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

GLOBAL GAW STATION JUNGFRAUJOCH SWITZERLAND NOVEMBER 2021

WCC-Empa Report 21/3

Submitted to the World Meteorological Organization by

C. Zellweger and B. Buchmann

WMO World Calibration Centre WCC-Empa

Empa, Dübendorf, Switzerland

Acknowledgements

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

WCC-Empa acknowledges logistical, technical and scientific support by the International Foundation High Altitude Research Stations Jungfraujoch + Gornergrat HFSJG and the Jungfraujoch station staff.

WCC-Empa Report 21/3

Contact Information:

GAW World Calibration Centre WCC-Empa
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution - Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

CONTENTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 4th system and performance audit by WCC-Empa[1] at the global GAW station Jungfraujoch (JFJ) was conducted from 1 - 2 November 2021 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at JFJ, 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
Dr Michael Schibig	Climate and Environmental Physics Institute, University of Bern
Dr Martin Steinbacher	Empa Dübendorf, National Air Pollution Monitoring Network
Mr David Steger	Empa Dübendorf, National Air Pollution Monitoring Network

This report summarises the assessment of the Jungfraujoch 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 Jungfraujoch GAW station, the national focal point for GAW in Switzerland, 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 JFJ research facility is managed by the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG). As an international organization, the Foundation is dedicated to providing the infrastructure and support for scientific research of international significance. The parameters of the audit scope are measured by Empa as part of the National Air Pollution Monitoring Network (NABEL), a joint project of Empa with the Federal Office for the Environment (FOEN). The Climate and Environmental Physics Institute (CEP) of the University of Bern contributes with additional CO_2 measurements. Empa's GHG and CO measurements are also part of the Integrated Carbon Observation System (ICOS) Research Infrastructure. Details of the organisation are available from the corresponding websites and links therein.

HFSJG:	http://www.hfsjg.ch/en/home/
Empa:	http://www.empa.ch/web/s503/nabel
FOEN:	http://www.bafu.admin.ch/luft/index.html?lang=en
University of Bern:	http://www.climate.unibe.ch
ICOS:	https://www.icos-switzerland.ch/

Station Location and Access

The high altitude research station Jungfraujoch (46.5475°N, 7.9851°E, 3580 m a.s.l.) is situated on a mountain saddle in the central Swiss Alps between the mountains of Jungfrau (4158 m a.s.l.) to the west and Mönch (4099 m a.s.l.) to the east. The International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG) runs the research station and provides the infrastructure

[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.

and support for scientific research. Due to its unique location, the year-round accessibility, and the excellent infrastructure, the Jungfraujoch research station is well suited for long-term ground-based monitoring of trace gases in the free troposphere. Due to its location in central Europe, and its proximity to anthropogenic greenhouse gas source regions, it is also an appropriate study site for European regional source allocations during pollution events. Year-round access to JFJ is possible by train.

More information is available from GAWSIS (https://gawsis.meteoswiss.ch).

Station Facilities

Several laboratories are available at the Jungfraujoch research station. The measurements of the audit scope are made in the Sphinx building, which was renovated in 2021. Compared to the last audit by WCC-Empa in 2015, the air conditioning of the laboratory significantly improved. However, temperature fluctuations of a few degrees are still a problem for some of the measurements. Besides the large number of permanent measurements, limited space is available for campaign based experiments.

Measurement Programme

The JFJ 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. The last update was made in April 2021, and the information was mostly up-to-date. However, some details regarding instrumentation needs to be re-visited and corrected.

> **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 April 2022, the following JFJ data of the scope of the audit were available at the World Data Centres:

Submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (three data sets, covering the period from 1991-2021)

NABEL/Empa, submission to World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2005-2021), CO_2 (2010-2021), CO (1996-2021), N_2O (2005-2021)

University of Bern/CEP, submission to WDCGG:
CO_2 (2004-2020)

Data shown in this report was accessed on 12 April 2022. All data of the scope of the audit has been submitted with a submission delay of less than one year. Continuation of this timely submission practice is recommended.

GHG and CO data is independently analysed by Empa and the ICOS Atmosphere Thematic Centre (ATC). Currently, the data evaluated by Empa is submitted to WDCGG except for N_2O, for which the ATC data is taken. The switch from Empa-processed to ATC-processed N_2O data was implemented in summer 2020 with the change of the N_2O analyser type. Data evaluated by ATC may be submitted as independent data series in the future. ICOS ATC is currently working on an automated data exchange between ICOS Carbon Portal and WDCGG.

Data Review

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

Documentation

All information is entered in electronic log books. For the measurements made by Empa, an electronic tool (UWEDAT - Maintenance Tool) is available to document all relevant information on instruments and the station. All instrument manuals are available at the site, and the reviewed information was comprehensive and up to date.

Air Inlet System

The current main inlet for trace gas observations was installed in 1994 about 5 m above the upper research platform, and about 10 m above the public platform. It is a stainless steel inlet reaching approximately 2 m above the laboratory roof with an inner diameter of 90 mm, and a flow rate of about 50 m^3 air per hour. The inlet system is heated to keep the air stream temperature at the lower end of the main manifold at 10°C. From there, a manifold flushed with 100 l/min serves as sampling ports for most analysers. The O_3 instrument is connected to the glass manifold through about 2 m of ¼" perfluoroalcoxy (PFA) tubing. The greenhouse gas (GHG) instruments are directly connected to the main stainless steel inlet by ¼" Synflex tubing. The pressure and temperature in the manifold, and the flow rates in the tubing to the GHG instruments are recorded.

About 10 years ago, it was realized that local emissions from the nearby tourist infrastructure occasionally lead to contamination of the atmospheric samples. This has been confirmed by the WCC-Empa audit in 2015 with parallel measurement using a different inlet location.

In 2020, an additional inlet system was installed about 30 m to the north-east of the tourist platform. The inlet system consists of two heated bundles with three tubes of 12 mm outer diameter (OD) Synflex-1300 tubing, and one heated bundle with 12 mm OD Synflex-1300, PFA, and PTFE tubing. The inlet location is at a lower altitude (3561 ± 2 m a.s.l.) than the tourist platform (3571.8 m a.s.l.). A full description of the new inlet system is given by Vollmer et al. (2020). This inlet is referred as the north-east inlet in this report.

Measurements of the parameters of the scope of the audit are still made using the old inlet system. The new system is currently used for the measurements of halogenated compounds. Parallel measurements of CO_2, CH_4 and CO from the default inlet and the north-east inlet were launched shortly after the audit when implementing a separate GHG instrument for continuous sampling from the north-east inlet.

Both inlet systems are adequate regarding material and residence times, and no change is required. However, it should be considered to measure GHG using the new system to minimise the influence of local pollution.

> **Recommendation 2 (*, minor, 2022)**
> *It should be considered to use the new air inlet system for the measurements of greenhouse gases to minimise the influence of the nearby tourist infrastructure on the measurements.*

Surface Ozone Measurements

Surface ozone measurements at JFJ were established in 1986, and continuous time series are available since then.

Instrumentation. JFJ is currently equipped with two ozone analysers (Thermo Scientific 49i). There are clearly defined master and backup instruments since the backup instrument's main purpose is to provide O_3 data for the correction of nitrogen oxides amount fractions in its dedicated measurement and data processing system. However, data from the backup instrument can be fed into the main O_3 data stream in case of persistent failures of the main instrument.

Standards. No standard is available at the site. However, two transfer standards (Thermo Scientific 49i-PS) are available at NABEL/Empa. One of them is used twice per year to verify the calibration of the JFJ instrument. The NABEL transfer standards have traceability to the Standard Reference Photometer (SRP) (Serial No. 15) of Empa. Indicative quality checks are performed every 49 hours when sampling ozone-free air and about 80 nmol mol^{-1} of O_3 for about 15 minutes each to verify the correct operation of the instrument. To do so, O_3 is produced by an external ozone generator.

Data Acquisition. The data acquisition system at JFJ is based on a commercial solution by Breitfuss GmbH (Easy-Comp, Anacomp and Anavis). The whole system including backup policy, data transfer and evaluation is fully adequate.

Intercomparison (Performance Audit). The JFJ 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 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 JFJ data acquisition system. The data was treated in the same way as ambient air measurements, and the following correction based on the last calibration with the NABEL transfer standards was applied, where X_{O3} is the unbiased O_3 amount fraction, and OA the reading of the analyser:

X_{O3} (nmol mol^{-1}) = ([OA] -0.25 nmol mol^{-1}) * 1.0015 (1a)

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 #1233255708 (BKG -0.7 nmol mol^{-1}, COEF 1.010):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -0.28 nmol mol^{-1}) / 1.0015 (1b)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.10e-05 * X_{O3}^2) (1c)

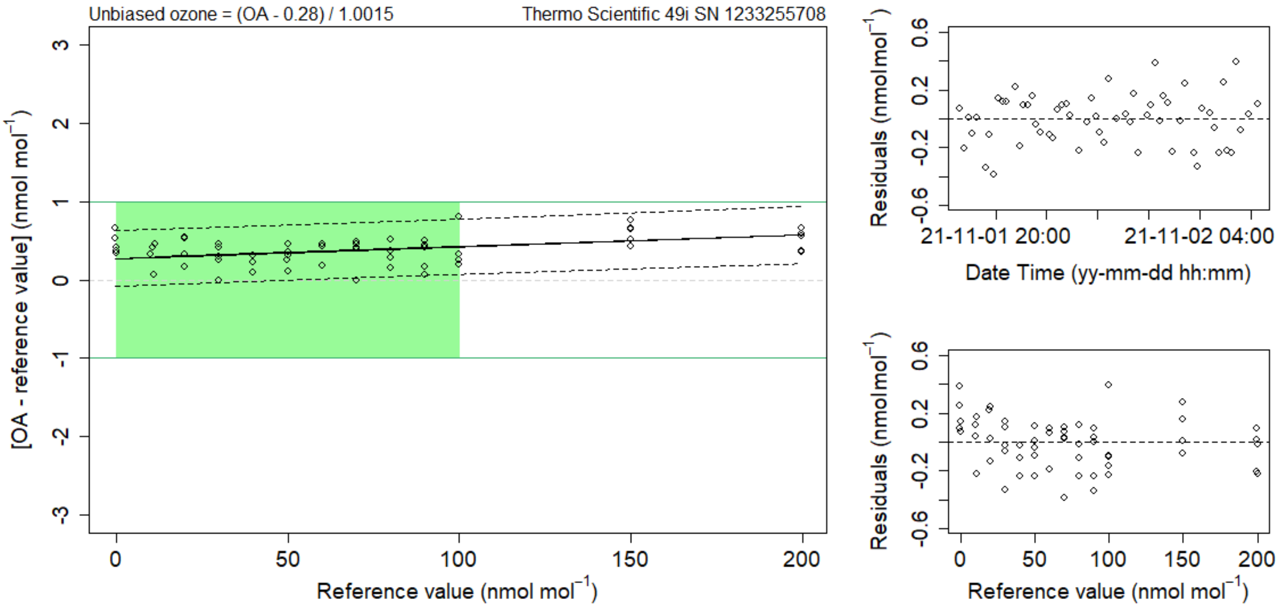

Figure 1. *Left: Bias of the JFJ ozone analyser (Thermo Scientific 49i #1233255708, BKG -0.7 nmol mol^{-1}, COEF 1.010) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant 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 JFJ ozone analyser was within the WMO/GAW DQOs over the entire measured range. Due to the good agreement, no further action is required.

Carbon Monoxide Measurements

Continuous measurements of CO at JFJ started in 1996 using non-dispersive infrared (NDIR) technique. For several years, CO was also simultaneously measured with gas chromatography / reduction gas detection and gas chromatography / flame ionization detection after methanisation of CO (Zellweger et al., 2009; Bond et al., 2011). Near-infrared Cavity Ringdown Spectroscopy (CRDS) measurements started in 2012, and an Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument was run from 2014 to 2020. In August 2020, a CO/N_2O CRDS mid-infrared analyser was added. Currently, the CO data of the near-IR CRDS instrument is considered as the master measurement despite inferior short-term precision of the near-IR instrument but due to the excellent mid- to long-term stability in the near-IR CRDS's instrument response.

Instrumentation. The following instruments are currently available:
Picarro G2401 (near-IR CRDS) with a Nafion dryer (MD-070-144S-2), and Picarro G5310 (mid-IR CRDS) using a Nafion dryer (MD-070-144S-2) to dry the sample air.

Standards. Several reference standards from the ICOS Flask and Calibration Laboratory (FCL), as well as working standards and target gas cylinders are available at JFJ. An overview of available standards is shown in Table 9 in the Appendix.

Calibration scheme of the Picarro G2401:

Weekly calibrations using three reference standards are made automatically. All standards are measured for 30 min, and the first 10 min are discarded due to stabilization time of the instrument. The calibration cycle is repeated four times, and only the last three runs are used for the calibration. In addition to the reference standards, CO-free air of the JFJ zero air system followed by a Sofnocat 423 cartridge is measured every fourth day. Daily measurements of a short term target gas are made, and a long term target gas is measured every 15 days.

ICOS ATC calibration procedure: ICOS ATC determines the calibration function based on a linear regression using the three reference standards. CO-free air is not used in the ICOS ATC calibration scheme. The data between the calibrations is linearly interpolated.

Empa calibration procedure: Empa applies a low-path filter (loess) to the calibration gas readings and determines the calibration function based on a linear regression using the three calibration gases (plus zero air for CO) for each ambient air measurement individually. The evaluation is made monthly and includes 10 days of data from the previous and the following month to minimize issues of diverging low-path filter fits at the very beginning and the very end of the month.

Calibration scheme of the Picarro G5310:

Calibrations using three reference standards are automatically made every three days. The calibration cycle is repeated four times, and only the last three runs are used for the calibration. In addition, measurements of a short term target gas are made every 10 hours, a short term working standard is measured daily, and a long term target gas is measured every 15 days.

ICOS ATC calibration procedure: ICOS ATC determines the calibration function based on a linear regression using the three calibration gases. The data between the calibrations is linearly interpolated. The readings (or analyser output) during calibration gas sampling are adjusted based on the measurements of the short term working standard to compensate for potential short-term drifts in instrument response.

Empa calibration procedure: Empa determines the calibration function based on a linear regression using the three standard gases similar to the approach applied to the G2401 data (see above). The evaluation is made monthly and includes one week of data from the previous and the following month. No corrections for drift based on the WS measurements is applied.

Data Acquisition. CO data from the CRDS instrument are sent to the central data acquisition system at JFJ to facilitate visual on-site inspection, e.g. during maintenance visits, and to forward the data along with all other measured variables to a server at Empa where time series from all 16 stations of the Swiss National Air Pollution Monitoring Network are continuously updated and displayed. This allows easy and remote visual inspection by the operators. However, high-resolution (5-sec averages) raw data files directly accessed from the CRDS hard disk are used for the processing of the data, including separation of the data into ambient air, calibration gas, and quality control datasets, analysis of the calibration gas measurements and application of the calibration function to the ambient air and target gas readings. Highest resolution (1 to 2 seconds resolution) raw data files are sent daily to ICOS ATC where processing is performed. See Hazan et al. (2016) for details of the ATC processing.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JFJ instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The data was independently processed by Empa and ICOS ATC. The following equations characterise the instrument bias, and the results are further illustrated in Figures 2 to 5 with respect to the WMO GAW DQOs (WMO, 2020):

Picarro G2401 #1732-CFKADS-2133 (Empa analysis):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 0.56 nmol mol^{-1}) / 0.9914 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (0.6 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2b)

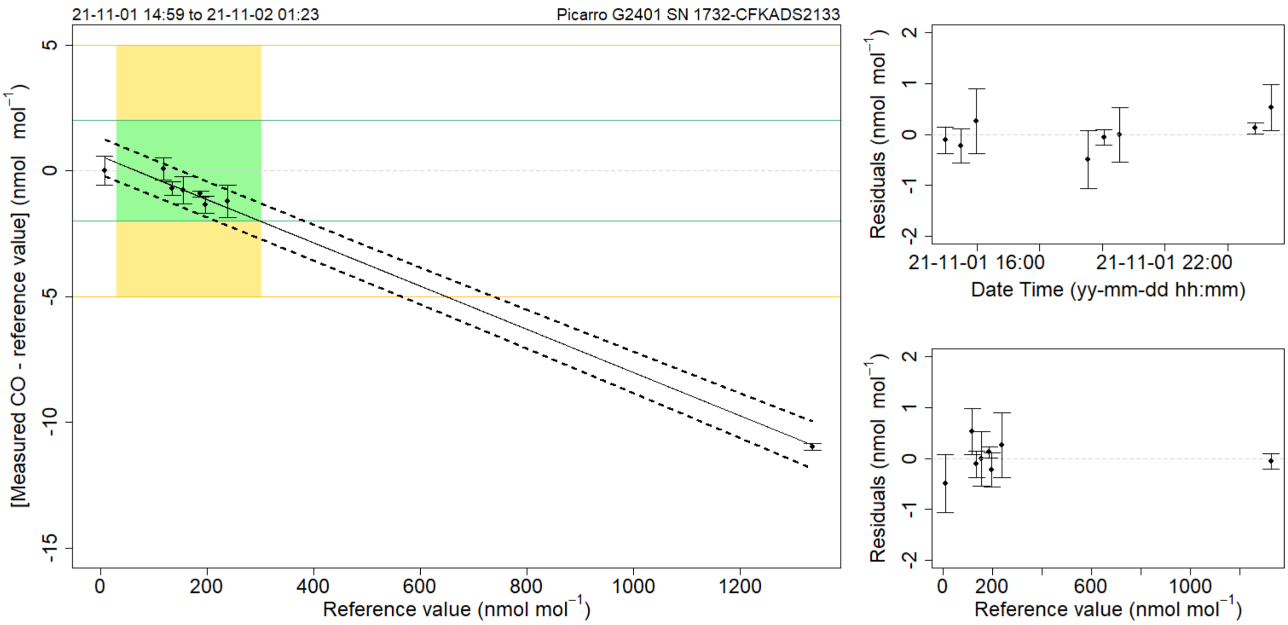

Figure 2. *Left: Bias of the JFJ Picarro G2401 #1732-CFKADS-2133 carbon monoxide instrument (Empa analysis) with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard 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 JFJ. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #1732-CFKADS-2133 (ICOS ATC analysis):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 14.71 nmol mol^{-1}) / 0.9411 (2c)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (11.9 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2d)

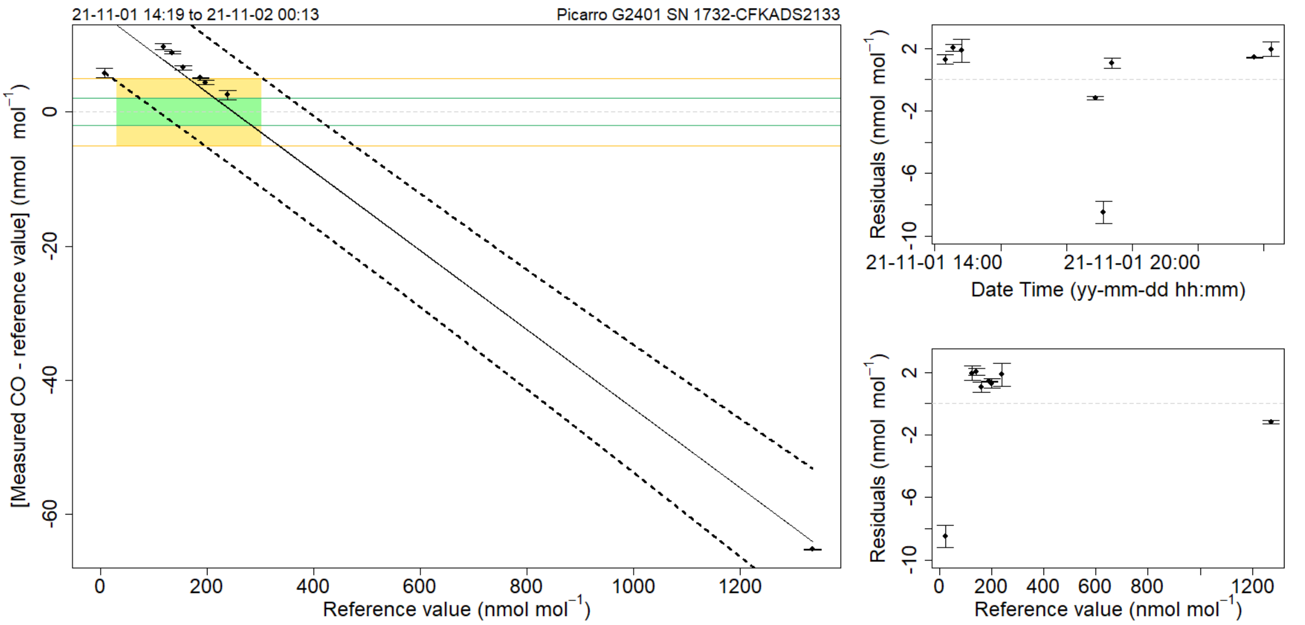

Figure 3. *Same as above, ICOS ATC analysis.*

Picarro G5310 #5097-PPU-JKADS5106 (Empa analysis):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 2.90 nmol mol^{-1}) / 1.0020 (2e)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (0.8 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2f)

