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System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide at the Global GAW Station Hohenpeissenberg Germany June/July 2020

WEATHER CLIMATE WATER

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Empa
Materials Science and Technology

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

GLOBAL GAW STATION HOHENPEISSENBERG GERMANY JUNE/JULY 2020

Submitted to the World Meteorological Organization by
C. Zellweger, M. Steinbacher and B. Buchmann
WMO World Calibration Centre WCC-Empa
Empa, Dübendorf, Switzerland

R. Steinbrecher
WMO World Calibration Centre WCC-N_2O
Institute of Meteorology and Climate Research (IMK-IFU)
Garmisch-Partenkirchen, Germany

WCC-Empa Report 20/1

Chair, Publications Board
World Meteorological Organization (WMO)
7 bis, avenue de la Paix
P.O. Box 2300
CH-1211 Geneva 2, Switzerland

Tel.: +41 (0) 22 730 84 03
Fax: +41 (0) 22 730 81 17
Email: Publications@wmo.int

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WCC-Empa Report 20/1

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

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The fourth system and performance audit by WCC-Empa[1] at the global GAW station Hohenpeissenberg (HPB) was conducted from 30 June–2 July 2020 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at HPB, 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 Christian Plass-Dülmer	Hohenpeissenberg, station manager, head of the observatory
Dr Robert Holla	Hohenpeissenberg, station scientist, GAW observations
Dr Dagmar Kubistin	Hohenpeissenberg, station scientist, head trace gases
Ms Marita Hoffmann	Hohenpeissenberg, station technician, GAW observations
Dr Matthias Lindauer	Hohenpeissenberg, station scientist, ICOS observations
Dr Jennifer Müller-Williams	Hohenpeissenberg, station scientist, ICOS observations
Mr Thomas Deromedis	Hohenpeissenberg, station technician, ICOS observations

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

The report is distributed to the station manager of Hohenpeissenberg, the national focal point for GAW in Germany, 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 meteorological observatory at Hohenpeissenberg is operated by the German Meteorological Service (DWD), and has a long history of meteorological and climatological observations starting in 1781. In 1995, the observatory became a Global Station of the GAW programme. HPB hosts one of the most extensive measurement programmes of the GAW network, and observed parameters cover all focal areas of GAW.

Since 2015, HPB is also part of the Integrated Carbon Observation System (ICOS), which aims at standardizing greenhouse gas observations in Europe. HPB was labelled as a class 1 station in 2017 (Yver-Kwok et al., 2021).

Scientist, technicians and administrative staff are directly working at the observatory. An overview of the measurement programme can be found on the station website (http://www.dwd.de/mohp).

Station Location and Access

The HPB observatory (47.80150°N, 11.0096°E, 985 m a.s.l.) is situated in the foothills of the Alps, approximately 55 km southwest of Munich. ICOS measurements, i.e. observations of CO_2, CH_4 and CO in the context of this audit, are made on a 159 m tall telecommunication tower, located approximately 1.1 km east of the observatory (47.80124°N, 11.00993°E). The

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[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.

locations, both of the observatory and the tall tower, are fully adequate for the intended purpose. Year-round access to HPB is possible by car.

Further information is available from the GAW Station Information System (GAWSIS) (https://gawsis.meteoswiss.ch), the station (http://www.dwd.de/mohp) and the ICOS web (https://www.icos-cp.eu/observations/atmosphere/stations) sites.

Station Facilities

Extensive laboratory and office space is available. The infrastructure is ideally supporting research projects and long-term atmospheric observations. The HPB observatory, together with the tall tower facilities, is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Measurement Programme

The HPB observatory hosts a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured species is available from GAWSIS and the station web site (http://www.dwd.de/mohp). HPB also participates in the cooperative flask sampling network run by the National Oceanic and Atmospheric Administration (NOAA) since 2006. The NOAA flasks are sampled at the HPB observatory.

The information available from GAWSIS was reviewed as part of the audit; however, updating was not possible due to limited access to GAWSIS at the time of the audit.

> **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 August 2021, the following HPB data of the scope of the audit were available at the World Data Centres:

Status at the World Data Centre for Reactive Gases (WDCRG):

O_3 (three data sets, 1971–2010, with large data gap from 1995–2007 and 2012-2019).

Another data set (2008–2010) was also available, but it contained clearly invalid data. Data was automatically transferred from WDCGG to WDCRG in 2019, which obviously worked not as it should. For example, data of 2011 was not transferred and incorrect time stamps were stated. Data directly submitted to WDCRG must have been modified by the WDCRG internal release process introducing wrong metadata information in part of the files.

The observed inconsistencies were discussed with HPB staff, and the following issues were identified:

- Data from the early period (1971–1994) should be in one data series, and should not contain the data from 2007–2010. The time stamp showed a time shift of -15 days.
- Data from 1995–2011 needs to be corrected (time is in UTC+1, should be UTC).
- Data from 2012–2020 is compliant with WDCRG data policy, but a wrong data header needs to be corrected.
- Two datasets with identical file names exist for 2008–2010. The invalid files need to be removed.

Recommendation 2 (*, critical, 2021)**

Ozone data available at WDCRG needs to be checked and corrected. The invalid data set needs to be withdrawn. The inconsistencies were caused by the automatic transfer from WDCGG to WDCRG and during the WDCRG internal release process. The revision process has already been initiated by HPB staff.

DWD, submission to World Data Centre for Greenhouse Gases (WDCGG):
CO (1995–2010)

DWD (ICOS), submission to WDCGG:
CH_4 (2015–2021), CO (2015–2021), CO_2 (2015–2021), N_2O (2017–2021)

NOAA, submission to WDCGG:
CO_2 (2006–2020), CH_4 (2006–2020), CO (2006–2020)

Data shown in this report was accessed on 19 August 2021.

Recommendation 3 (*, important, ongoing)**

Data has been submitted for all parameters of the scope of the audit. The submission delay varies depending on the parameter, but most data was timely submitted with a delay of one to two years. Data submission is an obligation of all GAW stations. It is recommended to continue with the current practice, and submit data to the corresponding data centres at least in yearly intervals. One hourly data must be submitted for all parameters.

Data Review

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

Documentation

All information is entered in electronic and handwritten log books. The instrument manuals are available at the site. The reviewed information was comprehensive and up-to-date.

Air Inlet System

GAW laboratory: The design of the air inlet system (O_3 and CO) has not been changed since the last audit by WCC-Empa. The inlet is located on the terrace 2 m above the laboratory, and it is protected against rain water and snow. From there instruments are connected by ¼" PFA tubing.

ICOS tall tower: The air intakes at the ICOS tower are located at three different sampling heights (50 m, 93 m, and 131 m). Direct sampling lines (Synflex 1300, 8 mm OD) lead inside the tower from the intake location to the laboratory in the basement of the tower using a flushing pump (KNF Neuberger NO34.1.2AN.18) with a flow rate of 4.5 l/min.

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

Surface Ozone Measurements

Surface ozone measurements at HPB (GAW laboratory) were established in 1971, and continuous time series are available since then.

Instrumentation. HPB is currently equipped with two ozone analysers (Thermo Scientific 49i and 49C).

Standards. A Thermo Scientific 49C-PS ozone calibrator with traceability to the WMO/GAW reference is available. The ozone standard is used every three months to calibrate the ozone analysers. The calibration settings are not changed. A correction function based on the calibrations is applied to the data.

> **Recommendation 4 (*, minor, 2022)**
>
> *Two instruments (Thermo Scientific 49C-PS and 49C) are reaching the end of the expected lifetime, and replacement should be considered.*

Data Acquisition. All instruments at HPB use a central LabView based data acquisition software, and remote access to the data is possible. The data acquisition system is appropriate, and no further action is required.

Intercomparison (Performance Audit). All three instruments at HPB were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomized sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. The result of the comparisons is summarized 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 HPB data acquisition system. Ozone analyser data was corrected based on the last calibration with the HPB ozone standard prior to the audit with is the same treatment as for ambient air. The following equations characterize the bias of instruments and the remaining uncertainty after compensation of the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the ozone absorption cross section of 11.476x10^{-18} cm^2 molecule^{-1} (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49C #56028-306 (BKG -0.0 nmol mol^{-1}, SPAN 1.000), corrected for the bias using the last calibration with the HPB reference:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.08 nmol mol^{-1}) / 1.0161 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.08e-05 * X_{O3}^2) (1b)

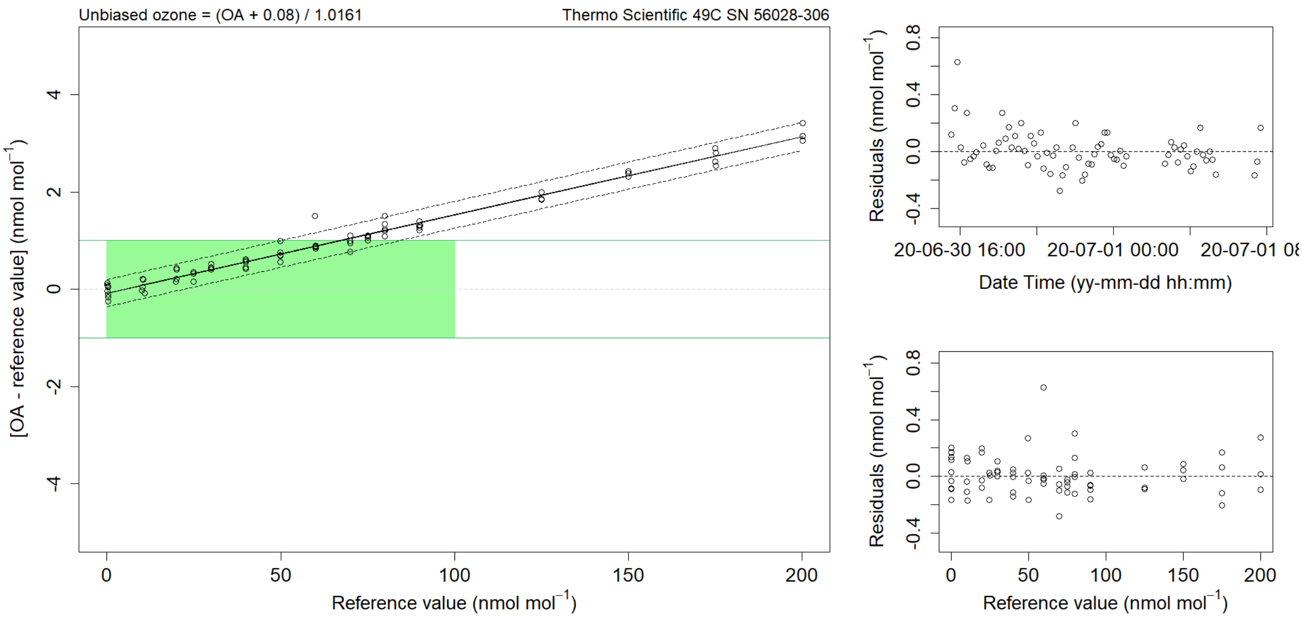

Figure 1. Left: Bias of the HPB ozone analyser (Thermo Scientific 49C #56028-306, BKG 0.0 nmol mol^{-1}, COEF 1.000), corrected for the bias using the last calibration with the HPB reference, with respect to the SRP as a function of mole fraction. Each point represents the average of the last five one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Thermo Scientific 49i #632519672 (BKG 0.0 nmol mol^{-1}, SPAN 1.000), corrected for the bias using the last calibration with the HPB reference:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.21 nmol mol^{-1}) / 1.0168 (1c)

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

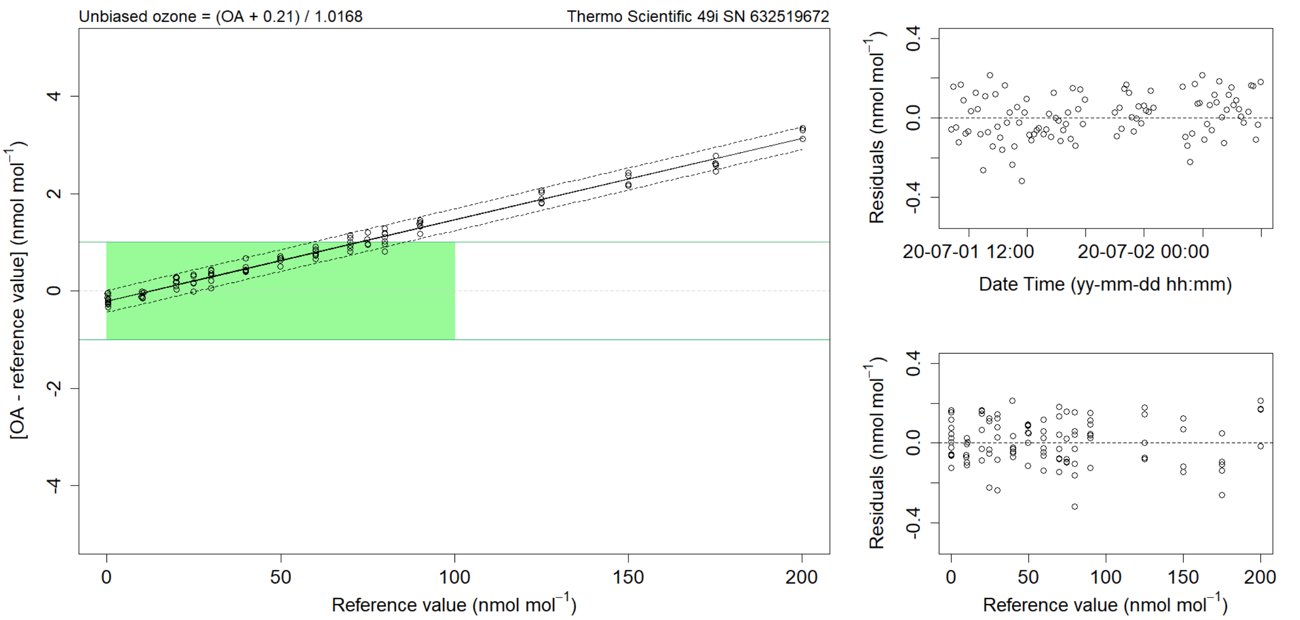

Figure 2. Same as above for the HPB Thermo Scientific 49i #632519672 ozone analyser.

Thermo Scientific 49C-PS #423807729 (BKG 0.0 nmol mol^{-1}, SPAN 1.024, initial comparison with unadjusted pressure sensor):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OC] - 0.14 nmol mol^{-1}) / 1.0176 (1e)

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

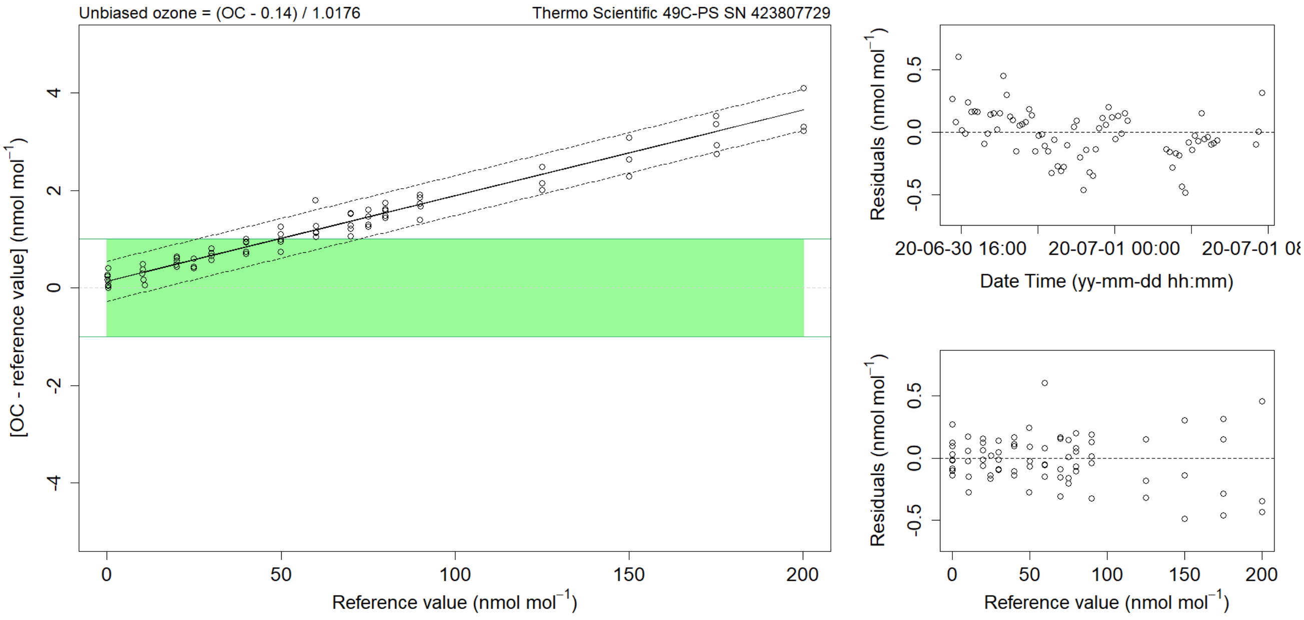

Figure 3. Left: Bias of the HPB ozone calibrator (Thermo Scientific 49C-PS #423807729, BKG 0.0 nmol mol^{-1}, COEF 1.024, unadjusted pressure sensor) with respect to the SRP as a function of mole fraction. Each point represents the average of the last five one-minute values at a given level. The green 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).

After the first comparison of the 49C-PS ozone calibrator, the reading of the internal pressure sensor was checked, and a disagreement outside the acceptable limit was found. Thus, the pressure sensor was adjusted and the comparison was repeated.

Thermo Scientific 49C-PS #423807729 (BKG 0.0 nmol mol^{-1}, SPAN 1.024, final comparison with adjusted pressure sensor):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OC] - 0.00 nmol mol^{-1}) / 1.0113 (1g)

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

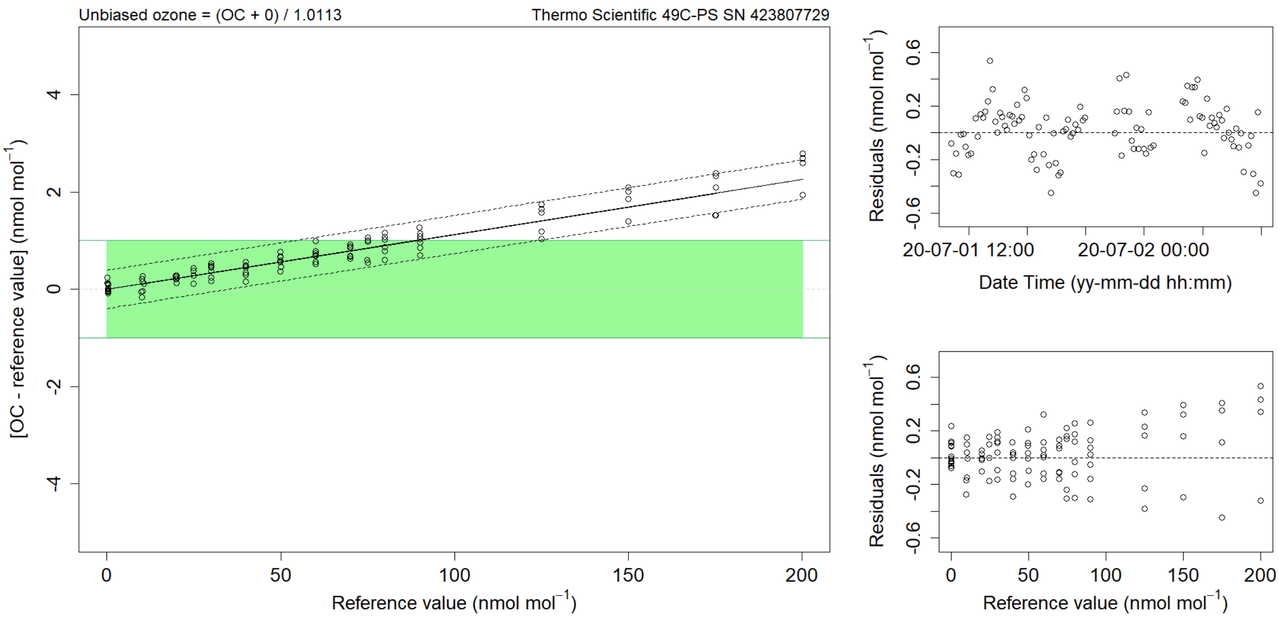

Figure 4. As above for the Thermo Scientific 49C-PS #423807729 ozone calibrator after adjustment of the pressure sensor.

