 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 (TS) and the PAL 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 11.476x10^{-18} cm^2 molecule^{-1} (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #1192744581 (BKG -0.2 nmol mol^{-1}, SPAN 0.987):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -0.91 nmol mol^{-1}) / 0.9941 (1a)

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

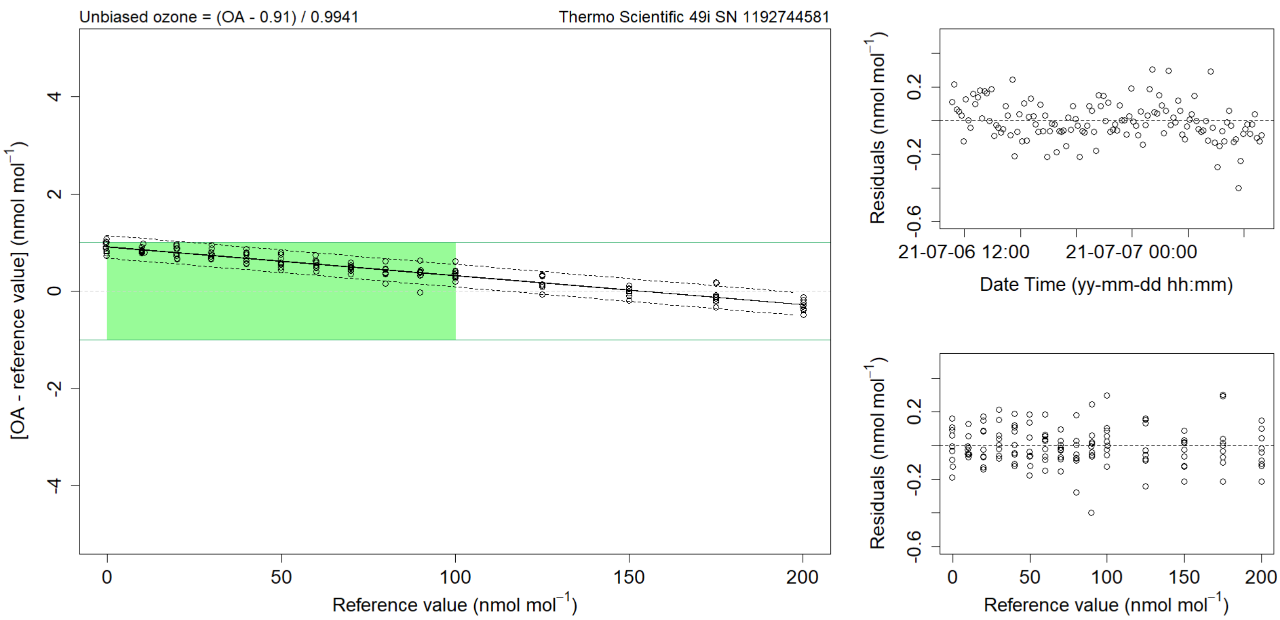

Figure 1. *Left: Bias of the PAL ozone analyser (Thermo Scientific 49i #1192744581, BKG -0.2 nmol mol^{-1}, COEF 0.987) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant 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 result of the PAL ozone analyser was within the WMO/GAW DQOs over the entire measured range. The observed zero offset was most likely due to an issue with the WCC-Empa zero air system. It was noted that the zero point was drifting, and the final comparison shown above was made after a long stabilisation period of about 24 hours. Tests were made after the audit at the WCC-Empa laboratory, and the effect disappeared after replacement of the activated charcoal cartridge.

Carbon Monoxide Measurements

Continuous measurements of CO at PAL started in 2004 using gas chromatographic (GC) systems, and Cavity Ringdown Spectroscopy (CRDS) measurements started in 2011. An Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument was added 2013.

Instrumentation. The following instruments are currently available:
Pallas GAW measurements: Picarro G2401 (CRDS) without drying system, and LGR 913-0015-0002 (OA-ICOS) with a Nafion dryer (MD-070-96S-2). ICOS: Picarro G2401 using a Nafion dryer (MD-070-144S-2) to dry the sample air. Comparisons were only made with the GAW instruments of Pallas.

Standards. Several reference standards from the GAW Central Calibration Laboratory (CCL), as well as working standards and target gas cylinders filled by FMI are available at PAL. An overview of available standards is shown in Table 5 in the Appendix. In addition, standards from the ICOS Flask and Calibration Laboratory (FCL) are available for the ICOS measurements.

Calibration procedure of the GAW Picarro instrument: Calibrations using the reference standards are made manually during station visits about 5 times per year. Nine reference standards are analysed together with the WS and target gas. Each standard is measures for 18 minutes, and only the last 9 minutes of the cycle is averaged. The sequence is repeated three times, but only the last two runs are used to ensure proper flushing of the lines and pressure regulators. To compensate for instrument drift, a working standard is automatically measured every 7 hours for 15 minutes, and a target gas is analysed every 25 hours for 15 minutes.

Calibration procedure of the GAW LGR instrument: Calibrations using the reference standards are made manually during station visits about 5 times per year. Seven reference standards are analysed together with the WS and target gas. Each standard is measures for 9 minutes, and only the last 3 minutes of the cycle is averaged. The sequence is repeated three to four times. The first run is rejected to ensure proper flushing of the lines and pressure regulators. To compensate for instrument drift, a working standard is automatically measured every 3 hours for 8 minutes, and a target gas is analysed every 13 hours for 9 minutes.

Intercomparison (Performance Audit). The comparisons involved repeated challenges of the PAL 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 2 and 3 with respect to the WMO GAW DQOs (WMO, 2020):

Picarro G2401 #306-CFKADS-2066 (instrument without dryer):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 2.35 nmol mol^{-1}) / 0.9979 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.1 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2b)

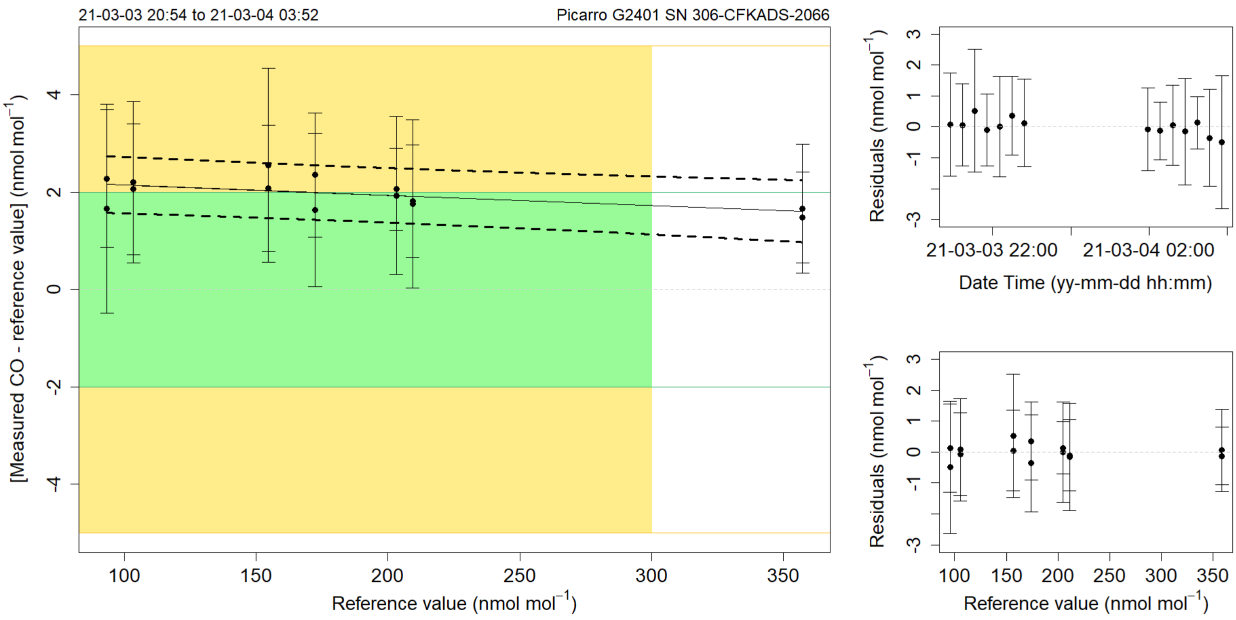

Figure 2. *Left: Bias of the PAL Picarro G2401 #306-CFKADS-2066 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of 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 PAL. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

LGR 913-0015-0002 #13-0055:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 5.69 nmol mol^{-1}) / 0.9842 (2c)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.3 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2d)

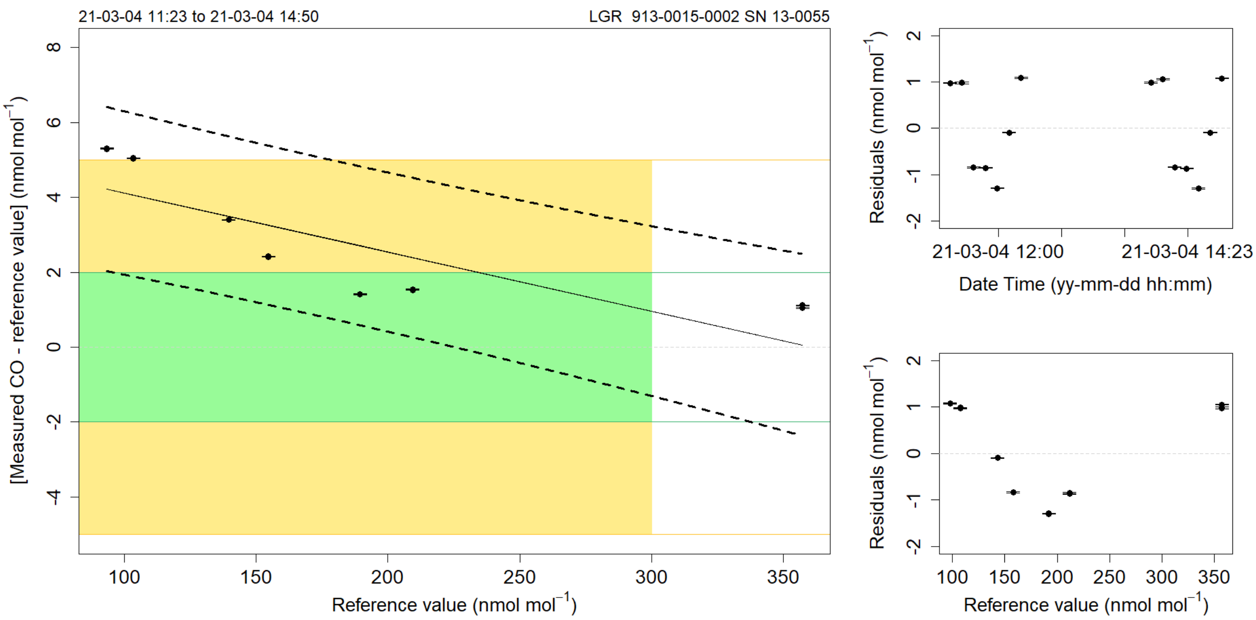

Figure 3. *Same as above, for the LGR 913-0015-0002 #13-0055 instrument.*

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 all instruments in the relevant amount fraction range. The Picarro instrument showed an almost constant offset of about 2 nmol mol^{-1}, which potentially could be caused by zero drift of the instrument. The Los Gatos analyser had a significant mole fraction dependency of the bias, which needs further attention.

> **Recommendation 6 (**, important, 2022)**
> *The reason for the non-linear behaviour of the Los Gatos instrument needs to be identified, and corrective actions must be made.*

Stability of CO in reference standards at low amount fractions remains a significant challenge, and therefore, the following recommendation is made:

> **Recommendation 7 (*, minor, 2021)**
> *The CRDS measurement technique shows a linear response for CO in the amount fraction range from at least 0 to 1000 nmol mol^{-1}. To minimise the influence of standard drift, WCC-Empa recommends that the calibration strategy focuses on higher CO mole fractions (300 to 1000 nmol mol^{-1}), and also includes CO free air (or N_2 6.0) to compensate for a zero offset.*

Methane Measurements

Continuous measurements of CH_4 at PAL started in 2004 using GC / flame ionization detection (FID). Since 2009 CH_4 measurements are made using CRDS technique, and the GC/FID system is no longer in operation.

Instrumentation. The following instruments are currently available:
Pallas GAW measurements: Picarro G2401 (CRDS) without drying system.
ICOS: Picarro G2401 using a Nafion dryer (MD-070-144S-2) to dry the sample air.
Comparisons were only made with the GAW instruments of Pallas.

Standards. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PAL GAW 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 results are 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 #306-CFKADS-2066 (instrument without dryer):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.39 nmol mol^{-1}) / 0.9990 (3a)

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

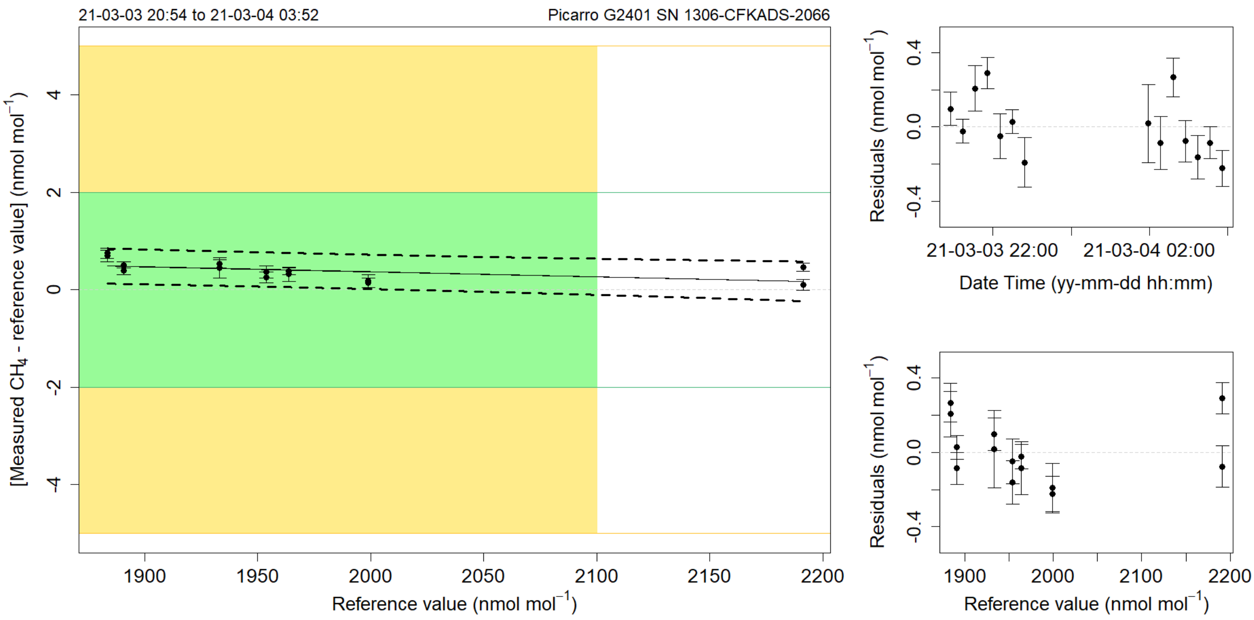

Figure 4. *Left: Bias of the Picarro G2401 #306-CFKADS-2066 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement 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 PAL. 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 within the WMO/GAW compatibility goal was found, and no significant dependency of the bias on the amount fraction was observed. This indicates that the whole system, including calibration procedures and standards gases, is fully appropriate, and no further action is required at present.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at PAL commenced in 1999 using NDIR technique and continuous data is available since then. Since 2009 CO_2 measurements are made using CRDS technique.