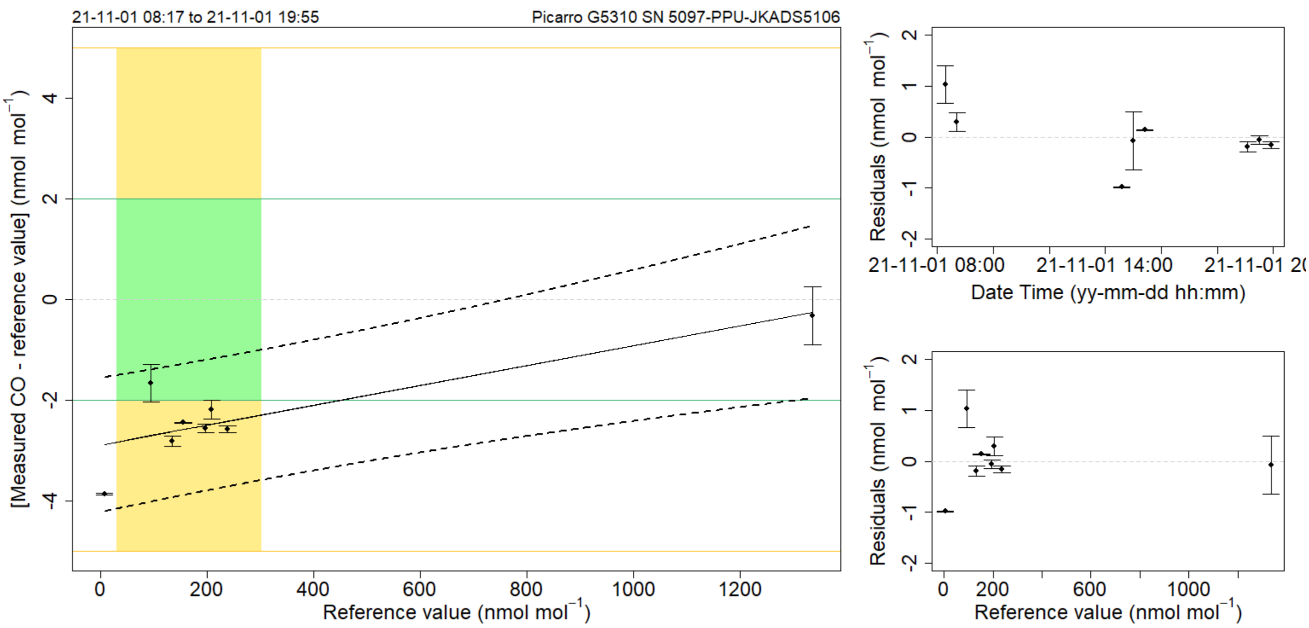

Figure 4. *Left: Bias of the JFJ Picarro G5310 #5097-PPU-JKADS5106 carbon monoxide instrument (Empa analysis) with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard 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 JFJ. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G5310 #5097-PPU-JKADS5106 (ICOS ATC analysis):

Unbiased CO mixing ratio:	X_{CO} (nmol mol^{-1}) = (CO - 2.71 nmol mol^{-1}) / 1.0018	(2g)
Remaining standard uncertainty:	u_{CO} (nmol mol^{-1}) = sqrt (0.8 nmol mol^{-1} + 1.01e-04 * X_{CO}^2)	(2h)

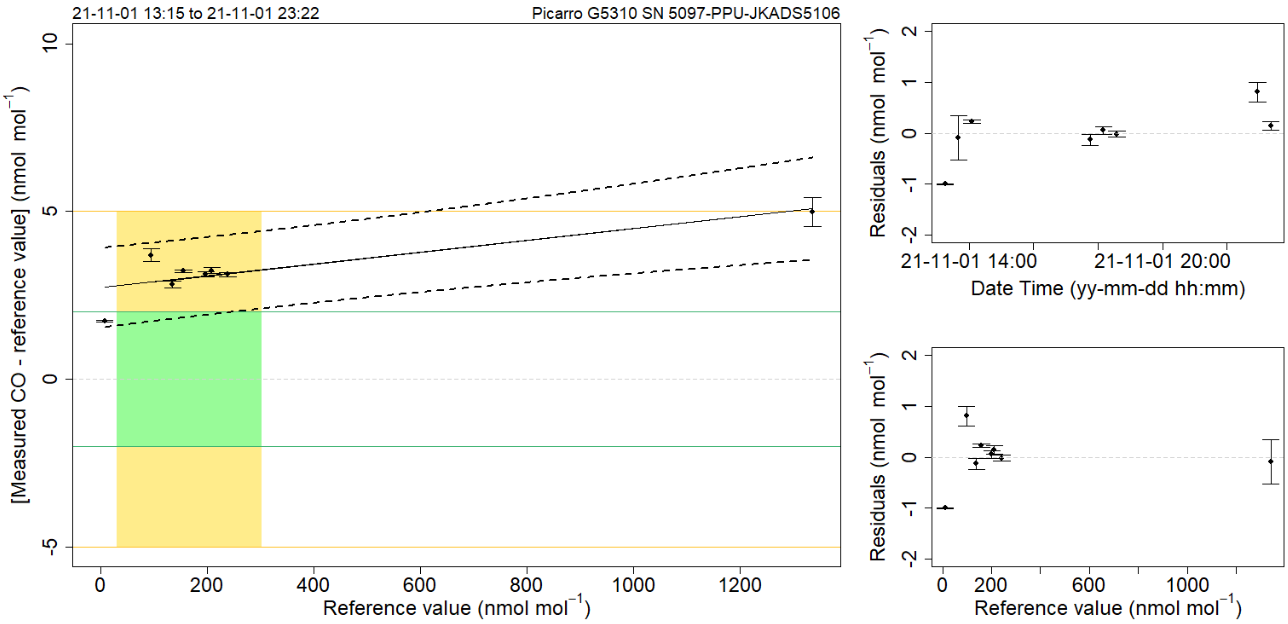

Figure 5. *Same as above, ICOS ATC analysis.*

The ICOS ATC standards were measured for CO on the WCC-Empa travelling instrument during the audit, and these standards were also measured at WCC-Empa when they were delivered by the ICOS ATC between 2015 and 2019. The results of these measurements are summarised in Table 1.

Table 1. *ICOS ATC CO standards analysed by WCC-Empa at JFJ during the audit and at WCC-Empa after delivery of the standards by the ICOS ATC. The ICOS ATC assigned value of the tank as well as the difference between the ICOS ATC assigned value and the WCC analysis at JFJ, and a drift rate per year based on the two WCC-Empa analyses is also given.*

Cylinder ID	Date of analysis @JFJ	CO by WCC @JFJ (nmol mol^{-1})	Date of analysis @WCC-Empa	CO by WCC @WCC (nmol mol^{-1})	ICOS ATC assigned (nmol mol^{-1})	ATC-WCC @JFJ 2021 (nmol mol^{-1})	ATC-WCC @WCC 2015/19 (nmol mol^{-1})	Drift (nmol mol^{-1} y^{-1})
D175443	2021-11-02	75.31	2015-07-15	72.18	71.95	-3.37	-0.23	0.50
D175446	2021-11-02	310.57	2015-07-15	304.07	304.89	-5.69	0.82	1.03
D175450	2021-11-01	122.61	2019-03-17	119.70	122.71	0.10	3.01	1.11
D175452	2021-11-01	206.88	2015-07-15	200.49	201.92	-4.96	1.43	1.01
D175447	2021-11-02	131.44	2019-05-10	128.86	129.02	-2.42	0.16	1.04
D570048	2021-11-02	74.35	2018-07-18	69.29	70.05	-4.30	0.76	1.54
D570049	2021-11-02	154.48	2018-07-18	150.76	150.20	-4.28	-0.56	1.13
D570050	2021-11-02	304.82	2018-07-18	302.27	300.35	-4.47	-1.92	0.77

The agreement between the ICOS ATC assigned values and WCC-Empa was mostly within the WMO/GAW network compatibility goals for the measurements that were carried out at WCC-Empa after the delivery of the standards between 2015 and 2019. On average, the bias between the ICOS ATC and WCC-Empa was 0.43 nmol mol^{-1}. The bias increased significantly until 2021 due to drift of the CO amount fraction in the standards. The drift rates that were estimated based on the measurements of the standards between 2015 and 2019 at WCC-Empa and 2021 at JFJ range from 0.5 to 1.5 nmol mol^{-1} y^{-1}, with an average of 1.0 nmol mol^{-1} y^{-1}. The average drift is in very good agreement with the drift that ICOS ATC assumes for their standards, which is 1.1 nmol mol^{-1} y^{-1}. Once the calibration gases are re-calibrated at ICOS FCL, data will be re-processed considering real drifts of the composition of the cylinder fillings. However, relatively large differences are observed between individual cylinders, which complicates the correction of drift related changes in the calibration standards. Therefore, a calibration strategy based on standards with high CO amount fractions and zero air should be considered as an alternative.

Recommendation 3 (*, minor, 2022)
The CRDS measurement technique shows a linear response for CO in the amount fraction range at least from 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, and also includes CO free air (or N_2 6.0) to compensate for a zero offset. When standards with an amount fraction larger than 500 nmol mol^{-1} are used, the linearity of the analyser and the traceability to the CCL needs to be checked.

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} in the relevant amount fraction range except for the ICOS ATC analysis of the Picarro 2401 analyser.

A large difference was observed between the Empa and the ICOS ATC analysis for CO, especially for the Picarro G2401 analyser. ICOS ATC assumes a linear drift for the CO standards of 1.1 nmol y^{-1}, but drift rates differ between standards. The fact that Empa does not consider standard drift may partly explain the observed bias. Other differences in the Empa and ATC data streams include different raw data files (5-sec averages vs. 1 to 2 sec data), different interpolation in between calibrations (lowess fit vs. linear fit), and the use of CO-free air as a forth reference point (for Empa-processing only). The main cause for the differences in the final data is still unidentified. The difference in the input files is expected to be negligible.

Recommendation 4 (*, critical, 2022)**
The difference between the Empa and the ICOS ATC analysis of the Picarro G2401 instrument needs further attention, and the reason must be identified.

Methane Measurements

Continuous measurements of CH_4 at JFJ started in 2005 using GC / flame ionization detection (FID). Since January 2010 CH_4 measurements are made using CRDS technique. The GC/FID still ran next to the CRDS analyser until summer 2016 but is now no longer in operation.

Instrumentation. The following instrument is currently used:
Picarro G2401 (near-IR CRDS) with a Nafion dryer (MD-070-144S-2).

Standards and calibration. See Carbon Monoxide Measurements. No CH_4-free air is used as forth reference point for the calibration.

Data Acquisition. See CO.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JFJ instrument with randomised CH_4 levels from travelling standards. The analysis was carried out by Empa and the ICOS ATC. The results of the comparison are summarised and illustrated below.

The following equation characterises the instrument bias. The results are further illustrated in Figure 6 and 7 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1732-CFKADS-2133 (Empa analysis):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.61 nmol mol^{-1}) / 0.9988 (3a)

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

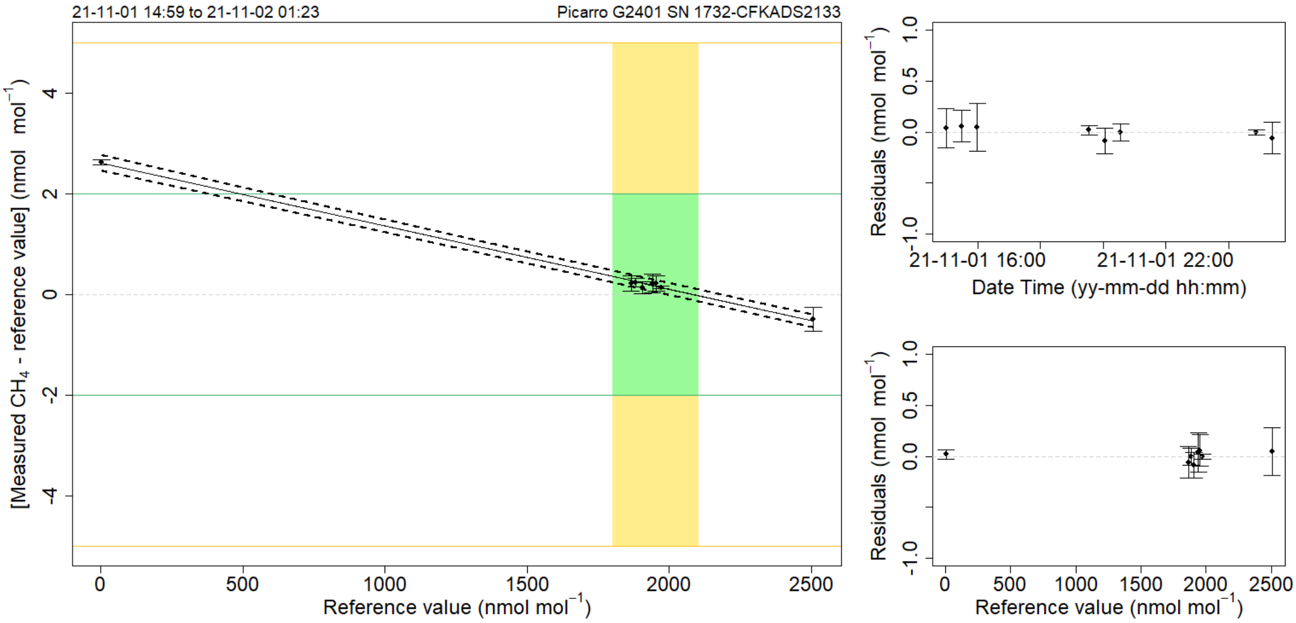

Figure 6. *Left: Bias of the Picarro G2401 #1732-CFKADS-2133 instrument (Empa analysis) with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation 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 JFJ. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #1732-CFKADS-2133 (ICOS ATC analysis):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 1.85 nmol mol^{-1}) / 0.9991 (3c)

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

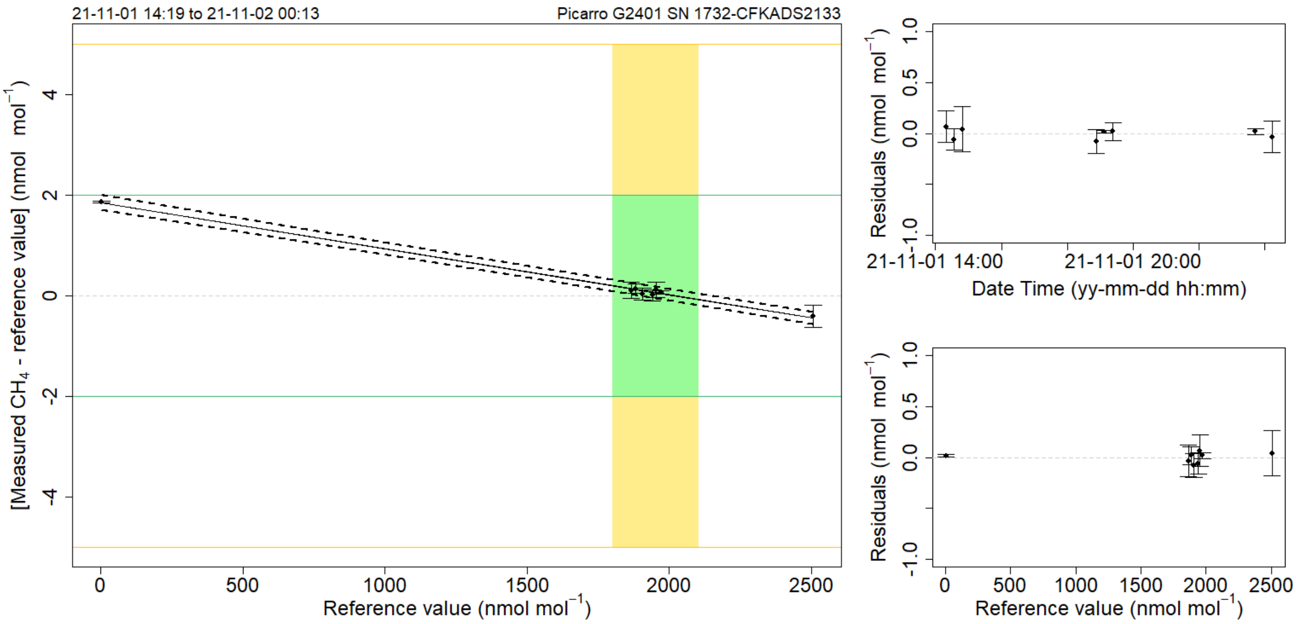

Figure 7. *Same as above, ICOS ATC analysis.*

The ICOS ATC standards were measured for CH_4 on the WCC-Empa travelling instrument during the audit, and these standards were also measured at WCC-Empa when they were delivered by the ICOS ATC between 2015 and 2019. The results of these measurements are summarised in Table 2.

Table 2. *ICOS ATC CH_4 standards analysed by WCC-Empa at JFJ during the audit and at WCC-Empa after delivery of the standards by the ICOS ATC. The ICOS ATC assigned value of the tank as well as the difference between the ICOS ATC assigned value and the WCC analysis at JFJ, and a drift rate per year based on the two WCC-Empa analyses is also given.*

Cylinder ID	Date of analysis @JFJ	CH_4 by WCC @JFJ (nmol mol^{-1})	Date of analysis @WCC-Empa	CH_4 by WCC @WCC (nmol mol^{-1})	ICOS ATC assigned (nmol mol^{-1})	ATC-WCC @JFJ 2021 (nmol mol^{-1})	ATC-WCC @WCC 2015/19 (nmol mol^{-1})	Drift (nmol mol^{-1} y^{-1})
D175443	2021-11-02	1784.46	2015-07-15	1785.06	1784.58	0.12	-0.48	-0.09
D175446	2021-11-02	2151.32	2015-07-15	2151.77	2151.00	-0.32	-0.77	-0.07
D175450	2021-11-01	1919.69	2019-03-17	1919.57	1919.58	-0.11	0.01	0.05
D175452	2021-11-01	2070.16	2015-07-15	2070.47	2070.10	-0.06	-0.37	-0.05
D175447	2021-11-02	1923.95	2019-05-10	1923.61	1924.05	0.10	0.44	0.14
D570048	2021-11-02	1788.36	2018-07-18	1788.22	1788.45	0.09	0.23	0.04
D570049	2021-11-02	1953.71	2018-07-18	1953.62	1953.70	-0.01	0.08	0.03
D570050	2021-11-02	2158.42	2018-07-18	2158.40	2158.14	-0.28	-0.26	0.01

The agreement between the ICOS ATC assigned values and WCC-Empa was well within the WMO/GAW network compatibility goals for the measurements that were carried out at WCC-Empa after the delivery of the standards between 2015 and 2019, and also for the measurements made during this audit. The bias between WCC-Empa and the ICOS ATC was not significantly different from zero. Furthermore, none of the standards showed a significant drift. The excellent result of the standard comparison is in good agreement with the comparisons carried out at JFJ.

The result of the comparison can be summarised as follows:

Excellent agreement well with the WMO/GAW compatibility goal was found in the relevant amount fraction range. A small dependency of the bias on the amount fraction was observed, which may be due to remaining inconsistencies of the used calibration standards. 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 at present. In contrast to CO, the analysis of the methane data by Empa and the ICOS ATC showed no relevant bias.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at JFJ were started by CEP in 2004 using NDIR technique, and continuous data is available since then. Since 2009, additional CO_2 measurements are made by Empa using CRDS technique.

Instrumentation. The following instruments are currently available:
Picarro G2401 (near-IR CRDS) with a Nafion dryer (MD-070-144S-2) operated by Empa, and a Sick Maihak S710 NDIR spectrometer with a cryogenic dryer (FC-100D21, FTS systems, USA) operated by CEP.

Standards and calibration. Empa CDRS Instrument: See Carbon Monoxide Measurements. No CO_2-free air is used as forth reference point for the calibration. CEP NDIR analyser: The Measurements are done in a cyclic sequence of 18 h. Each sample or gas is measured for 6 min, but only the last 115 s of a 6 min period is used for amount fraction determination to allow for signal stabilisation. At the beginning of each sequence, the system is calibrated with two reference gases (high and low span), and a working gas is measured between two ambient air measurements to correct for short-term variations (Schibig et al., 2015).

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JFJ instruments with randomised CO_2 levels from travelling standards. The data of the Empa analyser was independently processed by Empa and ICOS ATC. It should also be noted that the Empa data has been processed on the WMO-X2007 CO_2 calibration scale, whereas ICOS ATC and CEP used the WMO-X2019 CO_2 calibration scale. ICOS ATC released the CO_2 data on the WMO-X2019 scale shortly after the end of the audit (in early February 2022). Nominal values of the reference gases were only available in late 2021, thus, Empa decided to continue processing its CO_2 data on the WMO-X2007 scale until the end of 2021 and to switch to WMO-X2019 in January 2022. The results of the comparisons are summarised and illustrated below.