The results of the comparisons can be summarized as follows:

The comparison of both ozone analysers and the initial comparison of the HPB ozone standard showed a bias of approximately 1.7% compared to the WCC-Empa reference. This confirms that the internal calibration has successfully been implemented.

The bias can be explained as follows:

Part of the bias was due to an incorrect pressure sensor reading of the HPB ozone calibrator, which was reading low by 0.58%. The comparison with the adjusted pressure sensor showed better agreement with the WCC-Empa reference, but still a bias of approximately 1.1%. The HPB ozone calibrator was also compared at the WCC-Empa calibration laboratory in 2017, and the 1.1% bias was already observed at that time. The correction function to compensate for the bias was not implemented in the HPB data correction. This bias, together with the bias of the pressure sensor reading, explains the deviation found during this audit. Therefore, the following recommendations are made:

Recommendation 5 (*, critical, 2020)**

The pressure sensor of the ozone calibrator needs to be checked against the HPB reference pressure, and adjusted in case of significant deviations (> 1 hPa) prior to ozone calibrations.

Recommendation 6 (*, critical, 2020)**

The HPB ozone reference needs to be corrected for the bias with respect to the WMO/GAW reference value. The corresponding correction function

Conventional true value = (0.9893 x TEI 49C-PS #423807729 - 0.03) nmol mol^{-1}

is given in the WCC-Empa calibration certificate #5214016813-O3 from 11 September 2017, which is available at HPB. The current audit confirmed that this correction function is still valid.

Carbon Monoxide Measurements

Continuous measurements of CO at HPB started in 1995 using Non-dispersive Infrared Absorption technique (NDIR). This system was later replaced by a Vacuum UV Resonance Fluorescence (VURF) analyser, which is still available at the GAW laboratory. At the ICOS tower, CO is also measured with Cavity Ringdown Spectroscopy, and an Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument was added recently.

***Instrumentation*.** The following instruments are currently available: GAW laboratory: Aerolaser AL5001 (VURF); ICOS tower: Picarro G2401 (CRDS) (two analysers) and LGR 913-0015 (OA-ICOS). The sample air is dried with Nafion driers for all instruments except one Picarro G2401, which measures humid air.

Standards. GAW laboratory (VURF): A working standard from AirLiquide with an amount fraction of about 1 ppm is available for the calibration of the VURF instrument. In addition, three NOAA laboratory standards are available. The NOAA standards are used to assign values to the working standard. The working standard and the internal zero (Sofnocat® 423) of the VURF instrument are then used every seven hours for automatic calibrations of the analyser.

ICOS tower (CRDS and OA-ICOS): Laboratory standards, working (only OA-ICOS) and target gases are available from the ICOS Flask and Calibration Laboratory (FCL). These standards have traceability to the current WMO/GAW calibration scales. Calibrations using the laboratory standards are made every 15 days, and the WS is measured every seven hours to correct for drift (only OA-ICOS).

A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the HPB instruments with randomized carbon monoxide levels using WCC-Empa travelling standards. The following equations characterize the instrument bias, and the results are further illustrated in Figures 5 and 6 with respect to the WMO GAW DQOs (WMO, 2020):

Aerolaser AL5001 #142:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 1.46 nmol mol^{-1}) / 0.9908 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (2.4 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2b)

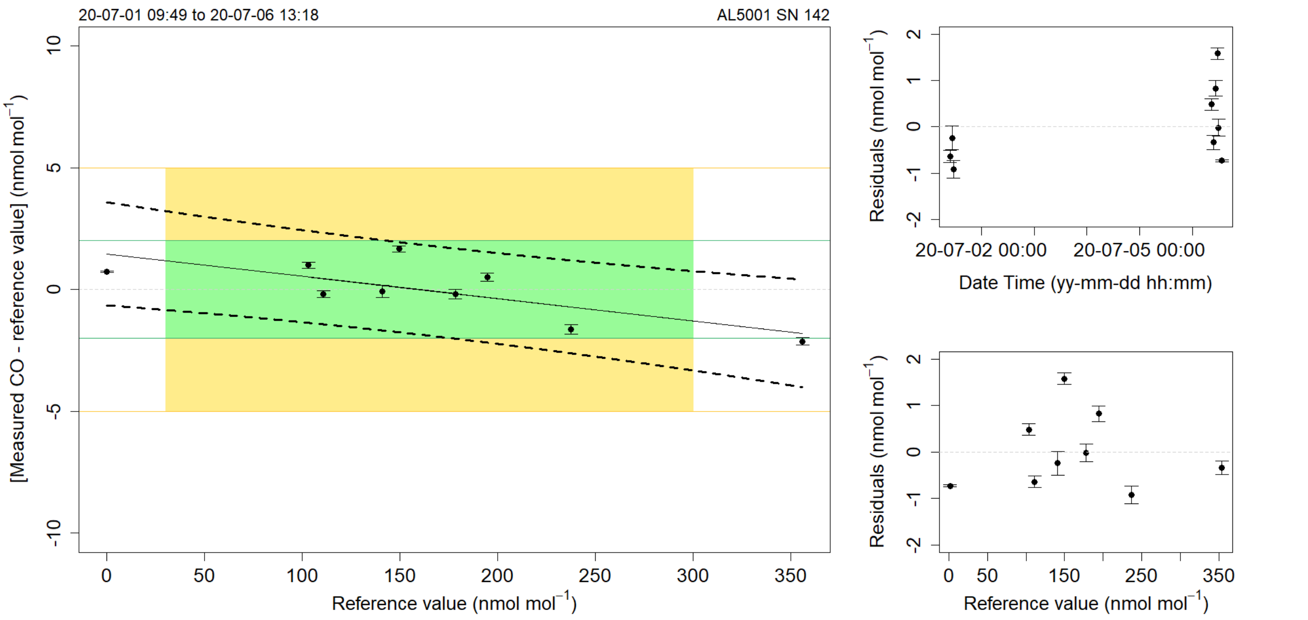

Figure 5. Left: Bias of the HPB Aerolaser AL5001 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for HPB. 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 #1670-CFKADS2120 (instrument without dryer):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 4.92 nmol mol^{-1}) / 0.9847 (2c)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (3.6 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2d)

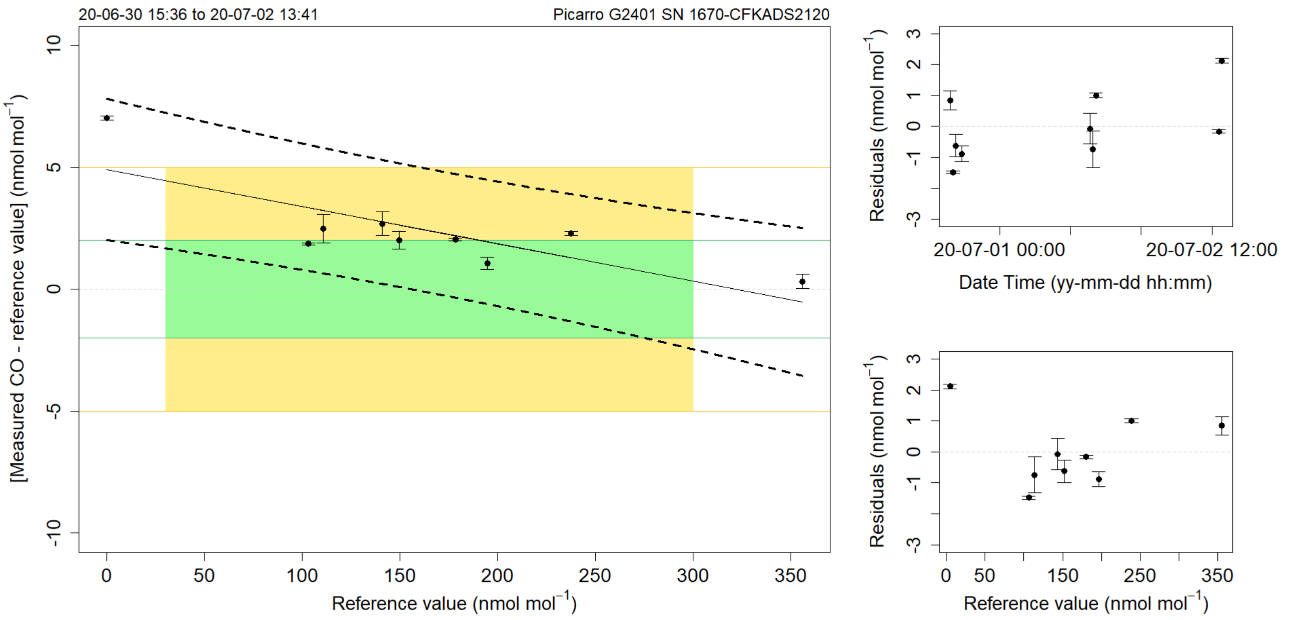

Figure 6. Same as above, for the Picarro G2401 #1670-CFKADS2120 instrument.

Picarro G2401 #2322-CFKADS2192 (instrument with Nafion dryer):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 4.38 nmol mol^{-1}) / 0.9850 (2e)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (4.0 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2f)

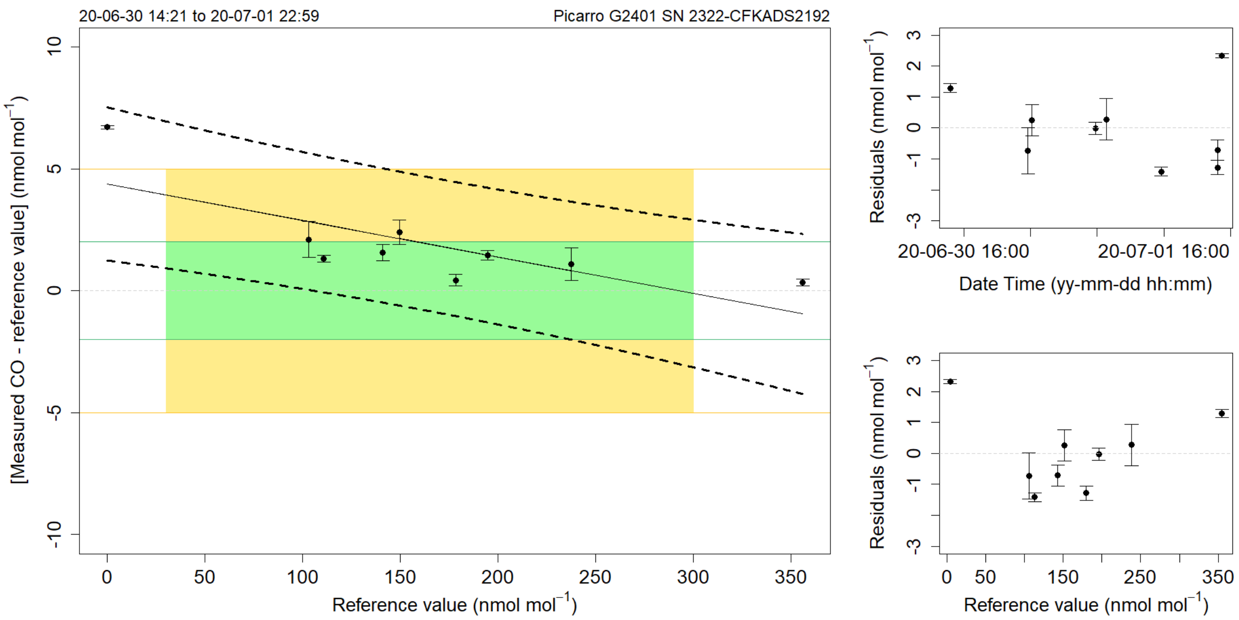

Figure 7. Same as above, for the Picarro G2401 #2322-CFKADS2192 instrument.

LGR 913-0015 #US4300160200001043:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 2.82 nmol mol^{-1}) / 0.9920 (2g)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.2 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2h)

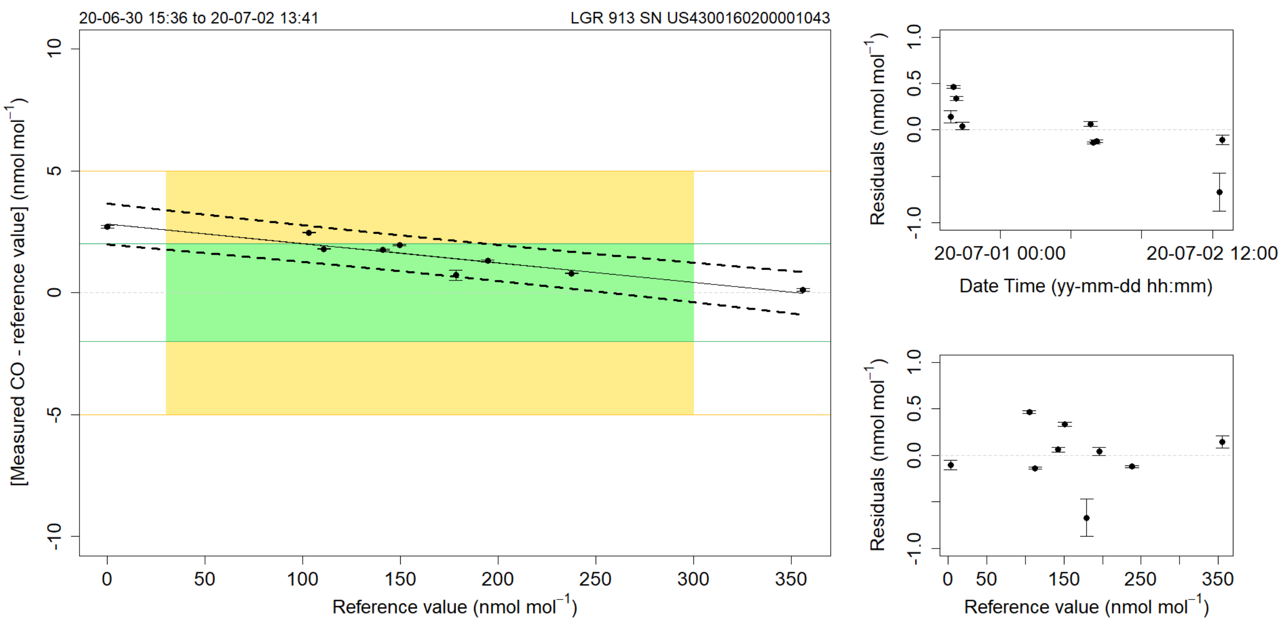

Figure 8. Same as above, for the LGR 913-0015 #US4300160200001043 instrument.

The results of the comparisons can be summarized as follows:

The comparison results were within the extended network compatibility goal of 5 nmol mol^{-1} for all instruments. The Picarro instruments of the ICOS programme were measuring slightly higher compared to WCC-Empa, while the agreement with the Aerolaser system of the GAW laboratory and the ICOS LGR instrument was slightly better. Furthermore, all comparisons showed a mole fraction dependent bias. The ICOS systems measured all significantly high at low mole fractions (zero offset), but the agreement at highest amount fraction was within the compatibility goal for all ICOS instruments. The zero offset was not observed for the Aerolaser system, which was measuring within the compatibility goals for amount fractions up to 200 nmol mol^{-1}. Most likely, the differences can be attributed to the use of different calibration standards. Within the ICOS programme an estimated drift of 1.1 ppb CO /year of the calibration standards cylinders is assumed. At intervals of 3–4 years the concentrations of the cylinder content is re-measured by the ICOS Calibration laboratory. The actual drift is applied to the measured mixing ratio and might lead to a correction of the reported CO mixing ratio. Stability of CO in reference standards at low amount fractions remains a significant challenge, and therefore, the following recommendation is made:

Recommendation 7 (, important, 2021)**

Since all CO measurement techniques used at HPB are expected to have a linear response in the amount fraction range from 0 to 1000 nmol mol^{-1}, the calibration strategy should focus on higher CO mole fractions (300 to 1000 nmol mol^{-1}) and also include CO free air (or N_2 6.0) to compensate for a zero offset.

Methane Measurements

Continuous measurements of CH_4 at HPB (GAW laboratory) started in 2010 using a CRDS instrument. At that time, measurements were made on a provisional basis in the GAW observatory, and were discontinued after the ICOS measurements commenced in 2015. Continuous data is available since 2015.

Instrumentation. Two Picarro G2401 CRDS analysers, one with and one without sample air drying.

Standards. Laboratory standards and target gases are available from the ICOS Flask and Calibration Laboratory (FCL). These standards have traceability to the current WMO/GAW calibration scales. Calibrations using the laboratory standards are made every 15 days.