Instrumentation. The following instruments are currently available:
Pallas GAW measurements: Picarro G2401 (CRDS) without drying system.
ICOS: Picarro G2401 using a Nafion dryer (MD-070-144S-2) to dry the sample air.
Comparisons were only made with the GAW instruments of Pallas.

Standards. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PAL instrument with randomised CO_2 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 5 with respect to the relevant mole fraction range and the WMO/GAW compatibility goal and extended compatibility goal (WMO, 2020).

Picarro G2401 #306-CFKADS-2066 (instrument without dryer):

Unbiased CO_2 mixing ratio: X_{CO2} (μmol mol^{-1}) = (CO_2 – 0.50 μmol mol^{-1}) / 0.99875 (4a)

Remaining standard uncertainty: u_{CO2} (μmol mol^{-1}) = sqrt (0.001 μmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4b)

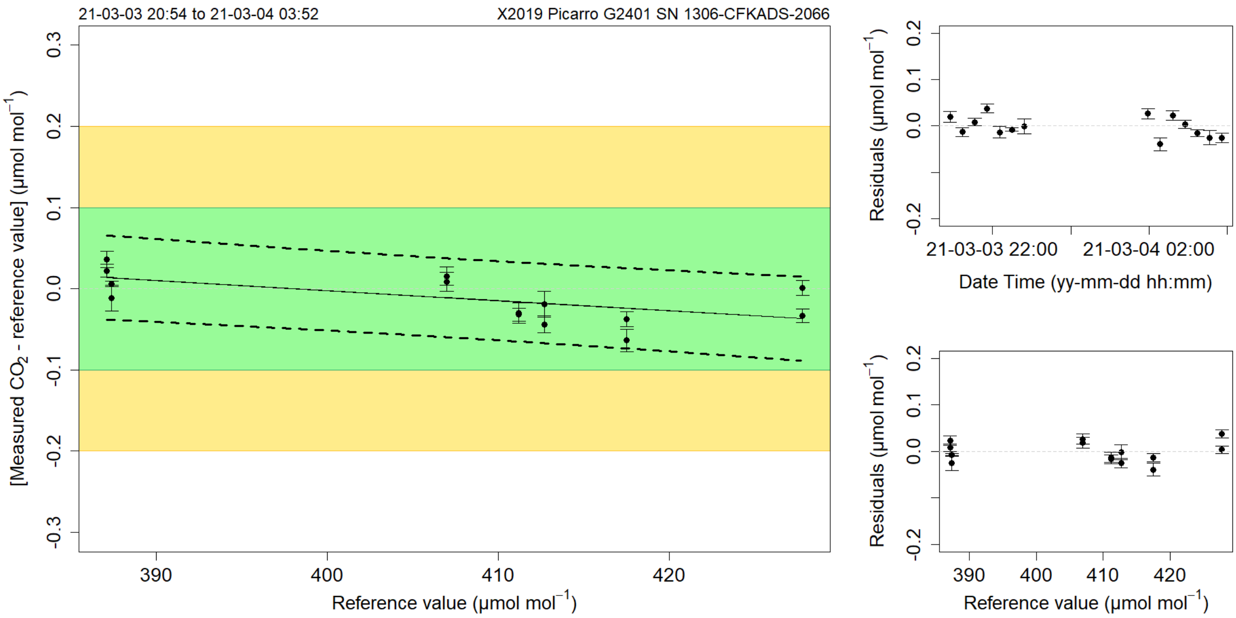

Figure 5. *Left: Bias of the Picarro G2401 #306-CFKADS-2066 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement 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 PAL. 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 Pallas GAW CRDS instrument showed agreement well within the WMO/GAW network compatibility goal, and were already reported on the WMO-X2019 CO_2 calibration scale (Hall et al., 2020). No significant amount fraction dependency of the bias was observed, which indicates that the entire measurement setup is fully appropriate.

Nitrous Oxide Measurements

Continuous measurements of N_2O at PAL started in 2004 using GC / electron capture detection (ECD). Since 2013 N_2O measurements are made using Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique, and the GC/ECD system is no longer in operation.

Instrumentation. LGR 913-0015-0002 (OA-ICOS) analyser (enhanced performance version) with a Nafion dryer (MD-070-96S-2).

Standards. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PAL 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 6 with respect to the WMO GAW DQOs (WMO, 2020):

LGR 913-0015-0002 #13-0055:

Unbiased N_2O mixing ratio:	X_{N2O} (nmol mol^{-1}) = (N_2O – 2.08) / 0.99322	(5a)
Remaining standard uncertainty:	u_{N2O} (nmol mol^{-1}) = sqrt (0.004 + 1.01e-07 * X_{N2O}^2)	(5b)

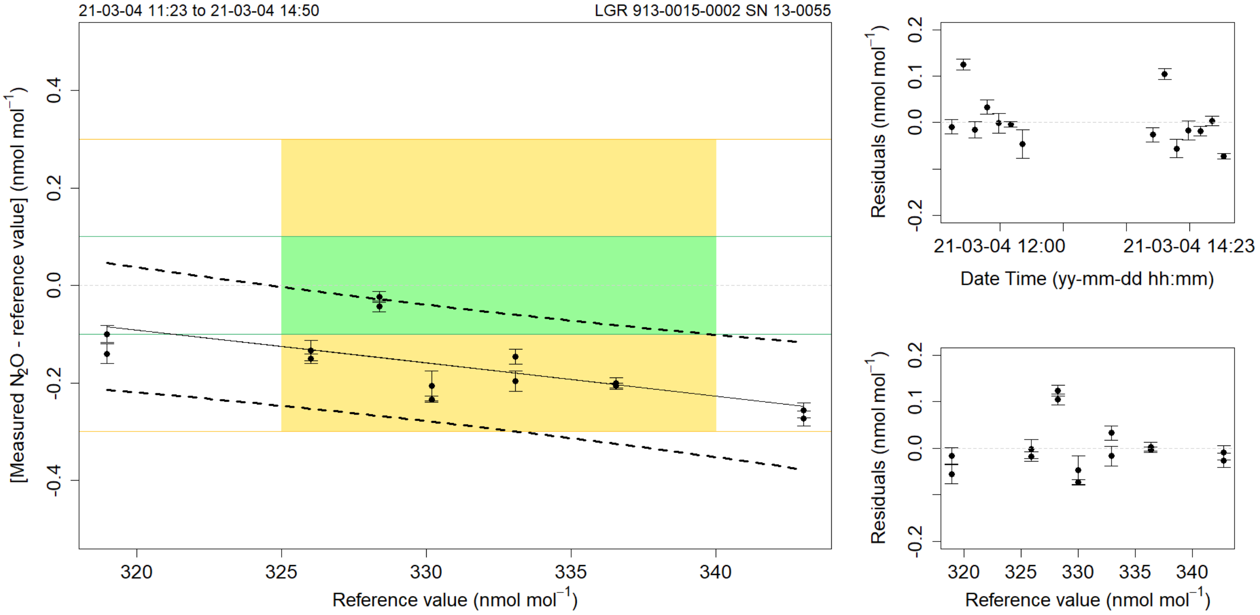

Figure 6. *Left: Bias of the LGR 913-0015 nitrous oxide analyser with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. 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 PAL. 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 between PAL and WCC-Empa was within the extended WMO/GAW network compatibility goal. Individual results showed a good repeatability, which confirms the functionality of the analytical system. The remaining bias is most likely dominated by the uncertainty of the reference standards, both from WCC-Empa and PAL. The analytical system is fully appropriate, and the limiting factor is most likely the uncertainty of the reference standards.

PAL PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the PAL 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 ppb 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 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 network goals in a certain mole fraction range. Figure 7 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 (excluding two outliers) are shown in Figure 8. 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 PAL audit are shown as coloured dots in Figure 7 and 8, 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 O_3, CH_4 and CO_2, and the extended WMO/GAW network compatibility goals were reached for the CRDS CO instrument and N_2O. The DQOs were not met for Los Gatos CO analyser due to a bias exceeding the goal at low mole fractions.

Table 1. *PAL 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**	**PAL within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**
O_3 (Thermo 49i #1192744581)	0 -100	nmol mol^{-1}	✓	64	NA
CO (Picarro G2401 CFKADS2066)	30 - 300	nmol mol^{-1}	✓	20	49
CO (LGR 913-0015)	30 - 300	nmol mol^{-1}	✗	20	49
CH_4 (Picarro G2401 CFKADS2066)	1750 - 2100	nmol mol^{-1}	✓	72	93
CO_2 (Picarro G2401 CFKADS2066)	380 - 450	µmol mol^{-1}	✓	44	70
N_2O (LGR 913-0015)	325 - 335	nmol mol^{-1}	✓	2	41

[1] Percentage of stations within the eDQO and DQO

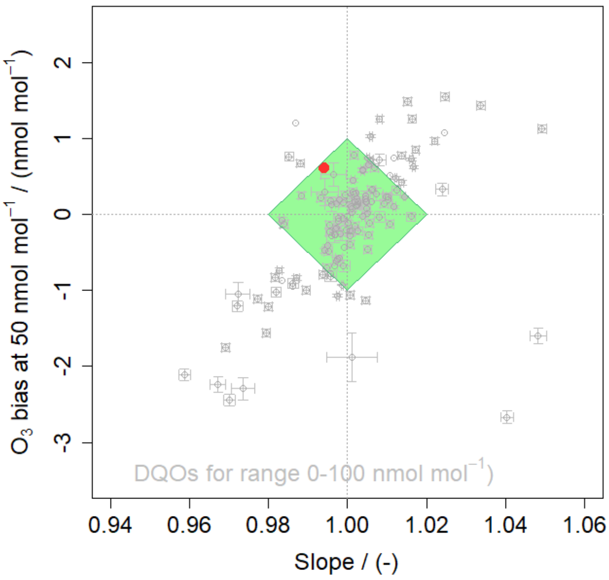

Figure 7. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the red dots shows the results of the PAL instrument. The uncertainty bars refer to the standard uncertainty, and the green area corresponds to the WMO/GAW DQO for surface ozone.*

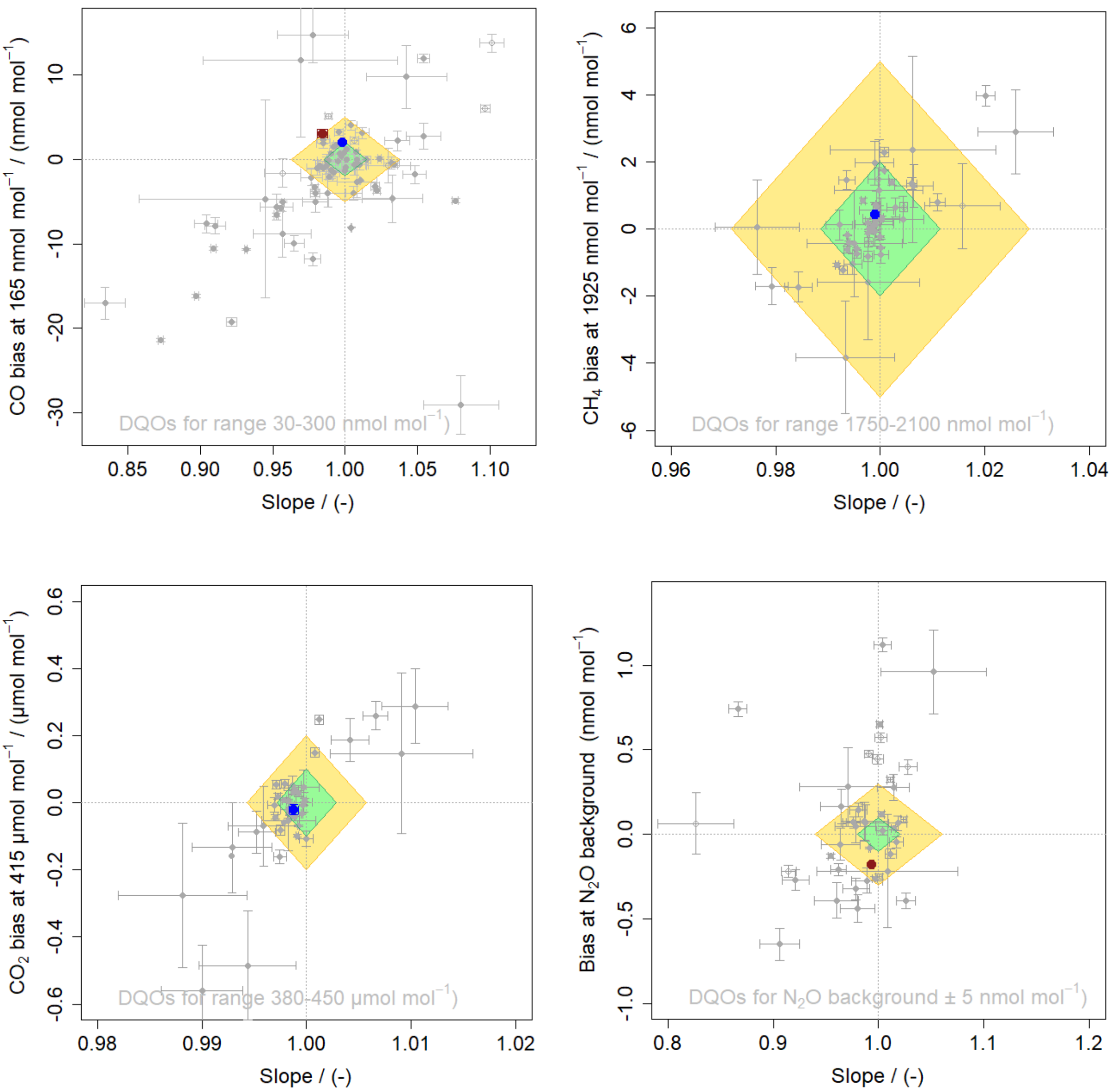

Figure 8. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show PAL results (dark red: LGR 913-0015, blue: Picarro G2401). 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 installed by the PAL station manager before the audit, and was running from 2 March through 6 July 2021 at PAL. The TI was connected to a separate independent inlet line (spare line of the ICOS inlet system) sampling from the same location as the PAL ICOS analysers. The TI was sampling air using the following sequence: 1745 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 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. The ICOS/PAL data shown here were processed by the ICOS Atmospheric Thematic Centre (ATC) and PAL.

Carbon monoxide comparison

Figure 9 shows the comparison of hourly CO measurements between the WCC-Empa TI and the PAL analysers. The corresponding deviation histograms are shown in Figure 10.

The deviation of the PAL measurements showed a similar pattern for both CRDS instrument, which was most likely caused by less stable measurements of the WCC-Empa TI. On average, the agreement was within the WMO/GAW network compatibility goals for the PAL instrument, while the ICOS analyser was within the extended WMO/GAW network compatibility goals. The comparison of ambient air showed a difference between the PAL and the ICOS CRDS instruments of about 3.5 nmol mol^{-1}.

Recommendation 8 (*, critical, 2022)**
The difference between the PAL and the ICOS CO measurements needs further attention, and the reason must be identified.