The following equations characterise the instrument bias. The results are further illustrated in Figure 8 to 10 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1732-CFKADS-2133 (Empa analysis, WMO-X2007 CO_2 calibration scale):

Unbiased CO_2 mixing ratio:	X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.31 µmol mol^{-1}) / 0.99905	(4a)
Remaining standard uncertainty:	u_{CO2} (µmol mol^{-1}) = sqrt (0.01 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2)	(4b)

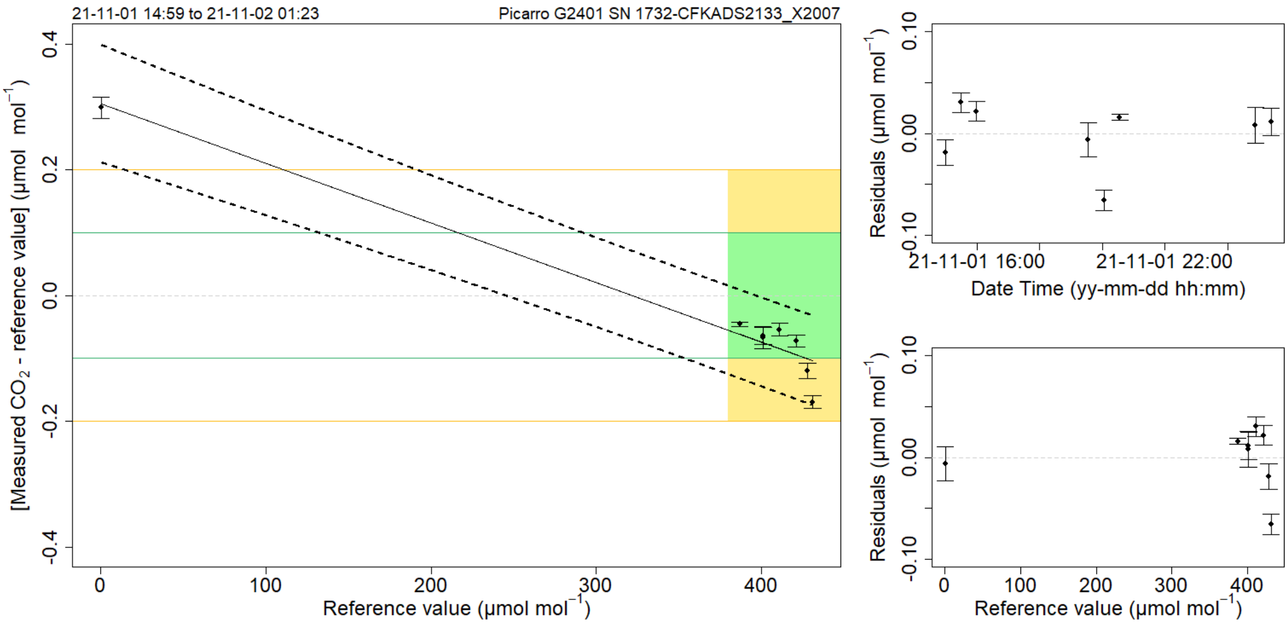

Figure 8. *Left: Bias of the Picarro G2401 #1732-CFKADS-2133 CO_2 instrument (Empa analysis, WMO-X2007 CO_2 calibration scale) with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty 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 JFJ. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #1732-CFKADS-2133 (ICOS ATC analysis, WMO-X2019 CO_2 calibration scale):

Unbiased CO_2 mixing ratio:	X_{CO2} (µmol mol^{-1}) = (CO_2 + 0.00 µmol mol^{-1}) / 0.99991	(4c)
Remaining standard uncertainty:	u_{CO2} (µmol mol^{-1}) = sqrt (0.01 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2)	(4d)

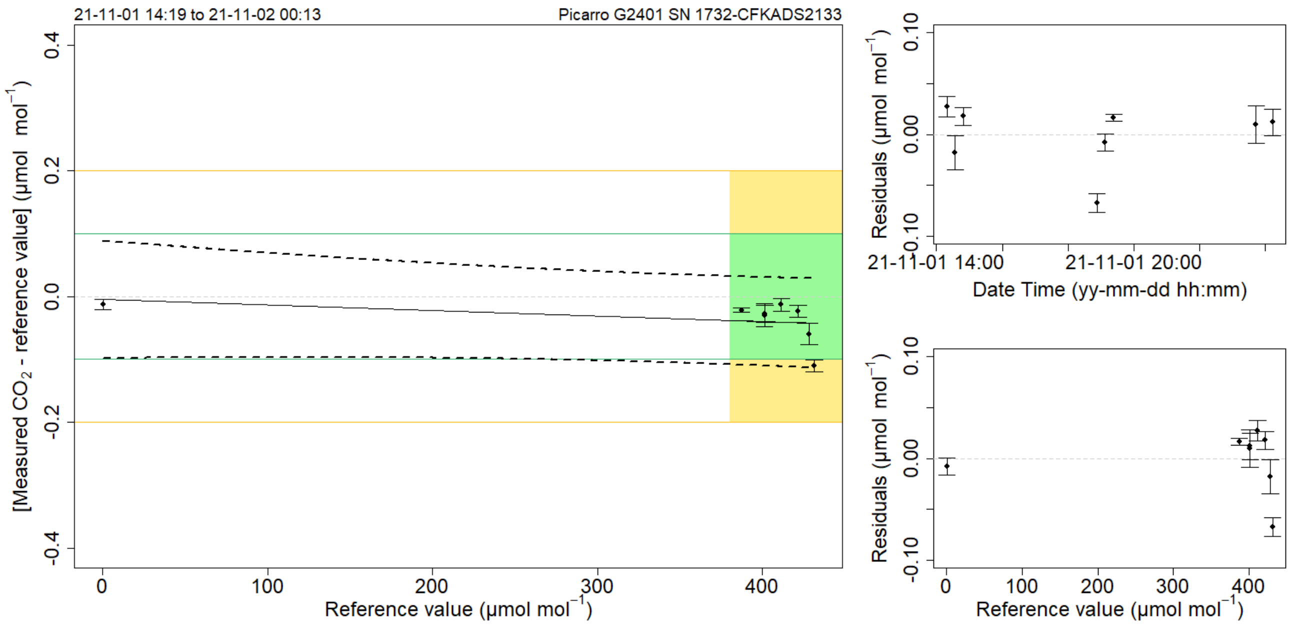

Figure 9. *Same as above, ICOS ATC analysis, WMO-X2019 CO_2 calibration scale.*

Maihak S710 (WMO-X2019 CO_2 calibration scale):

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 + 1.33 µmol mol^{-1}) / 1.00298 (4e)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.14 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4f)

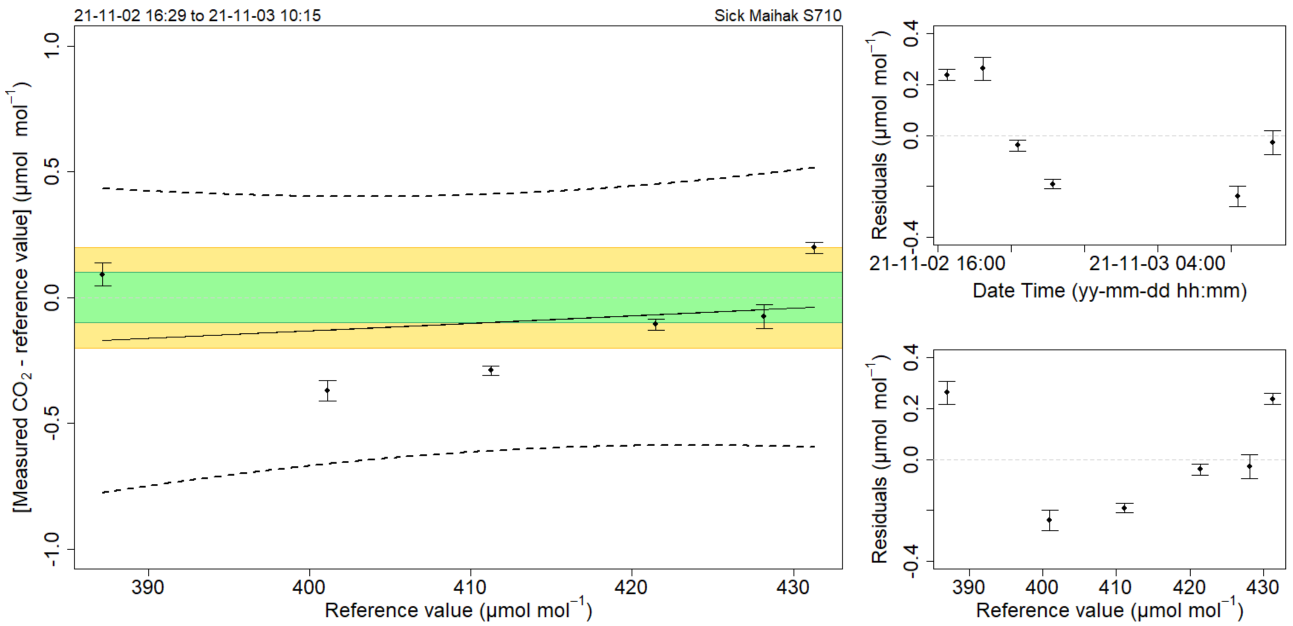

Figure 10. *Left: Bias of the Maihak S710 CO_2 instrument (WMO-X2019 CO_2 calibration scale) with respect to the WMO-X2019 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of 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 JFJ. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The ICOS ATC standards were measured for CO_2 on the WCC-Empa travelling instrument during the audit, and these standards were also measured at WCC-Empa when they were delivered by the ICOS ATC between 2015 and 2019. The results of these measurements are summarised in Table 3.

Table 3. *ICOS ATC CO_2 standards (WMO-X2007 CO_2 calibration scale) analysed by WCC-Empa at JFJ during the audit and at WCC-Empa after delivery of the standards by the ICOS ATC. The ICOS ATC assigned value of the tank as well as the difference between the ICOS ATC assigned value and the WCC analysis at JFJ, and a drift rate per year based on the two WCC-Empa analyses is also given.*

Cylinder ID	Date of analysis @JFJ	CO_2 by WCC @JFJ (µmol mol^{-1})	Date of analysis @WCC-Empa	CO_2 by WCC @WCC (µmol mol^{-1})	ICOS ATC assigned (µmol mol^{-1})	ATC-WCC @JFJ 2021 (µmol mol^{-1})	ATC-WCC @WCC 2015/19 (µmol mol^{-1})	Drift (µmol mol^{-1} y^{-1})
D175443	2021-11-02	375.02	2015-07-15	374.88	374.88	-0.14	0.01	0.02
D175446	2021-11-02	450.39	2015-07-15	450.12	450.19	-0.20	0.07	0.04
D175450	2021-11-01	404.63	2019-03-17	404.39	404.46	-0.17	0.07	0.09
D175452	2021-11-01	440.12	2015-07-15	439.95	439.93	-0.19	-0.02	0.03
D175447	2021-11-02	420.58	2019-05-10	420.47	420.51	-0.07	0.03	0.04
D570048	2021-11-02	374.45	2018-07-18	374.35	374.36	-0.09	0.02	0.03
D570049	2021-11-02	411.87	2018-07-18	411.77	411.74	-0.13	-0.03	0.03
D570050	2021-11-02	449.89	2018-07-18	449.78	449.71	-0.18	-0.07	0.03

The agreement between the ICOS ATC assigned values and WCC-Empa was well within the WMO/GAW network compatibility goals for the measurements that were carried out at WCC-Empa after the delivery of the standards between 2015 and 2019, with average bias between the ICOS ATC and WCC-Empa of 0.01 µmol mol^{-1}. A slightly larger bias of -0.15 µmol mol^{-1} was observed for the measurements carried out at JFJ, which is in agreement with the results of the TS comparisons. A drift rate was calculated based on the measurements of the ATC standards at WCC-Empa and the measurements of the standards at JFJ. The average drift was 0.04 µmol mol^{-1} y^{-1}; however, the drift rates should be treated with care, since they rely on a small number of measurements using a different set of calibration standards. These drift rates will also be determined at the ICOS ATC by a re-calibration at ICOS FCL after the use of the standards at JFJ. A correction of the data might be necessary based on these results.

The CO_2 standards of the University of Bern were measured on the WCC-Empa travelling instrument during the audit. The results of these measurements are summarised in Table 4.

Table 4. *University of Bern (CEP) CO_2 standards (WMO-X2019 CO_2 calibration scale) analysed by WCC-Empa at JFJ during the audit.*

Cylinder ID	Date of analysis @JFJ	CO_2 by WCC @JFJ (µmol mol^{-1})	CEP assigned (µmol mol^{-1})	CEP-WCC (µmol mol^{-1})
Lux3573	2021-11-02	428.74	428.81	0.07
Lux3581	2021-11-02	382.82	383.10	0.28
Lux3582	2021-11-02	421.46	421.30	-0.16

The difference of the CO_2 amount fraction assigned by CEP and measured by WCC-Empa is exceeding the WMO/GAW network compatibility goal. The results of the standard comparison are in agreement with the TS comparison of the performance audit. Re-calibration of the standards against CCL traceable standards is needed.

The result of the comparison can be summarised as follows:
The results were on average within the extended WMO/GAW network compatibility goal for the Picarro G2401 (Empa analysis) and the Sick Maihak S710 instrument. The ICOS ATC analysis of the Picarro G2401 analyser complied with the WMO/GAW network compatibility goal.

The remaining bias and uncertainty is largest for the Sick Maihak S710 instrument, most likely due to linearity issues of this instrument and biases in the assignment of the CO_2 amount fractions of the standards used for the calibration of the analyser. For this instrument, a clear amount fraction dependency of the bias was observed, and the CO_2 amount in the atmosphere might be underestimated at the current background level. The following recommendation is made:

Recommendation 5 (Sick Maihak S710 analyser only) (, important, 2022)**
It is recommended to re-calibrate the standards used for the calibration of the Sick Maihak S710 analyser. Furthermore, only a small number of standards is used to evaluate the non-linearity of the instrument. It is recommended to increase the number of standards for the evaluation of the non-linearity, and it must be made sure that the amount fraction of the calibration standards cover the entire relevant amount fraction range.

At the time of the audit, Empa was still using the WMO-X2007 CO_2 calibration scale, whereas the revised scale was retroactively implemented for the ICOS ATC analysis shortly after the end of the parallel measurements. The comparison with the WCC-Empa TS was made using the same calibration scale. The use of the revised scale may explain the slightly better results of the ICOS ATC analysis compared to Empa.

Recommendation 6 (, important, 2022)**
It is recommended to implement the WMO-X2019 CO_2 calibration for the data evaluation of the Picarro G2401 by Empa (Done in January 2022).

Nitrous Oxide Measurements

Continuous measurements of N_2O at JFJ started in 2005 using GC / electron capture detection (ECD). From 2015 to 2019, N_2O measurements were made using Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique. From 2020 onwards, N_2O measurements are made using a mid-IR CRDS analyser.

Instrumentation. Picarro G5310 (mid-IR CRDS) using a Nafion dryer (MD-070-144S-2) to dry the sample air.

Standards and calibration. See Carbon Monoxide Measurements (Picarro G5310).

Data Acquisition. See CO (Picarro G5310).

Intercomparison (Performance Audit). The comparison involved repeated challenges of the JFJ instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The data was independently processed by Empa and ICOS ATC. The following equations characterise the instrument bias, and the results are further illustrated in Figure 11 and 12 with respect to the WMO GAW DQOs (WMO, 2020):

Picarro G5310 #5097-PPU-JKADS5106 (Empa analysis):

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 2.46) / 1.0075 (5a)

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

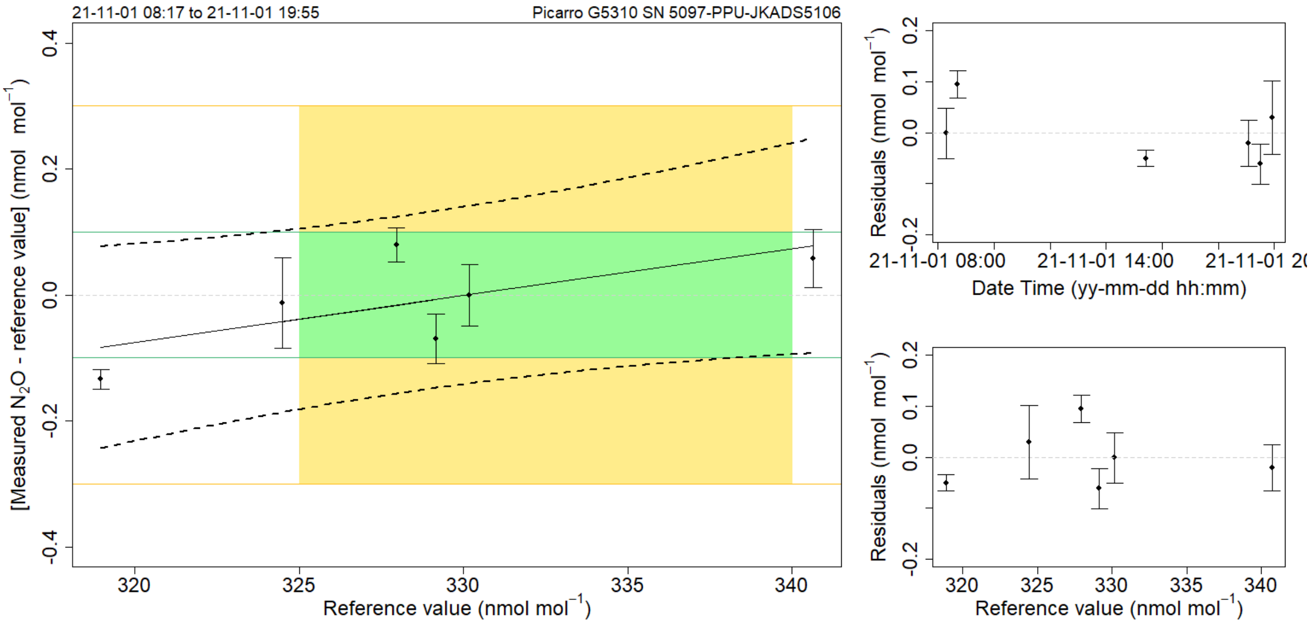

Figure 11. *Left: Bias of the Picarro G5310 nitrous oxide analyser (Empa analysis) with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual 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 JFJ. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G5310 #5097-PPU-JKADS5106 (ICOS ATC analysis):

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 2.97) / 1.0086 (5a)

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

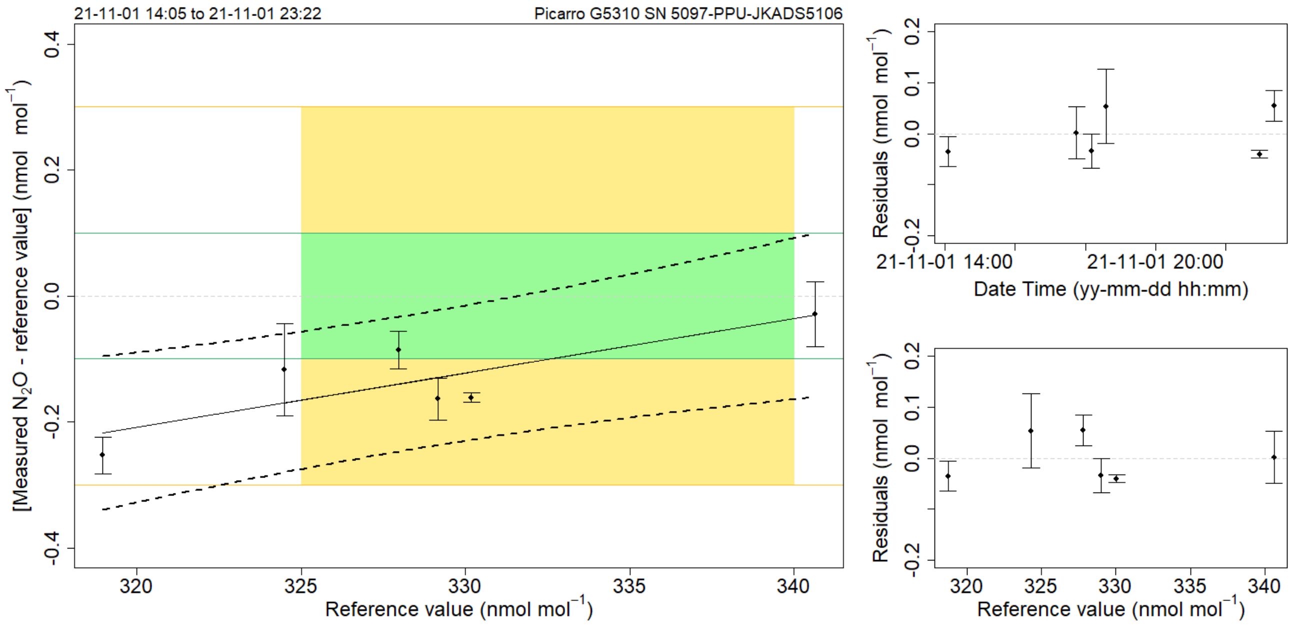

Figure 12. *Same as above, ICOS ATC analysis.*

The result of the comparison can be summarised as follows:

On average, the agreement between JFJ and WCC-Empa was within the WMO/GAW network compatibility goals for the Empa analysis, and within the extended goal for the ICOS ATC analysis of the data. The difference may be explained by the slightly different data analysis methods.

JFJ PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the JFJ 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 13 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 14. 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 JFJ audit are shown as coloured dots in Figure 13 and 14, and are also summarised in Table 5. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 5.

The results were within the DQOs for O_3 and CH_4, CO_2 was within the DQO for the ICOS ATC analysis of the Picarro instrument, and within the extended DQOs for the Empa analysis of the Picarro and the NDIR instrument of the University of Bern. N_2O results were also dependent on the data treatment, and were within the DQOs for the Empa analysis, but only within the extended DQO for the ICOS ATC data processing. CO results were within the extended DQOs for the mid-IR Picarro (G5310), but a large discrepancy was found for the near-IR instrument (Picarro G2401), where the Empa analysis was within the DQO, but the ICOS ATC analysis was not meeting even the extended DQO.