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

The following equation characterizes the instrument bias. The results are further illustrated in Figures 9 to 10 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1670-CFKADS2120 (instrument without dryer):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 1.93 nmol mol^{-1}) / 0.9990 (3a)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.3 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (3b)

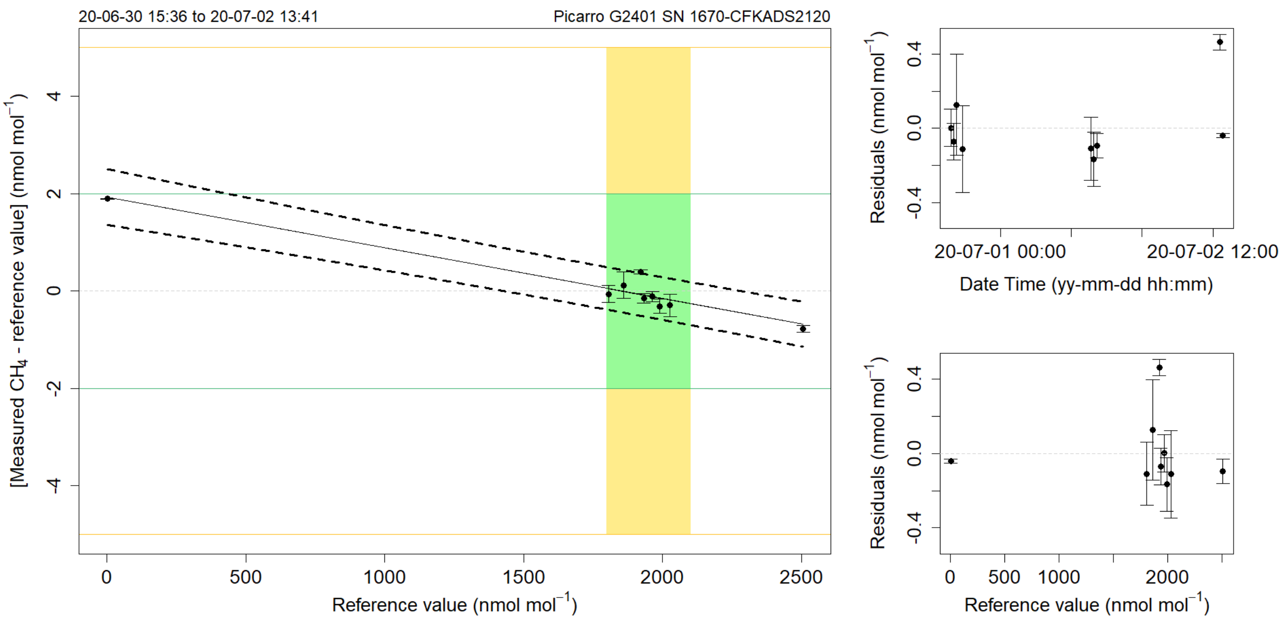

Figure 9. Left: Bias of the Picarro G2401 #1670-CFKADS2120 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for HPB. 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 #2322-CFKADS2192 (instrument with Nafion dryer):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 1.71 nmol mol^{-1}) / 0.9992 (3c)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.1 nmol mol^{-12} + 1.30e-07 * X_{CH4}^2) (3d)

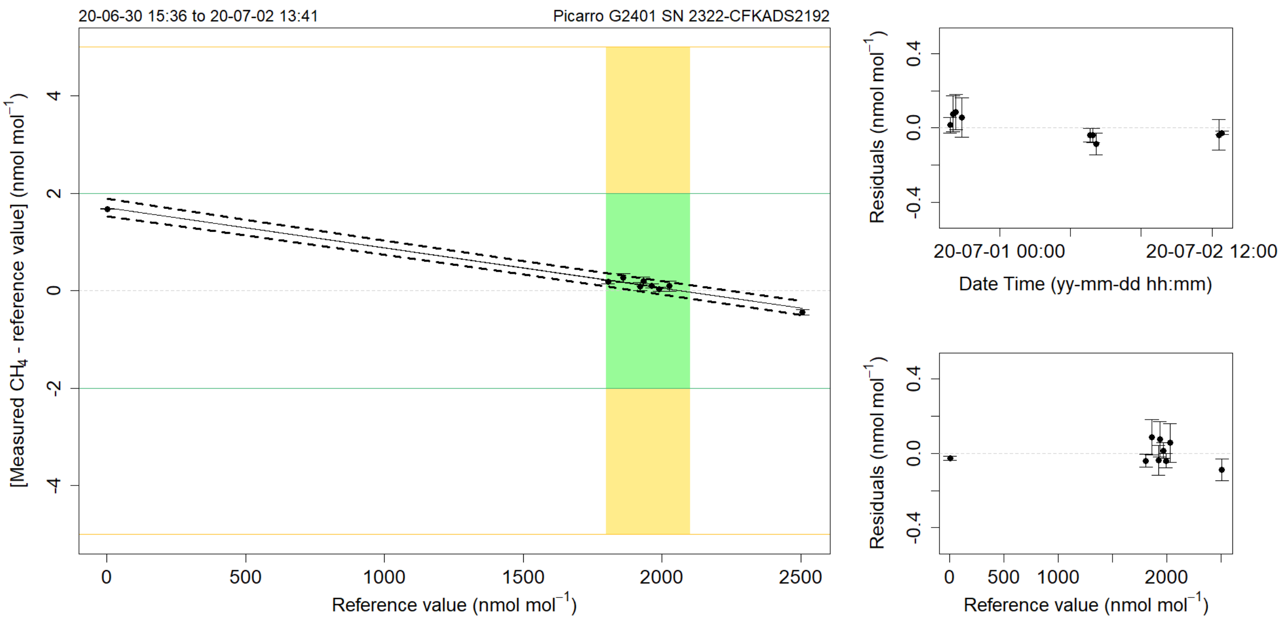

Figure 10. Same as above, for the Picarro G2401 #2322-CFKADS2192 methane analyser.

The result of the comparison can be summarized as follows:

Excellent agreement well with the WMO/GAW compatibility goal was found for both CRDS instruments. However, the small remaining bias was dependent on the amount fraction, and a significant offset was observed for methane free air. Most likely, this is due to the relatively small range covered by the standard gases used to calibrate the CRDS instruments, and the uncertainty of the calibration scale. Due to the small bias, no further action is required at present.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at HPB (GAW laboratory) started in 2010 using a CRDS instrument. At that time, measurements were made on a provisional basis in the GAW observatory, and were discontinued after the ICOS measurements commenced in 2015. Continuous data is available since 2015.

Instrumentation. Two Picarro G2401 CRDS analysers, one with and one without sample air drying.

Standards. Laboratory standards and target gases are available from the ICOS Flask and Calibration Laboratory (FCL). These standards have traceability to the current WMO/GAW calibration scales. Calibrations using the laboratory standards are made every 15 days.

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

The following equation characterizes the instrument bias. The result is further illustrated in Figure 11 and 12 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1670-CFKADS2120 (instrument without dryer):

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.25 µmol mol^{-1}) / 0.99923 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.006 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4b)

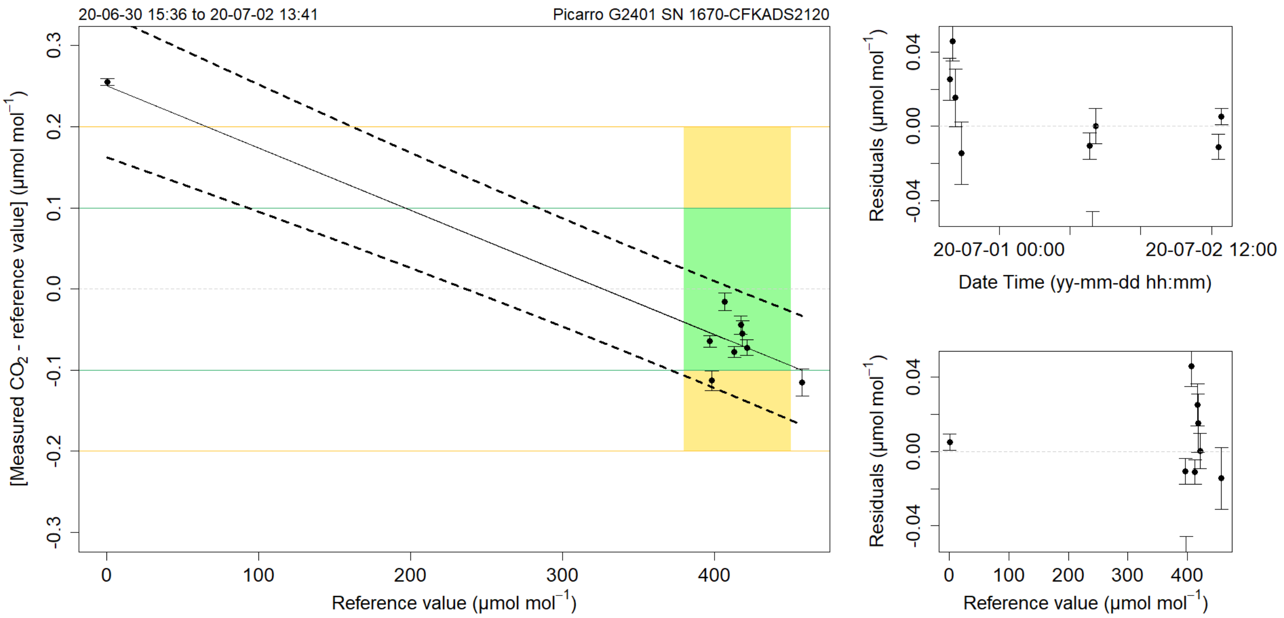

Figure 11. Left: Bias of the Picarro G2401 #1670-CFKADS2120 CO2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement 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 HPB. 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 #2322-CFKADS2192 (instrument with Nafion dryer):

Unbiased CO_2 mixing ratio: X_{CO2} (μmol mol^{-1}) = (CO_2 – 0.28 μmol mol^{-1}) / 0.99909 (4c)

Remaining standard uncertainty: u_{CO2} (μmol mol^{-1}) = sqrt (0.007 μmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4d)

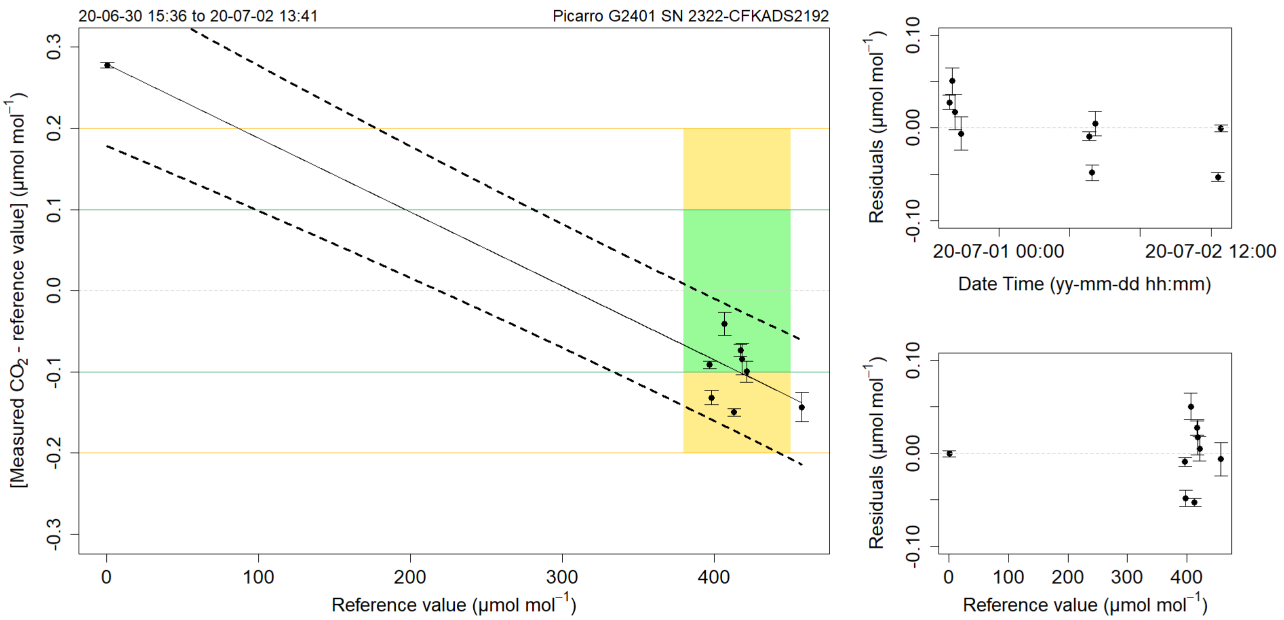

Figure 12. Same as above for the Picarro G2401 #2322-CFKADS2192 instrument.

The result of the comparison can be summarized as follows:

The ICOS CRDS instruments showed agreement within the WMO/GAW network compatibility goals (humid measurements) and the extended network compatibility goals (dry measurements). It is recommended to investigate if the slightly different performance of the two CRDS instruments is caused by the drying system. The bias further showed a mole fraction dependency and a significant zero offset. The reason for this is most likely a slightly different calibration strategy between WCC-Empa (calibrations are done with a set four reference standards and CO_2 free air), and ICOS (calibrations using a set of reference standards in the ambient mole fraction range), and a small remaining inconsistency in the WMO-X2007 calibration scale. Updating the calibrations to the new WMO-X2019 CO_2 calibration scale (Hall et al., 2020) will most likely reduce the bias.

Recommendation 8 (, important, 2021)**

It is recommended to update the data to the WMO-X2019 CO_2 calibration scale.

Nitrous Oxide Measurements

Continuous measurements of N_2O commenced in 2017 as part of the ICOS programme at the ICOS tower, and continuous time series are available since then.

Instrumentation. LGR 913-0015 (OA-ICOS) analyser (enhanced performance version).

Standards. Laboratory standards, working and target gases are available from the ICOS Flask and Calibration Laboratory (FCL). These standards have traceability to the current WMO/GAW calibration scales. Calibrations using the laboratory standards are made every 15 days, and the WS is measured every seven hours to correct for drift.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the HPB instrument with randomized nitrous oxide levels using WCC-Empa travelling standards. The following equations characterize the instrument bias, and the results are further illustrated in Figure 13 with respect to the WMO GAW DQOs (WMO, 2020):

LGR 913-0015 #US4300160200001043:

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 5.64) / 1.0168 (5a)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.04 + 1.01e-07 * X_{N2O}^2) (5b)

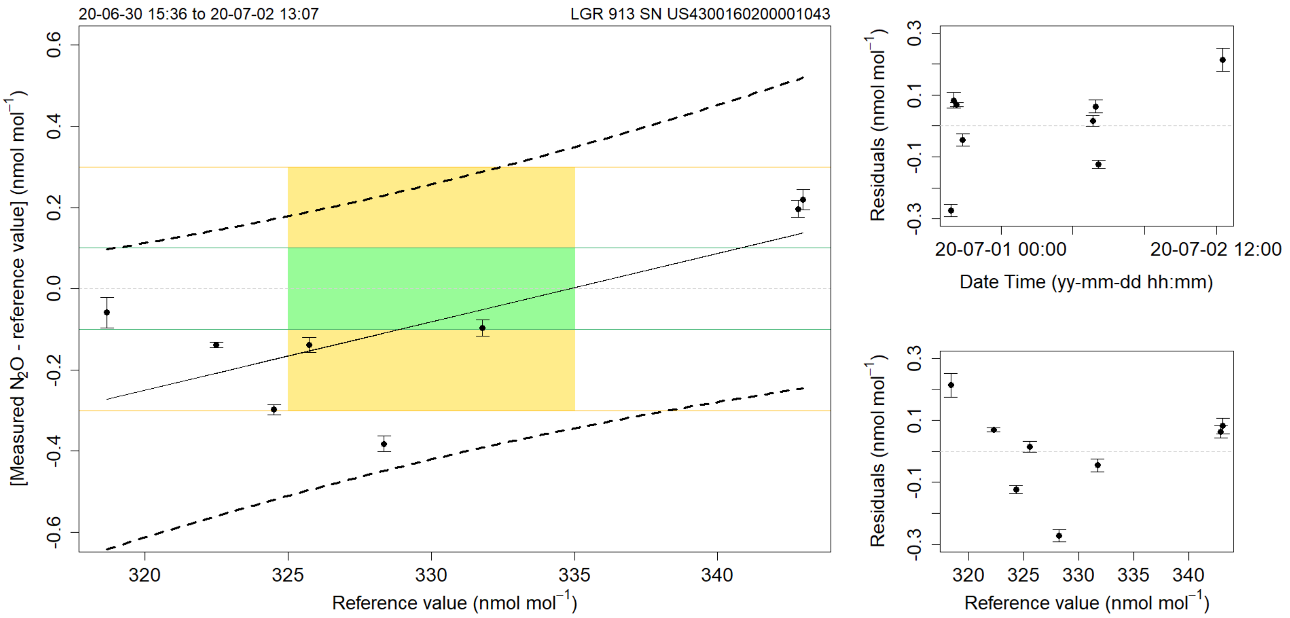

Figure 13. Left: Bias of the LGR 913-0015 nitrous oxide analyser with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for HPB. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The result of the comparison can be summarized as follows:

The average agreement between HPB and WCC-Empa was within the extended WMO/GAW network compatibility goals. Individual results showed a good repeatability, which confirms the functionality of the analytical system. The remaining bias is most likely dominated by the uncertainty of the reference standards, both from WCC-Empa and HPB. The analytical system is fully appropriate, and the limiting factor is most likely the uncertainty of the reference standards.

HPB PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the HPB performance audit to other station audits made by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO and N_2O, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions usually found in unpolluted air masses. For N_2O, the mole fraction range covers 10 ppb and depends on the time of the comparison due to the large annual increase combined with low variability (see Zellweger et al. (2019) for details). For surface ozone the mole fraction range of 0-100 ppb was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 14 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, while the results for CO, CH_4, CO_2 and N_2O (excluding two outliers) are shown in Figure 15. 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 HPB audit are shown as coloured dots in Figure 14 and 15, and are also summarized in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

The results were within the DQOs for CH_4 and one of the CRDS CO_2 instruments, and the extended WMO/GAW network compatibility goals were reached for the other CRDS CO_2, CO, and N_2O. The DQOs were not met for ozone measurements due to an uncorrected bias of the HPB ozone reference.

Table 1. HPB 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- 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	HPB within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]
O_3 (TEI 49C #56028-306)	0 -100	nmol mol^{-1}	✗	64	NA
O_3 (TEI 49i #632519672)	0 -100	nmol mol^{-1}	✗	64	NA
O_3 (TEI 49C-PS #423807729, initial)	0 -100	nmol mol^{-1}	✗	64	NA
O_3 (TEI 49C-PS #423807729, final)	0 -100	nmol mol^{-1}	✗	64	NA
CO (Aerolaser AL5001)	30 - 300	nmol mol^{-1}	✓ (green)	22	51
CO (Picarro G2401 CFKADS2120)	30 - 300	nmol mol^{-1}	✓ (orange)	22	51
CO (Picarro G2401 CFKADS2192)	30 - 300	nmol mol^{-1}	✓ (orange)	22	51
CO (LGR 913-0015)	30 - 300	nmol mol^{-1}	✓ (orange)	22	51
CH_4 (Picarro G2401 CFKADS2120)	1750 - 2100	nmol mol^{-1}	✓ (green)	70	93
CH_4 (Picarro G2401 CFKADS2192)	1750 - 2100	nmol mol^{-1}	✓ (green)	70	93
CO_2 (Picarro G2401 CFKADS2120)	380 - 450	µmol mol^{-1}	✓ (green)	40	67
CO_2 (Picarro G2401 CFKADS2192)	380 - 450	µmol mol^{-1}	✓ (orange)	40	67
N_2O (LGR 913-0015)	325 - 335	nmol mol^{-1}	✓ (orange)	2	36

[1] Percentage of stations within the eDQO and DQO

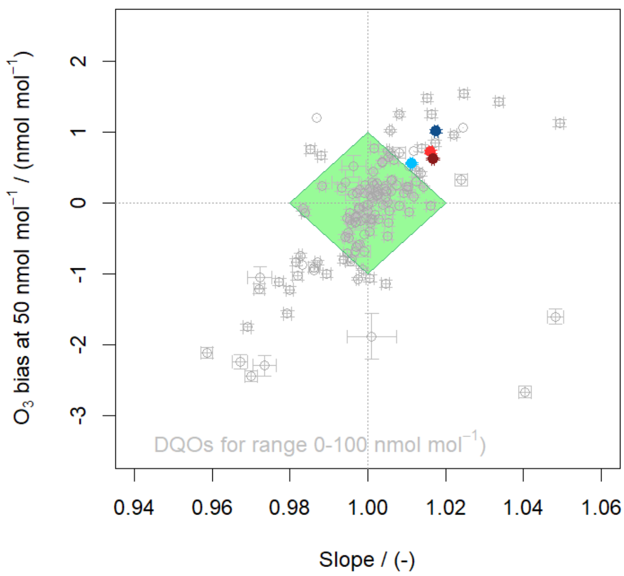

Figure 14. O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the results of the HPB instruments (red: TEI 49C #56028-306, dark red: TEI 49i #632519672, dark blue: TEI 49C-PS #423807729 with unadjusted pressure sensor, light blue: TEI 49C-PS #423807729 with adjusted pressure sensor). The green area corresponds to the WMO/GAW DQO for surface ozone.