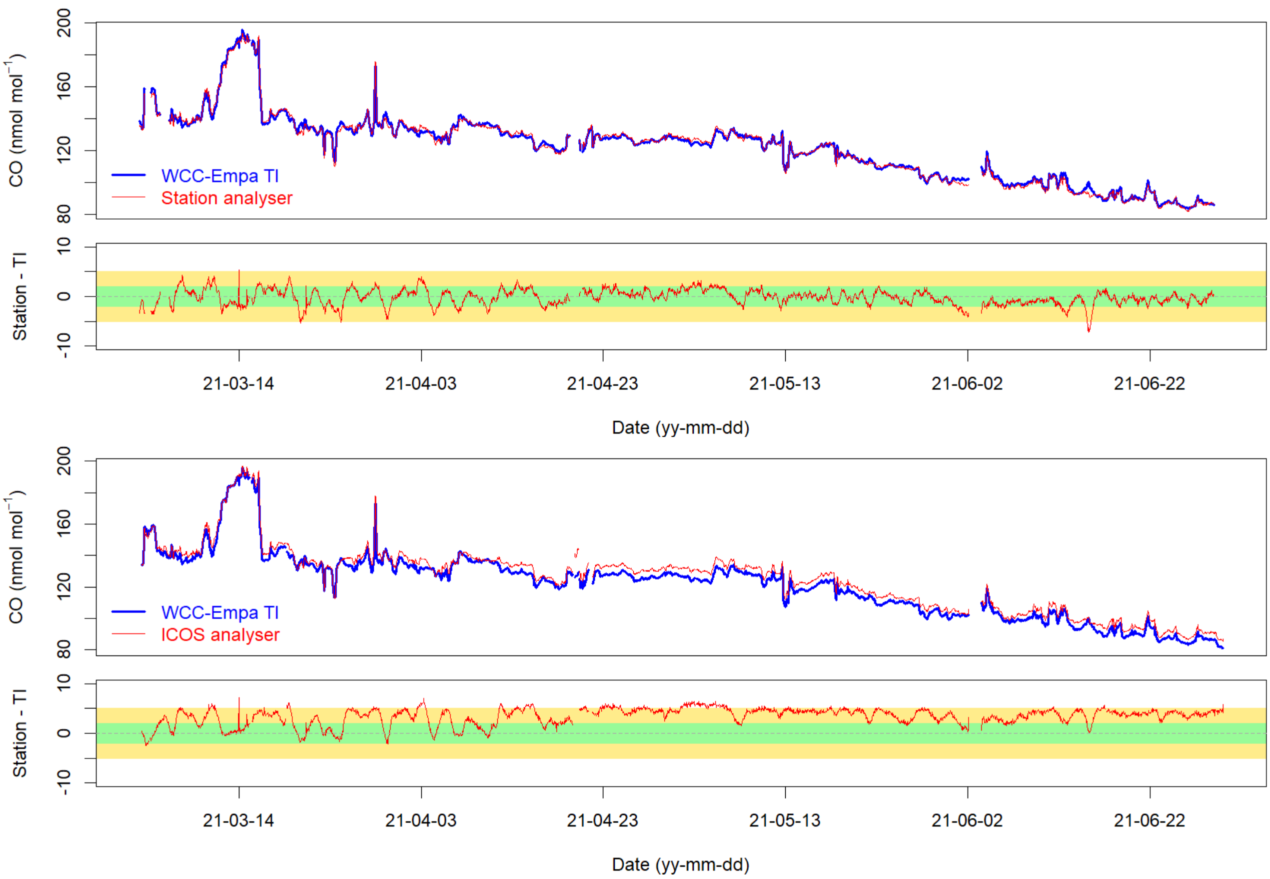

Figure 9. *Comparison of the Picarro G2401#306-CFKADS-2066 (instrument without dryer) (top) and the ICOS Picarro G2401#2037-CFKADS2164 (instrument with dryer) (bottom) analysers with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

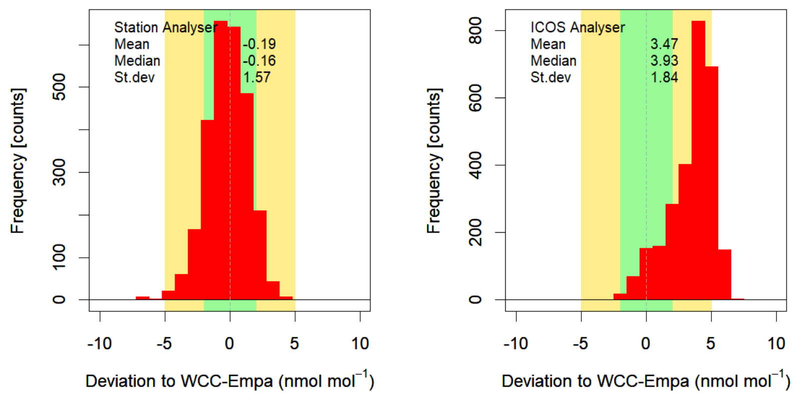

Figure 10. *Carbon monoxide deviation histograms for the Picarro G2401#306-CFKADS-2066 (instrument without dryer) (left) and the ICOS Picarro G2401#2037-CFKADS2164 (right).*

Methane

Figure 11 shows the comparison of hourly CH_4 between the WCC-Empa TI and the PAL CRDS instruments. The corresponding deviation histograms are shown in Figure 12. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers and the WCC-Empa TI. Excellent agreement within the WMO/GAW network compatibility goals was found between the TI and the PAL instruments, which confirms the results of the performance audit using traveling standards. The temporal variation was well captured by both instruments, which the ICOS analyser performing slightly better compared to the older PAL instrument.

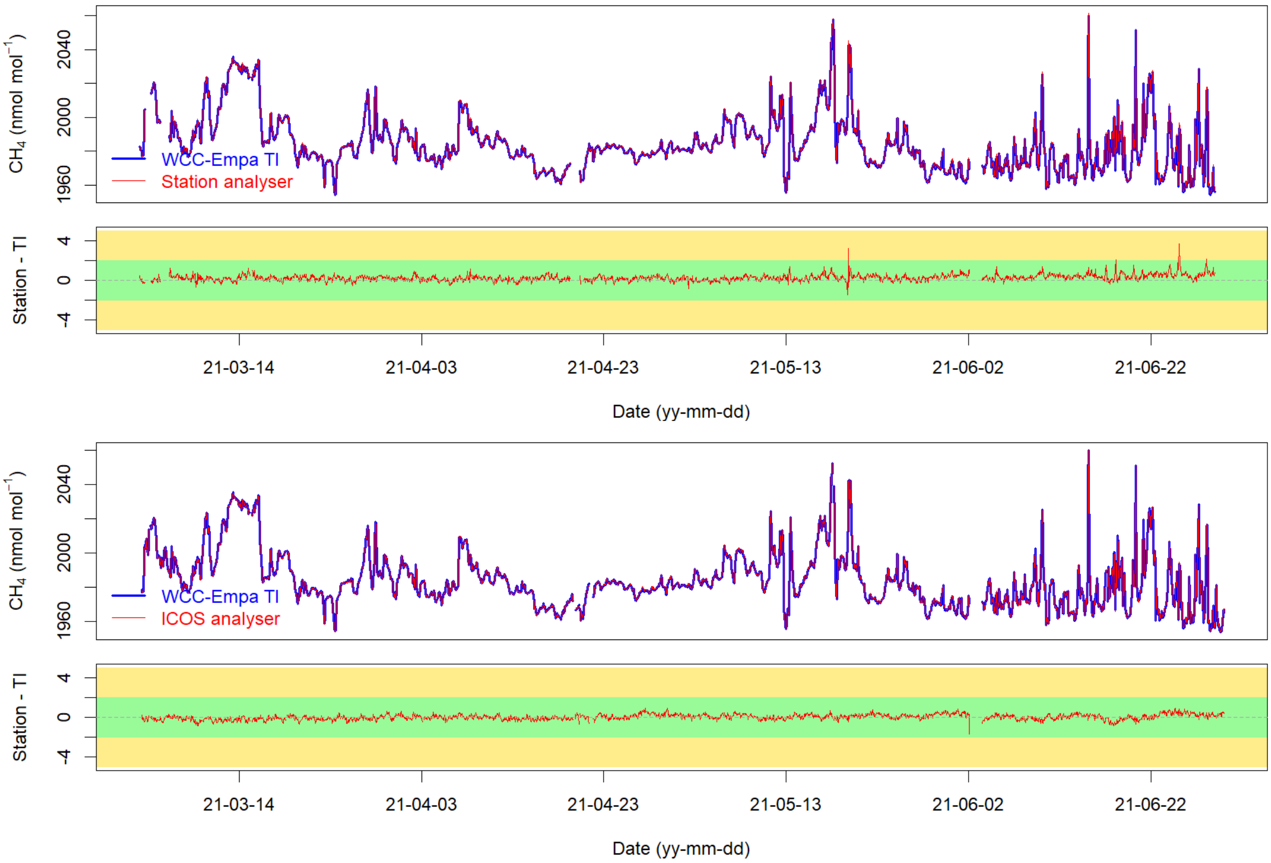

Figure 11. *Comparison of the PAL Picarro G2401#306-CFKADS-2066 (instrument without dryer) (top) and the Picarro G2401#2037-CFKADS2164 (instrument with dryer) (bottom) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

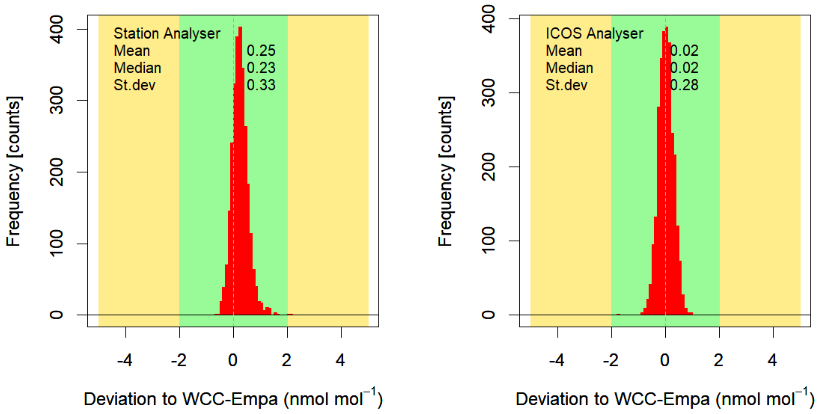

Figure 12. *Methane deviation histogram for the PAL Picarro G2401 G2401#306-CFKADS-2066 (left) and the Picarro G2401#2037-CFKADS2164 (right).*

Carbon dioxide

Figure 13 shows the comparison of hourly CO_2 between the WCC-Empa TI and the PAL CRDS instruments. The corresponding deviation histograms are shown in Figure 12. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers and the WCC-Empa TI. The temporal variability was well captured by both instruments, and no dependency of the bias on the amount fraction was observed. On average, the agreement was within the WMO/GAW network compatibility goal for the PAL instrument without the Nafion dryer, and within the extended compatibility goal for the ICOS instrument with a Nafion dryer. The results are in agreement with the bias observed during the travelling standard comparison.

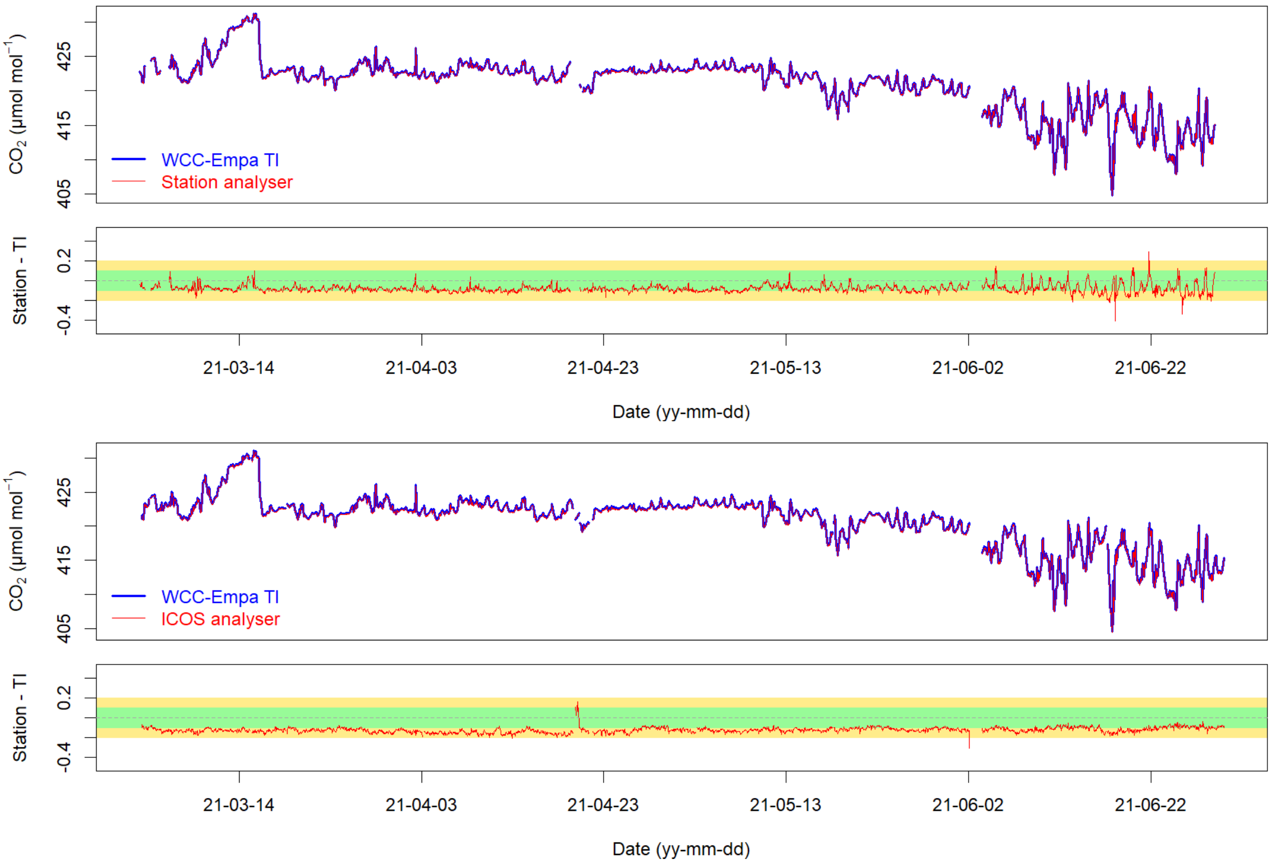

Figure 13. *Comparison of the PAL Picarro G2401 G2401#306-CFKADS-2066 (instrument without dryer) (top) and the Picarro G2401#2037-CFKADS2164 (instrument with dryer) (bottom) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data and the difference of the station instrument to the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

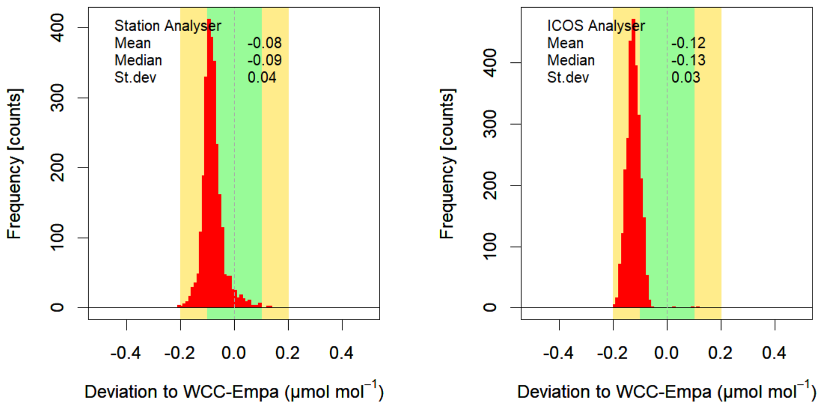

Figure 14. *Carbon dioxide deviation histogram of the PAL Picarro G2041 G2401#306-CFKADS-2066 (left) and the Picarro G2401#2037-CFKADS2164 (right) compared to WCC-Empa.*

CONCLUSIONS

The global GAW station Pallas is part of the Pallas Atmosphere-Ecosystem Supersite, which is one of the most important environmental research infrastructures in Finland and in the wider circumpolar region. The station offers extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects. It contributes to numerous European and global research programmes, such as GAW, the NOAA's cooperative air sampling network, ICOS, the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS), and the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP). Together with the Sodankylä station, where mainly observations of the upper atmosphere are made, it is a very significant contribution to the GAW programme.