Table 5. *JFJ 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**	**JFJ within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**
O_3 (Thermo 49i #1233255708)	0 -100	nmol mol^{-1}	✓	65	NA
CO (Picarro G2401 CFKADS2066, Empa analysis)	30 - 300	nmol mol^{-1}	✓	19	51
CO (Picarro G2401 CFKADS2066, ICOS ATC analysis)	30 - 300	nmol mol^{-1}	✗	19	51
CO (Picarro G5310 JKADS5106, Empa analysis)	30 - 300	nmol mol^{-1}	✓	19	51
CO (Picarro G5310 JKADS5106, ICOS ATC analysis)	30 - 300	nmol mol^{-1}	✓	19	51
CH_4 (Picarro G2401 CFKADS2066, Empa analysis)	1750 - 2100	nmol mol^{-1}	✓	73	94
CH_4 (Picarro G2401 CFKADS2066, ICOS ATC analysis)	1750 - 2100	nmol mol^{-1}	✓	73	94
CO_2 (Picarro G2401 CFKADS2066, Empa analysis)	380 - 450	µmol mol^{-1}	✓	44	72
CO_2 (Picarro G2401 CFKADS2066, ICOS ATC analysis)	380 - 450	µmol mol^{-1}	✓	44	72
CO_2 (Sick Maihak S710)	380 - 450	µmol mol^{-1}	✓	44	72
N_2O (Picarro G5310 JKADS5106, Empa analysis)	325 - 335	nmol mol^{-1}	✓	4	43
N_2O (Picarro G5310 JKADS5106, ICOS ATC analysis)	325 - 335	nmol mol^{-1}	✓	4	43

[1] Percentage of stations within the eDQO and DQO

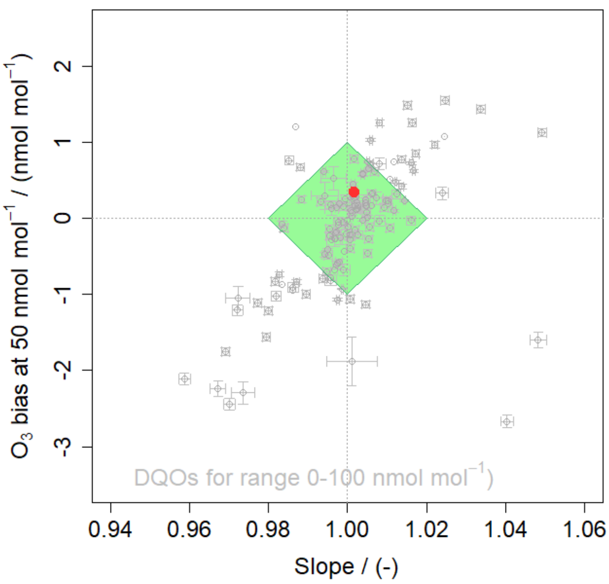

Figure 13. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the red dots shows the results of the JFJ instrument. The uncertainty bars refer to the standard uncertainty, and the green area corresponds to the WMO/GAW DQO for surface ozone.*

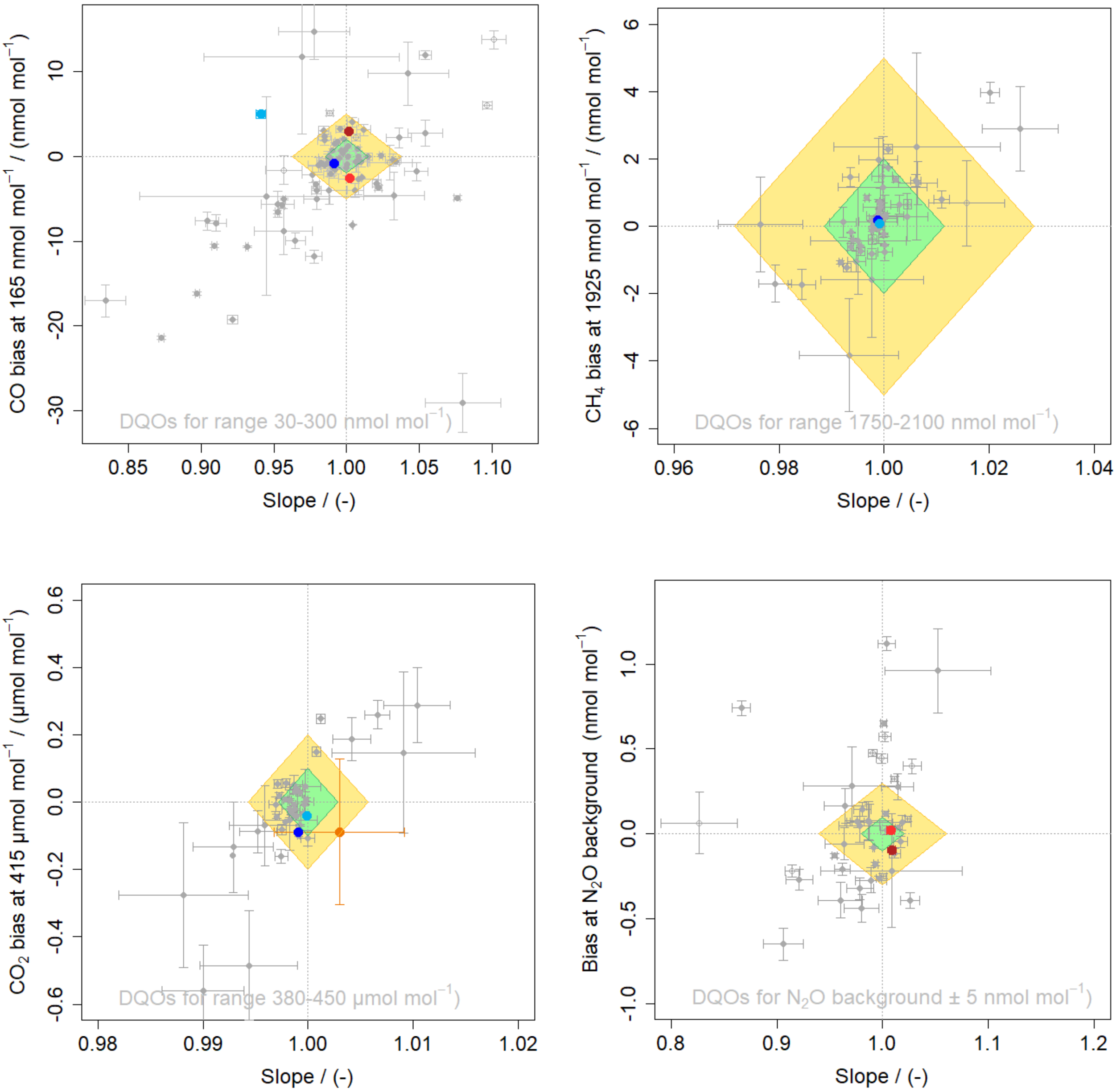

Figure 14. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show JFJ results (blue: Picarro G2401 Empa analysis, light blue: Picarro G2401 ICOS ATC analysis, red: Picarro G5310 Empa analysis, dark red: Picarro G5310 ICOS ATC analysis, orange: Sick Maihak S710). 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 3 November through 30 December 2021 at JFJ. The TI was connected to the NABEL inlet system, and was also sampling from a spare inlet line of the north-east inlet. The TI was sampling air using the following sequence: 1440 min ambient air from the NABEL inlet, then 300 min air from the north-east inlet 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. The JFJ data was independently processed by Empa and the ICOS ATC, and the results of both comparisons are shown below.

Carbon monoxide comparisons

Figure 15 shows the comparison of hourly CO measurements between the WCC-Empa TI and the JFJ Picarro G2401 analyser for the Empa (top) and the ICOS ATC analysis of the data (bottom). The corresponding deviation histograms are shown in Figure 16. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers and the WCC-Empa TI.

No significant influence of the inlet system was observed. The deviation was on average not significantly different when the WCC-Empa TI sampled from the north-east inlet. This indicates that both inlet systems are suitable; however, larger differences were observed during the WCC-Empa audit in 2015 during the summer months, when the NABEL inlet is more sensitive to activities on the tourist platform. To minimise the influence of the tourist activities, air sampling from the north-east inlet should be considered.

A large deviation exceeding 10 nmol mol^{-1} was found between the Empa and the ICOS ATC data evaluation of the Picarro G2401 data. Part of this difference may be explained by the fact the ATC assumes as constant drift in the calibration standards of 1.1 nmol y^{-1}. However, the date of the last ICOS ATC calibration of the standards in use is too recent to explain the entire bias. The reason for the different results of the Empa and the ICOS ATC analysis needs to be identified (see recommendation 4).

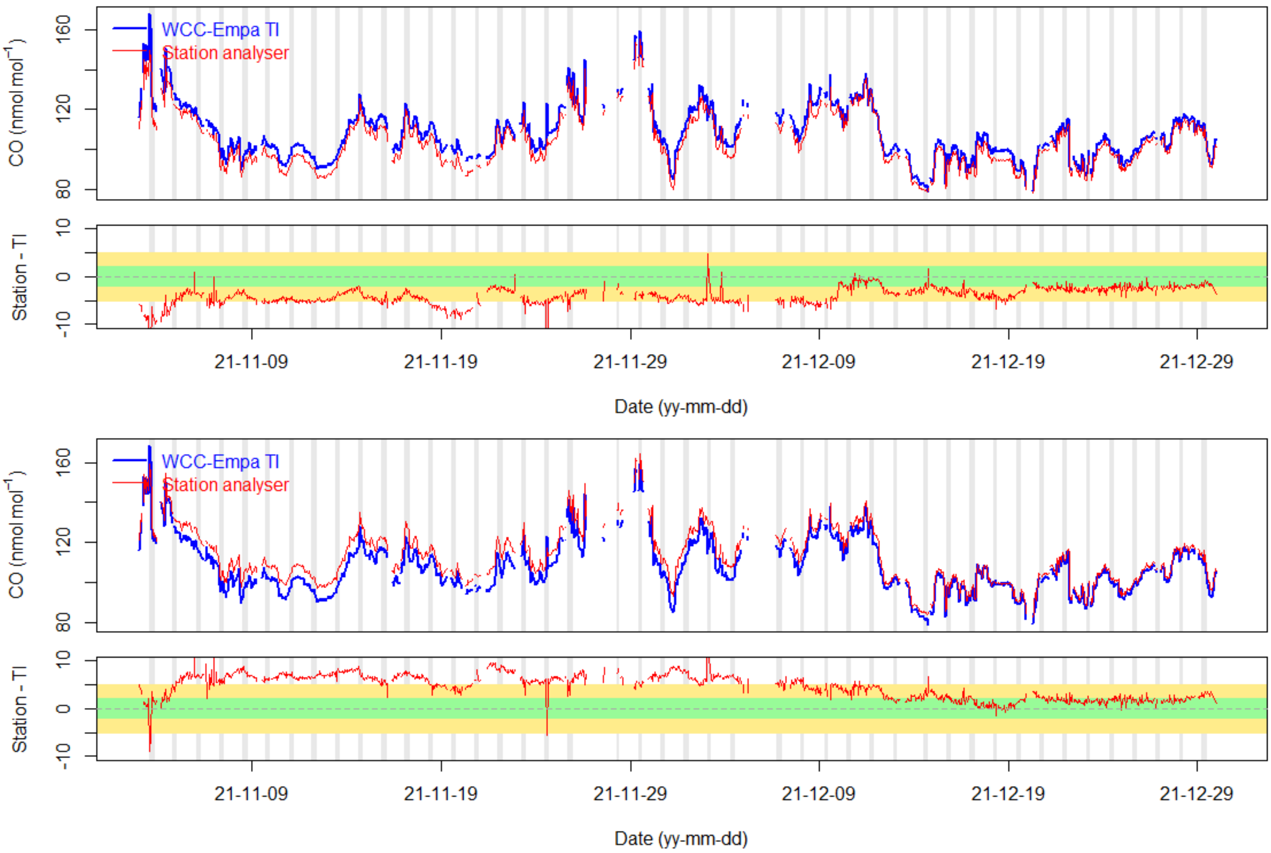

Figure 15. *Comparison of the Picarro G2401#1732-CFKADS-2133 (top: Empa analysis, bottom: ICOS ATC analysis) with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The grey areas correspond to times when the TI was sampling from the north-east inlet. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

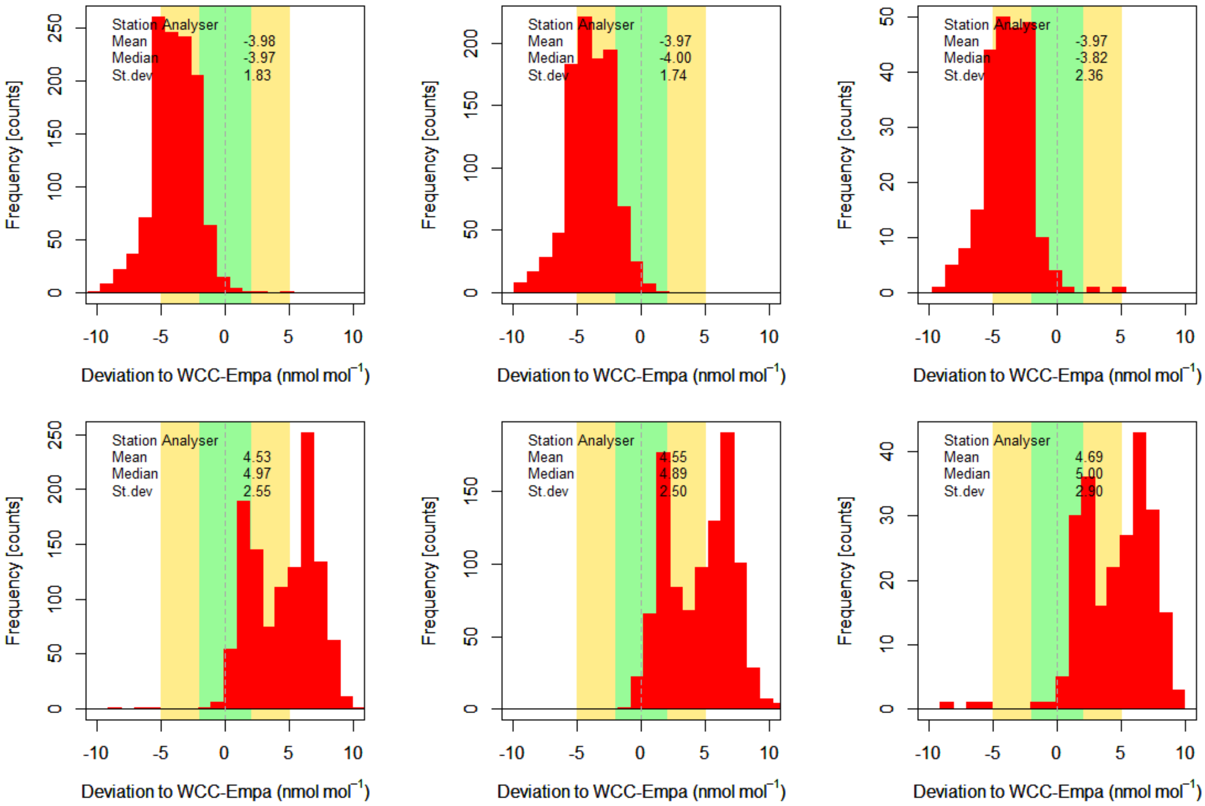

Figure 16. *Carbon monoxide deviation histograms for the Picarro G2401#1732-CFKADS-2133 analyser compared to the WCC-Empa TI. Top: left: Empa analysis, all data, middle: Empa analysis, TI sampling from the NABEL inlet, right: Empa analysis, TI sampling from the north-east inlet. Bottom: Same as top, for the ICOS ATC analysis.*

Figure 17 shows the comparison of hourly CO measurements between the WCC-Empa TI and the JFJ Picarro G5310 analyser for the Empa (top) and the ICOS ATC analysis of the data (bottom). The corresponding deviation histograms are shown in Figure 18.

The results of the parallel measurement are in better agreement with the TS comparison compared to the Picarro G2401 instrument. On average, the bias was within the extended GAW network compatibility goal for the Empa analysis, and within the GAW network compatibility goal for the ICOS ATC analysis. In this case, the drift correction applied by the ICOS ATC explains the better result compared to the Empa analysis. No significant influence of the inlet system was observed.

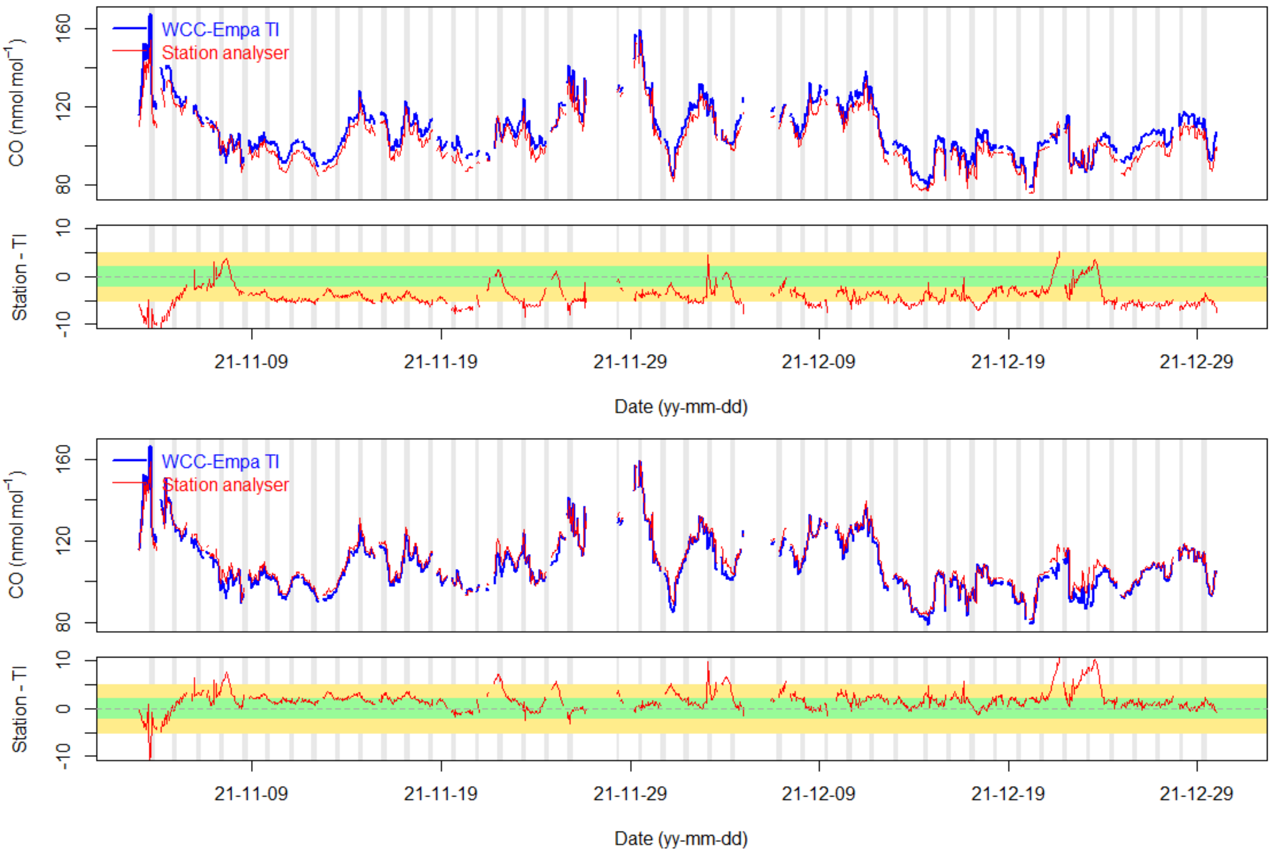

Figure 17. *Comparison of the Picarro G5310 #5097-PPU-JKADS5106 (top: Empa analysis, bottom: ICOS ATC analysis) with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The grey areas correspond to times when the TI was sampling from the north-east inlet. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

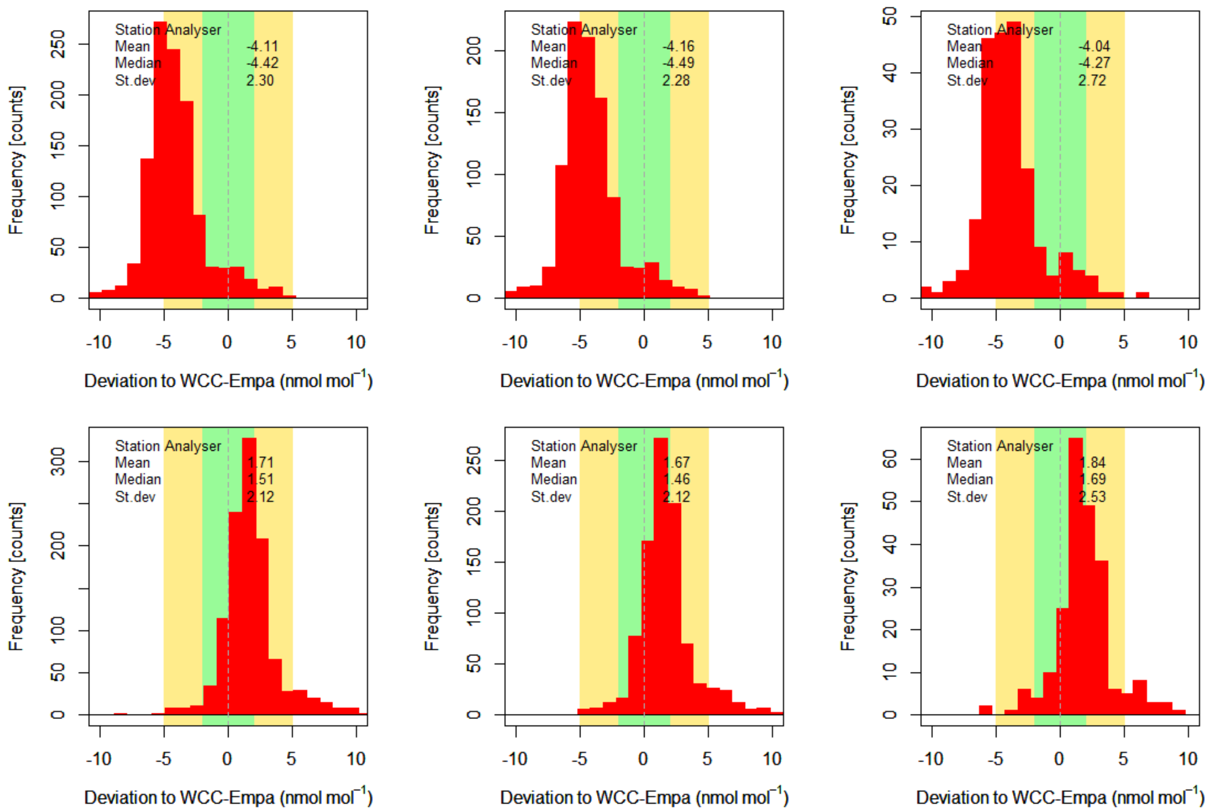

Figure 18. *Carbon monoxide deviation histograms for the Picarro G5310 #5097-PPU-JKADS5106 analyser compared to the WCC-Empa TI. Top: left: Empa analysis, all data, middle: Empa analysis, TI sampling from the NABEL inlet, right: Empa analysis, TI sampling from the north-east inlet. Bottom: Same as top, for the ICOS ATC analysis.*

Methane

Figure 19 shows the comparison of hourly CH_4 measurements between the WCC-Empa TI and the JFJ Picarro G2401 analyser for the Empa (top) and the ICOS ATC analysis of the data (bottom). The corresponding deviation histograms are shown in Figure 20. 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 JFJ instruments for both the Empa and the ICOS ATC analysis, which confirms the results of the performance audit using traveling standards. The temporal variation was well captured by both instruments.

No significant influence of the inlet system was observed. The deviation was on average not significantly different when the WCC-Empa TI sampled from the north-east inlet, but the variation of the bias was slightly higher, which is expected due to the different location of the air inlets.