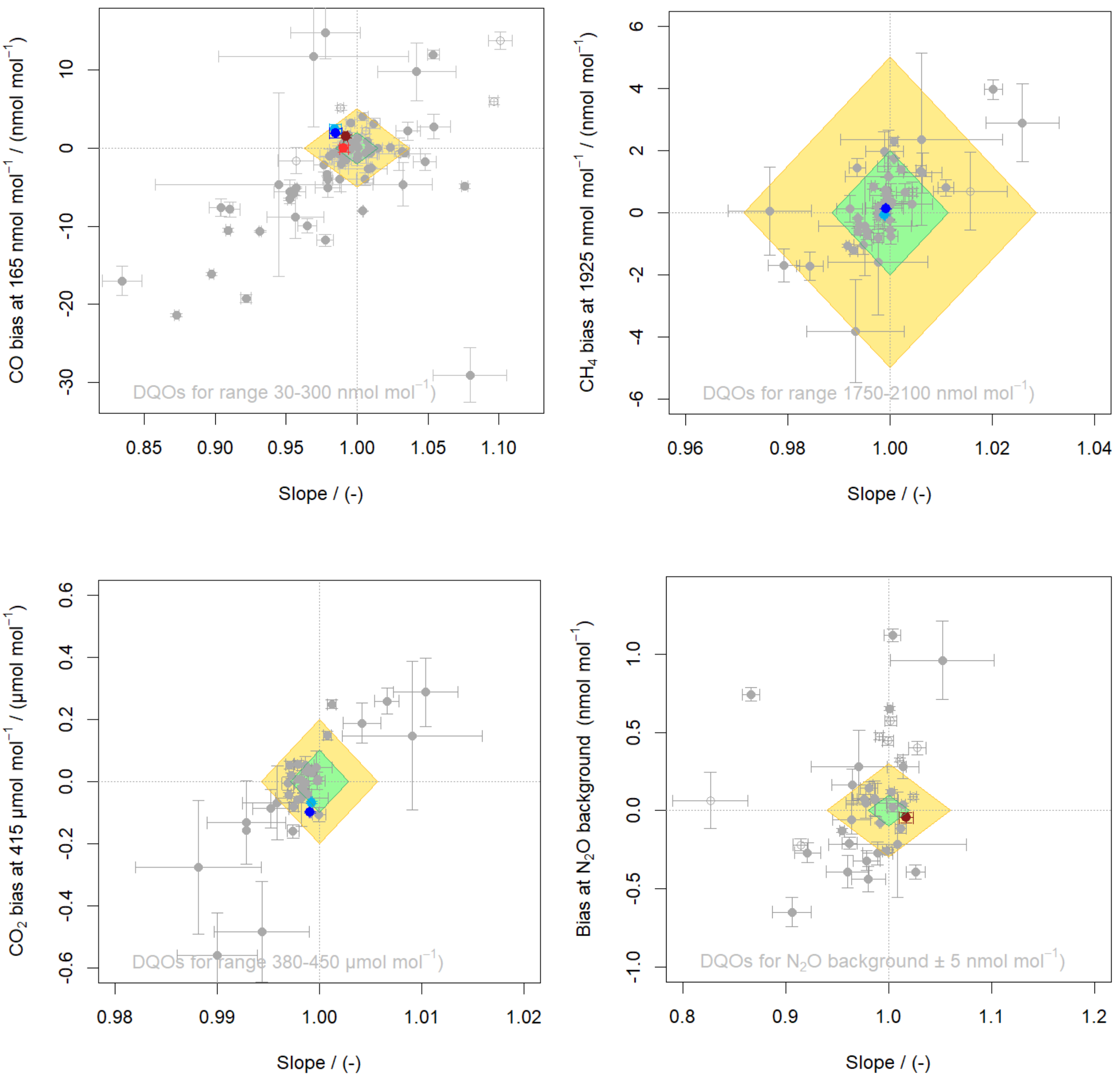

Figure 15. CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show HPB results (red: Aerolaser AL5001, light blue: Picarro G2401 #CFKADS2120, blue: Picarro G2401 #CFKADS2192, dark red: LGR 913-0015). 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 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 1 through 12 July 2020 at the ICOS tower, and then moved to the HPB GAW observatory until 4 August for the comparison with the Aerolaser CO system. The TI was connected to a separate independent inlet line sampling from the same location as the HPB analysers. At the ICOS tower, the TI only sampled air form the 131 m level. The TI was sampling air using the following sequence: 1445 min ambient air followed by 30 min measurement of three standard gases, each 10 min. The sample air was dried by a Nafion dryer (Model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum in the purge air flow. To account for the remaining effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The ICOS/HPB data shown here were processed by ICOS and HPB.

Carbon monoxide comparison with the Aerolaser instrument at the GAW observatory

Figure 16 shows the comparison of hourly CO measurements between the WCC-Empa TI and the HPB Aerolaser AL5001 analyser. The corresponding deviation histograms are shown in Figure 17.

The temporal variation was well captured by TI and the station analyser, and the agreement was on average within the WMO/GAW network compatibility goals, which confirms the results of the performance audit using travelling standards.

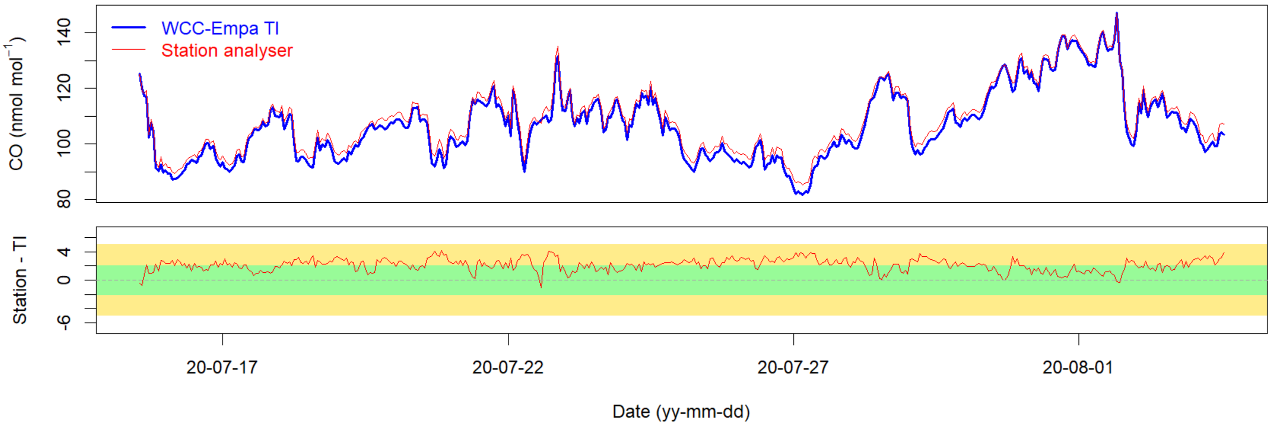

Figure 16. Comparison of the Aerolaser AL5001 analyser with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

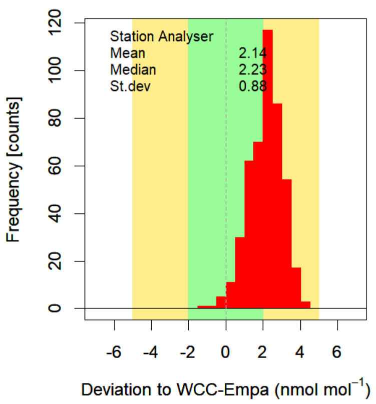

Figure 17. Carbon monoxide deviation histograms for the Aerolaser AL5001 analyser.

Carbon monoxide comparison at the ICOS tower

Figure 16 shows the comparison of hourly CO between the WCC-Empa TI and the Picarro G2401 and the LGR 913-0015 instruments. The TI was sampling from the 131 m level of the tower. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers at the 131 m level, which switched every 5 minutes between the three different sampling heights, and the WCC-Empa TI. The corresponding deviation histograms are shown in Figure 17.

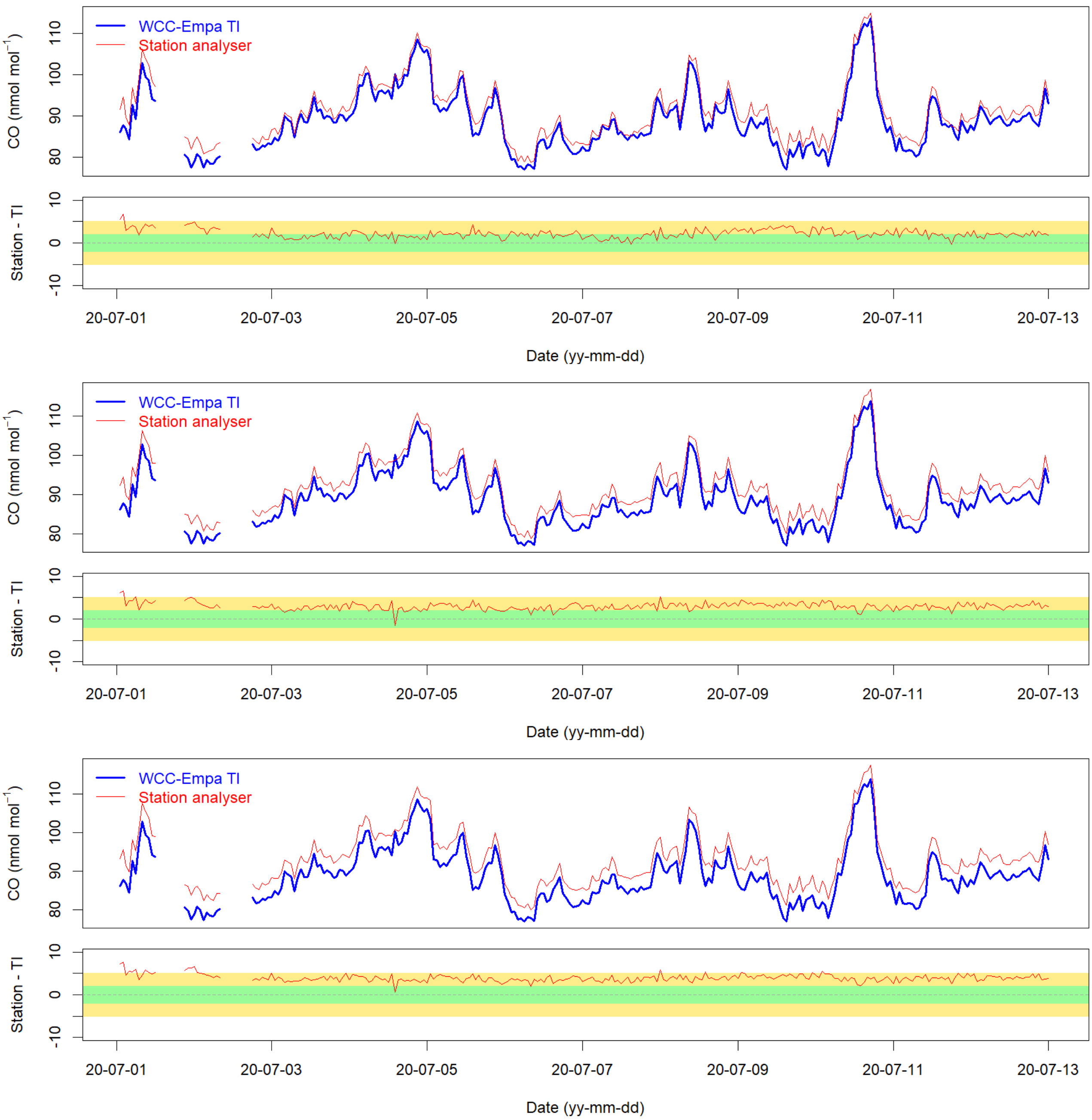

Figure 18. Comparison of the Picarro G2401#1670-CFKADS2120 (instrument without dryer) (top), the Picarro G2401#2322-CFKADS2192 (instrument with Nafion dryer) (middle) and the LGR 913-0015 (bottom) analysers with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

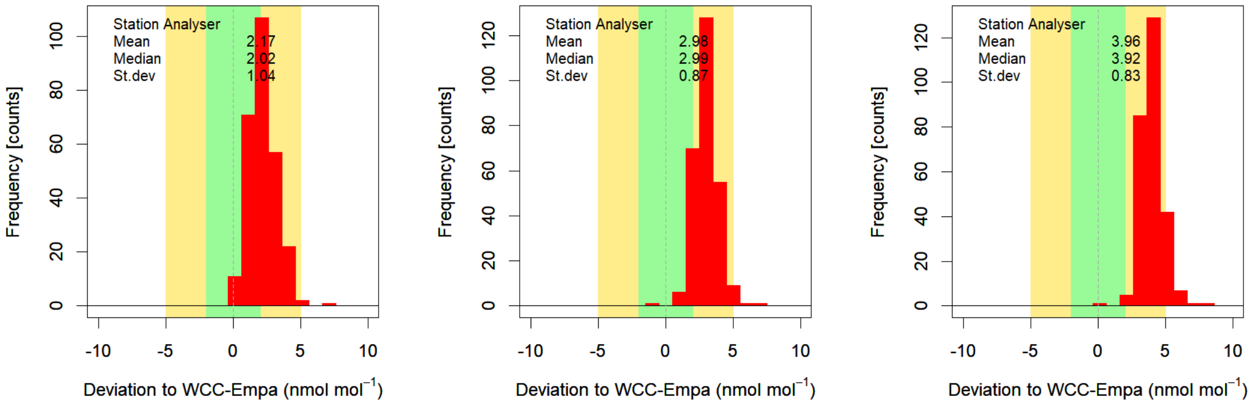

Figure 19. Carbon monoxide deviation histograms for the Picarro G2401#1670-CFKADS2120 (left), the Picarro G2401#2322-CFKADS2192 (middle) and the LGR 913-0015 (right).

On average, all ICOS CO analysers agreed within the extended WMO/GAW network compatibility goals with the TI. The deviation was similar to the one observed during the comparison of the travelling standards for the CRDS instrument, while the OA-ICOS analyser showed a slightly larger offset during the ambient air comparison. The reason for this should be explored.

Methane

Figure 20 shows the comparison of hourly CH_4 between the WCC-Empa TI and two Picarro instruments at the ICOS tower. The corresponding deviation histograms are shown in Figure 21. The TI was sampling from the 131 m level of the tower. 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 HPB instruments, which confirms the results of the performance audit using travelling standards. The temporal variation was well captured by both instruments.

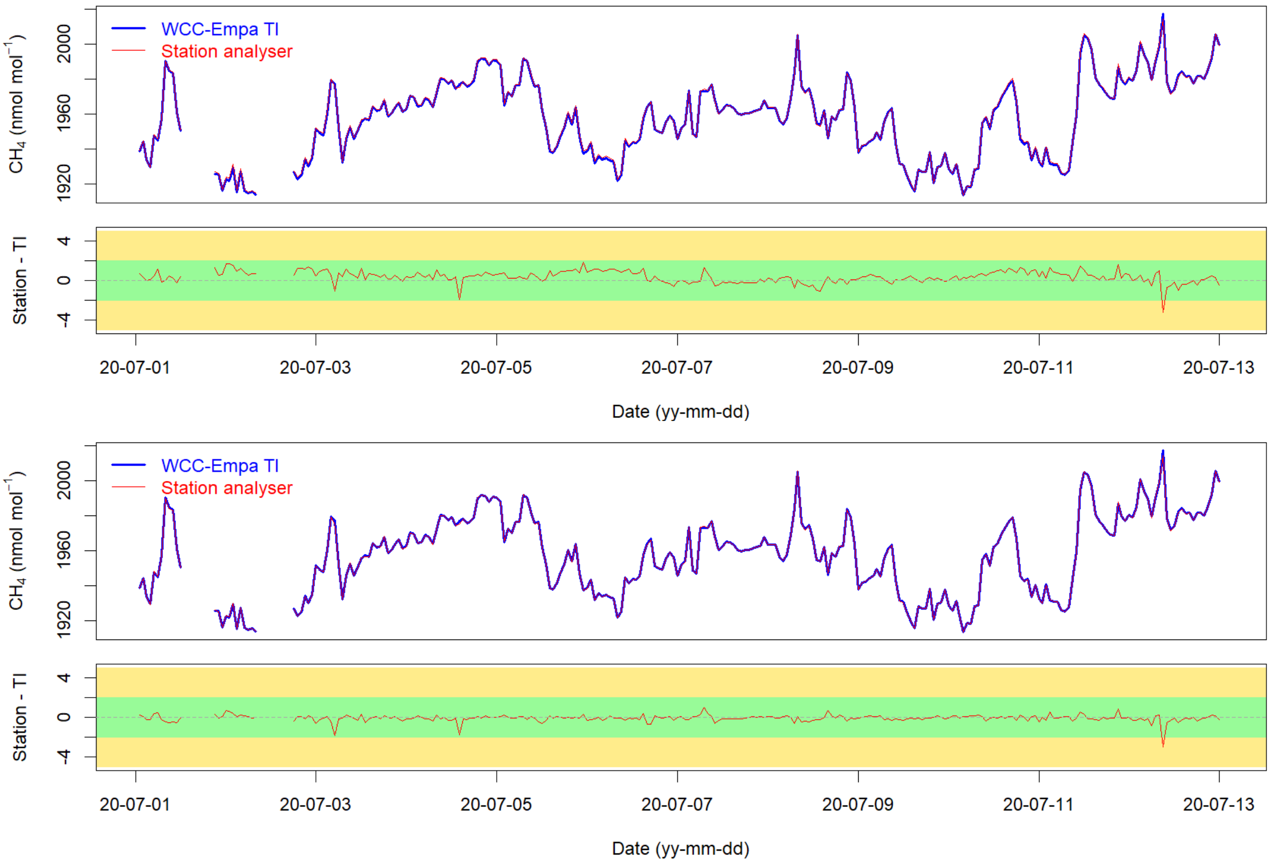

Figure 20. Comparison of the HPB Picarro G2401#1670-CFKADS2120 (top) and the Picarro G2401#2322-CFKADS2192 (bottom) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

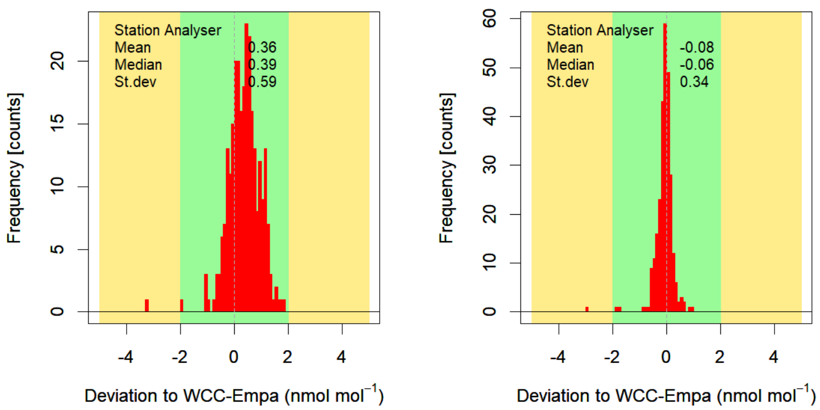

Figure 21. Methane deviation histogram for the HPB Picarro G2401 G2401#1670-CFKADS2120 (left) and the Picarro G2401#2322-CFKADS2192 (right).