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 PAL, 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 CFKADS2066	CO LGR 913 13-0055	CO Picarro G2401 CFKADS2164	CH_4 Picarro G2401 CFKADS2066	CH_4 Picarro G2401 CFKADS2164	CO_2 Picarro G2401 CFKADS2066	CO_2 Picarro G2401 CFKADS2164	N_2O LGR 913 13-0055
TS	✓	✓	(✓)	NA	✓	NA	✓	NA	✓
Air	NA	✓	NA	✓	✓	✓	✓	✓	NA

NA: no comparison was made

The continuation of the Pallas 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 PALLAS GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(4)	Year round access, can be difficult in spring and autumn
Facilities		
Laboratory and office space	(5)	Fully adequate, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable and stable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2	(5)	State of the art instrumentation
CO LGR 913	(4)	Adequate instrument, long-term support questionable
CO Picarro G2401	(4)	Adequate system
N_2O LGR 913	(5)	Adequate instrumentation
Standards		
O_3	(5)	Transfer standard with traceability to SRP at FMI
CO, CO_2, CH_4, N_2O (ICOS)	(5)	Full traceability to the GAW reference through ICOS FCL and on-site NOAA standards
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(5)	Skilled staff, appropriate procedures
Data submission	(3)	Data submitted except CO and N_2O

#0: inadequate thru 5: adequate.

Dübendorf, April 2022

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QA/SAC Switzerland

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Head of Department

APPENDIX

Data Review

The following figures show summary plots of PAL data accessed on 28 October 2021 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations. ICOS data are available at the ICOS Carbon Portal (https://www.icos-cp.eu/). Automated data transfer from ICOS Carbon Portal to WDCGG is currently in preparation but not yet implemented. Thus, ICOS data are not yet available in the GAW repository and are not reviewed here.

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

Surface ozone:

Two data sets were submitted, which are shown in the figures below.

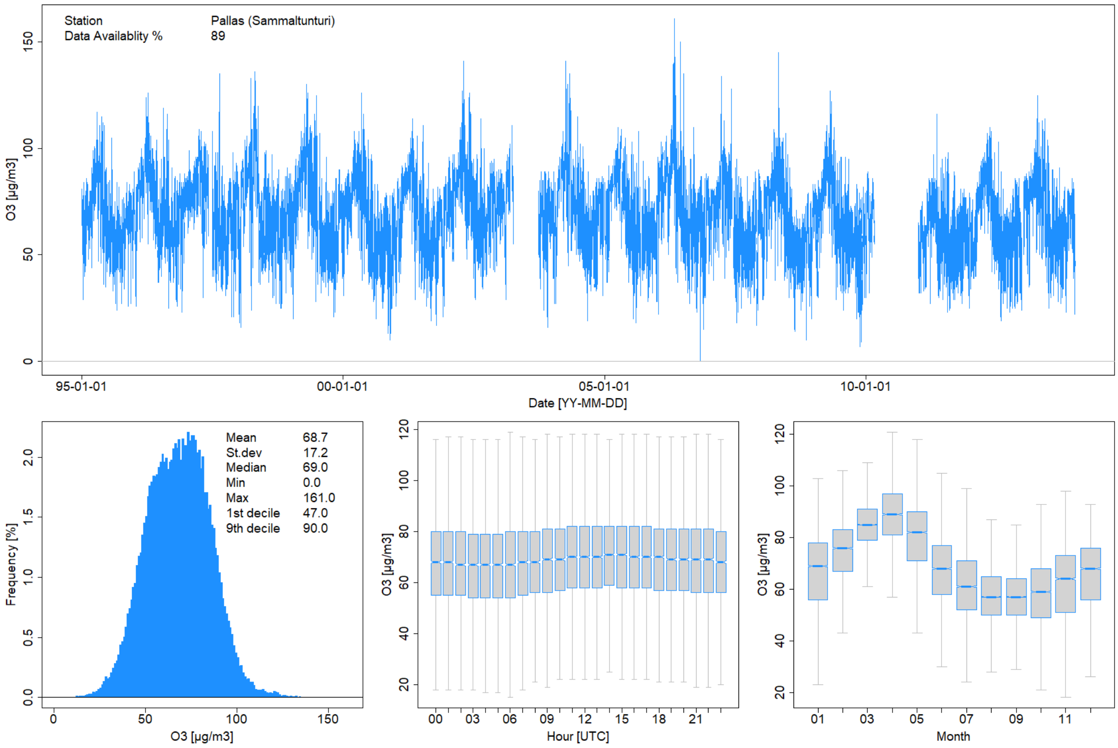

Figure 15. *O_3 data for the period from 1995 to 2013 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

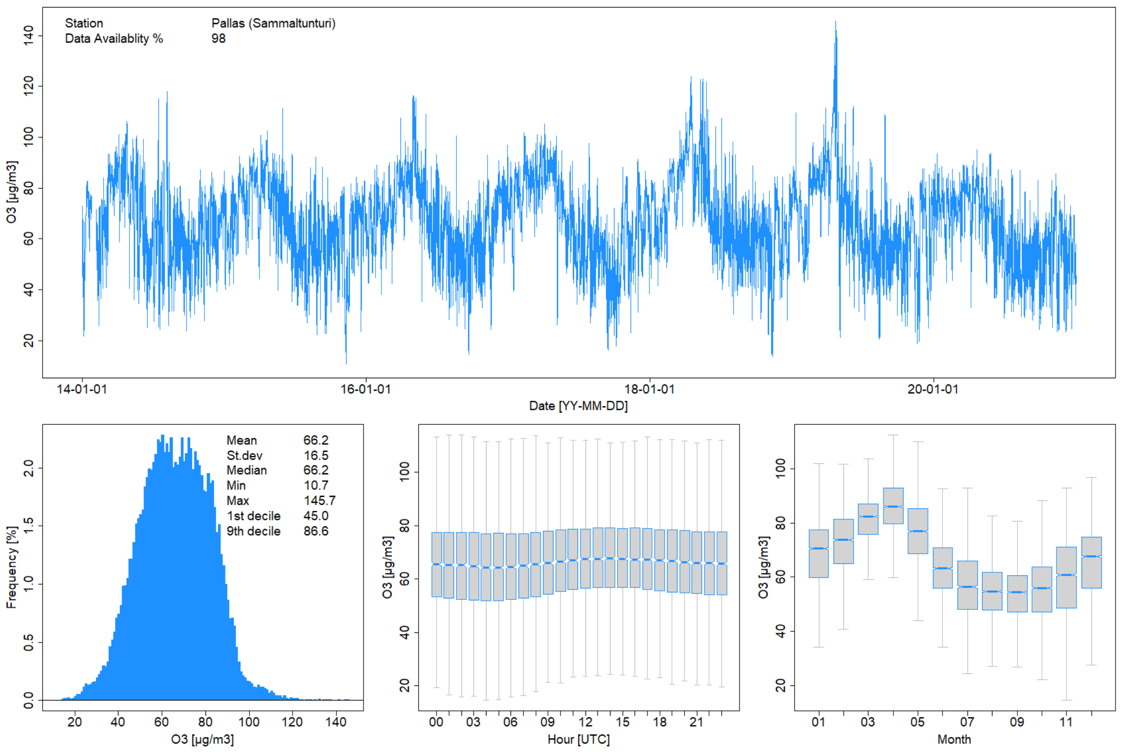

Figure 16. *O_3 data for the period from 2014 to 2020 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

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

Carbon monoxide:

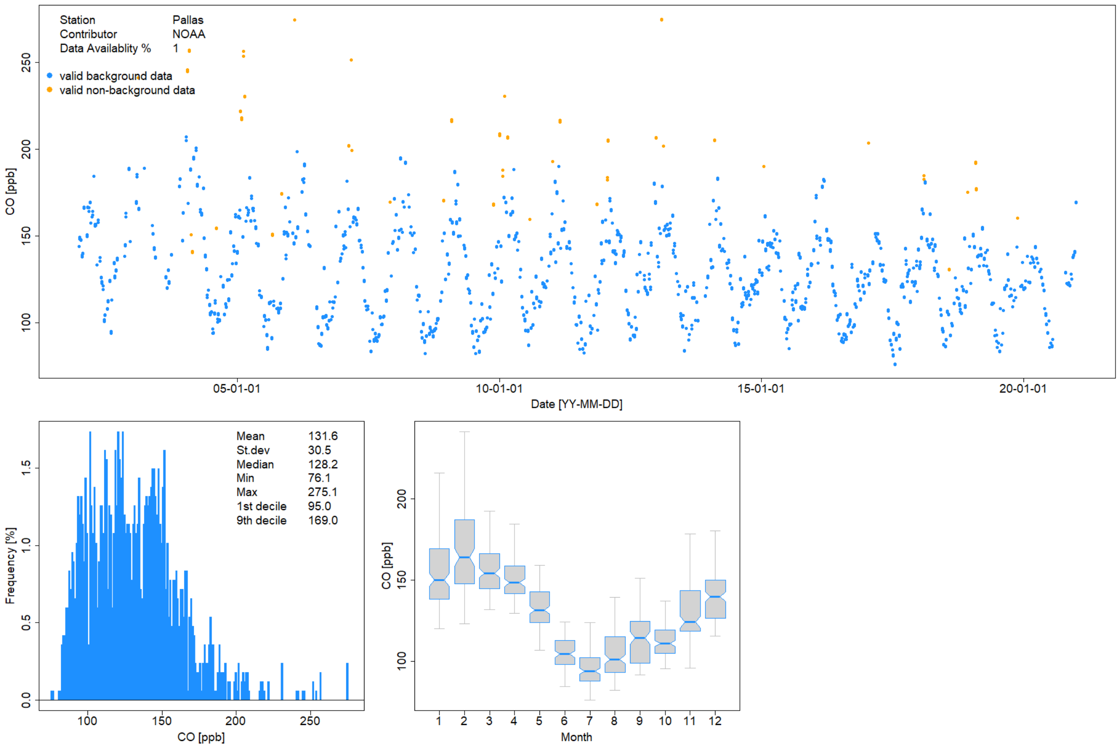

Figure 17. *NOAA CO flask data submitted to WDCGG, all valid data is shown. Top: Time series, individual flask analysis. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The NOAA data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.
- No CO data has been submitted by FMI.

Methane:

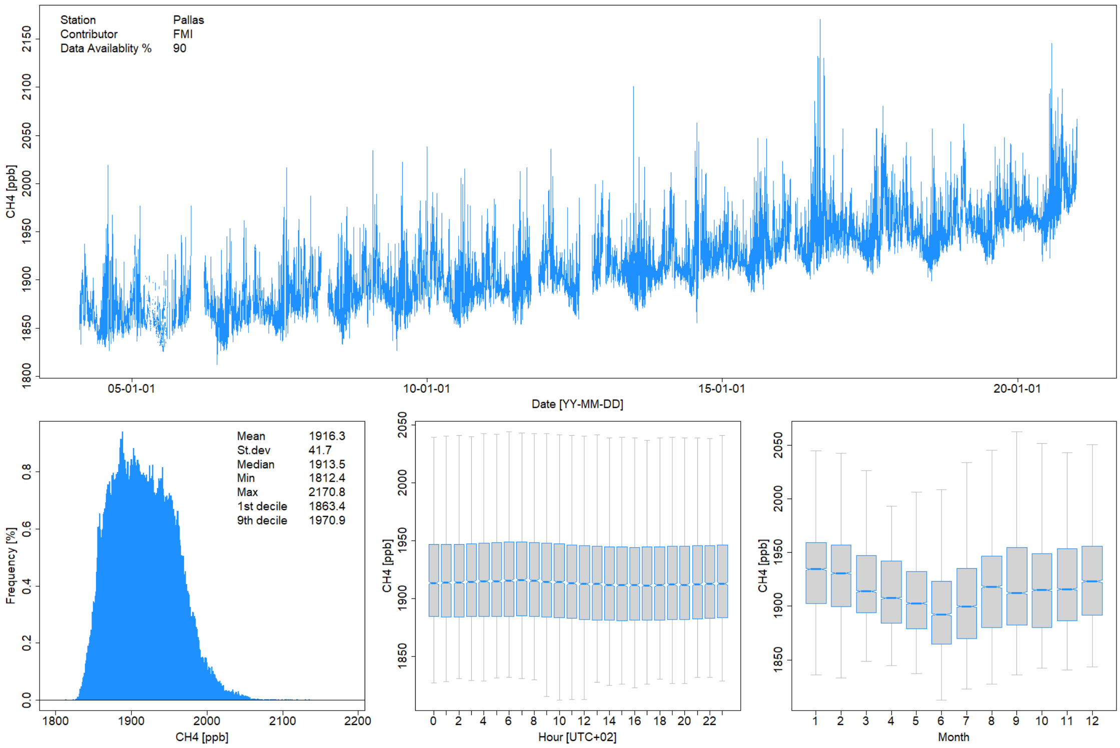

Figure 18. *Pallas in-situ CH_4 data (2004-2020) submitted by FMI. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

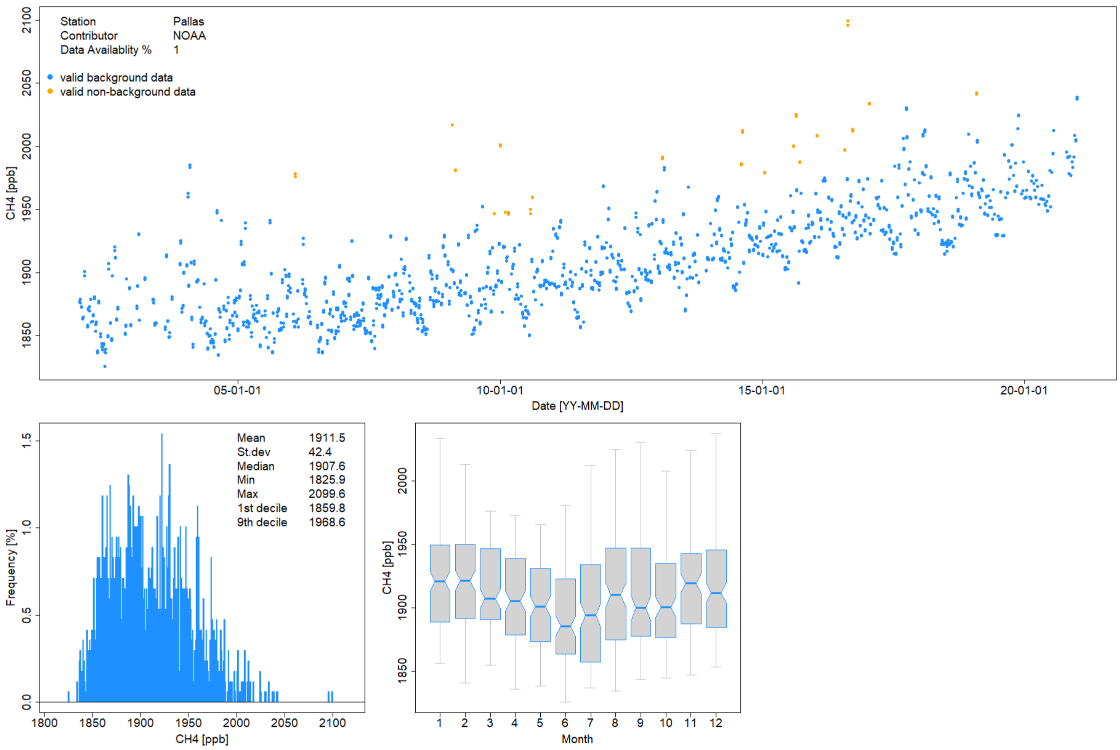

Figure 19. *Flask CH_4 data sampled at Pallas (2001-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, individual flask analysis.. Bottom: Left: frequency distribution, Right: seasonal*

variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

- Both FMI and NOAA data series look sound. Continued comparisons of the data series is encouraged.