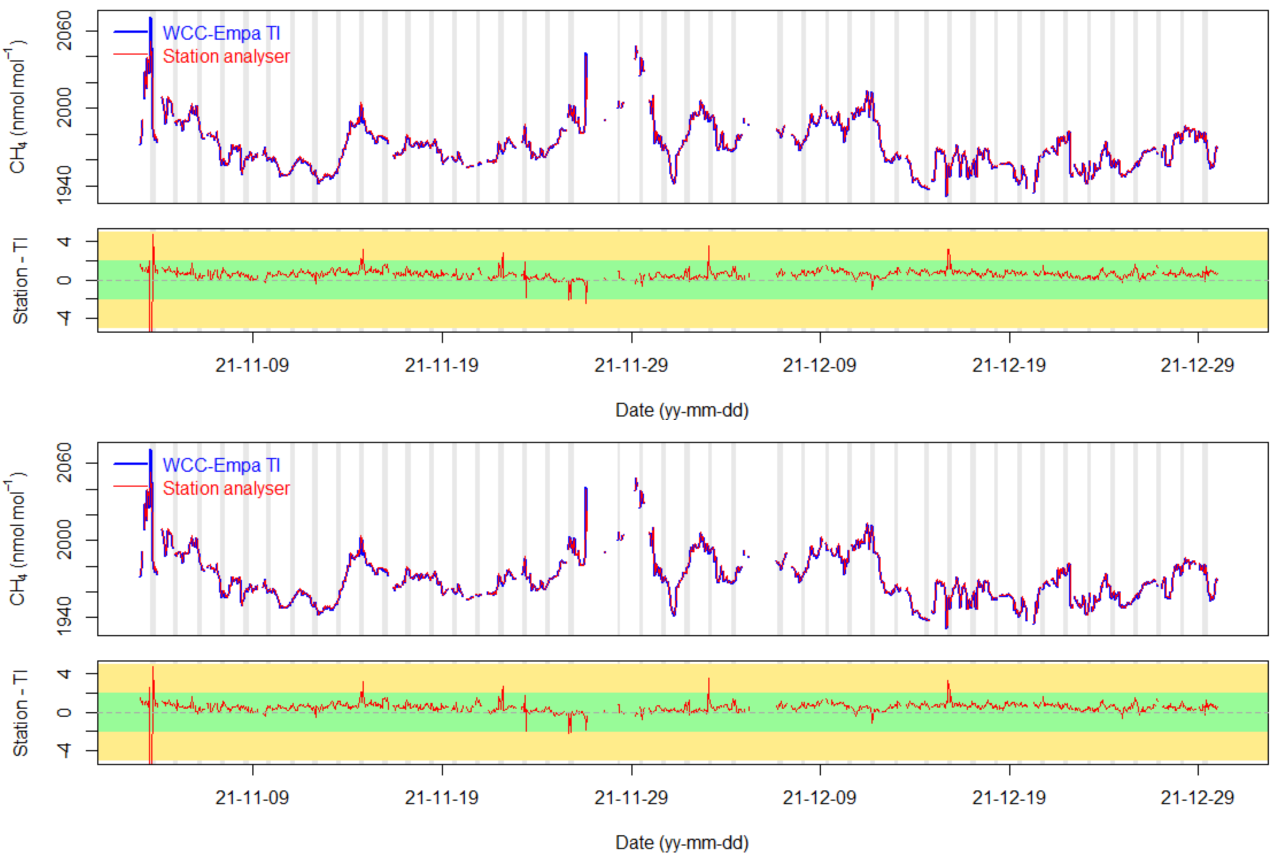

Figure 19. *Comparison of the Picarro G2401#1732-CFKADS-2133 (top: Empa analysis, bottom: ICOS ATC analysis) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The grey areas correspond to times when the TI was sampling from the north-east inlet. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

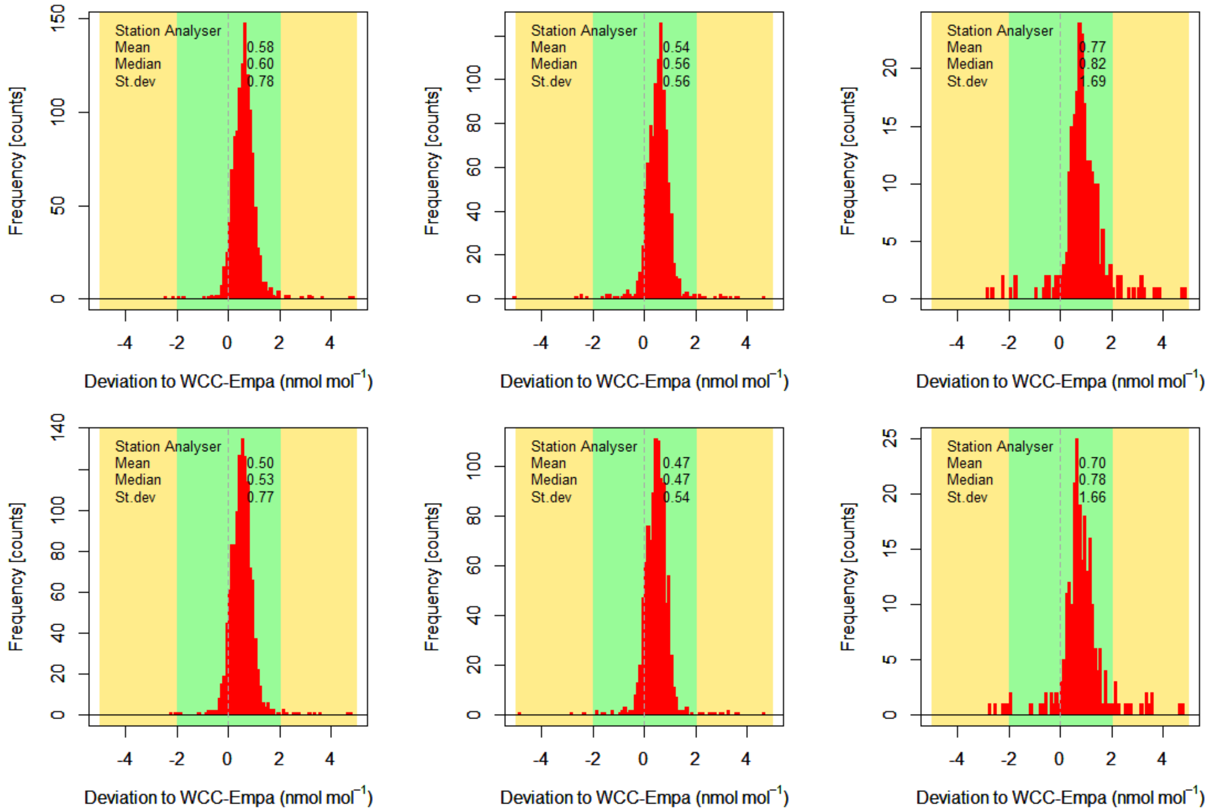

Figure 20. *Methane deviation histograms for the Picarro G2401#1732-CFKADS-2133 analyser compared to the WCC-Empa TI. Top: left: Empa analysis, all data, middle: Empa analysis, TI sampling from the NABEL inlet, right: Empa analysis, TI sampling from the north-east inlet. Bottom: Same as top, for the ICOS ATC analysis.*

Carbon dioxide

Figure 21 shows the comparison of hourly CO_2 measurements between the WCC-Empa TI and the JFJ Picarro G2401 analyser for the Empa (top) and the ICOS ATC analysis of the data (bottom). The corresponding deviation histograms are shown in Figure 20. 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 extended WMO/GAW network compatibility goal for both the Empa and the ICOS ATC analysis. The results are in relatively good agreement with the bias observed during the travelling standard comparison. No significant influence of the inlet system was observed.

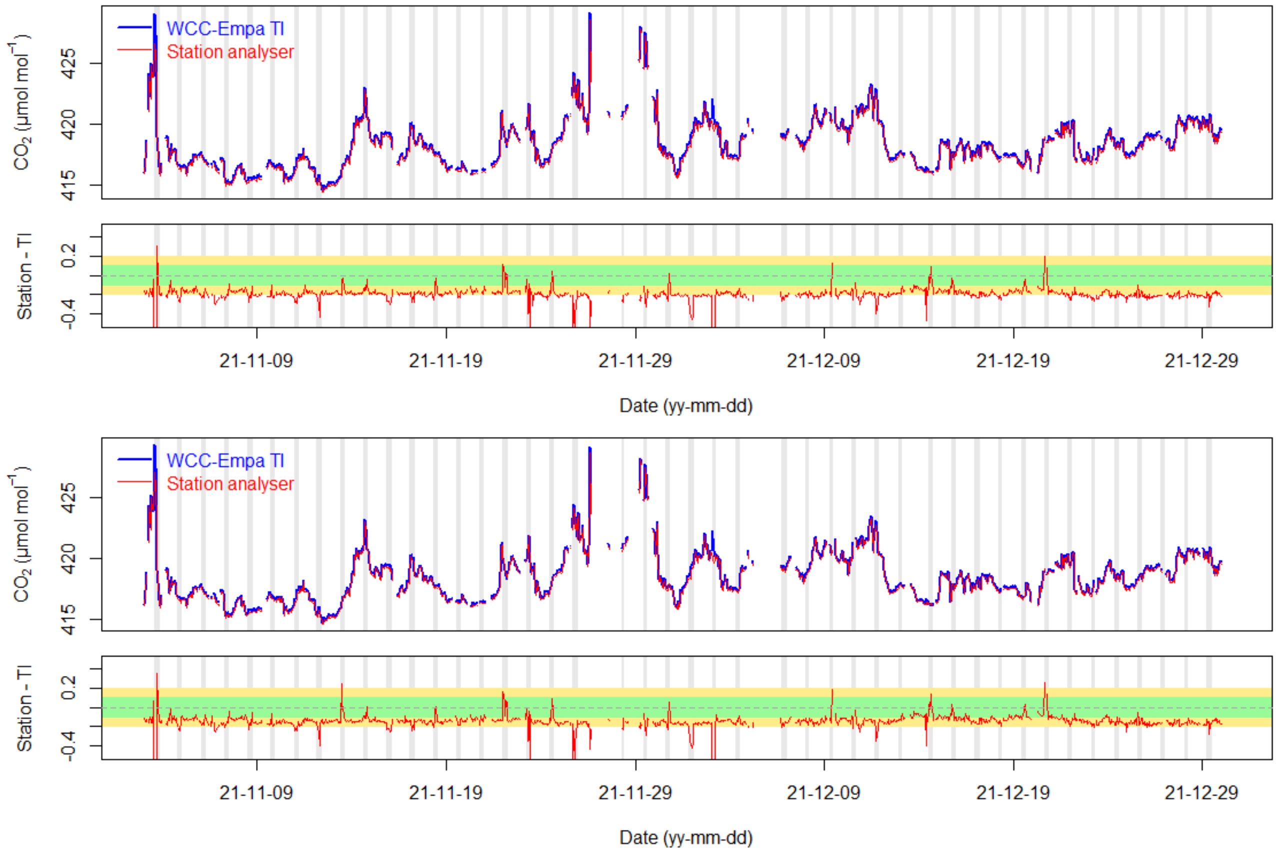

Figure 21. *Comparison of the Picarro G2401#1732-CFKADS-2133 (top: Empa analysis, bottom: ICOS ATC analysis) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The grey areas correspond to times when the TI was sampling from the north-east inlet. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

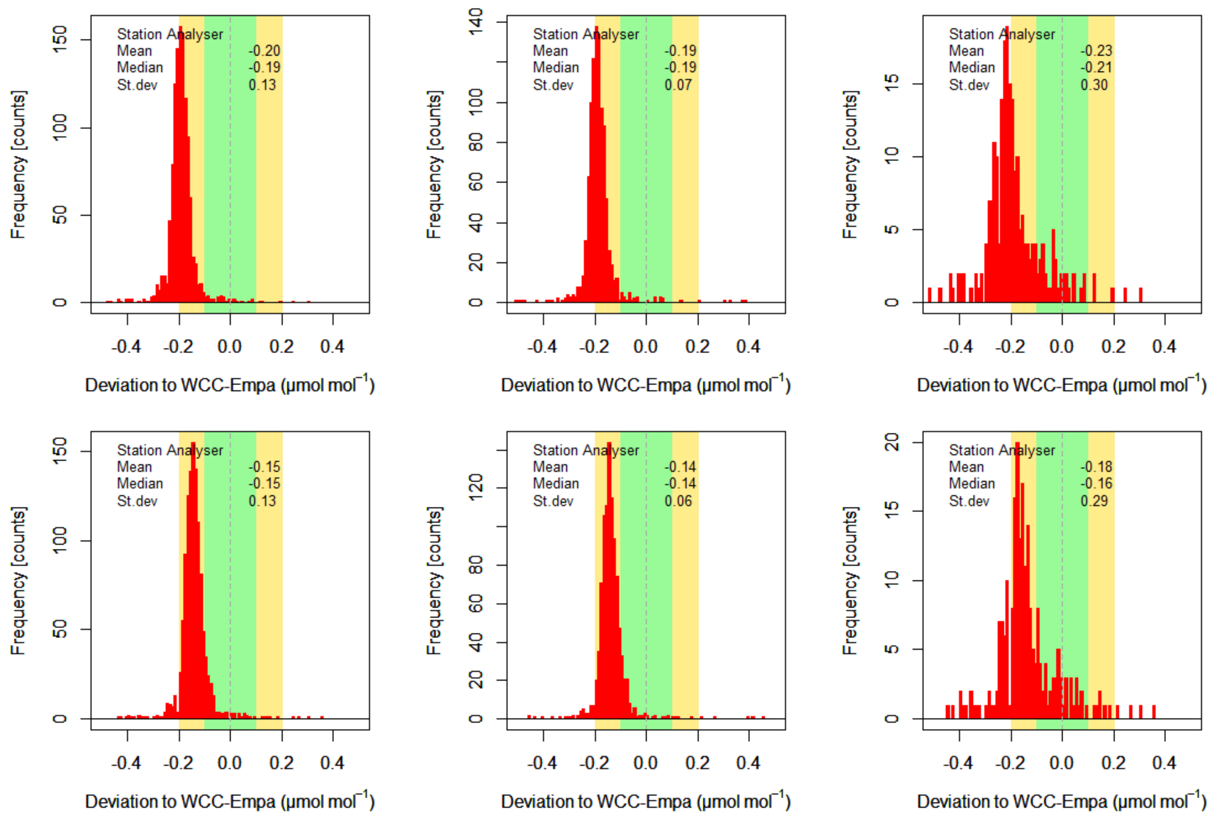

Figure 22. *Carbon dioxide deviation histograms for the Picarro G2401#1732-CFKADS-2133 analyser compared to the WCC-Empa TI. Top: left: Empa analysis, all data, middle: Empa analysis, TI sampling from the NABEL inlet, right: Empa analysis, TI sampling from the north-east inlet. Bottom: Same as top,* for the ICOS ATC analysis.

Figure 23 shows the comparison of hourly CO_2 measurements between the WCC-Empa TI and the JFJ Sick Maihak S710 analyser. The corresponding deviation histograms are shown in Figure 24. 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 of the ambient CO_2 amount fraction was well captured by both instruments. The average bias was -0.30±0.22 (1σ) µmol mol-1, which is comparable to the difference observed by the comparison of the travelling standards. This difference is slightly exceeding the extended WMO/GAW compatibility goal. The observed bias can be attributed to the calibration of the Sick Maihak S710 analyser, and the results would improve if the WCC-Empa assigned values for the calibration standards are used.

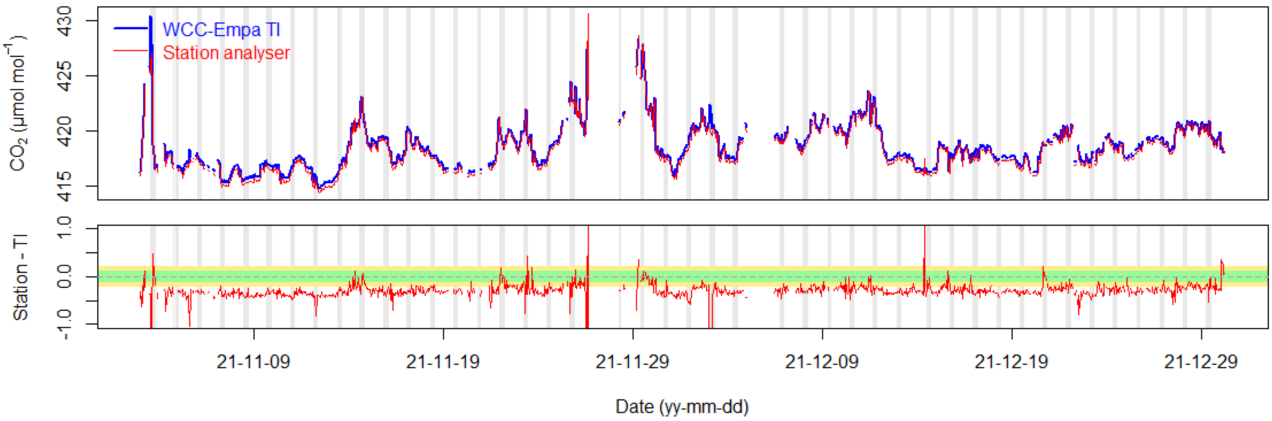

Figure 23. *Comparison of the Sick Maihak S710 analyser with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The grey areas correspond to times when the TI was sampling from the north-east inlet. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

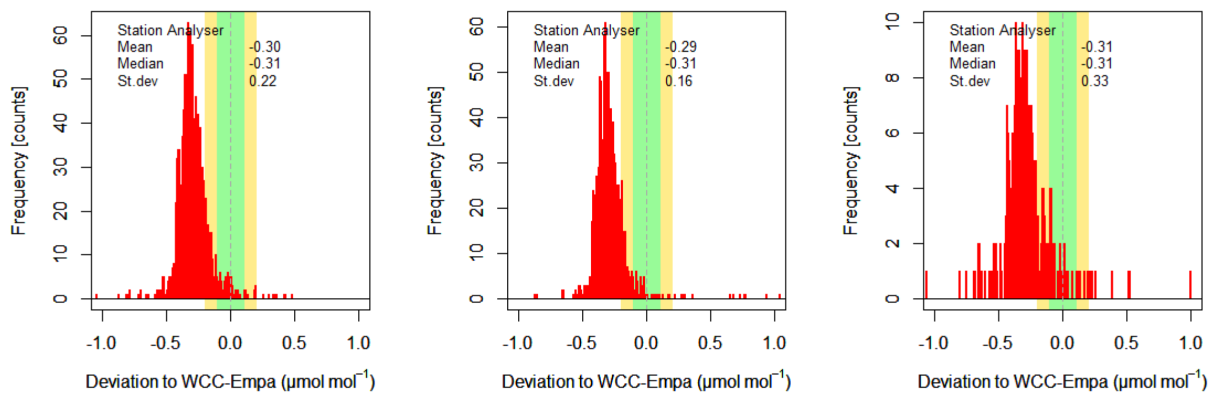

Figure 24. *Carbon dioxide deviation histograms for the Sick Maihak S710 analyser compared to the WCC-Empa TI. Left: all data, middle: TI sampling from the NABEL inlet, right: TI sampling from the north-east inlet.*

CONCLUSIONS

The global GAW station Jungfraujoch 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. The JFJ GAW activities are well embedded in the national and international research landscape, which makes it a very important contribution to the WMO/GAW programme. Thus, the continuation of the Jungfraujoch 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.

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, the observed bias in the CO measurements varied between different measurement techniques, and also between different analysis approaches by Empa and the ICOS ATC of the same technique. Currently, the data is independently analysed by Empa and the ICOS ATC, and different data sets for the same measurements should be avoided. Table 6 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Please note that Table 6 refers only to the mole fractions relevant to JFJ, whereas Table 5 further above covers a wider mole fraction range.

Table 6. *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 Empa analysis	CO Picarro G2401 ICOS ATC analysis	CO Picarro G5310 Empa analysis	CO Picarro G5310 ICOS ATC analysis	CH_4 Picarro G2401 Empa analysis	CH_4 Picarro G2401 ICOS ATC analysis	CO_2 Picarro G2401 Empa analysis	CO_2 Picarro G2401 ICOS ATC analysis	CO_2 Sick Maihak S710	N_2O Picarro G5310 Empa analysis	N_2O Picarro G5310 ICOS ATC analysis
TS	✓	✓	(✓)	✓	✓	✓	✓	(✓)	(✓)	(✓)	✓	(✓)
Air	NA	✓	✓	✓	✓	✓	✓	✓	✓	✗	NA	NA

NA: no comparison was made

SUMMARY RANKING OF THE JUNGFRAUJOCH GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access
Facilities		
Laboratory and office space	(4)	Adequate, with limited space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(3)	Temperature fluctuations
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 Picarro G2401	(5)	State of the art instrumentation
CO_2 Sick Maihak S710	(3)	Linearity issues
CO Picarro G2401	(4)	Adequate instrument
CO/ N_2O Picarro G5310	(5)	State of the art instrumentation
Standards		
O_3	(5)	Transfer standard with traceability to SRP at Empa
CO, CO_2, CH_4, N_2O	(5)	Full traceability to the GAW reference through ICOS FCL and NOAA standards at Empa and University of Bern
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(4)	Skilled staff, appropriate procedures, but difference between Empa and ICOS ATC
Data submission	(5)	Timely submission of all parameters

#0: inadequate thru 5: adequate.

Dübendorf, August 2022

Dr C. Zellweger
WCC-Empa

Dr B. Buchmann
Head of Department

APPENDIX

Data Review

The following figures show summary plots of JFJ data accessed on 12 April 2022 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

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

Surface ozone:

The ozone time series submitted to WDCRG is shown below. The three data sets covering different periods were combined to be displayed in one figure.

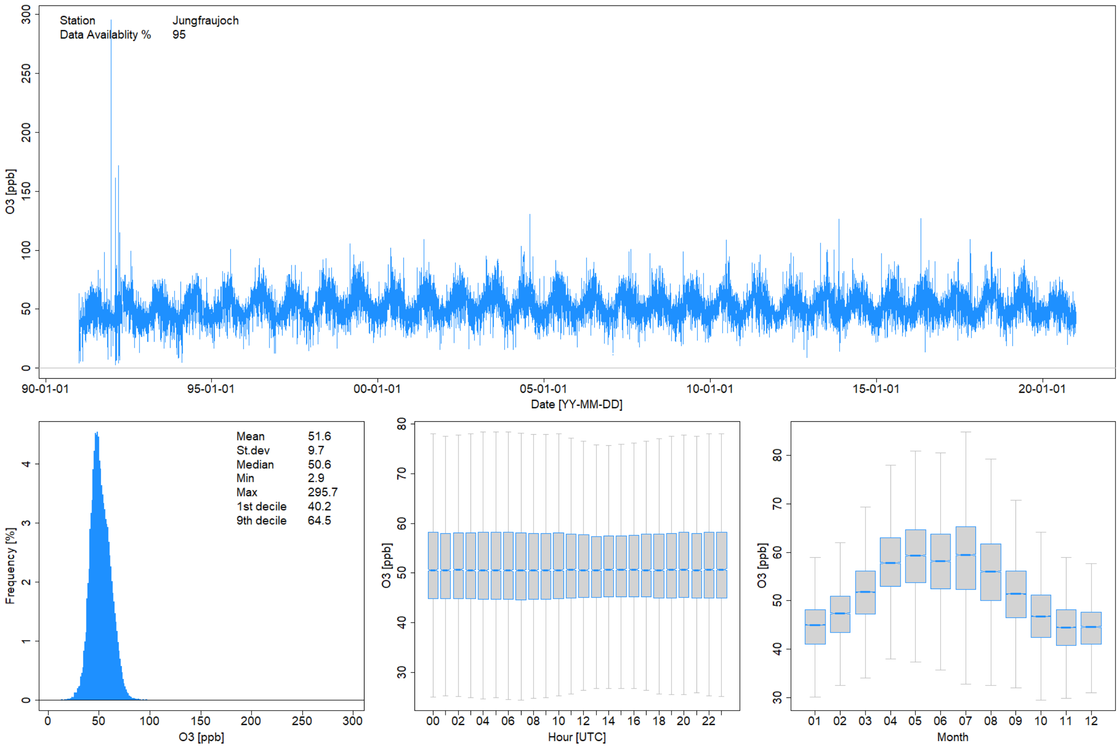

Figure 25. *O_3 data for the period from 1991 to 2021 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data sets looks sound with respect to mole fraction, trend, seasonal and diurnal variation.
- The variation is higher for the earliest period of the time series, and a few extremely high ozone amount were reported.