Carbon dioxide

Figure 22 shows the comparison of hourly CO_2 between the WCC-Empa TI and the two ICOS/HPB Picarro, and Figure 23 shows the corresponding deviation histogram. The TI was sampling from the 131 m level of the tower. 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 is well captured by both instruments, and no dependency of the bias on the amount fraction was observed. On average, the agreement was within the WMO/GAW compatibility goal for the CRDS instrument without the Nafion dryer, and within the extended compatibility goal for the instrument with a dryer. These results are in agreement with the bias observed during the travelling standard comparison.

Figure 22. Comparison of the HPB Picarro G2401 G2401#1670-CFKADS2120 (top) and the Picarro G2401#2322-CFKADS2192 (bottom) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

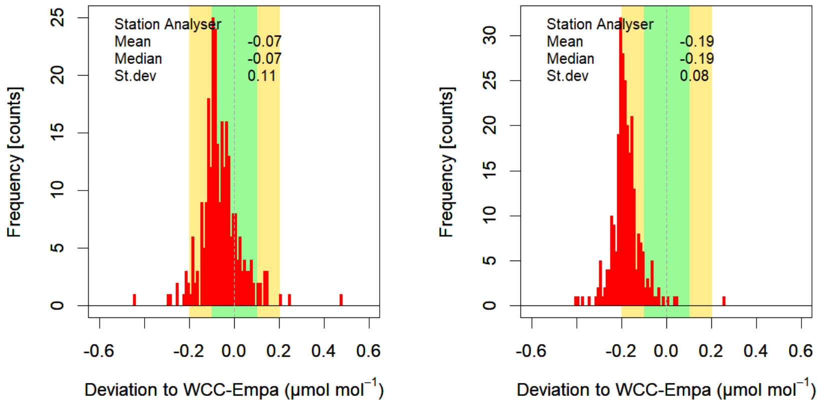

Figure 23. Carbon dioxide deviation histogram of the HPB Picarro G2041 G2401#1670-CFKADS2120 (left) and the Picarro G2401#2322-CFKADS2192 (right) compared to WCC-Empa.

CONCLUSIONS

The global GAW station Hohenpeissenberg 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, which makes it a very significant contribution to the GAW programme. The recent extension of the measurements by the greenhouse gas observations at the nearby tall tower as part of the ICOS network is a valuable addition to the already comprehensive measurement programme. Many parameters are redundantly measured using different instruments or analytical techniques, which enables internal comparison and strengthens the quality of the measurements.

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

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

Comparison type	O_3 (all instruments)	CO Aerolaser AL5001	CO Picarro G2401 CFKADS2120	CO Picarro G2401 CFKADS2120	CO LGR 913-0015	CH_4 Picarro G2401 CFKADS2120	CH_4 Picarro G2401 CFKADS2120	CO_2 Picarro G2401 CFKADS2120	CO_2 Picarro G2401 CFKADS2120	N_2O LGR 913-001
Audit with TS	(✓)	✓	✓	✓	✓	✓	✓	✓	✓	✓
Ambient air comparison	NA	✓	✓	✓	✓	✓	✓	✓	✓	NA

NA no ambient air comparisons were made for O_3 and N_2O

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

SUMMARY RANKING OF THE HOHENPEISSENBERG GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access.
Facilities		
Laboratory and office space	(5)	Fully adequate, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable and stable
General Management and Operation		
Organization	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2	(5)	State of the art instrumentation
CO Aerolaser AL5001	(4)	Adequate instrument, long-term support questionable
CO Picarro G2401	(4)	Adequate systems, drying recommended
CO LGR 913-0015	(5)	Adequate instrumentation
Standards		
O_3	(4)	Known bias to GAW reference should be corrected
CO, CO_2, CH_4, N_2O (ICOS)	(5)	Full traceability to the GAW reference through ICOS FCL
CO (GAW, Aerolaser)	(4)	Calibration with working standard
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(5)	Skilled staff, appropriate procedures
Data submission	(4)	All data submitted, partly with more than 2 years delay.

#0: inadequate thru 5: adequate.

Dübendorf, October 2021

Dr C. Zellweger
WCC-Empa

Dr M. Steinbacher
QA/SAC Switzerland

Dr B. Buchmann
Head of Department

APPENDIX

Data Review

The following figures show summary plots of HPB data accessed on 22 December 2020 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations. ICOS measurements at the tower are made at three sampling heights, which were submitted as independent data sets.

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

Surface ozone:

The individual data sets available from WDCRG are shown independently. In total, three different data sets were available.

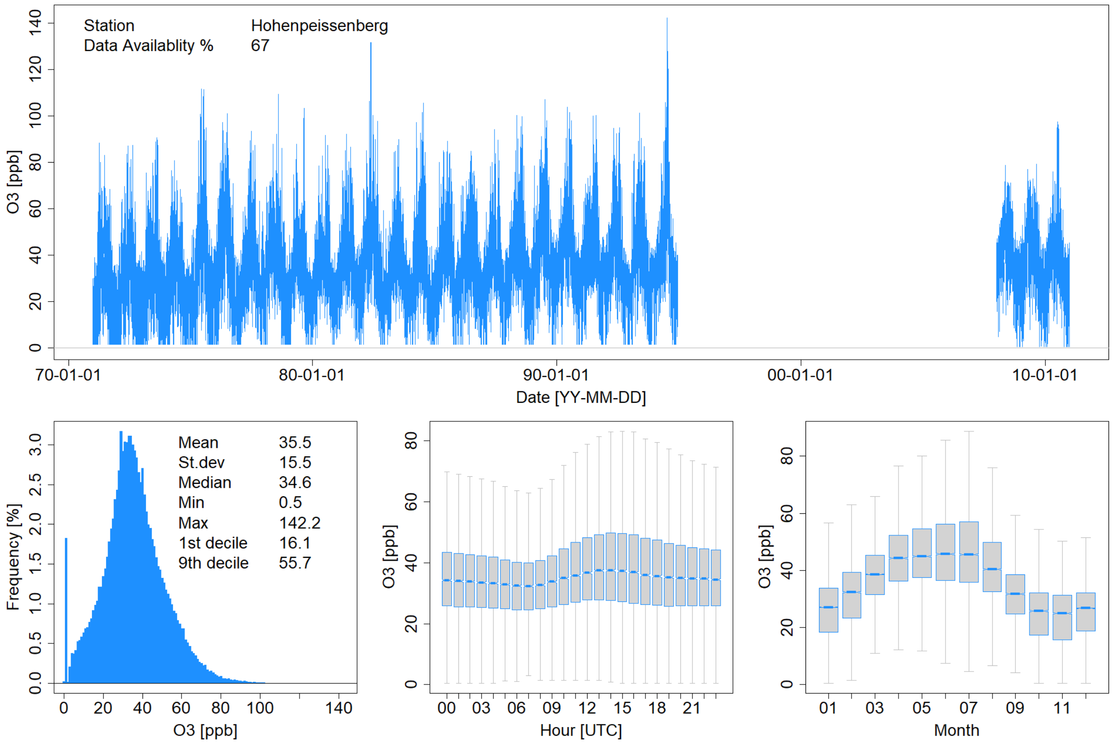

Figure 24. O_3 data for the period from 1971 to 2010 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

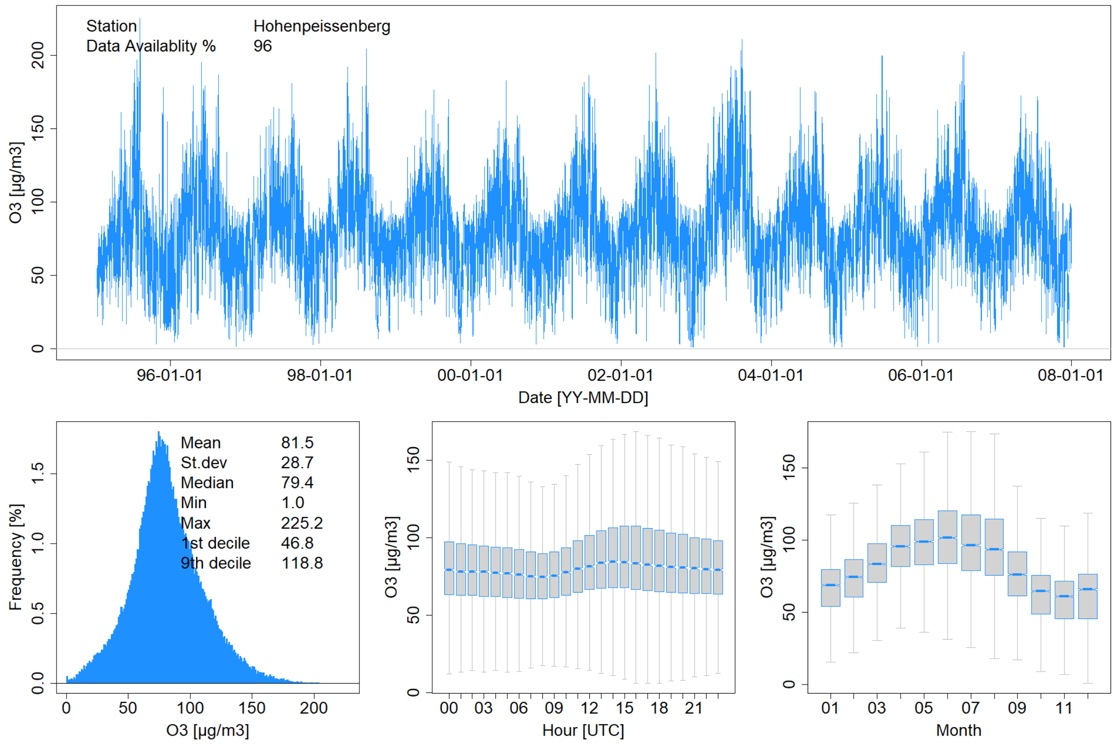

Figure 25. Same as above for the period 1995 to 2007.

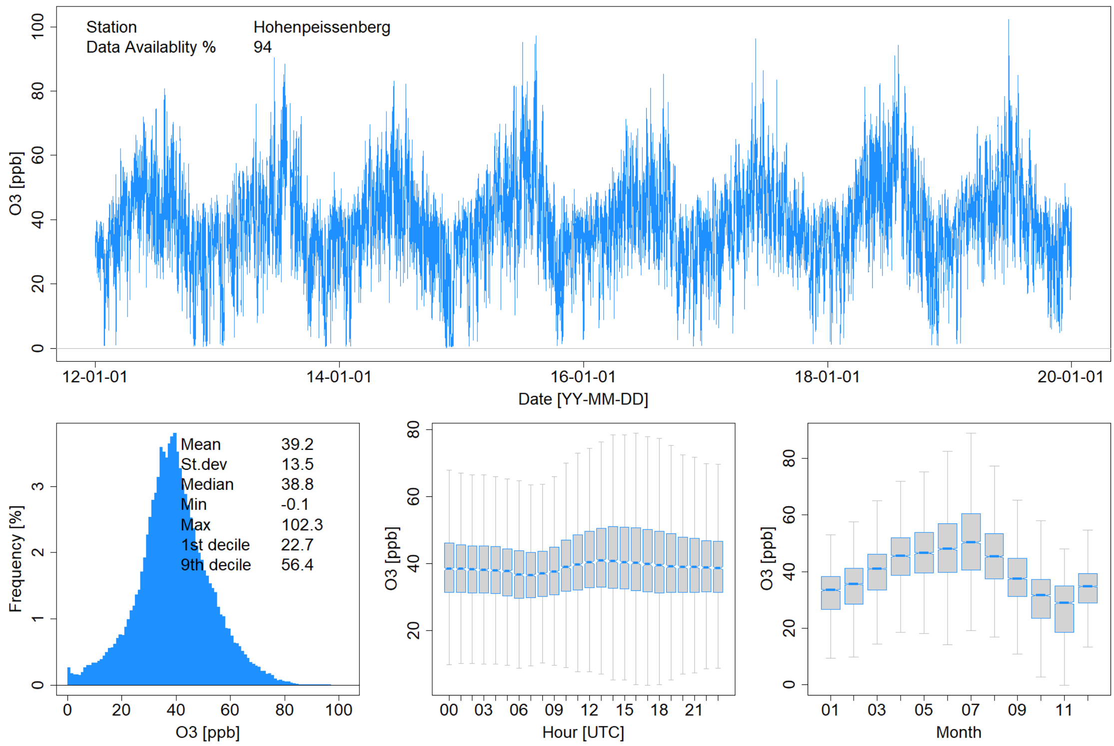

Figure 26. Same as above for the period 2012 to 2019.

- The data sets looks generally sound with respect to mole fraction, trend, seasonal and diurnal variation.
- The main difference between the two data sets is the frequency of measurements with zero ozone, which accounted approximately 2% for the first data set, and <0.2% for the second data set.

Carbon monoxide:

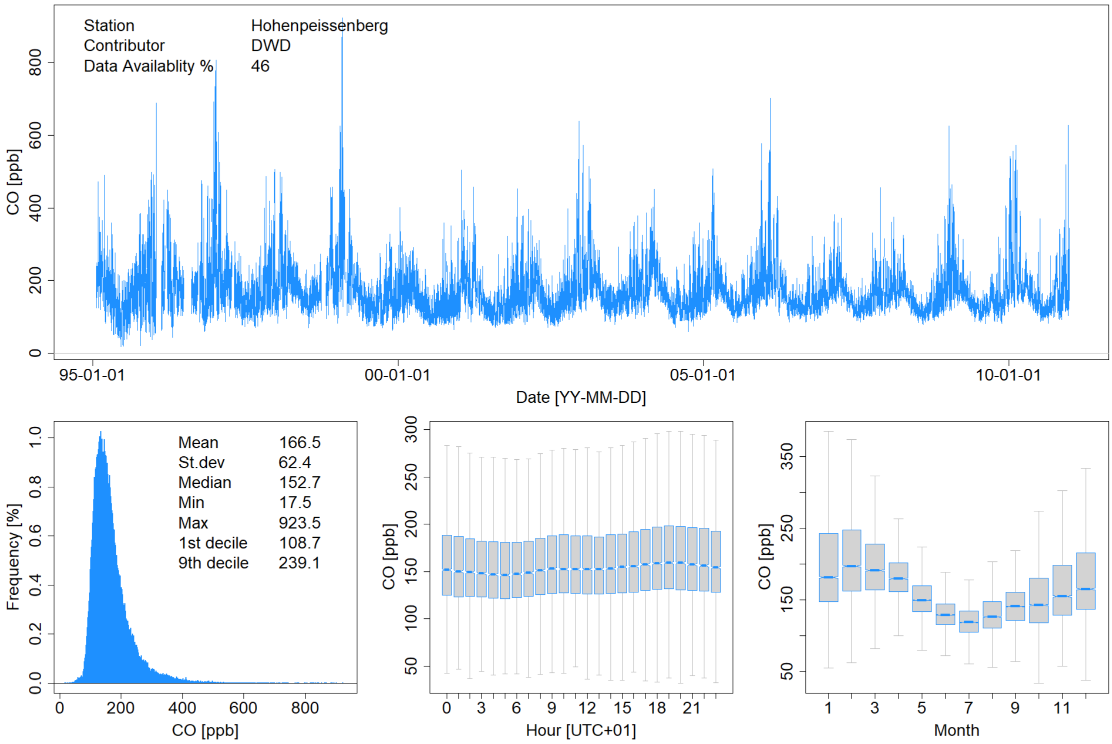

Figure 27. In-situ CO data submitted by DWD, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

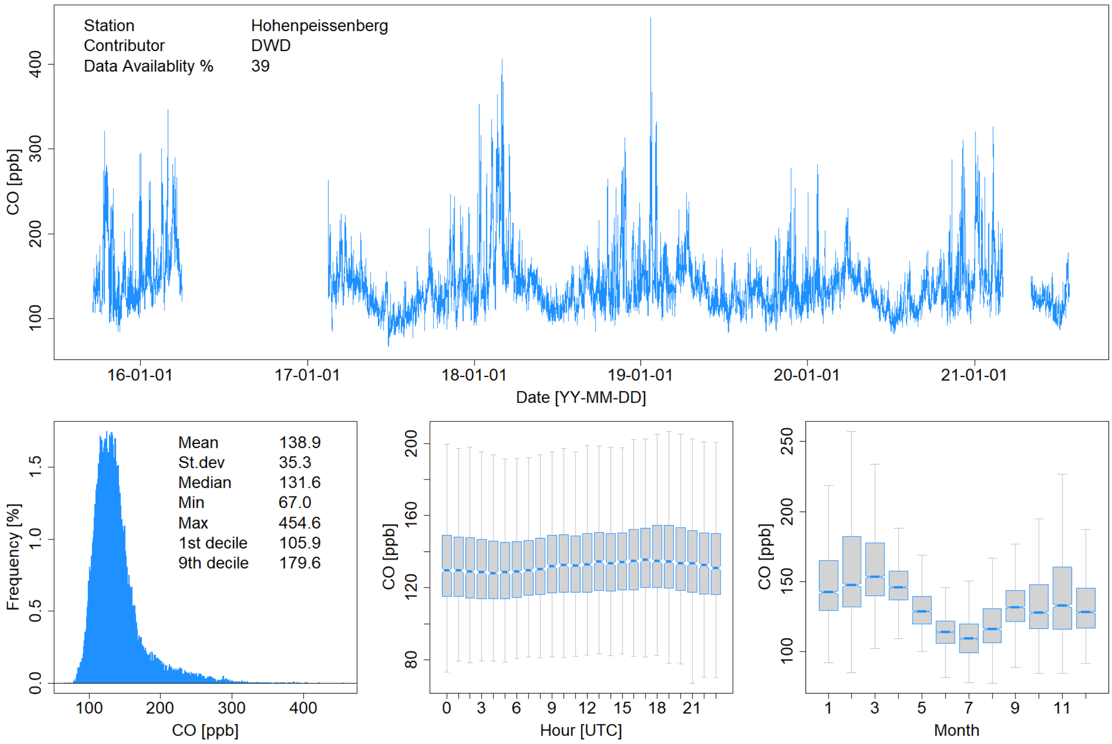

Figure 28. Same as above, for the ICOS instrument (until 2017-12-31 CRDS, afterwards OA-ICOS) sampling from the tower at the 50 m level.