Carbon dioxide:

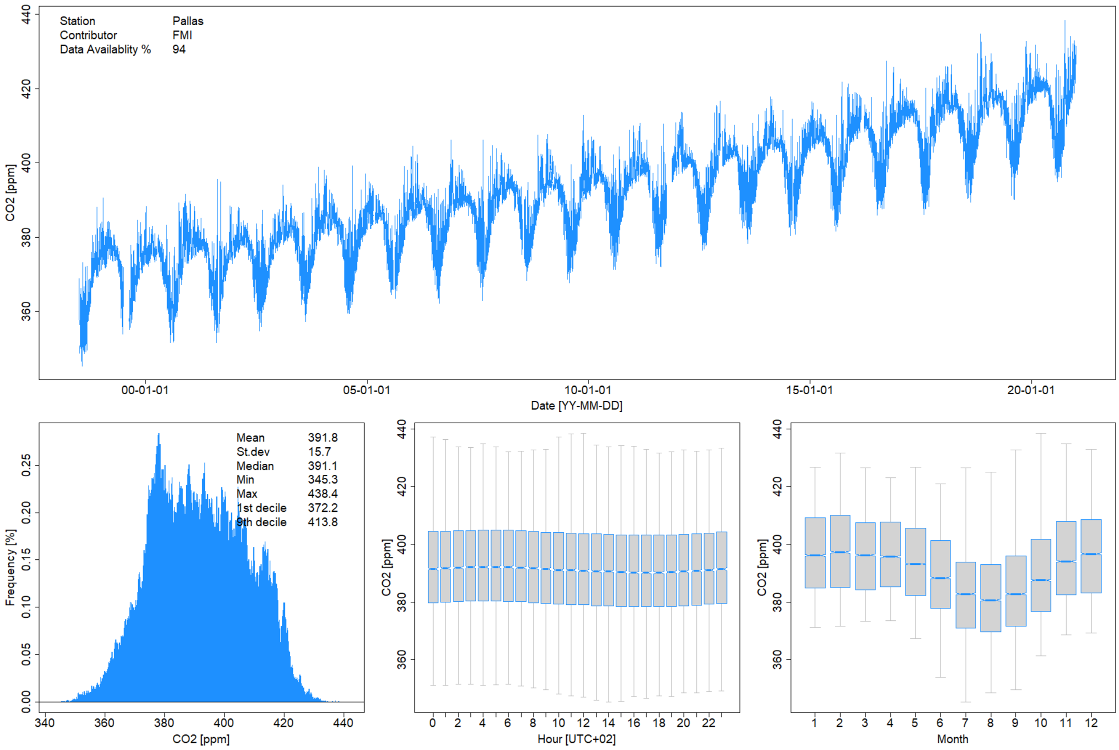

Figure 20. *Pallas in-situ CO_2 data (1998-2020) submitted by FMI. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

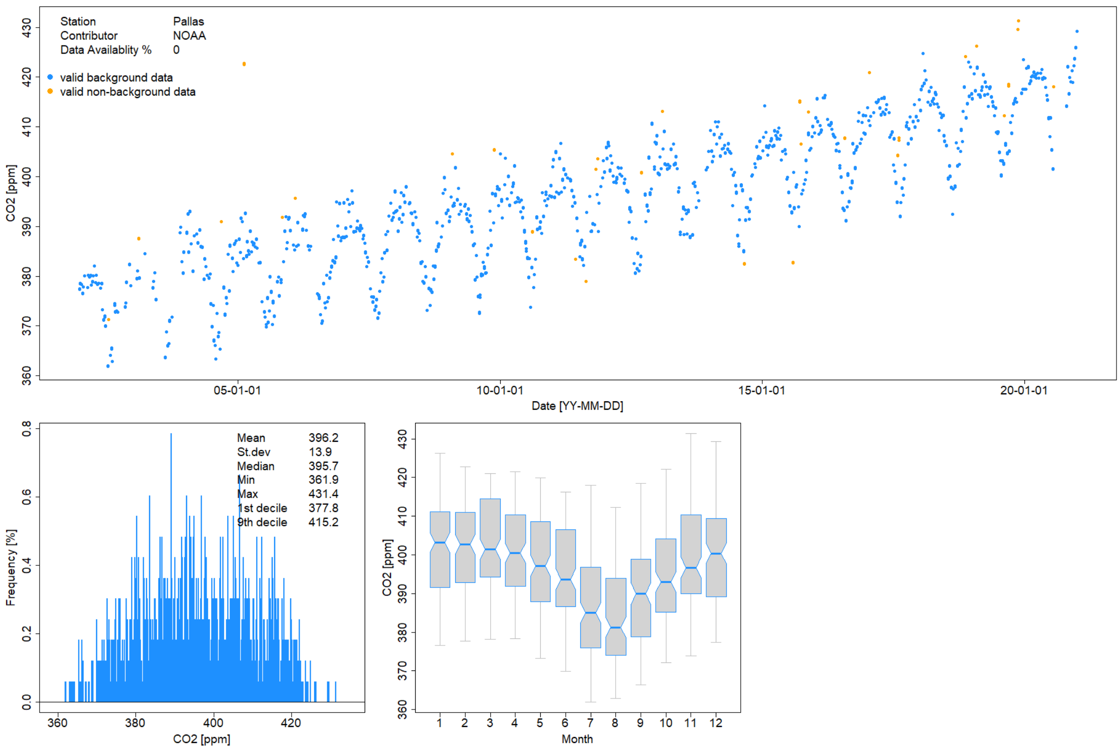

Figure 21. *Flask CO_2 data (2001-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, individual flask analysis. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- Both FMI and NOAA data series look sound. Continued comparisons of the data series is encouraged.

Nitrous oxide:

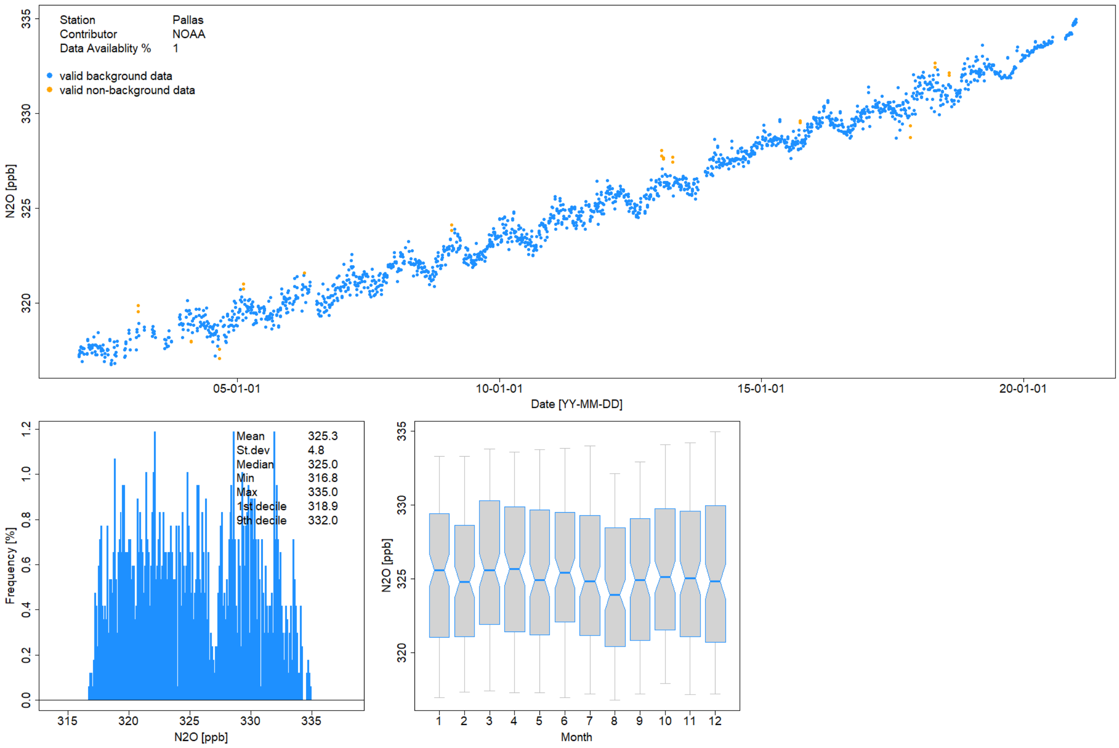

Figure 22. *Flask N_2O data (2001-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, individual flask analysis. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The NOAA flask data set looks sound. Comparison with the in-situ data is encouraged.
- The variability of the NOAA flask data became significantly smaller after 2019.
- FMI has not yet submitted N2O in-situ data.

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 PAL data acquisition systems.

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

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG -0.3, COEF 0.991
Pressure readings (hPa)	Ambient 949.8;TS 951.1, (no adjustment was made)
PAL analyser (OA)	
Model, S/N	Thermo Scientific 49i #1192744581
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.2 nmol mol^{-1}, COEF 0.987
Pressure readings (hPa)	Ambient 949.7; OA 947.9 (no adjustment was made)

Results

Each ozone level was applied for 10 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 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. *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the PAL ozone analyser (OA) Thermo Scientific 49i #1192744581 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 (%)**
2021-07-06 11:06	-0.41	0.07	0.62	0.08	1.03	NA
2021-07-06 11:16	29.89	0.07	30.83	0.24	0.94	3.14
2021-07-06 11:26	59.90	0.05	60.52	0.16	0.62	1.04
2021-07-06 11:36	99.96	0.05	100.34	0.35	0.38	0.38
2021-07-06 11:46	69.89	0.03	70.42	0.40	0.53	0.76
2021-07-06 11:56	149.94	0.10	149.84	0.15	-0.10	-0.07
2021-07-06 12:06	10.17	0.37	11.15	0.44	0.98	9.64
2021-07-06 12:16	39.89	0.08	40.57	0.13	0.68	1.70

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 (%)
2021-07-06 12:26	89.97	0.08	90.31	0.12	0.34	0.38
2021-07-06 12:36	124.98	0.10	125.31	0.16	0.33	0.26
2021-07-06 12:46	200.04	0.12	199.87	0.23	-0.17	-0.08
2021-07-06 12:56	49.90	0.05	50.66	0.23	0.76	1.52
2021-07-06 13:06	79.93	0.05	80.55	0.20	0.62	0.78
2021-07-06 13:16	174.99	0.07	174.88	0.22	-0.11	-0.06
2021-07-06 13:26	19.88	0.09	20.84	0.18	0.96	4.83
2021-07-06 13:36	-0.34	0.16	0.74	0.15	1.08	NA
2021-07-06 13:46	9.89	0.07	10.74	0.18	0.85	8.59
2021-07-06 13:56	49.86	0.06	50.66	0.21	0.80	1.60
2021-07-06 14:06	124.95	0.07	125.03	0.25	0.08	0.06
2021-07-06 14:16	99.96	0.07	100.26	0.15	0.30	0.30
2021-07-06 14:26	199.99	0.09	199.68	0.30	-0.31	-0.16
2021-07-06 14:36	174.97	0.04	174.78	0.23	-0.19	-0.11
2021-07-06 14:46	39.90	0.11	40.53	0.27	0.63	1.58
2021-07-06 14:56	19.91	0.05	20.79	0.13	0.88	4.42
2021-07-06 15:06	79.98	0.11	80.45	0.33	0.47	0.59
2021-07-06 15:16	59.96	0.06	60.43	0.13	0.47	0.78
2021-07-06 15:26	89.96	0.10	90.58	0.15	0.62	0.69
2021-07-06 15:36	149.99	0.08	149.80	0.20	-0.19	-0.13
2021-07-06 15:46	69.89	0.04	70.32	0.06	0.43	0.62
2021-07-06 15:56	29.90	0.07	30.67	0.20	0.77	2.58
2021-07-06 16:06	-0.21	0.10	0.58	0.26	0.79	NA
2021-07-06 16:16	99.95	0.05	100.37	0.22	0.42	0.42
2021-07-06 16:26	39.90	0.04	40.45	0.30	0.55	1.38
2021-07-06 16:36	89.95	0.06	90.35	0.29	0.40	0.44
2021-07-06 16:46	125.00	0.04	125.30	0.10	0.30	0.24
2021-07-06 16:56	79.98	0.06	80.44	0.23	0.46	0.58
2021-07-06 17:06	9.88	0.16	10.71	0.11	0.83	8.40
2021-07-06 17:16	19.84	0.07	20.57	0.11	0.73	3.68
2021-07-06 17:26	69.94	0.06	70.53	0.10	0.59	0.84
2021-07-06 17:36	149.98	0.04	149.94	0.36	-0.04	-0.03
2021-07-06 17:46	59.96	0.08	60.55	0.28	0.59	0.98
2021-07-06 17:56	175.00	0.13	174.66	0.30	-0.34	-0.19
2021-07-06 18:06	49.89	0.10	50.44	0.21	0.55	1.10
2021-07-06 18:16	200.01	0.06	199.72	0.15	-0.29	-0.14
2021-07-06 18:26	29.87	0.04	30.58	0.27	0.71	2.38
2021-07-06 18:36	-0.31	0.11	0.42	0.20	0.73	NA
2021-07-06 18:46	29.87	0.06	30.54	0.20	0.67	2.24
2021-07-06 18:56	59.94	0.04	60.43	0.24	0.49	0.82
2021-07-06 19:06	99.94	0.11	100.21	0.24	0.27	0.27
2021-07-06 19:16	69.92	0.08	70.27	0.24	0.35	0.50
2021-07-06 19:26	150.06	0.06	150.10	0.10	0.04	0.03
2021-07-06 19:36	9.95	0.09	10.74	0.16	0.79	7.94
2021-07-06 19:46	40.00	0.07	40.76	0.30	0.76	1.90
2021-07-06 19:56	89.95	0.08	90.34	0.25	0.39	0.43
2021-07-06 20:06	125.00	0.10	125.14	0.21	0.14	0.11
2021-07-06 20:16	200.05	0.07	199.56	0.18	-0.49	-0.24