Carbon monoxide:

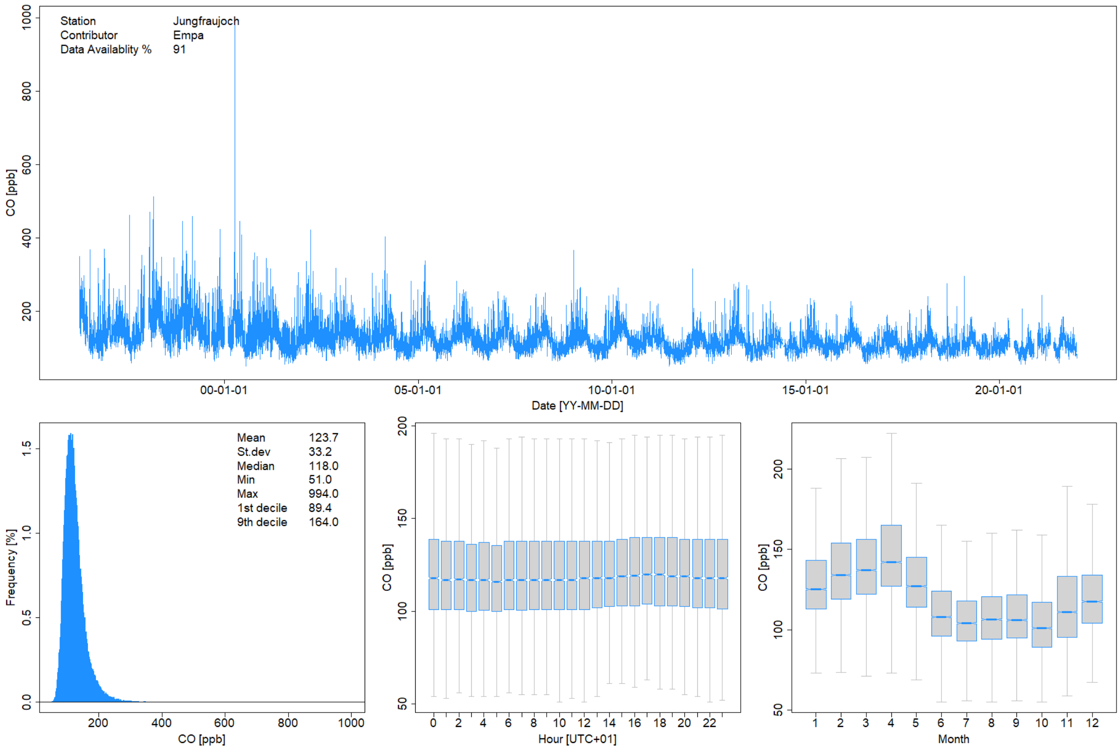

Figure 26. *JFJ CO in-situ data (1996-2021) submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The JFJ CO data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Episodes with elevated CO amount fraction became less frequent over time.

Methane:

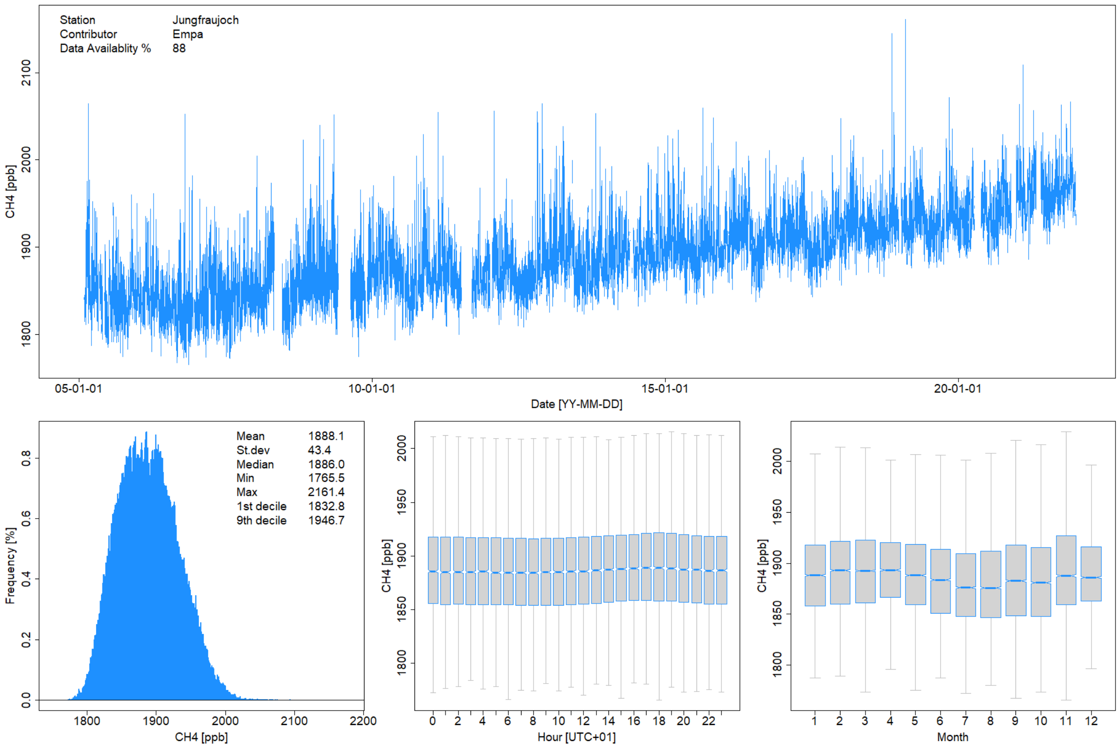

Figure 27. *Jungfraujoch in-situ CH_4 data (2005-2021) submitted by Empa. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The JFJ CH_4 data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

Carbon dioxide:

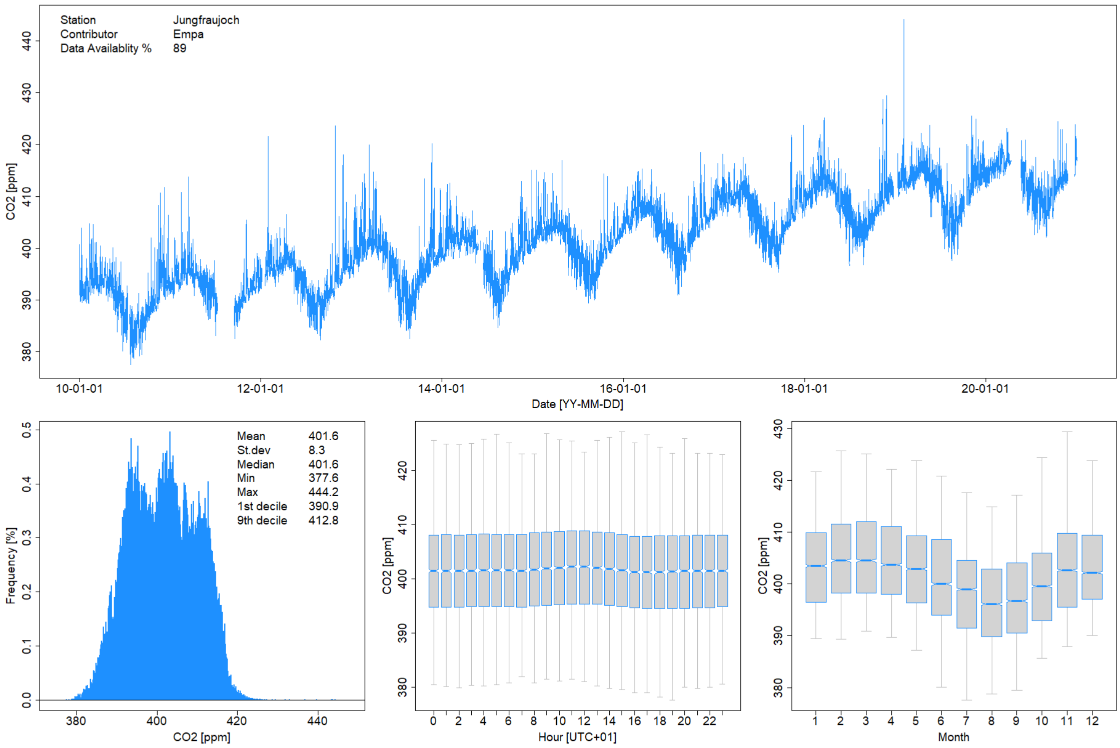

Figure 28. *Jungfraujoch in-situ CO_2 data (2010-2021) submitted by Empa. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

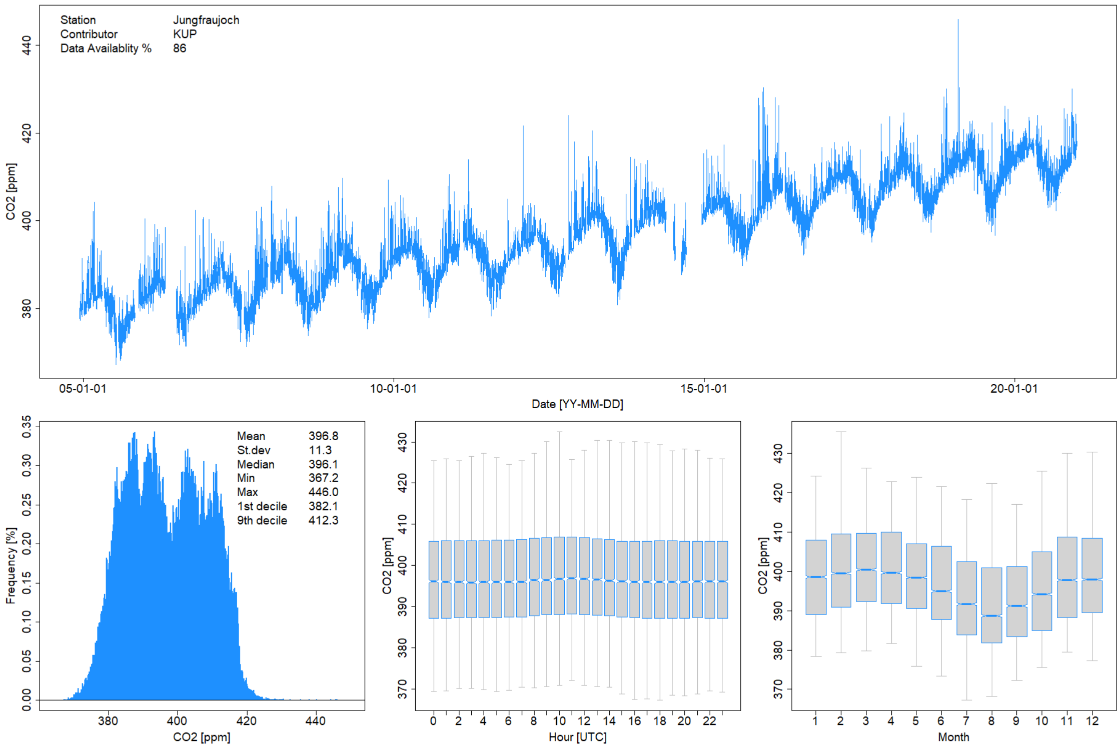

Figure 29. *Jungfraujoch in-situ CO_2 data (2005-2021) submitted by the University of Bern. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- Both the Empa and the University of Bern CO_2 data series look sound with respect to mole fraction, trend, seasonal and diurnal variation. Continued comparisons of the data series is encouraged.

Nitrous oxide:

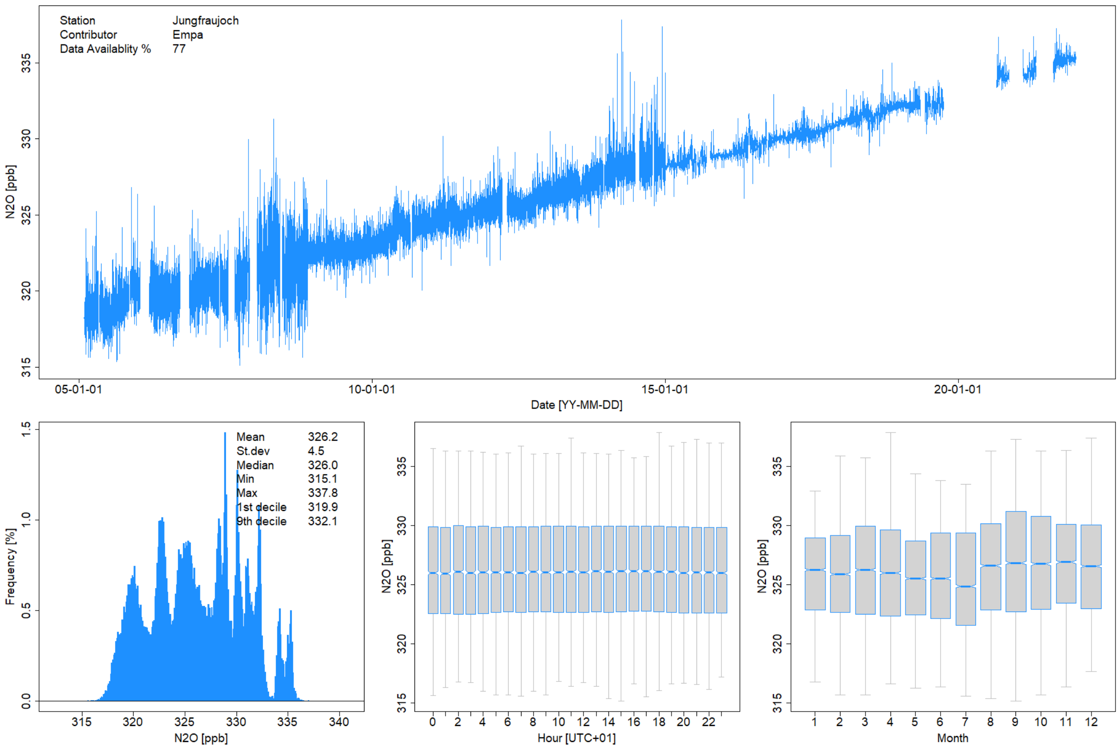

Figure 30. *Jungfraujoch in-situ N_2O data (2005-2021) submitted by Empa. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The N_2O data series looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Two distinctly different periods can be distinguished, before and after 2015. These periods represent different measurement techniques, and clearly show the advantage of the spectroscopic techniques used from 2015 onwards.
- Data of the GC/ECD system showed high variability in the first three years of the measurements.

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 7 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 JFJ data acquisition systems.

Table 7. *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 1.009
Pressure readings (hPa)	Ambient 645.3;TS 645.3, (no adjustment was made)
JFJ analyser (OA)	
Model, S/N	Thermo Scientific 49i #1233255708
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.7 nmol mol^{-1}, COEF 1.010
Pressure readings (hPa)	Ambient 645.3; OA 647.1 (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 7 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 8. *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the JFJ ozone analyser (OA) Thermo Scientific 49i #1233255708 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 (%)**
2021-11-01 18:36	0.06	0.28	0.41	0.21	0.35	NA
2021-11-01 18:46	199.74	0.14	200.11	0.25	0.37	0.19
2021-11-01 18:56	50.01	0.16	50.37	0.25	0.36	0.72
2021-11-01 19:06	99.90	0.21	100.22	0.28	0.32	0.32
2021-11-01 19:16	149.84	0.05	150.36	0.27	0.52	0.35
2021-11-01 19:36	89.88	0.16	89.94	0.31	0.06	0.07
2021-11-01 19:46	39.93	0.22	40.15	0.56	0.22	0.55
2021-11-01 19:56	69.90	0.13	69.89	0.39	-0.01	-0.01

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 (%)
2021-11-01 20:06	30.01	0.25	30.48	0.39	0.47	1.57
2021-11-01 20:16	10.58	0.62	10.99	0.78	0.41	3.88
2021-11-01 20:26	79.92	0.17	80.43	0.22	0.51	0.64
2021-11-01 20:46	19.89	0.45	20.42	0.34	0.53	2.66
2021-11-01 20:56	59.98	0.11	60.16	0.22	0.18	0.30
2021-11-01 21:06	-0.06	0.20	0.31	0.13	0.37	NA
2021-11-01 21:16	199.68	0.04	200.35	0.29	0.67	0.34
2021-11-01 21:26	149.86	0.05	150.52	0.23	0.66	0.44
2021-11-01 21:36	50.02	0.21	50.34	0.43	0.32	0.64
2021-11-01 21:46	99.85	0.12	100.18	0.42	0.33	0.33
2021-11-01 22:06	79.86	0.15	80.15	0.28	0.29	0.36
2021-11-01 22:16	20.09	0.11	20.26	0.18	0.17	0.85
2021-11-01 22:26	59.95	0.14	60.38	0.33	0.43	0.72
2021-11-01 22:36	89.90	0.23	90.41	0.43	0.51	0.57
2021-11-01 22:46	29.95	0.25	30.38	0.31	0.43	1.44
2021-11-01 22:56	69.95	0.13	70.36	0.20	0.41	0.59
2021-11-01 23:16	10.87	0.70	10.95	0.72	0.08	0.74
2021-11-01 23:36	39.97	0.09	40.28	0.32	0.31	0.78
2021-11-01 23:46	0.02	0.17	0.43	0.13	0.41	NA
2021-11-01 23:56	199.76	0.09	200.35	0.23	0.59	0.30
2021-11-02 00:06	49.94	0.14	50.20	0.32	0.26	0.52
2021-11-02 00:16	99.92	0.08	100.18	0.22	0.26	0.26
2021-11-02 00:26	149.78	0.12	150.56	0.21	0.78	0.52
2021-11-02 00:46	89.79	0.13	90.21	0.26	0.42	0.47
2021-11-02 01:06	69.92	0.08	70.34	0.22	0.42	0.60
2021-11-02 01:16	30.00	0.16	30.30	0.22	0.30	1.00
2021-11-02 01:26	11.30	0.67	11.77	0.80	0.47	4.16
2021-11-02 01:36	79.89	0.12	80.05	0.31	0.16	0.20
2021-11-02 01:56	19.99	0.09	20.32	0.11	0.33	1.65
2021-11-02 02:06	59.98	0.13	60.44	0.38	0.46	0.77
2021-11-02 02:16	-0.19	0.33	0.47	0.17	0.66	NA
2021-11-02 02:26	199.81	0.19	200.37	0.33	0.56	0.28
2021-11-02 02:36	149.78	0.12	150.44	0.26	0.66	0.44
2021-11-02 02:46	49.98	0.22	50.45	0.26	0.47	0.94
2021-11-02 02:56	99.94	0.11	100.14	0.49	0.20	0.20
2021-11-02 03:16	79.82	0.15	80.20	0.26	0.38	0.48
2021-11-02 03:26	19.97	0.35	20.52	0.31	0.55	2.75
2021-11-02 03:46	89.81	0.13	89.98	0.32	0.17	0.19
2021-11-02 03:56	29.96	0.09	29.95	0.18	-0.01	-0.03
2021-11-02 04:06	69.90	0.24	70.36	0.35	0.46	0.66
2021-11-02 04:26	10.13	0.34	10.47	0.35	0.34	3.36
2021-11-02 04:36	30.02	0.20	30.28	0.30	0.26	0.87
2021-11-02 04:46	39.93	0.26	40.03	0.60	0.10	0.25
2021-11-02 04:56	-0.09	0.56	0.43	0.09	0.52	NA
2021-11-02 05:06	199.78	0.14	200.13	0.35	0.35	0.18
2021-11-02 05:16	50.03	0.25	50.15	0.41	0.12	0.24
2021-11-02 05:26	99.85	0.06	100.66	0.23	0.81	0.81
2021-11-02 05:36	149.85	0.11	150.28	0.23	0.43	0.29

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 (%)
2021-11-02 05:56	89.88	0.12	90.33	0.21	0.45	0.50
2021-11-02 06:16	69.97	0.07	70.46	0.26	0.49	0.70

Calibration Standards for CO, CH_4, CO_2 and N_2O

Table 9 shows and overview of available standard gases for the calibration of the CO, CH_4, CO_2 and N2O instruments. The measurements made by Empa are calibrated with standards provided by the ICOS FCL with full traceability to the CCL. The University of Bern uses three working standards with traceability to CCL standards through CEP.

Table 9 *Calibration standards at JFJ 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 (X2007*) (µmol mol^{-1})	Usage
D175452	NA	201.92	2070.10	439.93	Picarro G2401, ICOS FCL standard
D175450	329.43	119.76	1899.34	400.01	Picarro G2401, ICOS FCL standard
D175444	329.86	151.67	1958.87	409.96	Picarro G2401, ICOS FCL standard
D175443	319.90	71.95	1784.58	374.88	Picarro G2401, ICOS FCL standard
D175446	344.76	304.89	2151.00	450.19	Picarro G2401, ICOS FCL standard
D175447	331.75	129.02	1924.05	420.51	Picarro G5310, ICOS FCL standard
D570048	318.53	70.05	1788.45	374.36	Picarro G5310, ICOS FCL standard
D570049	326.94	150.20	1953.70	411.74	Picarro G5310, ICOS FCL standard
D570050	342.14	300.35	2158.14	449.71	Picarro G5310, ICOS FCL standard
D570051	336.97	200.33	2077.51	439.78	Picarro G5310, ICOS FCL standard
D570052	326.26	120.87	1908.34	399.52	Picarro G5310, ICOS FCL standard
Lux3582	NA	NA	NA	421.30	University Bern CO_2 standard
Lux3581	NA	NA	NA	383.10	University Bern CO_2 standard
Lux3573	NA	NA	NA	428.81	University Bern CO_2 standard

* University of Bern standards are on the WMO-X2019 CO_2 scale

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 10 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 JFJ data acquisition system.