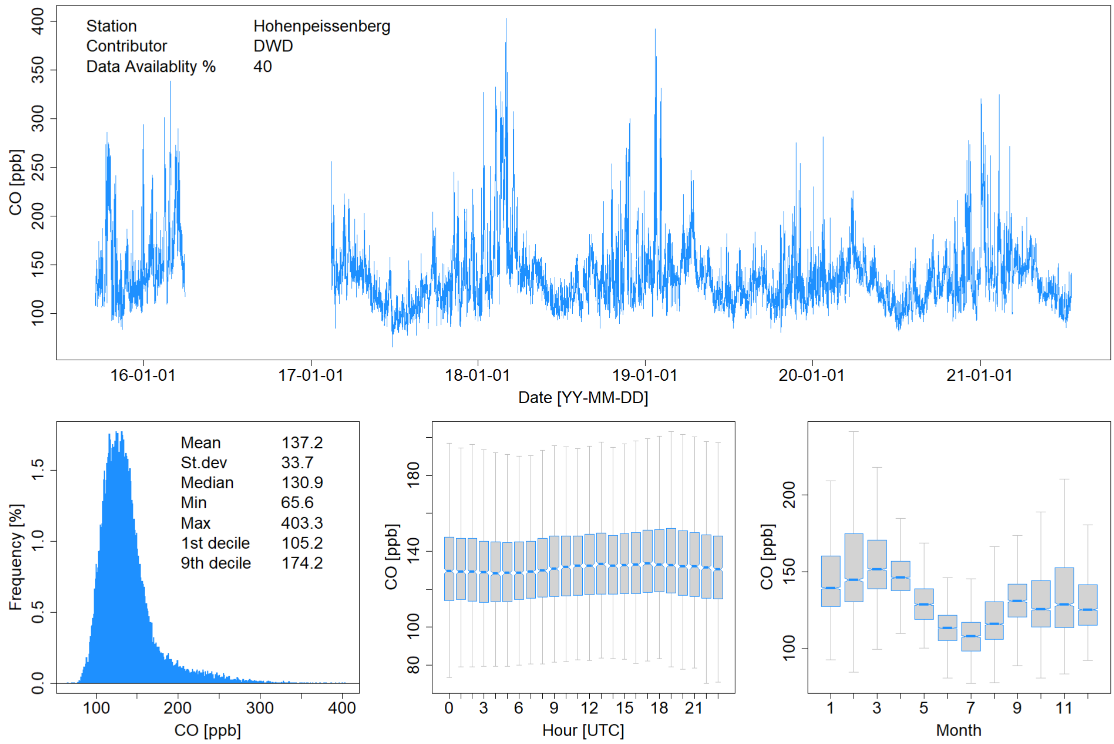

Figure 29. Same as above, for the ICOS instrument sampling from the tower at the 93 m level.

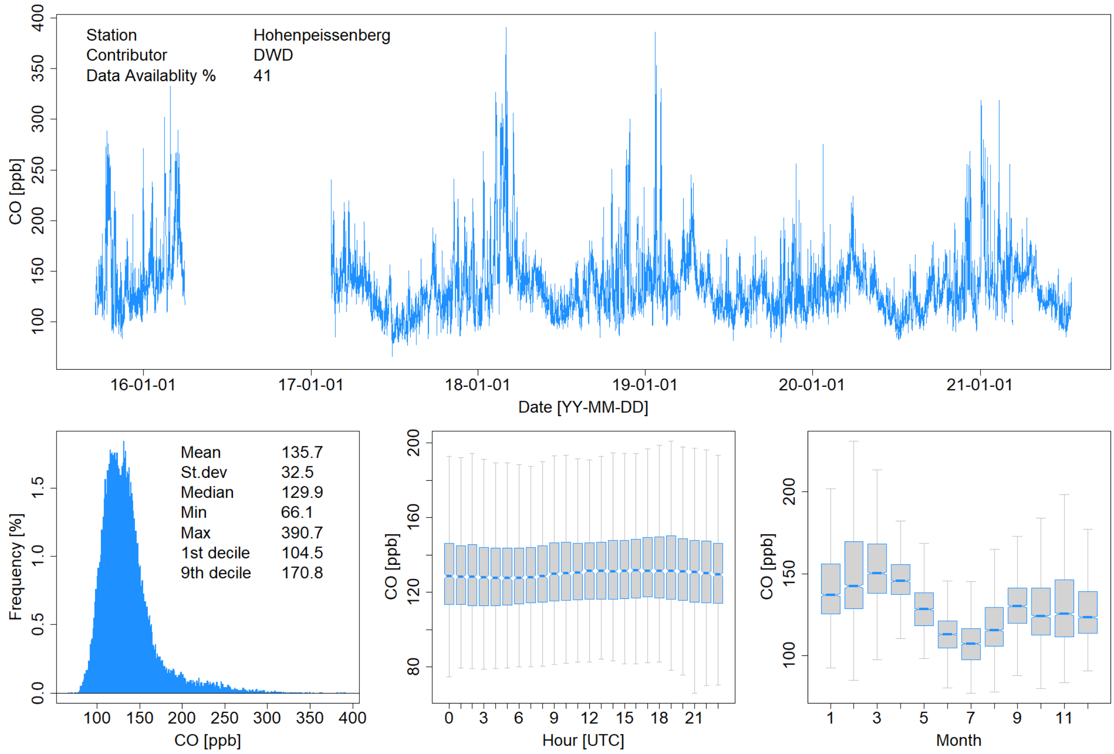

Figure 30. Same as above, for the ICOS instrument sampling from the tower at the 131 m level.

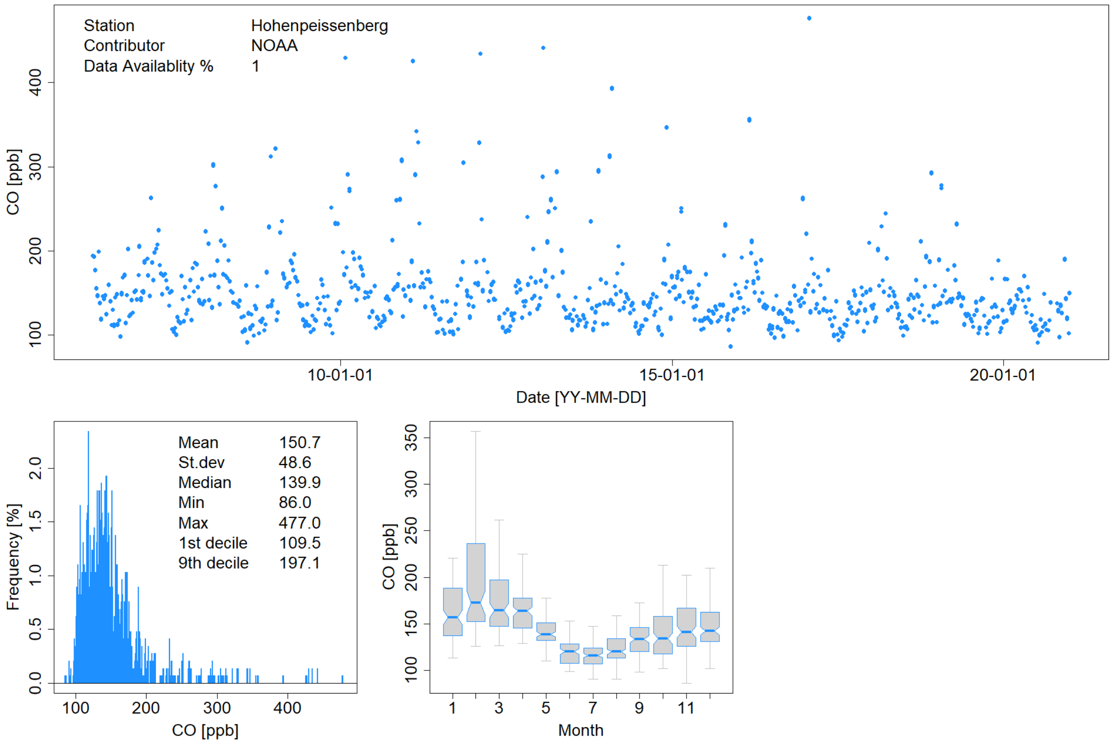

Figure 31. NOAA CO flask data submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

- All data sets (DWD, ICOS, and NOAA) look sound with respect to mole fraction, trend, seasonal and diurnal variation.

Methane:

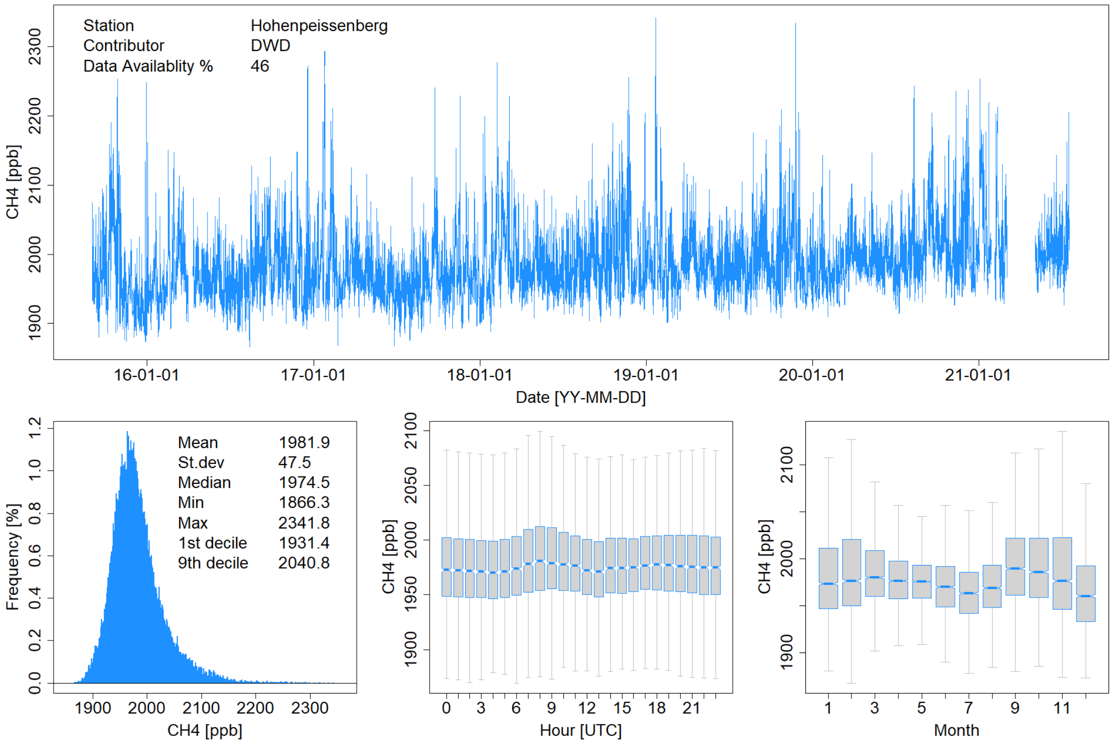

Figure 32. In-situ CH4 data (2015-2021) submitted by DWD from the tower at the 50 m level. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

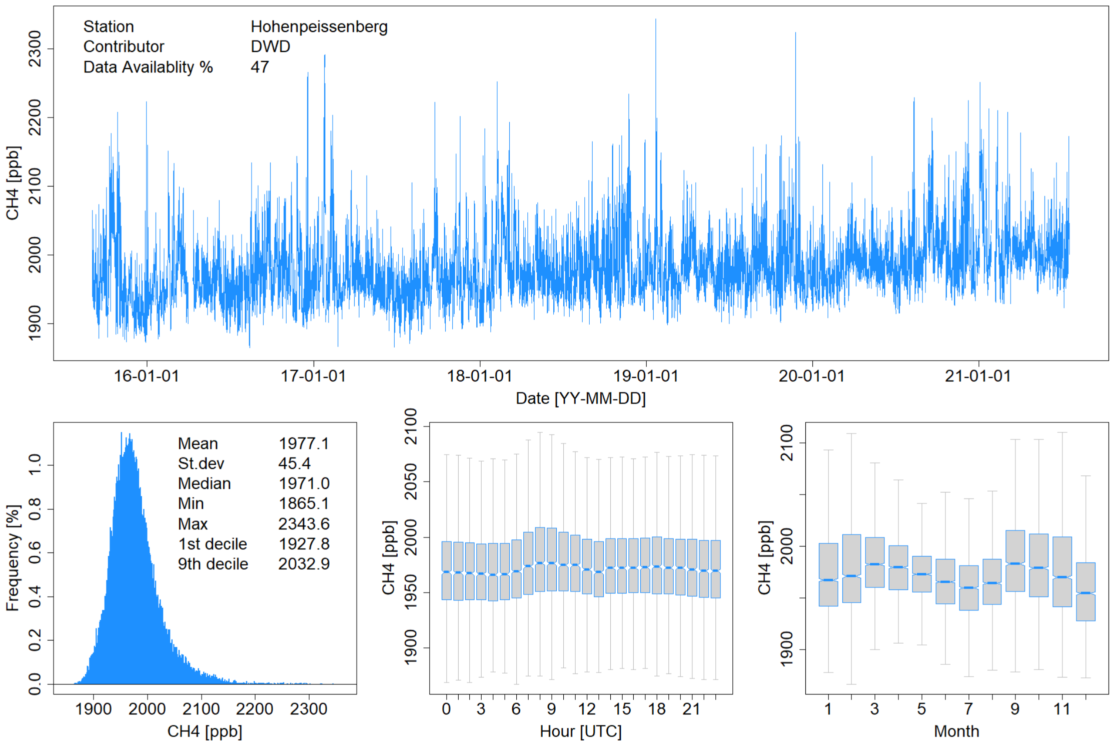

Figure 33. Same as above, for the 93 m level of the tower.

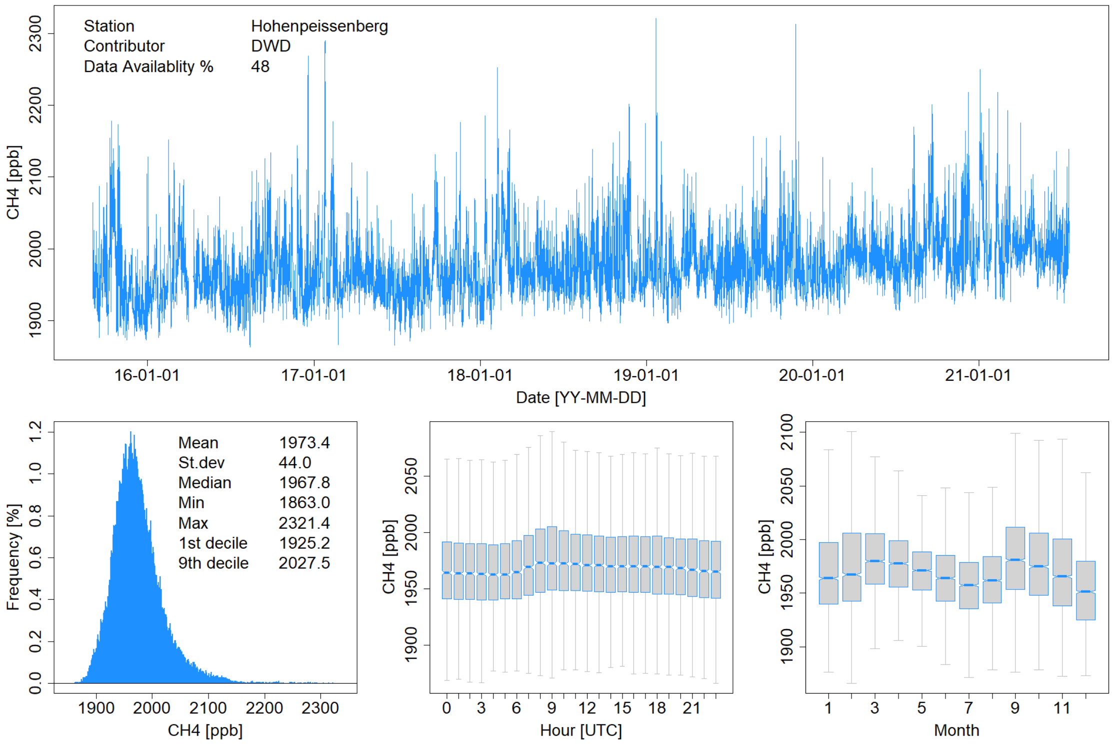

Figure 34. Same as above, for the 131 m level of the tower.

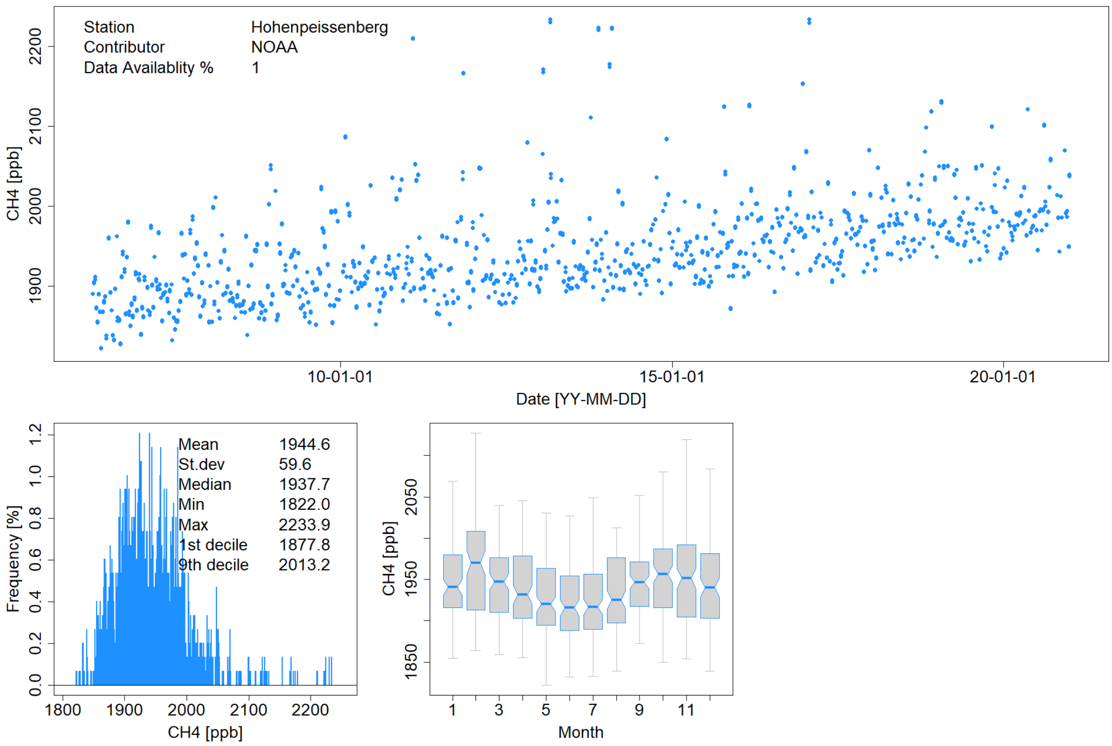

Figure 35. Flask CH4 data sampled at the GAW laboratory (2006-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

- All data looks generally sound. Continued comparisons of the data series is encouraged.