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 (%)
2021-07-06 20:26	49.94	0.09	50.49	0.27	0.55	1.10
2021-07-06 20:36	79.94	0.06	80.30	0.23	0.36	0.45
2021-07-06 20:46	174.98	0.10	174.83	0.36	-0.15	-0.09
2021-07-06 20:56	19.93	0.12	20.81	0.12	0.88	4.42
2021-07-06 21:06	-0.50	0.10	0.48	0.16	0.98	NA
2021-07-06 21:16	9.91	0.15	10.69	0.16	0.78	7.87
2021-07-06 21:26	49.91	0.09	50.34	0.25	0.43	0.86
2021-07-06 21:36	124.99	0.03	125.31	0.47	0.32	0.26
2021-07-06 21:46	99.96	0.06	100.37	0.27	0.41	0.41
2021-07-06 21:56	200.03	0.06	199.91	0.11	-0.12	-0.06
2021-07-06 22:06	175.01	0.06	174.89	0.17	-0.12	-0.07
2021-07-06 22:16	39.95	0.06	40.73	0.12	0.78	1.95
2021-07-06 22:26	19.88	0.10	20.61	0.10	0.73	3.67
2021-07-06 22:36	80.00	0.07	80.38	0.20	0.38	0.47
2021-07-06 22:46	59.96	0.07	60.49	0.24	0.53	0.88
2021-07-06 22:56	89.94	0.09	90.26	0.16	0.32	0.36
2021-07-06 23:06	149.99	0.06	150.10	0.25	0.11	0.07
2021-07-06 23:16	69.97	0.05	70.47	0.20	0.50	0.71
2021-07-06 23:26	29.94	0.04	30.68	0.16	0.74	2.47
2021-07-06 23:36	-0.31	0.13	0.51	0.10	0.82	NA
2021-07-06 23:46	99.90	0.05	100.25	0.23	0.35	0.35
2021-07-06 23:56	39.95	0.10	40.81	0.23	0.86	2.15
2021-07-07 00:06	89.91	0.04	90.29	0.24	0.38	0.42
2021-07-07 00:16	124.93	0.07	125.07	0.29	0.14	0.11
2021-07-07 00:26	79.90	0.09	80.25	0.11	0.35	0.44
2021-07-07 00:36	9.94	0.12	10.85	0.18	0.91	9.15
2021-07-07 00:46	19.94	0.06	20.59	0.20	0.65	3.26
2021-07-07 00:56	69.93	0.11	70.41	0.17	0.48	0.69
2021-07-07 01:06	150.01	0.07	150.06	0.09	0.05	0.03
2021-07-07 01:16	59.90	0.08	60.65	0.19	0.75	1.25
2021-07-07 01:26	175.03	0.07	175.21	0.19	0.18	0.10
2021-07-07 01:36	49.89	0.03	50.55	0.18	0.66	1.32
2021-07-07 01:46	200.03	0.04	199.80	0.12	-0.23	-0.11
2021-07-07 01:56	29.89	0.08	30.78	0.25	0.89	2.98
2021-07-07 02:06	-0.34	0.09	0.66	0.20	1.00	NA
2021-07-07 02:16	29.83	0.04	30.49	0.22	0.66	2.21
2021-07-07 02:26	59.94	0.05	60.56	0.18	0.62	1.03
2021-07-07 02:36	99.93	0.10	100.55	0.19	0.62	0.62
2021-07-07 02:46	69.94	0.13	70.41	0.12	0.47	0.67
2021-07-07 02:56	149.95	0.08	149.99	0.20	0.04	0.03
2021-07-07 03:06	9.95	0.11	10.79	0.18	0.84	8.44
2021-07-07 03:16	39.91	0.10	40.71	0.21	0.80	2.00
2021-07-07 03:26	89.97	0.02	90.41	0.15	0.44	0.49
2021-07-07 03:36	125.00	0.08	125.09	0.23	0.09	0.07
2021-07-07 03:46	200.04	0.09	199.66	0.19	-0.38	-0.19
2021-07-07 03:56	49.90	0.06	50.48	0.23	0.58	1.16
2021-07-07 04:06	79.99	0.06	80.43	0.32	0.44	0.55
2021-07-07 04:16	175.03	0.07	174.95	0.17	-0.08	-0.05

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 (%)
2021-07-07 04:26	19.90	0.11	20.85	0.10	0.95	4.77
2021-07-07 04:36	-0.39	0.06	0.52	0.17	0.91	NA
2021-07-07 04:46	10.68	0.18	11.47	0.22	0.79	7.40
2021-07-07 04:56	49.89	0.05	50.44	0.19	0.55	1.10
2021-07-07 05:06	124.98	0.11	125.09	0.29	0.11	0.09
2021-07-07 05:16	100.04	0.05	100.36	0.15	0.32	0.32
2021-07-07 05:26	200.06	0.06	199.67	0.25	-0.39	-0.19
2021-07-07 05:36	175.06	0.09	175.23	0.20	0.17	0.10
2021-07-07 05:46	39.89	0.05	40.53	0.16	0.64	1.60
2021-07-07 05:56	19.93	0.13	20.59	0.16	0.66	3.31
2021-07-07 06:06	79.94	0.04	80.10	0.23	0.16	0.20
2021-07-07 06:16	59.93	0.10	60.34	0.15	0.41	0.68
2021-07-07 06:26	89.96	0.08	90.28	0.19	0.32	0.36
2021-07-07 06:36	150.03	0.03	149.93	0.12	-0.10	-0.07
2021-07-07 06:46	69.93	0.09	70.42	0.18	0.49	0.70
2021-07-07 06:56	29.86	0.04	30.65	0.28	0.79	2.65
2021-07-07 07:06	-0.39	0.08	0.50	0.13	0.89	NA
2021-07-07 07:16	99.94	0.01	100.14	0.11	0.20	0.20
2021-07-07 07:26	39.92	0.08	40.49	0.12	0.57	1.43
2021-07-07 07:36	89.92	0.08	89.90	0.19	-0.02	-0.02
2021-07-07 07:46	124.99	0.11	124.92	0.33	-0.07	-0.06
2021-07-07 07:56	79.96	0.09	80.32	0.37	0.36	0.45
2021-07-07 08:06	9.90	0.14	10.70	0.23	0.80	8.08
2021-07-07 08:16	19.89	0.15	20.66	0.11	0.77	3.87
2021-07-07 08:26	69.92	0.07	70.34	0.26	0.42	0.60
2021-07-07 08:36	150.01	0.09	150.01	0.25	0.00	0.00
2021-07-07 08:46	59.98	0.06	60.57	0.14	0.59	0.98
2021-07-07 08:56	175.03	0.10	174.80	0.41	-0.23	-0.13
2021-07-07 09:06	49.91	0.09	50.41	0.42	0.50	1.00
2021-07-07 09:16	200.02	0.06	199.66	0.30	-0.36	-0.18

Calibration Standards for CO, CH_4, CO_2 and N_2O

Table 5 shows and overview of available standard gases for the calibration of the CO, CH_4, CO_2 and N_2O GAW instruments. A set of five NOAA standards at FMI serve as the reference, and the values of all other standards were assigned based on this set of standards. In addition, linear drift rates were determined for all CO standards, and amount fractions for a given time are calculated based on these drift rates.

Table 5 *Calibration standards at PAL as of November 2021.*

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
CB10181	279.60	98.13	1561.61	302.41	FMI, NOAA reference standard
CB10207	326.25	121.13	1876.70	395.33	FMI, NOAA reference standard
CB10188	330.00	237.46	1942.65	419.84	FMI, NOAA reference standard
CB10240	338.99	361.37	2039.87	449.01	FMI, NOAA reference standard
CB10210	349.41	455.08	2332.44	695.29	FMI, NOAA reference standard
CA04187	NA	142.06	1761.24	358.27	PAL, NOAA Standard, Picarro
CA04185	NA	156.65	1809.95	366.20	PAL, NOAA Standard, Picarro
CA04191	NA	204.99	1887.10	380.85	PAL, NOAA Standard, Picarro
CA04182	NA	160.31	1843.75	390.79	PAL, NOAA Standard, Picarro
CA04163	NA	165.18	1849.30	410.76	PAL, NOAA Standard, Picarro
CA04151	NA	418.27	2157.04	446.97	PAL, NOAA Standard, Picarro
CA06177	NA	77.60	1812.16	NA	PAL, NOAA Standard, Picarro
CA06249	NA	154.05	1945.29	NA	PAL, NOAA Standard, Picarro
CA06206	NA	238.45	1995.51	NA	PAL, NOAA Standard, Picarro
D609112	NA	140.00	1971.45	410.53	PAL, WS, Picarro
D489487	NA	144.40	1938.79	411.07	PAL, Target, Picarro
CA06177	NA	77.60	NA	NA	PAL, NOAA Standard, LGR
CA06249	NA	154.05	NA	NA	PAL, NOAA Standard, LGR
CA06206	NA	238.45	NA	NA	PAL, NOAA Standard, LGR
D232747	297.84	140.19	NA	NA	PAL, Station Standard, LGR
D232765	311.60	139.22	NA	NA	PAL, Station Standard, LGR
D232744	345.07	227.50	NA	NA	PAL, Station Standard, LGR
D232759	358.23	275.30	NA	NA	PAL, Station Standard, LGR
D348370	330.32	161.52	NA	NA	PAL, WS, LGR
D348379	330.34	167.27	NA	NA	PAL, Target, LGR

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 PAL data acquisition system.

Table 6. Experimental details of the PAL 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 14 and 15.	
Station Analyser (GAW) (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #306-CFKADS-2066
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference
Station Analyser (GAW) (CO, N_2O)	
Model, S/N	LGR 913-0015-0002 #13-0055
Principle	Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)
Drying system	PERMAPURE MD-070-96S-2 Nafion drier
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 7. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #306-CFKADS-2066 instrument (AL) 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 (%)
(21-03-03 21:13:30)	180318_FF61508	357.4	1.4	359.0	1.3	10	1.7	0.5
(21-03-04 02:17:30)	171204_FA01469	357.4	1.4	358.9	0.9	10	1.5	0.4
(21-03-03 20:54:30)	160622_FA02479	103.4	0.7	105.6	1.7	10	2.2	2.1
(21-03-04 01:58:30)	140514_FB03895	103.4	0.7	105.4	1.3	10	2.1	2.0
(21-03-03 21:51:30)	130819_FB03870	209.3	0.9	211.1	1.2	10	1.8	0.9
(21-03-04 02:55:30)	130819_FB03865	209.3	0.9	211.1	1.7	10	1.8	0.8
(21-03-03 22:10:30)	181129_FB03853	203.2	0.9	205.1	1.6	10	1.9	1.0
(21-03-04 03:14:30)	180318_FF61508	203.2	0.9	205.3	0.8	10	2.1	1.0
(21-03-03 21:32:30)	171204_FA01469	154.6	0.9	157.1	2.0	10	2.6	1.7
(21-03-04 02:36:30)	160622_FA02479	154.6	0.9	156.7	1.3	10	2.1	1.4
(21-03-03 22:29:30)	140514_FB03895	172.3	1.1	174.7	1.3	10	2.4	1.4
(21-03-04 03:33:30)	130819_FB03870	172.3	1.1	173.9	1.6	10	1.6	1.0
(21-03-03 22:48:30)	130819_FB03865	93.4	1.0	95.6	1.4	10	2.3	2.4
(21-03-04 03:52:30)	181129_FB03853	93.4	1.0	95.0	2.1	10	1.7	1.8

Table 8. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015-0002 #13-0055 instrument (AL) 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 (%)
(21-03-04 11:23:00)	171204_FA01469	103.4	0.7	108.4	0.0	3	5.0	4.9
(21-03-04 11:32:00)	180318_FF61508	357.4	1.4	358.4	0.0	3	1.0	0.3
(21-03-04 11:41:00)	130819_FB03870	154.6	0.9	157.0	0.0	3	2.4	1.6
(21-03-04 11:50:00)	160622_FA02479	209.3	0.9	210.8	0.0	3	1.5	0.7
(21-03-04 11:59:00)	180318_FF61500	189.4	0.8	190.8	0.0	3	1.4	0.8
(21-03-04 12:08:00)	171204_FA02769	139.5	0.8	142.9	0.0	3	3.4	2.4
(21-03-04 12:17:00)	181129_FB03853	93.4	1.0	98.7	0.0	3	5.3	5.7
(21-03-04 13:56:00)	171204_FA01469	103.4	0.8	108.4	0.0	3	5.1	4.9
(21-03-04 14:05:00)	180318_FF61508	357.4	0.3	358.5	0.0	3	1.1	0.3
(21-03-04 14:14:00)	130819_FB03870	154.6	0.3	157.0	0.0	3	2.4	1.6
(21-03-04 14:23:00)	160622_FA02479	209.3	0.2	210.8	0.0	3	1.5	0.7
(21-03-04 14:32:00)	180318_FF61500	189.4	0.8	190.8	0.0	3	1.4	0.7
(21-03-04 14:41:00)	171204_FA02769	139.5	0.6	142.9	0.0	3	3.4	2.4
(21-03-04 14:50:00)	181129_FB03853	93.4	0.8	98.7	0.0	3	5.3	5.7

Methane 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 PAL data acquisition system. The standards used for the calibration of the PAL instruments are shown in Table 5.

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. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #306-CFKADS-2066 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 (%)
(21-03-03 21:13:30)	180318_FF61508	1963.81	0.03	1964.19	0.06	10	0.38	0.02
(21-03-04 02:17:30)	171204_FA01469	1963.81	0.03	1964.13	0.14	10	0.32	0.02
(21-03-03 20:54:30)	160622_FA02479	1933.20	0.05	1933.73	0.09	10	0.53	0.03
(21-03-04 01:58:30)	140514_FB03895	1933.20	0.05	1933.65	0.21	10	0.45	0.02
(21-03-03 21:51:30)	130819_FB03870	2191.22	0.05	2191.68	0.08	10	0.46	0.02
(21-03-04 02:55:30)	130819_FB03865	2191.22	0.05	2191.32	0.11	10	0.10	0.00
(21-03-03 22:10:30)	181129_FB03853	1953.82	0.02	1954.18	0.12	10	0.36	0.02
(21-03-04 03:14:30)	180318_FF61508	1953.82	0.02	1954.07	0.12	10	0.25	0.01
(21-03-03 21:32:30)	171204_FA01469	1883.44	0.03	1884.13	0.12	10	0.69	0.04
(21-03-04 02:36:30)	160622_FA02479	1883.44	0.03	1884.19	0.10	10	0.75	0.04
(21-03-03 22:29:30)	140514_FB03895	1890.78	0.11	1891.28	0.06	10	0.50	0.03
(21-03-04 03:33:30)	130819_FB03870	1890.78	0.11	1891.17	0.09	10	0.39	0.02
(21-03-03 22:48:30)	130819_FB03865	1998.97	0.02	1999.15	0.13	10	0.18	0.01
(21-03-04 03:52:30)	181129_FB03853	1998.97	0.02	1999.11	0.10	10	0.14	0.01

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 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 PAL data acquisition system. The standards used for the calibration of the PAL instruments are shown in Table 5.