Table 10. Experimental details of the JFJ 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 24 and 25.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #1732-CFKADS-2133
Principle	Near-IR CRDS
Drying system	Nafion dryer
Station Analyser (CO, N_2O)	
Model, S/N	Picarro G5310 #5097-PPU-JKADS5106
Principle	Mid-IR CRDS
Drying system	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 11. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1732-CFKADS-2133 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 (%)
(21-11-01 14:59:00)	210420_FB03367	134.8	0.6	134.1	0.3	3	-0.7	-0.5
(21-11-01 19:33:00)	210412_FB03377	7.3	0.3	7.3	0.6	3	0.0	0.0
(21-11-01 15:29:00)	140514_FB03894	197.1	1.1	195.8	0.3	3	-1.4	-0.7
(21-11-01 20:03:00)	150601_FA02482	1336.3	0.8	1325.4	0.2	3	-11.0	-0.8
(21-11-02 00:53:00)	140514_FB03918	187.7	0.3	186.8	0.1	3	-0.9	-0.5
(21-11-01 15:59:00)	160622_FA02474	238.3	0.5	237.1	0.6	3	-1.2	-0.5
(21-11-01 20:33:00)	130819_FB03870	155.1	0.4	154.3	0.5	3	-0.8	-0.5
(21-11-02 01:23:00)	210415_FB03376	117.7	0.9	117.8	0.5	3	0.1	0.1

Table 12. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1732-CFKADS-2133 instrument (AL) (ICOS ATC 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 (%)
(21-11-01 23:43:00)	140514_FB03918	187.7	0.3	192.8	0.0	3	5.1	2.7
(21-11-01 18:53:00)	150601_FA02482	1336.3	0.8	1271.1	0.1	3	-65.2	-4.9
(21-11-02 00:13:00)	210415_FB03376	117.7	0.9	127.5	0.5	3	9.7	8.3
(21-11-01 19:23:00)	130819_FB03870	155.1	0.4	161.7	0.3	3	6.6	4.3
(21-11-01 14:34:00)	210420_FB03367	134.8	0.6	143.6	0.2	2	8.8	6.5
(21-11-01 19:08:00)	210412_FB03377	7.3	0.3	13.1	0.7	2	5.8	80.0
(21-11-01 14:19:00)	140514_FB03894	197.1	1.1	201.5	0.3	3	4.4	2.2
(21-11-01 14:49:00)	160622_FA02474	238.3	0.5	240.9	0.7	3	2.5	1.1

Table 13. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G5310 #5097-PPU-JKADS5106 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 (%)
(21-11-01 15:25:00)	130819_FB03870	155.1	0.4	152.7	0.0	3	-2.5	-1.6
(21-11-01 19:30:00)	140514_FB03894	197.1	1.1	194.5	0.1	3	-2.6	-1.3
(21-11-01 08:42:00)	140514_FB03912	208.1	0.9	205.9	0.2	3	-2.2	-1.1
(21-11-01 15:00:00)	150601_FA02482	1336.3	0.8	1336.0	0.6	3	-0.3	0.0
(21-11-01 19:55:00)	160622_FA02474	238.3	0.5	235.8	0.1	3	-2.6	-1.1
(21-11-01 08:17:00)	181129_FB03853	94.6	0.4	93.0	0.4	3	-1.7	-1.8
(21-11-01 14:35:00)	210412_FB03377	7.3	0.3	3.4	0.0	3	-3.9	-53.4
(21-11-01 19:05:00)	210420_FB03367	134.8	0.6	132.0	0.1	3	-2.8	-2.1

Table 14. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G5310 #5097-PPU-JKADS5106 instrument (AL) (ICOS ATC 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 (%)
(21-11-01 14:05:00)	130819_FB03870	155.1	0.4	158.3	0.0	3	3.2	2.1
(21-11-01 22:57:00)	181129_FB03853	94.6	0.4	98.3	0.2	3	3.7	3.9
(21-11-01 17:45:00)	210420_FB03367	134.8	0.6	137.6	0.1	3	2.8	2.1
(21-11-01 13:40:00)	150601_FA02482	1336.3	0.8	1341.3	0.4	3	5.0	0.4
(21-11-01 13:15:00)	210412_FB03377	7.3	0.3	9.0	0.0	3	1.7	23.9

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 (%)
(21-11-01 18:10:00)	140514_FB03894	197.1	1.1	200.2	0.1	3	3.1	1.6
(21-11-01 23:22:00)	140514_FB03912	208.1	0.9	211.3	0.1	3	3.2	1.6
(21-11-01 18:35:00)	160622_FA02474	238.3	0.5	241.5	0.1	3	3.1	1.3

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 10 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 JFJ data acquisition system. The standards used for the calibration of the JFJ instruments are shown in Table 9.

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 15. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1732-CFKADS-2133 instrument (AL) (Empa analysis) 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 (%)
(21-11-01 14:59:00)	210420_FB03367	1940.94	0.03	1941.15	0.19	3	0.21	0.01
(21-11-01 15:29:00)	140514_FB03894	1953.91	0.07	1954.12	0.16	3	0.21	0.01
(21-11-01 15:59:00)	160622_FA02474	2506.89	0.08	2506.40	0.24	3	-0.49	-0.02
(21-11-01 19:33:00)	210412_FB03377	2.48	0.32	5.10	0.04	3	2.62	105.65
(21-11-01 20:03:00)	150601_FA02482	1906.04	0.03	1906.17	0.12	3	0.13	0.01
(21-11-01 20:33:00)	130819_FB03870	1883.44	0.05	1883.68	0.08	3	0.24	0.01
(21-11-02 00:53:00)	140514_FB03918	1971.36	0.04	1971.49	0.03	3	0.13	0.01
(21-11-02 01:23:00)	210415_FB03376	1865.74	0.02	1865.95	0.16	3	0.21	0.01

Table 16. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1732-CFKADS-2133 instrument (AL) (ICOS ATC analysis) 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 (%)
(21-11-01 14:19:00)	140514_FB03894	1953.91	0.07	1954.03	0.16	3	0.12	0.01
(21-11-01 14:34:00)	210420_FB03367	1940.94	0.03	1940.94	0.11	2	0.00	0.00
(21-11-01 14:49:00)	160622_FA02474	2506.89	0.08	2506.48	0.22	3	-0.41	-0.02
(21-11-01 18:53:00)	150601_FA02482	1906.04	0.03	1906.06	0.12	3	0.02	0.00
(21-11-01 19:08:00)	210412_FB03377	2.48	0.32	4.34	0.01	2	1.86	75.00
(21-11-01 19:23:00)	130819_FB03870	1883.44	0.05	1883.58	0.09	3	0.14	0.01
(21-11-01 23:43:00)	140514_FB03918	1971.36	0.04	1971.42	0.03	3	0.06	0.00
(21-11-02 00:13:00)	210415_FB03376	1865.74	0.02	1865.84	0.16	3	0.10	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 10 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 JFJ data acquisition system. The standards used for the calibration of the JFJ instruments are shown in Table 9.

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 17. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2401 #1732-CFKADS-2133 instrument (AL) (Empa analysis) with the WCC-Empa TS (WMO-X2007 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 (%)
(21-11-01 14:59:00)	210420_FB03367	427.98	0.02	427.86	0.01	3	-0.12	-0.03
(21-11-01 19:33:00)	210412_FB03377	0.24	0.02	0.54	0.02	3	0.30	125.06
(21-11-01 15:29:00)	140514_FB03894	411.03	0.02	410.97	0.01	3	-0.05	-0.01
(21-11-01 20:03:00)	150601_FA02482	431.09	0.02	430.92	0.01	3	-0.17	-0.04
(21-11-02 00:53:00)	140514_FB03918	400.89	0.03	400.83	0.02	3	-0.07	-0.02
(21-11-01 15:59:00)	160622_FA02474	421.27	0.01	421.20	0.01	3	-0.07	-0.02
(21-11-01 20:33:00)	130819_FB03870	386.94	0.02	386.89	0.00	3	-0.05	-0.01
(21-11-02 01:23:00)	210415_FB03376	401.13	0.00	401.07	0.01	3	-0.06	-0.01

Table 18. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2401 #1732-CFKADS-2133 instrument (AL) (ICOS ATC analysis) 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 (%)
(21-11-01 19:08:00)	210412_FB03377	0.24	0.02	0.23	0.01	2	-0.01	-4.17
(21-11-01 14:34:00)	210420_FB03367	428.19	0.02	428.13	0.02	2	-0.06	-0.01
(21-11-01 23:42:40)	140514_FB03918	401.09	0.03	401.06	0.02	3	-0.03	-0.01
(21-11-02 00:13:00)	210415_FB03376	401.33	0.00	401.30	0.01	3	-0.03	-0.01
(21-11-01 19:23:00)	130819_FB03870	387.13	0.02	387.11	0.00	3	-0.02	-0.01
(21-11-01 14:19:00)	140514_FB03894	411.23	0.02	411.22	0.01	3	-0.01	0.00
(21-11-01 18:53:00)	150601_FA02482	431.30	0.02	431.19	0.01	3	-0.11	-0.03
(21-11-01 14:49:00)	160622_FA02474	421.48	0.01	421.46	0.01	3	-0.02	0.00

Table 19. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Maihak S710 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 (%)
(21-11-02 16:29:00)	150601_FA02482	431.30	0.02	431.50	0.02	10	0.20	0.05
(21-11-02 18:27:00)	130819_FB03870	387.13	0.02	387.22	0.05	10	0.09	0.02
(21-11-02 20:21:00)	160622_FA02474	421.48	0.01	421.37	0.02	10	-0.11	-0.03
(21-11-02 22:15:00)	140514_FB03894	411.23	0.02	410.94	0.02	10	-0.29	-0.07
(21-11-03 08:21:00)	140514_FB03918	401.09	0.03	400.72	0.04	10	-0.37	-0.09
(21-11-03 10:15:00)	210420_FB03367	428.19	0.02	428.11	0.05	10	-0.08	-0.02

Nitrous Oxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before 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 10 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 JFJ data acquisition system. The standards used for the calibration of the JFJ instruments are shown in Table 9.

Results

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

Table 20. *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) (Empa analysis) 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 (%)
(21-11-01 15:25:00)	130819_FB03870	318.96	0.04	318.83	0.02	3	-0.13	-0.04
(21-11-01 19:30:00)	140514_FB03894	329.16	0.01	329.09	0.04	3	-0.07	-0.02
(21-11-01 08:42:00)	140514_FB03912	327.96	0.03	328.04	0.03	3	0.08	0.02
(21-11-01 19:55:00)	160622_FA02474	324.49	0.01	324.48	0.07	3	-0.01	0.00
(21-11-01 08:17:00)	181129_FB03853	330.18	0.02	330.18	0.05	3	0.00	0.00
(21-11-01 19:05:00)	210420_FB03367	340.64	0.00	340.70	0.05	3	0.06	0.02

Table 21. *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) (ICOS ATC analysis) 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 (%)
(21-11-01 14:05:00)	130819_FB03870	318.96	0.04	318.71	0.03	3	-0.25	-0.08
(21-11-01 18:10:00)	140514_FB03894	329.16	0.01	329.00	0.03	3	-0.16	-0.05
(21-11-01 17:45:00)	210420_FB03367	340.64	0.00	340.61	0.05	3	-0.03	-0.01
(21-11-01 18:35:00)	160622_FA02474	324.49	0.01	324.37	0.07	3	-0.12	-0.04
(21-11-01 23:22:00)	140514_FB03912	327.96	0.03	327.87	0.03	3	-0.09	-0.03
(21-11-01 22:57:00)	181129_FB03853	330.18	0.02	330.02	0.01	3	-0.16	-0.05

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 1.009

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 **Error! Reference source not found.**. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 31). 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)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] + 0.05\ \text{nmol mol}^{-1}) / 1.0018 \qquad (6a)$$

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

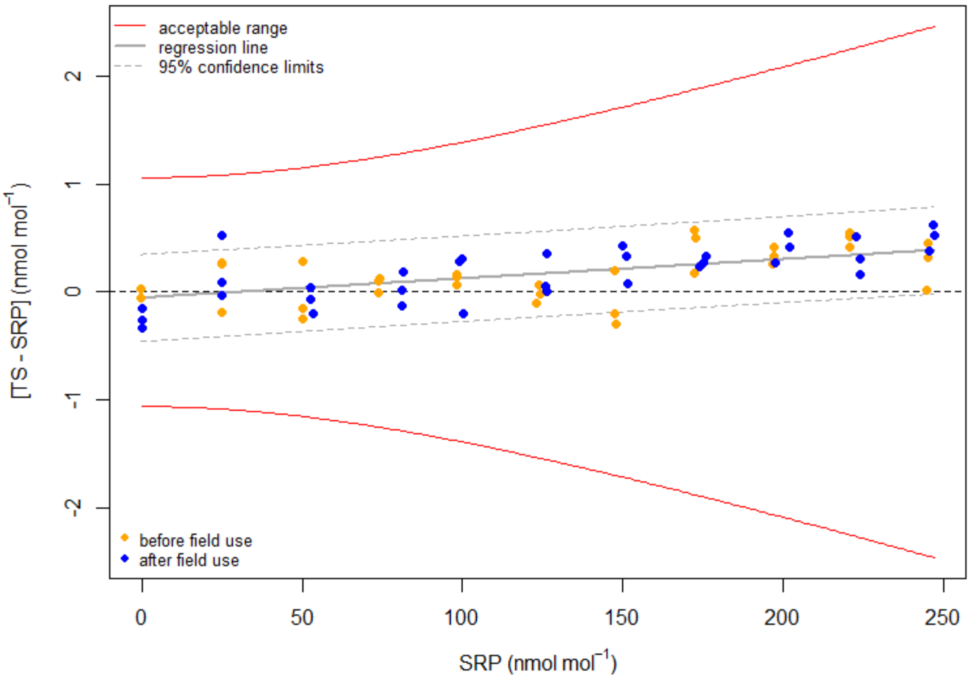

Figure 31. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 22. 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)
2021-10-05	1	0	0.12	0.27	-0.13	0.21
2021-10-05	1	75	74.19	0.14	74.32	0.26
2021-10-05	1	125	123.97	0.37	124.05	0.13
2021-10-05	1	50	50.36	0.22	50.12	0.20
2021-10-05	1	195	197.15	0.42	197.57	0.23
2021-10-05	1	220	220.54	0.42	220.96	0.15
2021-10-05	1	25	24.88	0.20	25.15	0.20
2021-10-05	1	150	147.81	0.33	147.52	0.14
2021-10-05	1	100	98.31	0.55	98.38	0.17
2021-10-05	1	175	172.55	0.29	173.06	0.26
2021-10-05	1	245	245.10	0.52	245.55	0.38
2021-10-05	2	75	73.88	0.60	73.99	0.21
2021-10-05	2	145	147.26	0.27	147.46	0.33
2021-10-05	2	25	24.91	0.23	25.18	0.16
2021-10-05	2	195	197.01	0.38	197.35	0.06
2021-10-05	2	170	172.07	0.27	172.64	0.19
2021-10-05	2	100	98.23	0.20	98.40	0.12
2021-10-05	2	50	50.35	0.37	50.20	0.21
2021-10-05	2	0	-0.12	0.23	-0.18	0.19
2021-10-05	2	125	124.44	0.31	124.42	0.21
2021-10-05	2	220	220.72	0.23	221.23	0.21
2021-10-05	2	245	244.93	0.27	245.25	0.17
2021-10-05	3	75	73.89	0.31	73.89	0.30
2021-10-05	3	25	25.15	0.56	24.96	0.17
2021-10-05	3	50	50.03	0.25	50.31	0.17
2021-10-05	3	100	98.05	0.30	98.19	0.23
2021-10-05	3	195	196.49	0.30	196.75	0.28
2021-10-05	3	125	123.05	0.20	122.95	0.25
2021-10-05	3	170	172.42	0.37	172.60	0.24
2021-10-05	3	145	147.40	0.19	147.20	0.22
2021-10-05	3	0	-0.07	0.27	-0.04	0.13
2021-10-05	3	220	220.79	0.57	221.34	0.58
2021-10-05	3	245	244.82	0.24	244.85	0.35
2022-01-15	4	0	0.21	0.36	-0.05	0.19
2022-01-15	4	55	53.26	0.30	53.05	0.19
2022-01-15	4	225	223.94	0.52	224.25	0.17
2022-01-15	4	125	126.33	0.55	126.69	0.24
2022-01-15	4	80	81.43	0.28	81.62	0.14
2022-01-15	4	25	24.76	0.31	25.28	0.18
2022-01-15	4	150	149.89	0.20	150.32	0.29
2022-01-15	4	175	175.25	0.26	175.52	0.13
2022-01-15	4	200	201.82	0.33	202.24	0.34
2022-01-15	4	100	99.72	0.33	100.03	0.28
2022-01-15	4	245	247.16	0.52	247.68	0.56

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-01-15	5	0	0.14	0.30	-0.01	0.22
2022-01-15	5	195	197.31	0.22	197.58	0.22
2022-01-15	5	55	52.64	0.50	52.57	0.21
2022-01-15	5	125	126.20	0.46	126.21	0.24
2022-01-15	5	150	151.23	0.20	151.57	0.23
2022-01-15	5	100	100.27	0.34	100.07	0.19
2022-01-15	5	245	246.63	0.46	247.26	0.22
2022-01-15	5	80	81.23	0.48	81.11	0.27
2022-01-15	5	225	223.99	0.42	224.15	0.36
2022-01-15	5	25	24.94	0.41	24.91	0.24
2022-01-15	5	175	173.90	0.31	174.14	0.23
2022-01-15	6	0	0.31	0.44	-0.02	0.17
2022-01-15	6	55	52.81	0.51	52.85	0.18
2022-01-15	6	25	25.12	0.28	25.21	0.25
2022-01-15	6	100	98.87	0.49	99.16	0.32
2022-01-15	6	245	245.65	0.28	246.04	0.19
2022-01-15	6	225	222.76	0.34	223.28	0.20
2022-01-15	6	175	176.06	0.24	176.40	0.18
2022-01-15	6	150	151.31	0.20	151.39	0.28
2022-01-15	6	125	125.79	0.17	125.84	0.32
2022-01-15	6	200	201.57	0.26	202.12	0.36
2022-01-15	6	80	81.22	0.46	81.24	0.33

#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 23 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 24 and 25, and Figures 32 to 35 show the analysis of the TS over time.

Table 23. *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 24. *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_FB03870	1360	1883.44	0.05	387.13	0.02	318.87	0.04	318.93	0.09
140514_FB03894	690	1953.91	0.07	411.23	0.02	329.16	0.04	329.14	0.08
140514_FB03912	1810	1952.43	0.02	401.71	0.00	328.01	0.03	327.98	0.02
140514_FB03918	1260	1971.36	0.04	401.09	0.03	322.61	0.03	322.62	0.04
150601_FA02482	1690	1906.04	0.03	431.30	0.02	327.02	0.04	326.56	0.03
160622_FA02474	1000	2506.89	0.08	421.48	0.01	324.44	0.03	324.48	0.01
181129_FB03853	1110	1998.97	0.02	412.69	0.00	330.12	0.01	330.17	0.02
210412_FB03377	1200	2.48	0.32	0.24	0.02	10.33	0.09	15.27	0.93
210415_FB03376	1970	1865.74	0.02	401.33	0.00	326.74	0.02	326.78	0.01
210420_FB03367	1900	1940.94	0.03	428.19	0.02	340.63	0.06	340.64	0.03

Table 25. *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_FB03870	1360	155.11	0.43	153.47	0.10	152.74	0.09
140514_FB03894	690	197.11	1.07	195.01	0.26	194.27	0.04
140514_FB03912	1810	208.07	0.87	206.20	0.06	205.25	0.06
140514_FB03918	1260	187.71	0.29	185.61	0.05	184.79	0.06
150601_FA02482	1690	1336.34	0.82	1331.87	1.17	1339.53	0.41
160622_FA02474	1000	238.34	0.45	236.49	0.09	235.32	0.06
181129_FB03853	1110	94.63	0.37	92.29	0.29	92.98	0.13
210412_FB03377	1200	7.25	0.26	6.53	0.22	6.64	0.15
210415_FB03376	1970	117.72	0.85	115.29	0.33	115.51	0.05
210420_FB03367	1900	134.78	0.58	131.96	0.15	132.19	0.23