Carbon dioxide:

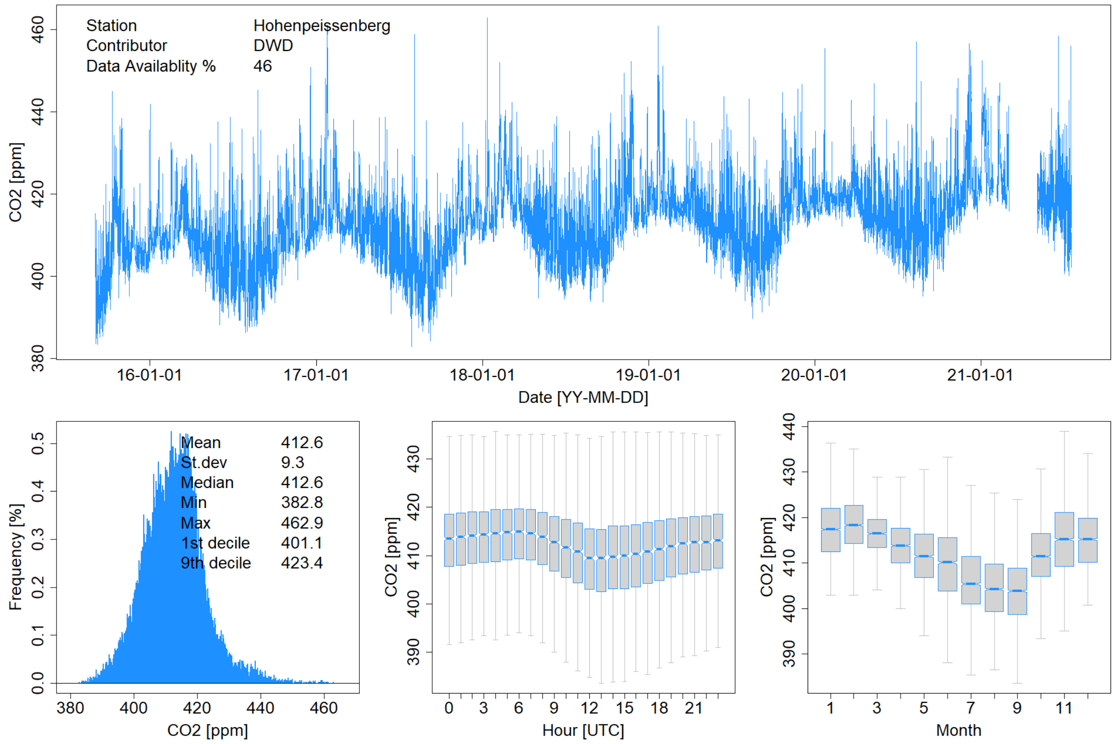

Figure 36. In-situ CO2 data (2015-2021) submitted by DWD from the tower at the 50 m level. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

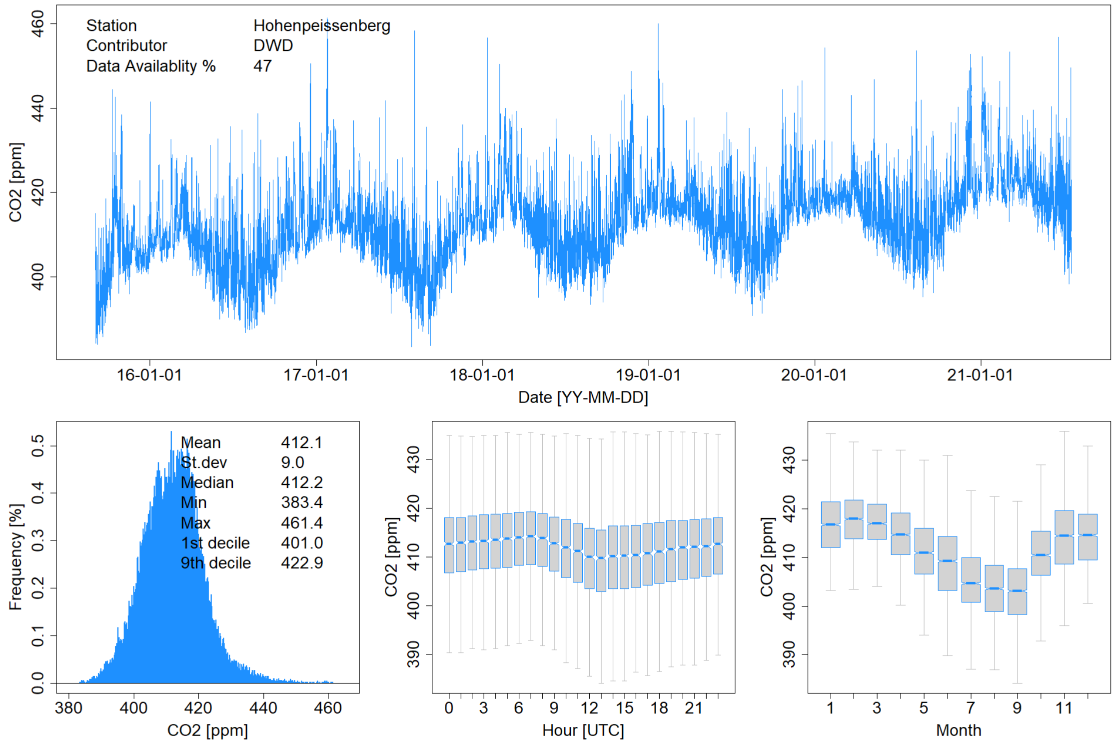

Figure 37. Same as above, for the 93 m level of the tower.

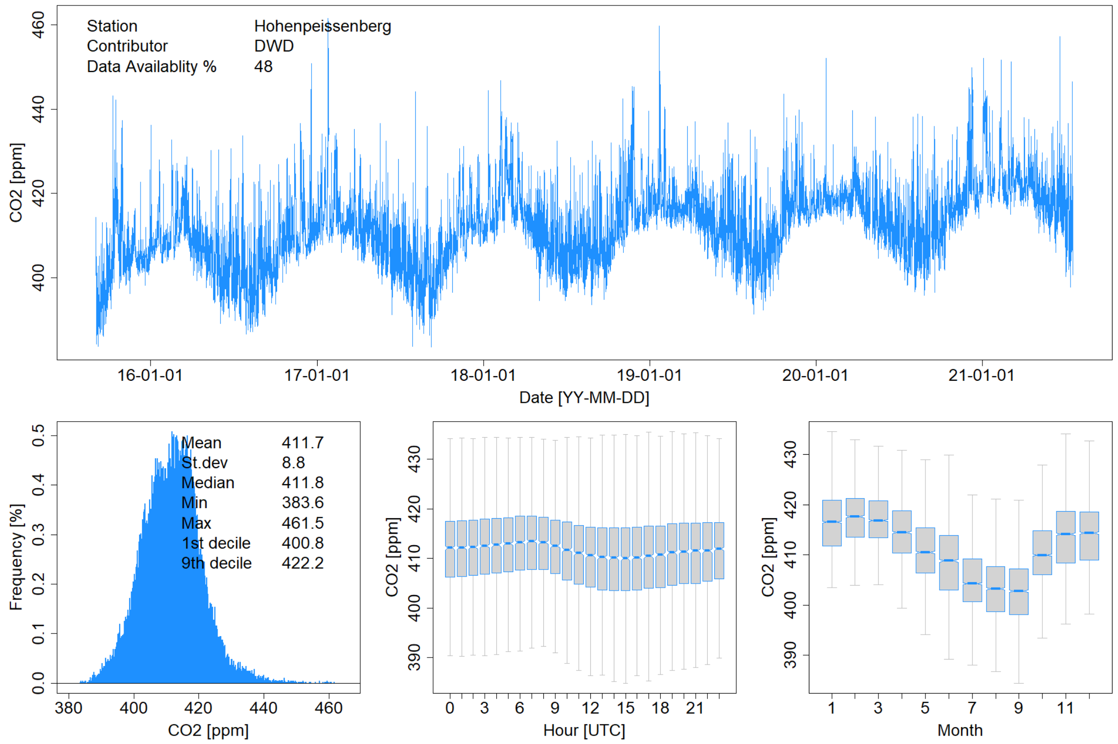

Figure 38. Same as above, for the 131 m level of the tower.

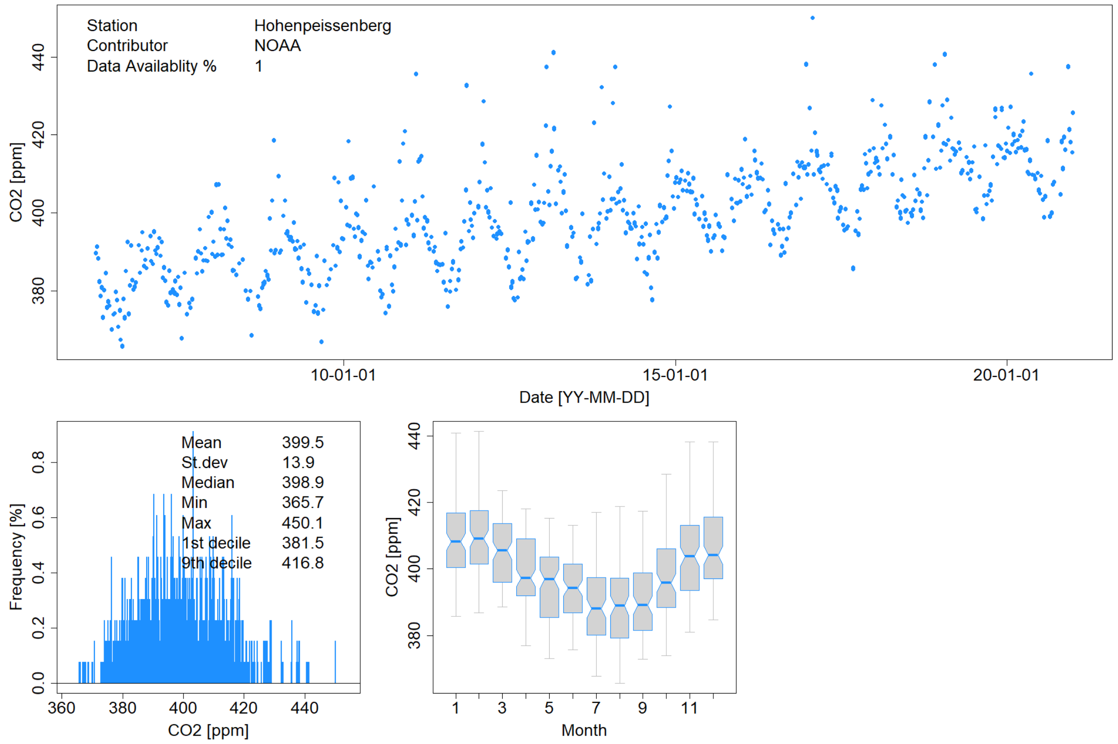

Figure 39. Flask CO2 data (2006-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

- All data sets look generally sound. Continued comparisons of the data series is encouraged.

Nitrous oxide:

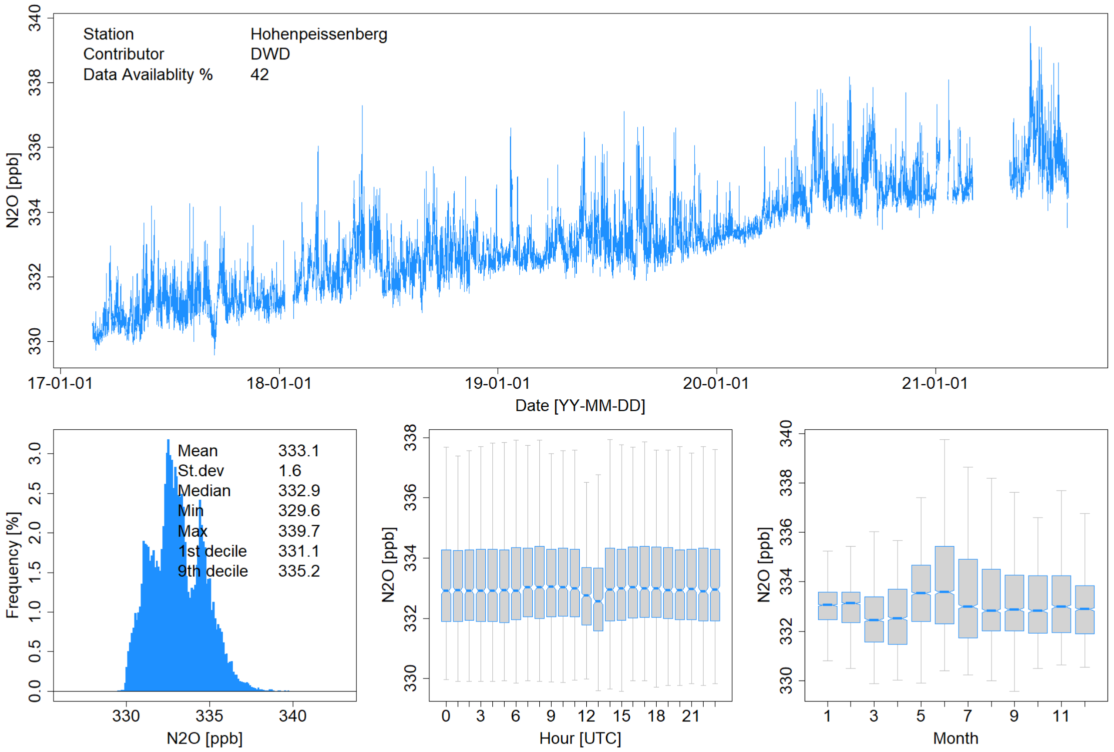

Figure 40. In-situ N2O data (2017-2021) submitted by DWD from the tower at the 50 m level. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

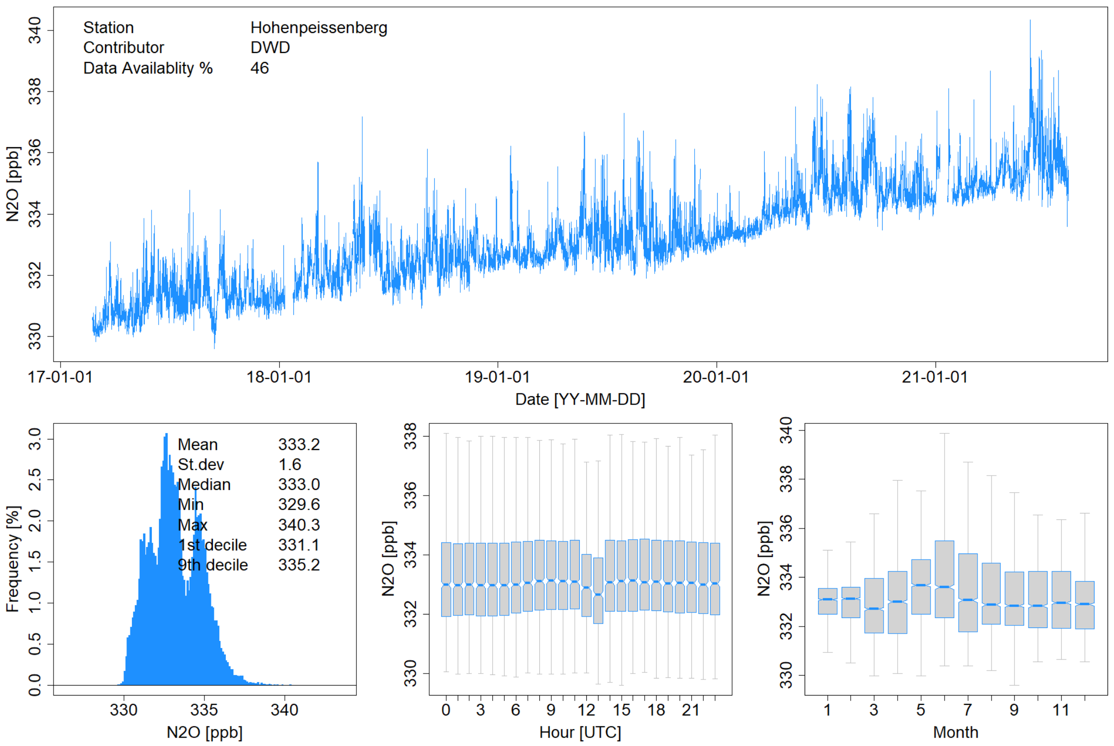

Figure 41. Same as above, for the 93 m level of the tower.

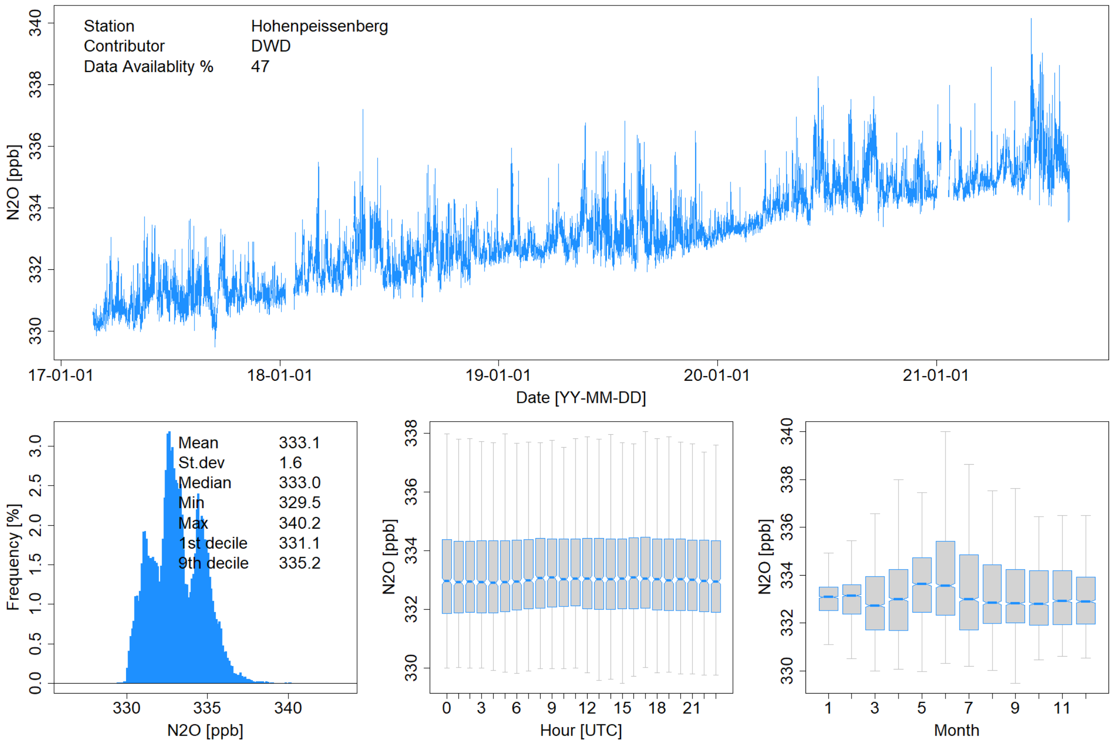

Figure 42. Same as above, for the 131 m level of the tower.