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 10. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2401 #306-CFKADS-2066 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 (%)
(21-03-03 21:13:30)	180318_FF61508	417.53	0.01	417.49	0.01	10	-0.04	-0.01
(21-03-04 02:17:30)	171204_FA01469	417.53	0.01	417.47	0.01	10	-0.06	-0.01
(21-03-03 20:54:30)	160622_FA02479	406.99	0.01	407.00	0.01	10	0.01	0.00
(21-03-04 01:58:30)	140514_FB03895	406.99	0.01	407.01	0.01	10	0.02	0.00
(21-03-03 21:51:30)	130819_FB03870	427.81	0.03	427.81	0.01	10	0.00	0.00
(21-03-04 02:55:30)	130819_FB03865	427.81	0.03	427.78	0.01	10	-0.03	-0.01
(21-03-03 22:10:30)	181129_FB03853	411.21	0.01	411.18	0.01	10	-0.03	-0.01
(21-03-04 03:14:30)	180318_FF61508	411.21	0.01	411.18	0.01	10	-0.03	-0.01
(21-03-03 21:32:30)	171204_FA01469	387.12	0.01	387.14	0.01	10	0.02	0.01
(21-03-04 02:36:30)	160622_FA02479	387.12	0.01	387.16	0.01	10	0.04	0.01
(21-03-03 22:29:30)	140514_FB03895	387.39	0.02	387.40	0.00	10	0.01	0.00
(21-03-04 03:33:30)	130819_FB03870	387.39	0.02	387.38	0.02	10	-0.01	0.00
(21-03-03 22:48:30)	130819_FB03865	412.70	0.02	412.68	0.02	10	-0.02	0.00
(21-03-04 03:52:30)	181129_FB03853	412.70	0.02	412.66	0.01	10	-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 PAL data acquisition system. The standards used for the calibration of the PAL 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 11. *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 (%)
(21-03-04 11:23:00)	171204_FA01469	343.03	0.02	342.77	0.02	3	-0.26	-0.08
(21-03-04 11:32:00)	180318_FF61508	328.37	0.01	328.35	0.01	3	-0.02	-0.01
(21-03-04 11:41:00)	130819_FB03870	318.97	0.02	318.87	0.02	3	-0.10	-0.03
(21-03-04 11:50:00)	160622_FA02479	333.07	0.01	332.92	0.02	3	-0.15	-0.05
(21-03-04 11:59:00)	180318_FF61500	326.01	0.01	325.88	0.02	3	-0.13	-0.04
(21-03-04 12:08:00)	171204_FA02769	336.55	0.02	336.34	0.01	3	-0.21	-0.06
(21-03-04 12:17:00)	181129_FB03853	330.17	0.01	329.96	0.03	3	-0.21	-0.06
(21-03-04 13:56:00)	171204_FA01469	343.03	0.02	342.76	0.02	3	-0.27	-0.08
(21-03-04 14:05:00)	180318_FF61508	328.37	0.01	328.33	0.01	3	-0.04	-0.01
(21-03-04 14:14:00)	130819_FB03870	318.97	0.02	318.83	0.02	3	-0.14	-0.04
(21-03-04 14:23:00)	160622_FA02479	333.07	0.01	332.87	0.02	3	-0.20	-0.06
(21-03-04 14:32:00)	180318_FF61500	326.01	0.01	325.86	0.01	3	-0.15	-0.05
(21-03-04 14:41:00)	171204_FA02769	336.55	0.02	336.35	0.01	3	-0.20	-0.06
(21-03-04 14:50:00)	181129_FB03853	330.17	0.01	329.94	0.01	3	-0.23	-0.07

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 #1171430027, BKG -0.3, COEF 0.991

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 12. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 23). 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)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] - 0.12\ \text{nmol mol}^{-1}) / 0.9993 \quad (6a)$$

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

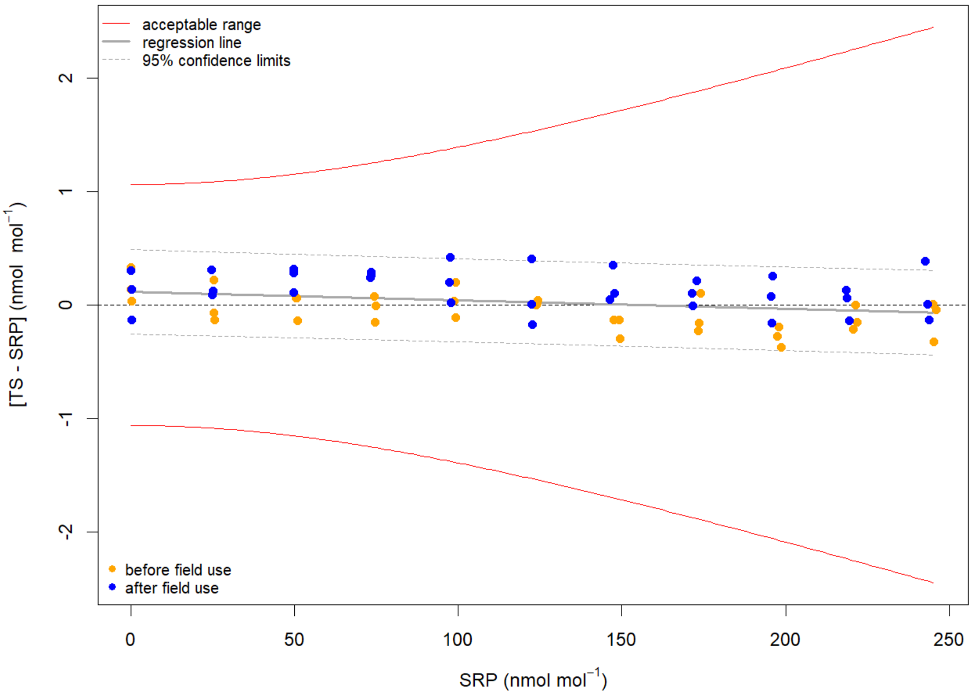

Figure 23. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 12. 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 (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2020-12-02	1	25	25.21	0.37	25.43	0.14
2020-12-02	1	0	173.45	0.29	173.29	0.11
2020-12-02	1	75	124.37	0.25	124.41	0.07
2020-12-02	1	125	0.02	0.37	0.15	0.11
2020-12-02	1	100	149.39	0.31	149.09	0.18
2020-12-02	1	175	74.68	0.24	74.67	0.10
2020-12-02	1	200	221.82	0.45	221.66	0.10
2020-12-02	1	150	99.14	0.28	99.33	0.09
2020-12-02	1	225	198.77	0.33	198.40	0.19
2020-12-02	1	50	50.67	0.31	50.73	0.06
2020-12-02	1	250	245.94	0.24	245.90	0.25
2020-12-02	2	150	173.40	0.31	173.17	0.11
2020-12-02	2	0	0.12	0.17	0.16	0.08
2020-12-02	2	175	149.08	0.30	148.95	0.31
2020-12-02	2	100	50.82	0.20	50.68	0.09
2020-12-02	2	200	99.08	0.29	98.97	0.16
2020-12-02	2	25	25.45	0.23	25.32	0.10
2020-12-02	2	75	221.28	0.27	221.28	0.19
2020-12-02	2	125	124.18	0.29	124.19	0.12
2020-12-02	2	50	197.95	0.27	197.76	0.19
2020-12-02	2	225	74.62	0.31	74.47	0.10
2020-12-02	2	250	245.14	0.25	245.15	0.23
2020-12-02	3	25	98.76	0.27	98.80	0.09
2020-12-02	3	125	74.22	0.38	74.29	0.09
2020-12-02	3	175	220.71	0.20	220.49	0.17
2020-12-02	3	75	-0.10	0.49	0.23	0.09
2020-12-02	3	0	173.99	0.52	174.09	0.47
2020-12-02	3	225	123.82	0.18	123.82	0.16
2020-12-02	3	150	25.35	0.41	25.28	0.18
2020-12-02	3	50	50.46	0.44	50.53	0.17
2020-12-02	3	100	197.44	0.40	197.17	0.14
2020-12-02	3	200	147.61	0.37	147.48	0.08
2020-12-02	3	245	245.25	0.36	244.93	0.22
2021-08-05	4	25	24.65	0.60	24.96	0.19
2021-08-05	4	170	171.61	0.40	171.60	0.08
2021-08-05	4	120	122.50	0.28	122.91	0.18
2021-08-05	4	0	-0.17	0.28	0.13	0.09
2021-08-05	4	150	147.75	0.35	147.86	0.16
2021-08-05	4	75	73.35	0.42	73.64	0.14
2021-08-05	4	220	219.42	0.37	219.28	0.15
2021-08-05	4	100	97.55	0.49	97.97	0.06
2021-08-05	4	195	195.98	0.42	196.23	0.08
2021-08-05	4	50	49.73	0.29	50.05	0.13
2021-08-05	4	245	243.91	0.35	243.77	0.21
2021-08-05	5	170	171.32	0.32	171.42	0.17

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2021-08-05	5	0	0.28	0.36	0.14	0.20
2021-08-05	5	145	147.27	0.27	147.62	0.08
2021-08-05	5	50	49.72	0.32	50.00	0.05
2021-08-05	5	95	97.39	0.39	97.59	0.15
2021-08-05	5	25	24.90	0.34	24.99	0.09
2021-08-05	5	220	218.44	0.46	218.58	0.08
2021-08-05	5	120	122.40	0.27	122.40	0.07
2021-08-05	5	195	195.54	0.32	195.62	0.14
2021-08-05	5	75	73.24	0.26	73.48	0.12
2021-08-05	5	245	242.69	0.37	243.07	0.18
2021-08-05	6	100	97.69	0.30	97.72	0.10
2021-08-05	6	75	73.38	0.42	73.64	0.10
2021-08-05	6	220	218.75	0.27	218.81	0.24
2021-08-05	6	0	0.11	0.28	0.25	0.11
2021-08-05	6	175	172.85	0.67	173.06	0.40
2021-08-05	6	125	122.61	0.39	122.44	0.18
2021-08-05	6	25	24.96	0.45	25.08	0.07
2021-08-05	6	50	49.78	0.24	49.89	0.08
2021-08-05	6	195	195.77	0.41	195.61	0.14
2021-08-05	6	145	146.31	0.21	146.36	0.10
2021-08-05	6	245	243.34	0.26	243.35	0.17

#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 13 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 14 and 15, and Figures 24 to 27 show the analysis of the TS over time.

Table 13. *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 14. *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, (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**
130819_FB03865	310	1890.78	0.11	387.39	0.02	319.94	0.02	320.00	0.02
130819_FB03870	1400	1883.44	0.03	387.12	0.01	318.87	0.04	318.97	0.02
140514_FB03895	1780	1953.82	0.02	411.21	0.01	329.07	0.01	329.08	0.02
160622_FA02479	1350	2191.22	0.05	427.81	0.03	333.05	0.04	333.07	0.01
171204_FA01469	850	1933.20	0.05	406.99	0.01	342.95	0.05	343.03	0.02
171204_FA02769	1370	1956.05	0.03	421.01	0.03	336.48	0.04	336.55	0.02
180318_FF61500	1880	1937.10	0.03	412.91	0.01	326.00	0.02	326.01	0.01
180318_FF61508	1000	1963.81	0.03	417.57	0.05	328.38	0.03	328.37	0.01
181129_FB03853	1790	1998.97	0.02	412.70	0.02	330.05	0.02	330.17	0.01

Table 15. *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, (L) LGR.*

TS	**Press. (psi)**	**CO (P) (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**	**CO (L) (nmol mol^{-1})**	**sd**
130819_FB03865	310	172.3	1.1	170.78	0.75	169.92	0.59
130819_FB03870	1400	154.59	0.89	153.2	0.37	152.48	0.12
140514_FB03895	1780	203.2	0.86	201.65	0.19	200.68	0.14
160622_FA02479	1350	209.3	0.87	207.78	0.07	206.8	0.14
171204_FA01469	850	103.38	0.71	101.98	0.24	102.47	0.03
171204_FA02769	1370	139.51	0.77	138.15	0.17	137.9	0.04
180318_FF61500	1880	189.41	0.78	187.59	0.1	186.66	0.04
180318_FF61508	1000	357.37	1.41	355.82	0.45	354.98	0.46
181129_FB03853	1790	93.36	1.04	91.92	0.32	92.5	0.19