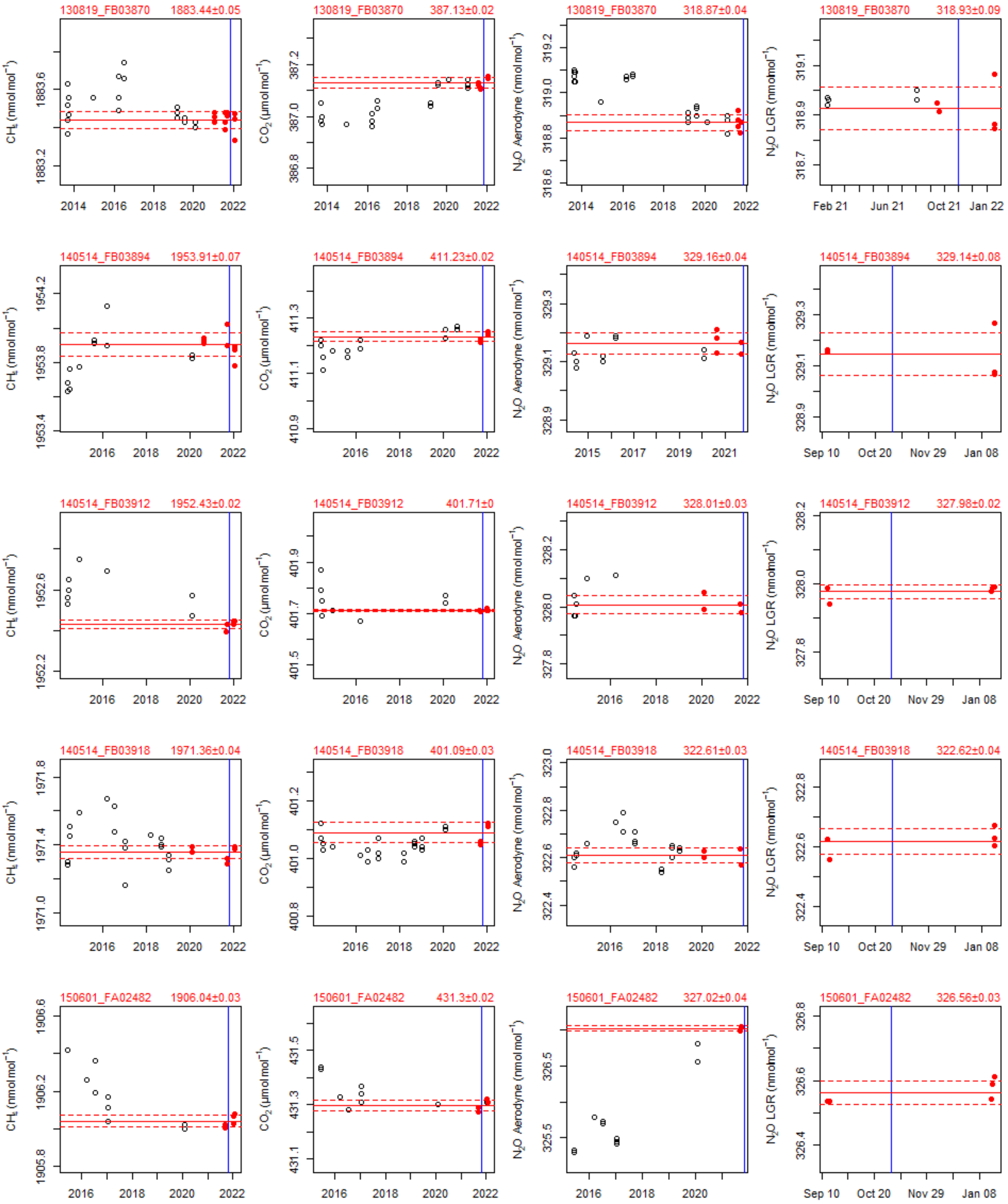

Figure 32. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

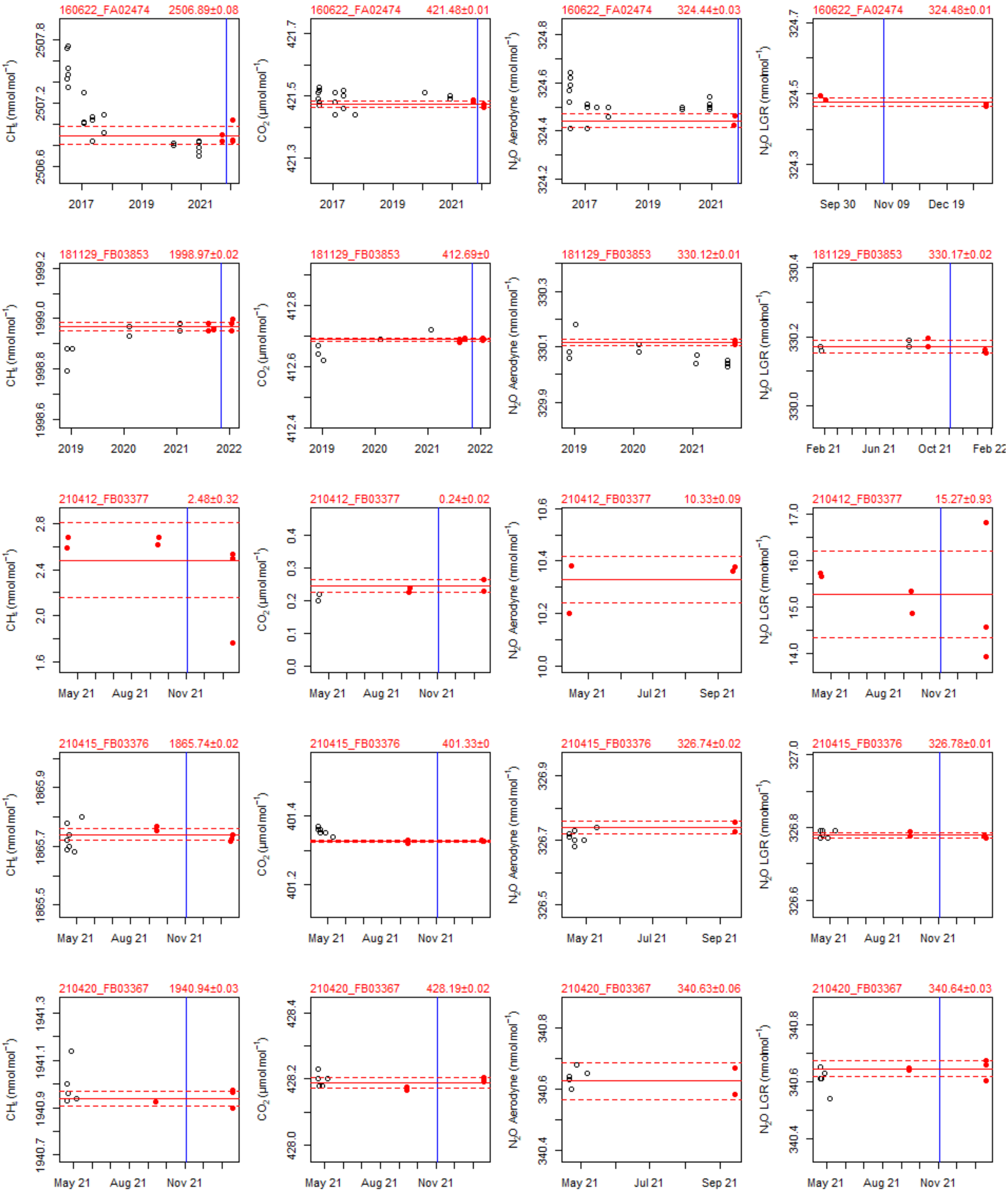

Figure 33. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

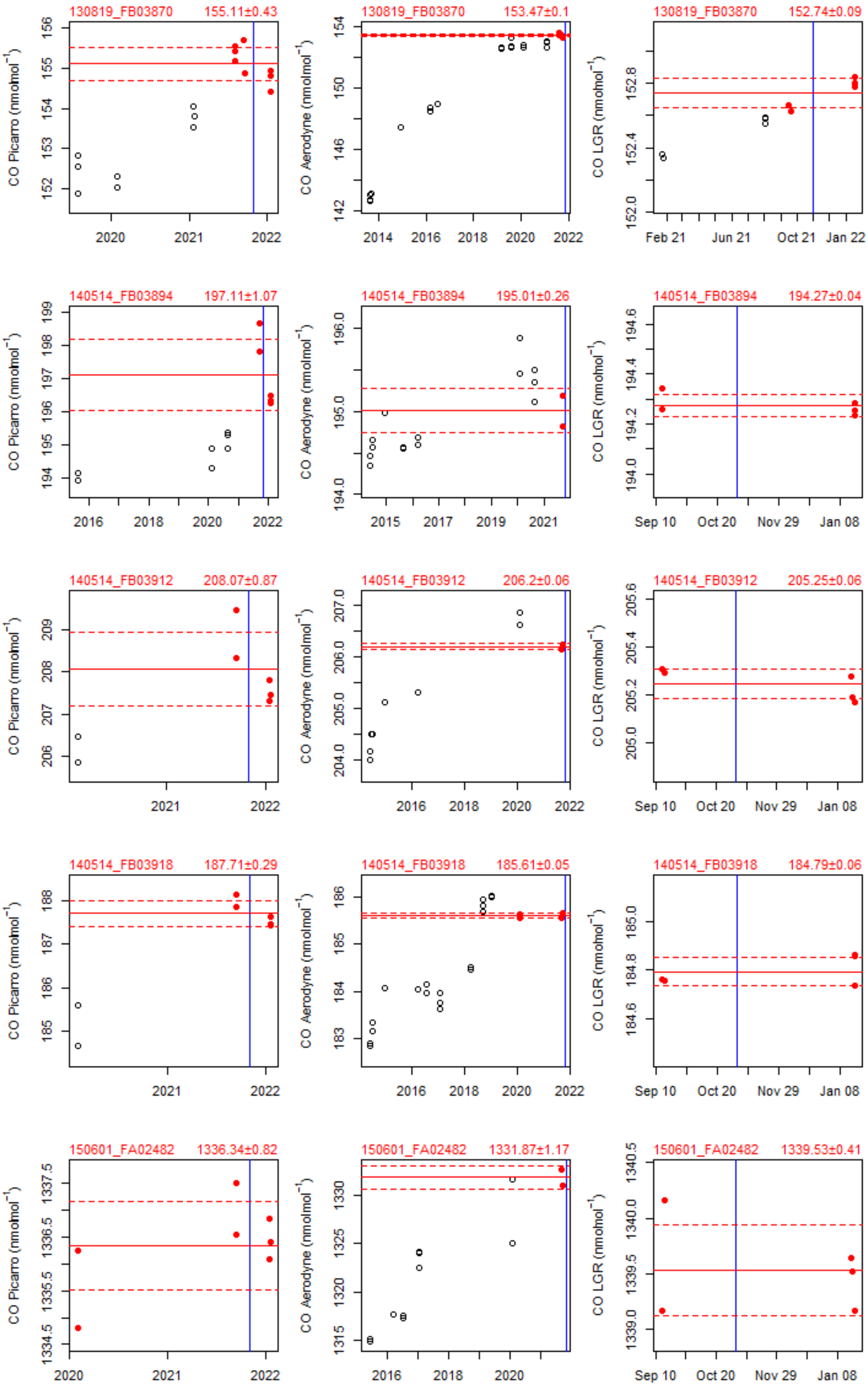

Figure 34. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

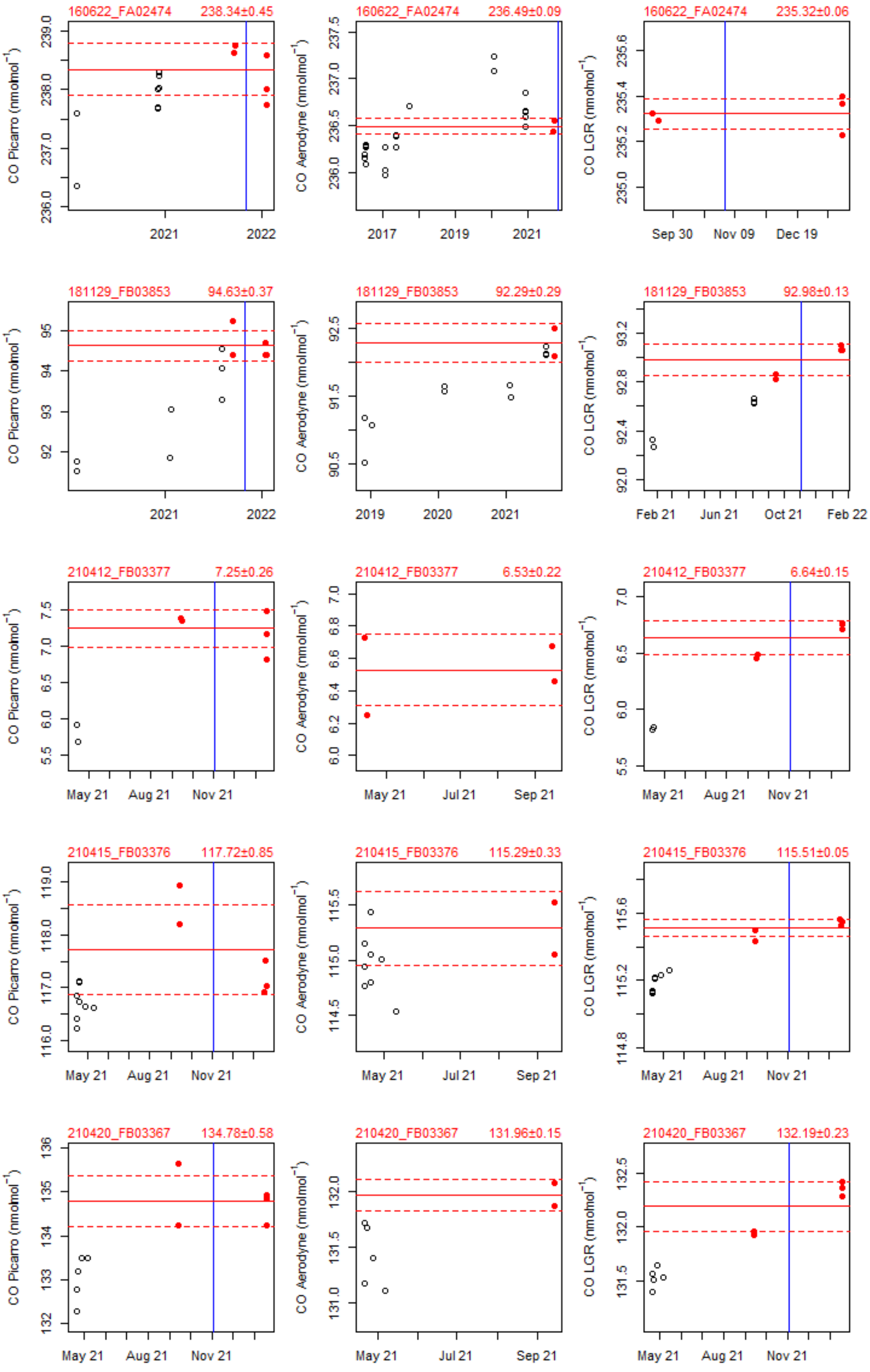

Figure 35. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. 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 1745 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.

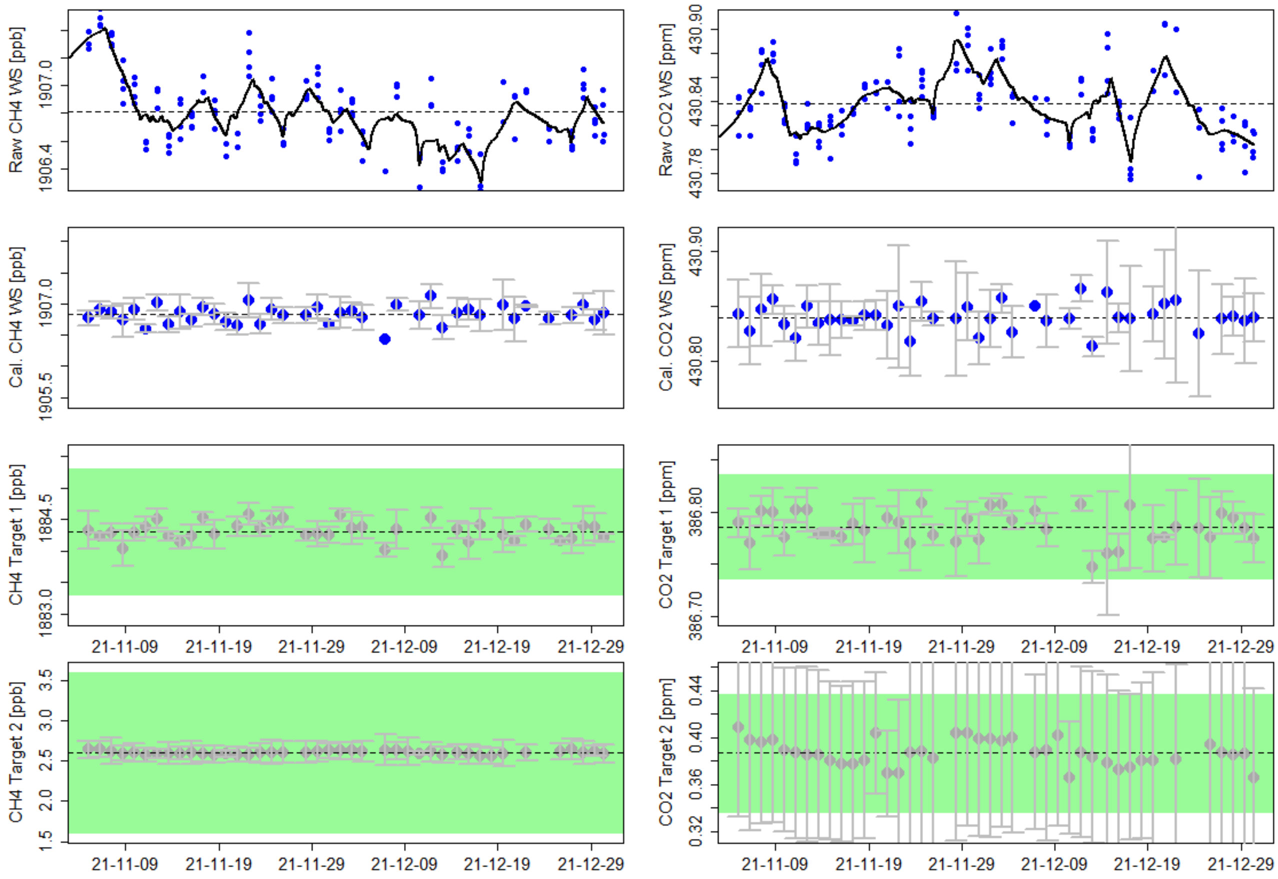

Figure 36. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower 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 1745 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.

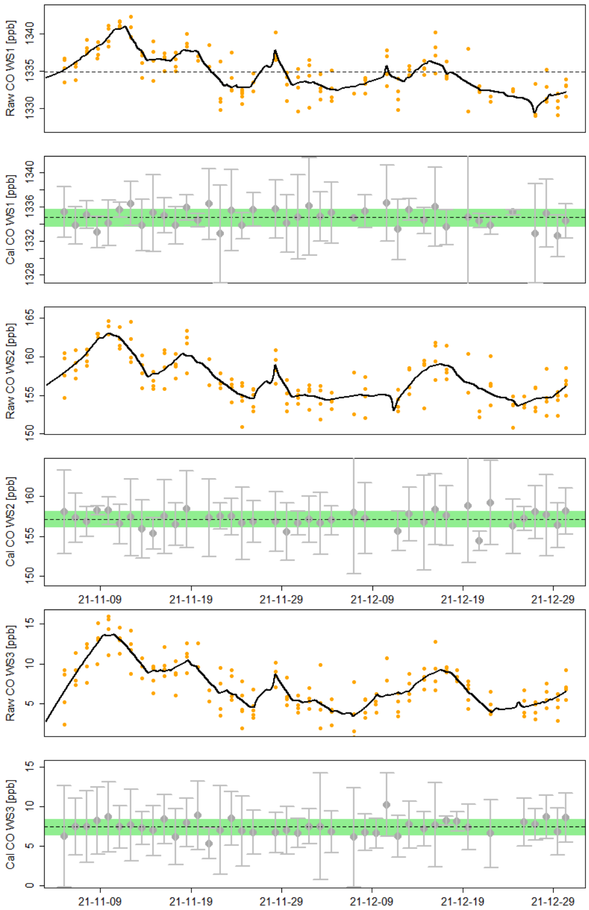

Figure 37. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

REFERENCES

Bond, S. W., Vollmer, M. K., Steinbacher, M., Henne, S., and Reimann, S.: Atmospheric molecular hydrogen (H2): observations at the high-altitude site Jungfraujoch, Switzerland, Tellus B, 63, 64-76, 2011.

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, Journal Of Geophysical Research-Atmospheres, 110, Article D18306, 2005.

Empa: Standard Operating Procedure (SOP), Measurement uncertainty of ozone measuring instruments and standards, 7th Edition from 13 February 2014 (available in German), Empa, Laboratory for Air Pollution / Environmental Technology, 2014.

Hall, B. D., Crotwell, A. M., Kitzis, D. R., Mefford, T., Miller, B. R., Schibig, M. F., and Tans, P. P.: Revision of the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) CO2 calibration scale, Atmos. Meas. Tech., 14, 3015-3032, 2021.

Hazan, L., Tarniewicz, J., Ramonet, M., Laurent, O., and Abbaris, A.: Automatic processing of atmospheric CO2 and CH4 mole fractions at the ICOS Atmosphere Thematic Centre, Atmos. Meas. Tech., 9, 4719-4736, 2016.

Hearn, A. G.: ABSORPTION OF OZONE IN ULTRA-VIOLET AND VISIBLE REGIONS OF SPECTRUM, Proceedings of the Physical Society of London, 78, 932-&, 1961.

Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, Journal of Geophysical Research-Atmospheres, 108, 4622, doi:4610.1029/2003JD003710, 2003.

Novelli, P. C., Masarie, K. A., Lang, P. M., Hall, B. D., Myers, R. C., and Elkins, J. W.: Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, Journal of Geophysical Research-Atmospheres, 108, 4464, doi:4410.1029/2002JD003031, 2003.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech., 6, 837-860, 2013.

Schibig, M. F., Steinbacher, M., Buchmann, B., van der Laan-Luijkx, I. T., van der Laan, S., Ranjan, S., and Leuenberger, M. C.: Comparison of continuous in situ CO2 observations at Jungfraujoch using two different measurement techniques, Atmos. Meas. Tech., 8, 57-68, 2015.

Vollmer, M. K., Steinbacher, M., Leuenberger, M. C., and Emmenegger, L.: The new 2020 air sampling inlet system at Jungfraujoch, Activity Report 2020 o the High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG), Bern, 2020.

WMO: 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019), Jeju Island, South Korea, 2-5 September 2019, GAW Report No. 255, World Meteorological Organization, Geneva, Switzerland, 2020.

WMO: Guidelines for Continuous Measurements of Ozone in the Troposphere, WMO TD No. 1110, GAW Report No. 209, World Meteorological Organization, Geneva, Switzerland, 2013.

WMO: Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland, 2007.

WMO: WMO Global Atmosphere Watch (GAW) Implementation Plan: 2016-2023, GAW report no. 228. , World Meteorological Organization, Geneva, Switzerland, 2017.

Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M., Kozlova, E., Spain, T. G., Steinbacher, M., van der Schoot, M. V., and Buchmann, B.: Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, Atmos. Meas. Tech., 9, 4737-4757, 2016.

Zellweger, C., Hüglin, C., Klausen, J., Steinbacher, M., Vollmer, M., and Buchmann, B.: Inter-comparison of four different carbon monoxide measurement techniques and evaluation of the long-term carbon monoxide time series of Jungfraujoch, Atmos. Chem. Phys., 9, 3491-3503, 2009.

Zellweger, C., Steinbacher, M., and Buchmann, B.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, Atmos. Meas. Tech., 5, 2555-2567, 2012.

Zellweger, C., Steinbrecher, R., Laurent, O., Lee, H., Kim, S., Emmenegger, L., Steinbacher, M., and Buchmann, B.: Recent advances in measurement techniques for atmospheric carbon monoxide and nitrous oxide observations, Atmos. Meas. Tech., 12, 5863-5878, 2019.

LIST OF ABBREVIATIONS

a.s.l	above sea level
ATC	Atmosphere Thematic Centre
BKG	Background
CEP	Climate and Environmental Physics Institute
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
FCL	Flask and Calibration Laboratory
FID	Flame Ionization Detection
FOEN	Federal Office for the Environment
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
HFSJG	High Altitude Research Stations Jungfraujoch and Gornergrat
ICOS	Integrated Carbon Observation System
ICOS-CAL	ICOS Central Analytical Laboratories
IR	Infrared
JFJ	Jungfraujoch GAW Station
LS	Laboratory Standard
NA	Not Applicable
NABEL	National Air Pollution Monitoring Network
NDIR	Non-Dispersive Infrared
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