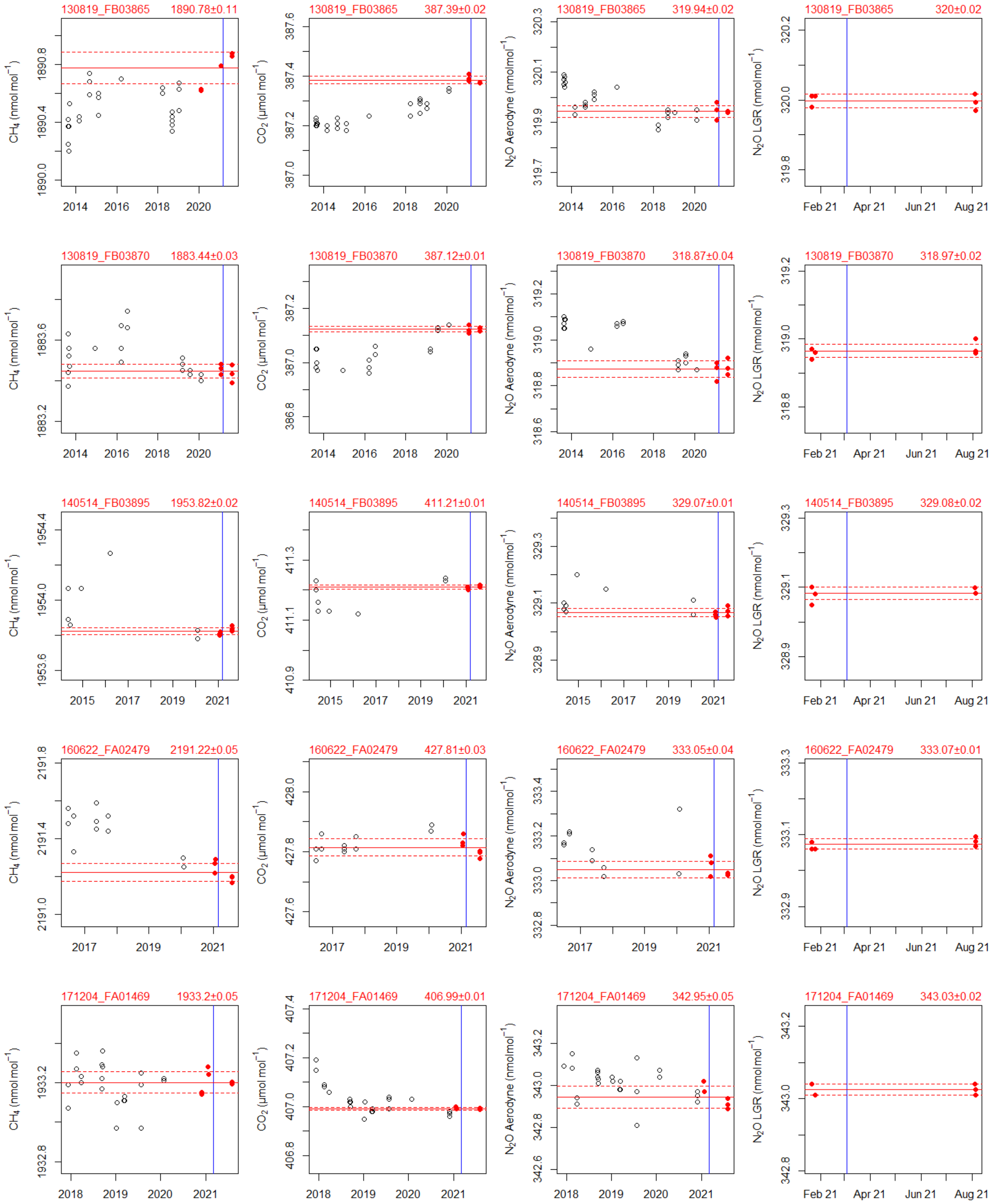

Figure 24. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

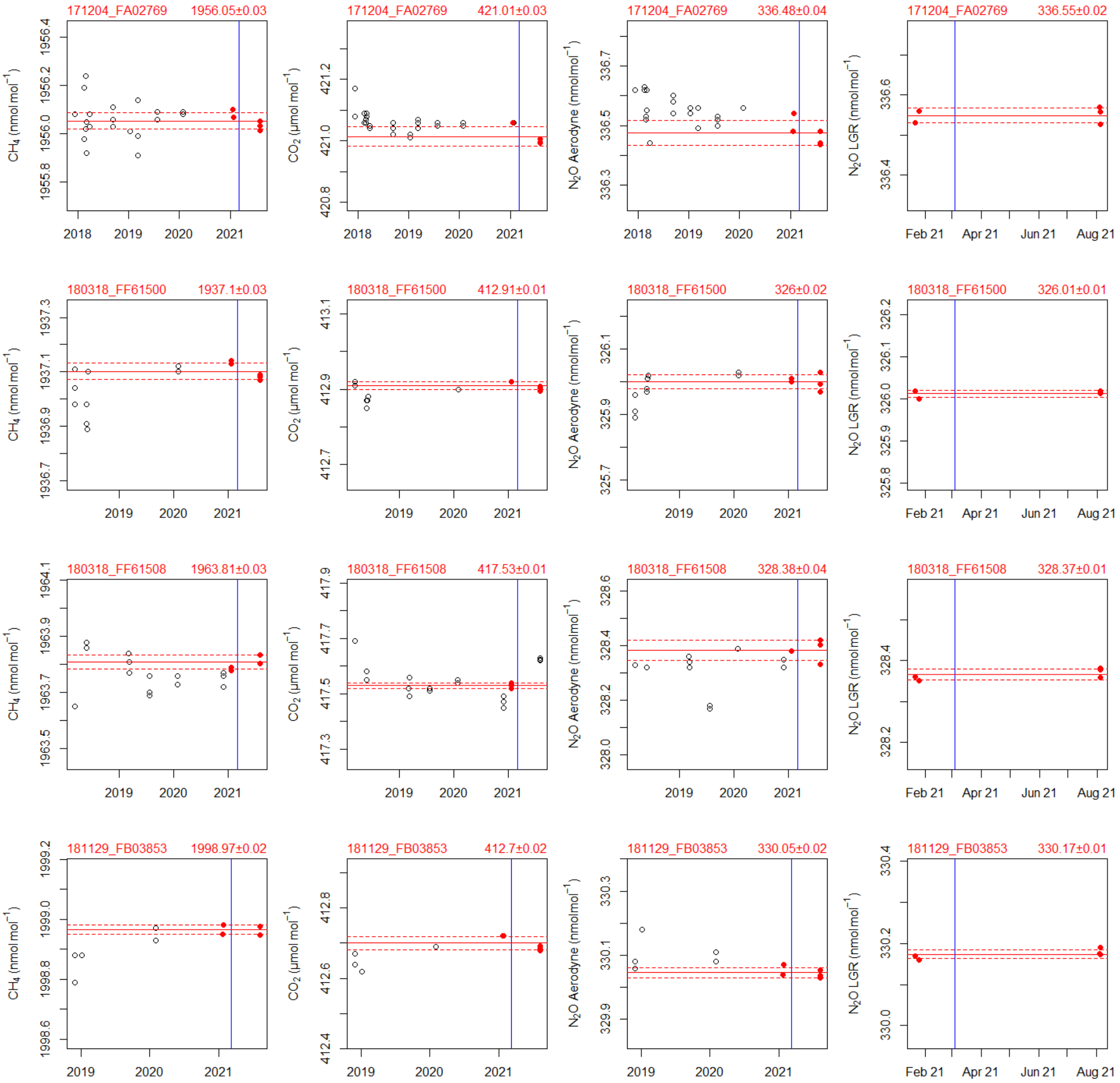

Figure 25. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

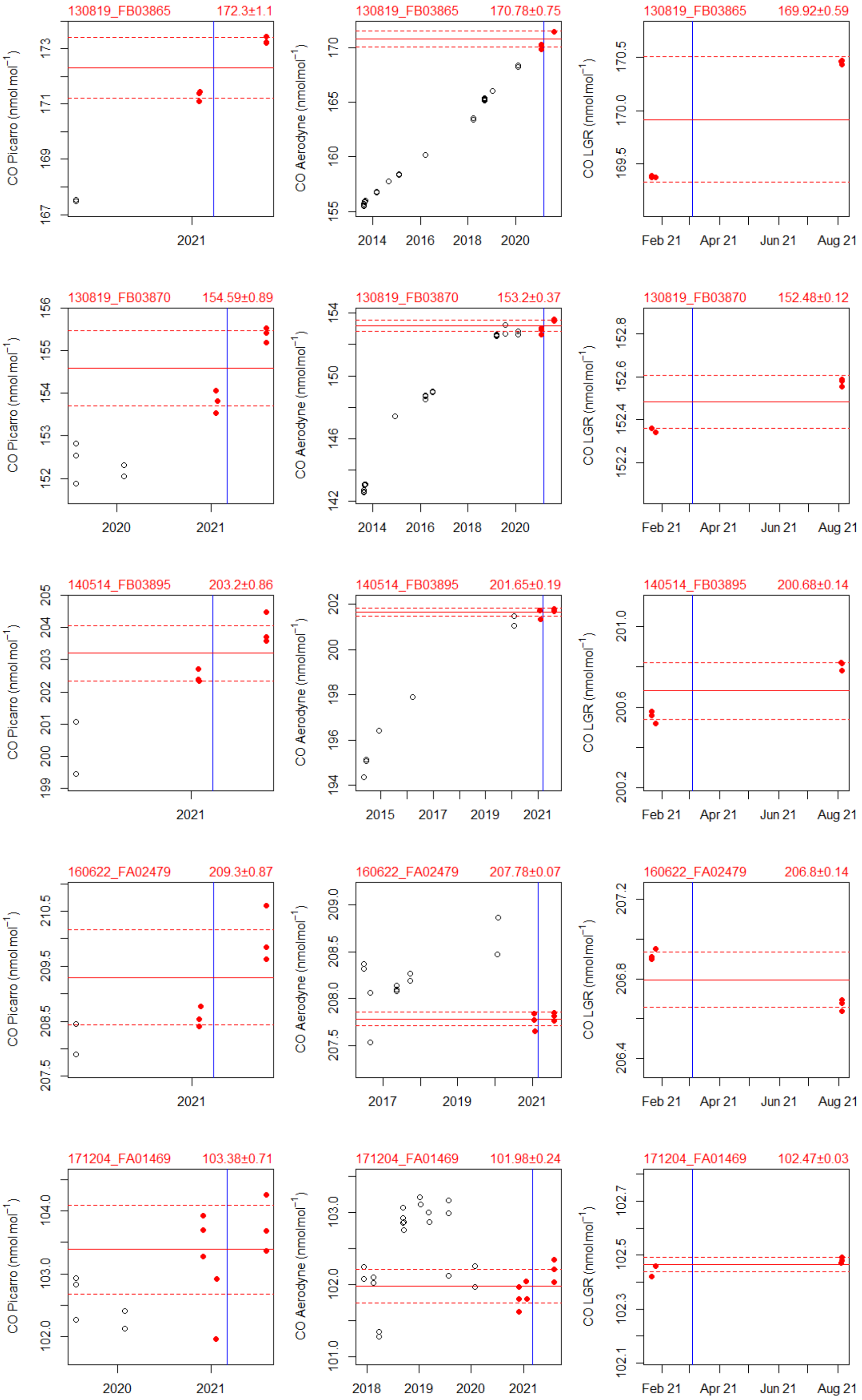

Figure 26. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

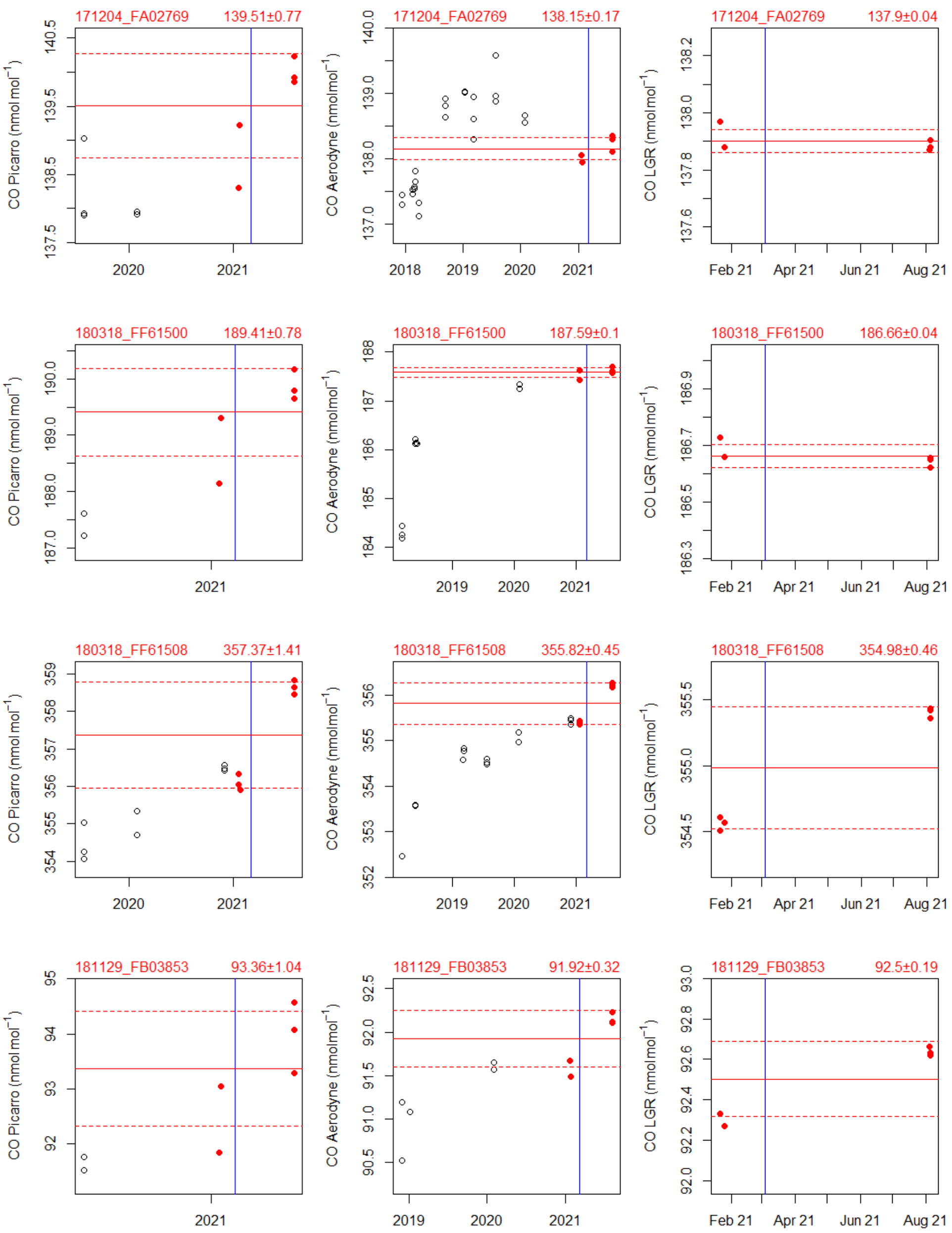

Figure 27. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. 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 1445 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. 0.1 ppb for CH_4 and 0.04 ppm for CO_2. With the exception of the first measurement, both target cylinders were within half of the WMO GAW compatibility goals.

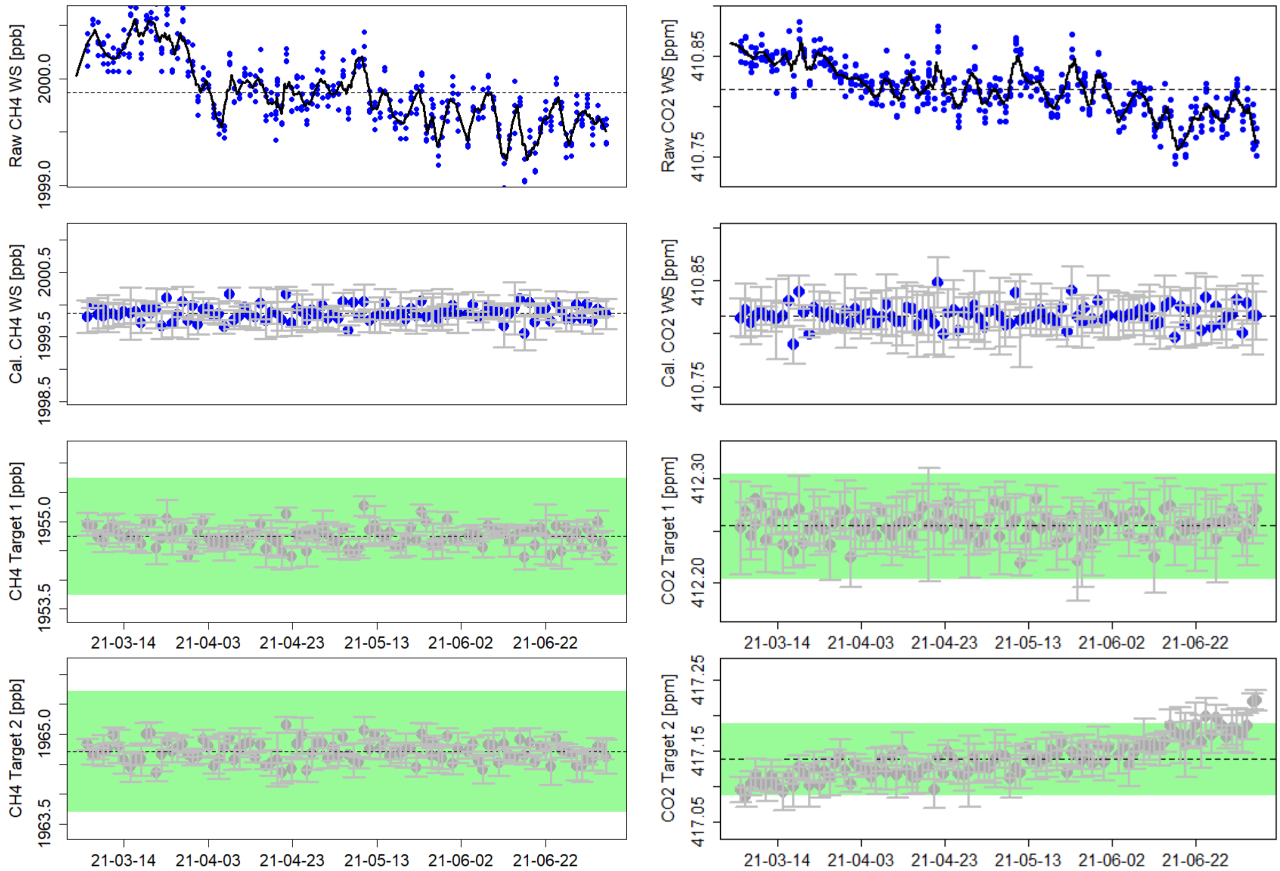

Figure 28. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower 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 1445 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.

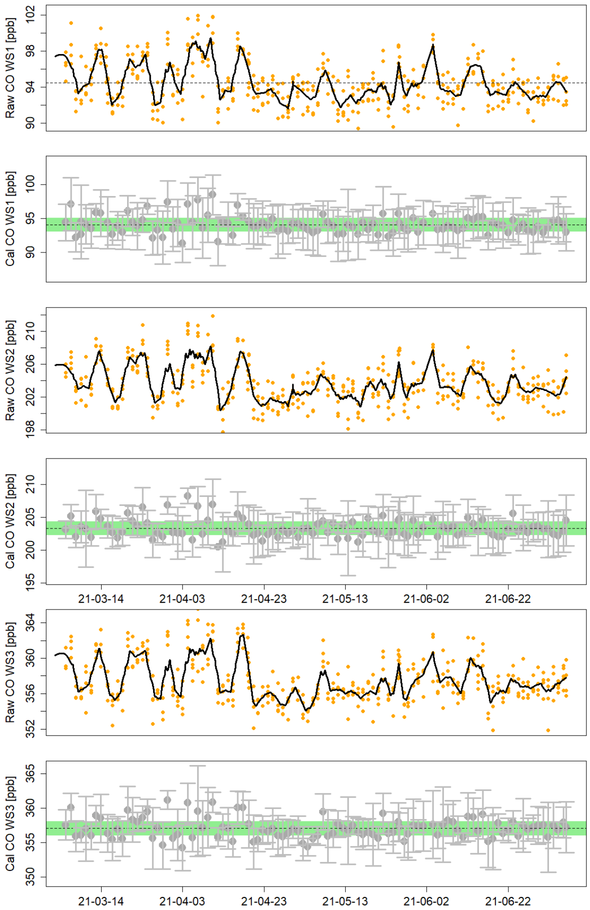

Figure 29. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels 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
ACTRIS	Aerosol, Clouds and Trace Gases Research Infrastructure
ATC	Atmospheric Thematic Centre (of ICOS)
ATV	All-Terrain Vehicle
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
EMEP	Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe
FID	Flame Ionization Detection
FMI	Finnish Meteorological Institute
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
PAL	Pallas GAW Station
ICOS	Integrated Carbon Observation System
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
PI	Principle Investigator
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