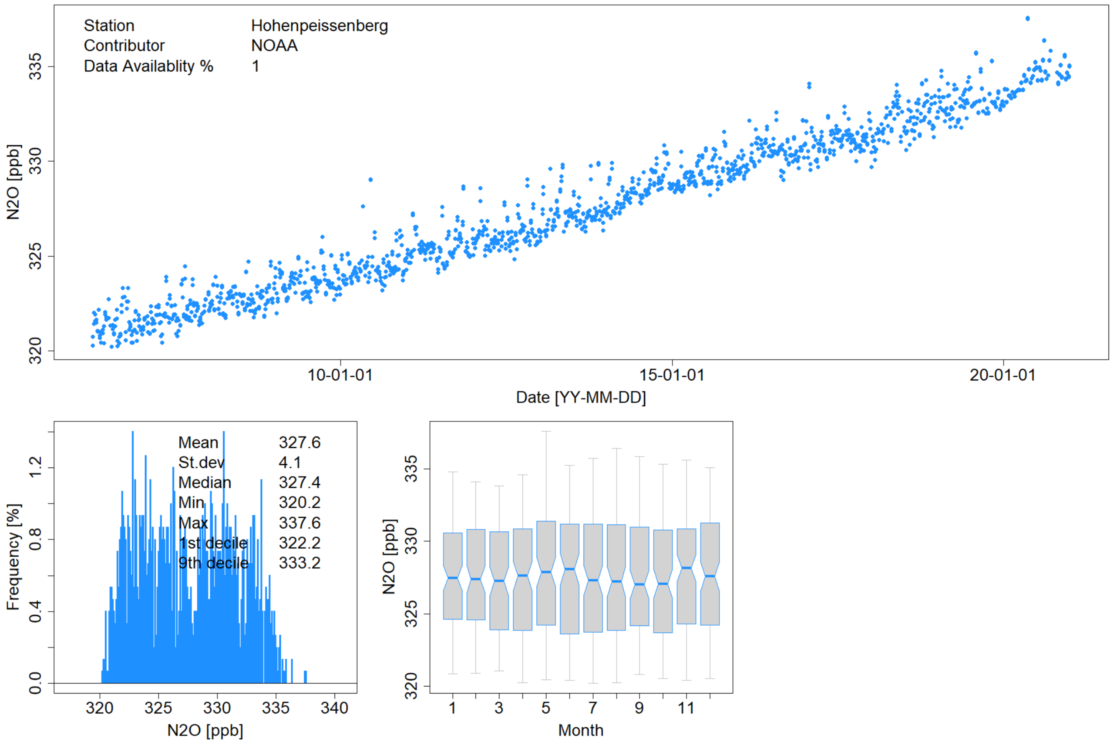

Figure 43. Flask N2O data (2006-2019) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

- The NOAA flask data set looks sound. Comparison with the in-situ data is encouraged.

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 randomized sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa and HPB data acquisition systems.

Table 3. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG -0.3, COEF 0.991
Pressure readings (hPa)	Ambient 903.4;TS 903.1, (no adjustment was made)
HPB analyser (OA)	
Model, S/N	Thermo Scientific 49C #56028-306
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG 0.0 nmol mol^{-1}, COEF 1.000
Pressure readings (hPa)	Ambient 901.8; OA 900.3 (no adjustment was made)
HPB analyser (OA)	
Model, S/N	Thermo Scientific 49i #632519672
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG 0.0 nmol mol^{-1}, COEF 1.000
Pressure readings (hPa)	Ambient 902.6; OA 903.3 (no adjustment was made)
HPB calibrator (OC)	
Model, S/N	Thermo Scientific 49C-PS #423807729
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	Initial comparison: BKG +0.0 nmol mol^{-1}, COEF 1.024 Final comparison: BKG +0.0 nmol mol^{-1}, COEF 1.024
Pressure readings (hPa)	Initial: Ambient 902.0; OC 895.9 (no adjustment was made during the initial comparison) Final: Ambient 901.4; OC 896.2 (adjusted to 901.4 for the final comparison)

Results

Each ozone level was applied for ten minutes, and the last five one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser values. The readings of the ozone analysers (OA) were also corrected based on calibrations with the HPB ozone reference. The same treatment as for ambient air analysis was applied.

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

Table 4. Five-minute aggregates computed from the last five of a total of ten one-minute values for the comparison of the HPB ozone analyser (OA) Thermo Scientific 49C #56028-306 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 (%)
2020-06-30 15:31	0.31	0.08	0.35	0.14	0.04	NA
2020-06-30 15:41	80.00	0.08	81.51	0.11	1.51	1.89
2020-06-30 15:51	59.90	0.23	61.41	1.26	1.51	2.52
2020-06-30 16:01	89.96	0.08	91.35	0.16	1.39	1.55
2020-06-30 16:11	19.90	0.10	20.06	0.10	0.16	0.80
2020-06-30 16:21	49.93	0.10	50.92	0.28	0.99	1.98
2020-06-30 16:31	70.00	0.09	70.99	0.29	0.99	1.41
2020-06-30 16:41	10.24	0.35	10.29	0.38	0.05	0.49
2020-06-30 16:51	39.93	0.06	40.49	0.21	0.56	1.40
2020-06-30 17:11	29.93	0.03	30.37	0.13	0.44	1.47
2020-06-30 17:21	0.33	0.06	0.16	0.17	-0.17	NA
2020-06-30 17:31	74.94	0.10	75.95	0.20	1.01	1.35
2020-06-30 17:41	175.03	0.07	177.65	0.18	2.62	1.50
2020-06-30 17:51	24.95	0.04	25.27	0.19	0.32	1.28
2020-06-30 18:01	125.02	0.06	127.02	0.21	2.00	1.60
2020-06-30 18:11	200.04	0.05	203.45	0.24	3.41	1.70
2020-06-30 18:21	150.02	0.08	152.45	0.21	2.43	1.62
2020-06-30 18:31	0.10	0.11	0.19	0.14	0.09	NA
2020-06-30 18:41	39.96	0.04	40.54	0.17	0.58	1.45
2020-06-30 18:51	10.53	0.66	10.73	0.76	0.20	1.90
2020-06-30 19:01	80.00	0.05	81.22	0.20	1.22	1.52
2020-06-30 19:11	19.95	0.10	20.39	0.07	0.44	2.21
2020-06-30 19:21	59.94	0.07	60.83	0.19	0.89	1.48
2020-06-30 19:31	89.91	0.13	91.18	0.27	1.27	1.41
2020-06-30 19:41	29.95	0.15	30.46	0.12	0.51	1.70
2020-06-30 19:51	69.93	0.06	71.03	0.33	1.10	1.57
2020-06-30 20:01	49.94	0.08	50.64	0.28	0.70	1.40
2020-06-30 20:11	0.21	0.11	0.27	0.27	0.06	NA
2020-06-30 20:21	79.94	0.06	81.03	0.23	1.09	1.36
2020-06-30 20:31	59.94	0.08	60.81	0.03	0.87	1.45
2020-06-30 20:41	89.95	0.08	91.15	0.11	1.20	1.33
2020-06-30 20:51	19.92	0.10	20.14	0.24	0.22	1.10
2020-06-30 21:01	49.92	0.10	50.67	0.28	0.75	1.50

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 (%)
2020-06-30 21:11	69.99	0.04	70.75	0.25	0.76	1.09
2020-06-30 21:21	10.81	0.30	10.73	0.34	-0.08	-0.74
2020-06-30 21:31	39.94	0.04	40.39	0.28	0.45	1.13
2020-06-30 21:51	29.92	0.13	30.35	0.17	0.43	1.44
2020-06-30 22:01	0.20	0.15	0.32	0.21	0.12	NA
2020-06-30 22:11	74.96	0.06	76.05	0.15	1.09	1.45
2020-06-30 22:21	175.07	0.16	177.60	0.28	2.53	1.45
2020-06-30 22:31	24.90	0.10	25.05	0.14	0.15	0.60
2020-06-30 22:41	124.96	0.05	126.81	0.14	1.85	1.48
2020-06-30 22:51	200.11	0.04	203.16	0.19	3.05	1.52
2020-06-30 23:01	150.01	0.07	152.32	0.19	2.31	1.54
2020-06-30 23:11	0.11	0.08	0.06	0.15	-0.05	NA
2020-06-30 23:21	39.91	0.07	40.53	0.24	0.62	1.55
2020-06-30 23:31	10.30	0.57	10.52	0.69	0.22	2.14
2020-06-30 23:41	79.96	0.06	81.30	0.25	1.34	1.68
2020-06-30 23:51	20.06	0.56	20.28	0.69	0.22	1.10
2020-07-01 00:01	59.95	0.11	60.78	0.19	0.83	1.38
2020-07-01 00:11	89.95	0.11	91.25	0.16	1.30	1.45
2020-07-01 00:21	29.90	0.08	30.30	0.15	0.40	1.34
2020-07-01 00:31	69.94	0.07	70.89	0.16	0.95	1.36
2020-07-01 00:41	49.94	0.09	50.63	0.20	0.69	1.38
2020-07-01 02:41	0.28	0.11	0.12	0.11	-0.16	NA
2020-07-01 02:51	74.95	0.09	76.05	0.07	1.10	1.47
2020-07-01 03:01	175.07	0.08	177.88	0.30	2.81	1.61
2020-07-01 03:11	24.89	0.08	25.24	0.12	0.35	1.41
2020-07-01 03:21	124.98	0.05	126.83	0.25	1.85	1.48
2020-07-01 03:31	200.06	0.11	203.21	0.25	3.15	1.57
2020-07-01 03:41	150.00	0.03	152.38	0.10	2.38	1.59
2020-07-01 03:51	0.26	0.17	0.15	0.12	-0.11	NA
2020-07-01 04:01	39.93	0.08	40.35	0.33	0.42	1.05
2020-07-01 04:11	10.09	0.21	10.07	0.27	-0.02	-0.20
2020-07-01 04:21	79.92	0.05	81.13	0.24	1.21	1.51
2020-07-01 04:31	20.04	0.42	20.44	0.69	0.40	2.00
2020-07-01 04:41	59.96	0.07	60.82	0.19	0.86	1.43
2020-07-01 04:51	89.98	0.07	91.28	0.16	1.30	1.44
2020-07-01 05:01	29.92	0.08	30.32	0.17	0.40	1.34
2020-07-01 05:11	69.95	0.05	70.94	0.19	0.99	1.42
2020-07-01 05:21	49.94	0.08	50.50	0.18	0.56	1.12
2020-07-01 07:21	0.29	0.11	0.05	0.17	-0.24	NA
2020-07-01 07:31	74.96	0.07	76.01	0.13	1.05	1.40
2020-07-01 07:41	175.01	0.09	177.91	0.12	2.90	1.66

Table 5. Five-minute aggregates computed from the last five of a total of ten one-minute values for the comparison of the old HPB ozone analyser (OA) Thermo Scientific 49i # 632519672 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 (%)
2020-07-01 10:48	0.27	0.15	0.00	0.19	-0.27	NA
2020-07-01 10:58	79.89	0.05	81.17	0.35	1.28	1.60
2020-07-01 11:08	59.96	0.07	60.71	0.28	0.75	1.25
2020-07-01 11:18	90.03	0.09	91.20	0.25	1.17	1.30
2020-07-01 11:28	19.91	0.11	20.20	0.27	0.29	1.46
2020-07-01 11:38	49.94	0.10	50.65	0.29	0.71	1.42
2020-07-01 11:48	69.97	0.06	70.85	0.27	0.88	1.26
2020-07-01 11:58	9.86	0.08	9.74	0.21	-0.12	-1.22
2020-07-01 12:08	39.91	0.05	40.40	0.43	0.49	1.23
2020-07-01 12:28	29.96	0.03	30.37	0.32	0.41	1.37
2020-07-01 12:38	0.26	0.14	0.09	0.24	-0.17	NA
2020-07-01 12:48	74.95	0.04	75.91	0.15	0.96	1.28
2020-07-01 12:58	175.08	0.09	177.53	0.24	2.45	1.40
2020-07-01 13:08	24.87	0.03	25.18	0.24	0.31	1.25
2020-07-01 13:18	125.04	0.11	126.85	0.16	1.81	1.45
2020-07-01 13:28	200.07	0.07	203.43	0.21	3.36	1.68
2020-07-01 13:38	150.03	0.07	152.19	0.50	2.16	1.44
2020-07-01 13:48	0.24	0.09	0.15	0.08	-0.09	NA
2020-07-01 13:58	39.91	0.10	40.32	0.28	0.41	1.03
2020-07-01 14:08	10.22	0.32	10.08	0.43	-0.14	-1.37
2020-07-01 14:18	79.89	0.11	80.86	0.31	0.97	1.21
2020-07-01 14:28	19.95	0.09	20.24	0.28	0.29	1.45
2020-07-01 14:38	59.97	0.07	60.74	0.15	0.77	1.28
2020-07-01 14:48	89.98	0.07	91.31	0.21	1.33	1.48
2020-07-01 14:58	29.88	0.09	29.93	0.18	0.05	0.17
2020-07-01 15:08	69.94	0.04	70.76	0.28	0.82	1.17
2020-07-01 15:18	49.93	0.10	50.60	0.30	0.67	1.34
2020-07-01 15:28	0.27	0.18	0.03	0.24	-0.24	NA
2020-07-01 15:38	79.92	0.06	80.72	0.13	0.80	1.00
2020-07-01 15:48	59.99	0.06	60.81	0.24	0.82	1.37
2020-07-01 15:58	89.92	0.05	91.31	0.27	1.39	1.55
2020-07-01 16:08	19.94	0.12	19.98	0.36	0.04	0.20
2020-07-01 16:18	49.92	0.07	50.43	0.39	0.51	1.02
2020-07-01 16:28	69.98	0.08	70.86	0.39	0.88	1.26
2020-07-01 16:38	9.97	0.14	9.86	0.32	-0.11	-1.10
2020-07-01 16:48	39.98	0.09	40.39	0.30	0.41	1.03
2020-07-01 17:08	29.97	0.09	30.18	0.21	0.21	0.70
2020-07-01 17:18	0.25	0.09	-0.02	0.14	-0.27	NA
2020-07-01 17:28	74.93	0.08	75.99	0.17	1.06	1.41
2020-07-01 17:38	175.03	0.03	177.66	0.23	2.63	1.50
2020-07-01 17:48	24.96	0.10	25.29	0.26	0.33	1.32
2020-07-01 17:58	124.99	0.06	126.87	0.24	1.88	1.50
2020-07-01 18:08	200.06	0.10	203.19	0.17	3.13	1.56
2020-07-01 18:18	149.99	0.08	152.18	0.11	2.19	1.46

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 (%)
2020-07-01 18:28	0.24	0.11	-0.03	0.21	-0.27	NA
2020-07-01 18:38	39.94	0.08	40.37	0.19	0.43	1.08
2020-07-01 18:48	10.15	0.30	10.13	0.45	-0.02	-0.20
2020-07-01 18:58	79.92	0.11	80.94	0.24	1.02	1.28
2020-07-01 19:08	19.93	0.09	20.20	0.20	0.27	1.35
2020-07-01 19:18	59.94	0.08	60.59	0.21	0.65	1.08
2020-07-01 19:28	89.98	0.06	91.32	0.20	1.34	1.49
2020-07-01 19:38	29.95	0.07	30.38	0.32	0.43	1.44
2020-07-01 19:48	69.95	0.08	70.88	0.20	0.93	1.33
2020-07-01 19:58	49.94	0.09	50.65	0.24	0.71	1.42
2020-07-01 21:58	0.29	0.13	0.11	0.10	-0.18	NA
2020-07-01 22:08	74.94	0.05	75.89	0.31	0.95	1.27
2020-07-01 22:18	175.05	0.05	177.82	0.50	2.77	1.58
2020-07-01 22:28	24.95	0.09	25.11	0.39	0.16	0.64
2020-07-01 22:38	125.03	0.05	127.06	0.14	2.03	1.62
2020-07-01 22:48	200.10	0.10	203.41	0.45	3.31	1.65
2020-07-01 22:58	149.99	0.06	152.41	0.14	2.42	1.61
2020-07-01 23:08	0.25	0.10	0.04	0.28	-0.21	NA
2020-07-01 23:18	39.90	0.10	40.29	0.24	0.39	0.98
2020-07-01 23:28	10.17	0.34	10.12	0.48	-0.05	-0.49
2020-07-01 23:38	79.95	0.07	81.14	0.29	1.19	1.49
2020-07-01 23:48	19.91	0.09	20.00	0.23	0.09	0.45
2020-07-01 23:58	59.94	0.05	60.79	0.25	0.85	1.42
2020-07-02 00:08	89.99	0.05	91.32	0.23	1.33	1.48
2020-07-02 00:18	29.93	0.08	30.25	0.17	0.32	1.07
2020-07-02 00:28	69.94	0.08	71.03	0.29	1.09	1.56
2020-07-02 00:38	50.00	0.06	50.67	0.28	0.67	1.34
2020-07-02 02:38	0.19	0.11	0.13	0.27	-0.06	NA
2020-07-02 02:48	74.95	0.12	75.89	0.29	0.94	1.25
2020-07-02 02:58	175.04	0.04	177.62	0.32	2.58	1.47
2020-07-02 03:08	24.98	0.07	24.96	0.12	-0.02	-0.08
2020-07-02 03:18	124.98	0.09	126.78	0.26	1.80	1.44
2020-07-02 03:28	200.06	0.07	203.37	0.22	3.31	1.65
2020-07-02 03:38	150.01	0.06	152.38	0.10	2.37	1.58
2020-07-02 03:48	0.15	0.08	0.02	0.11	-0.13	NA
2020-07-02 03:58	39.86	0.12	40.53	0.28	0.67	1.68
2020-07-02 04:08	10.26	0.43	10.11	0.40	-0.15	-1.46
2020-07-02 04:18	79.92	0.10	81.01	0.09	1.09	1.36
2020-07-02 04:28	19.92	0.08	20.10	0.29	0.18	0.90
2020-07-02 04:38	59.99	0.04	60.72	0.18	0.73	1.22
2020-07-02 04:48	90.00	0.05	91.41	0.40	1.41	1.57
2020-07-02 04:58	29.95	0.11	30.32	0.33	0.37	1.24
2020-07-02 05:08	69.97	0.04	71.12	0.14	1.15	1.64
2020-07-02 05:18	49.93	0.08	50.56	0.26	0.63	1.26
2020-07-02 05:28	0.27	0.09	-0.07	0.17	-0.34	NA
2020-07-02 05:38	79.94	0.08	81.11	0.30	1.17	1.46
2020-07-02 05:48	59.95	0.08	60.86	0.20	0.91	1.52
2020-07-02 05:58	89.98	0.07	91.43	0.17	1.45	1.61

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 (%)
2020-07-02 06:08	19.93	0.16	20.11	0.21	0.18	0.90
2020-07-02 06:18	49.90	0.09	50.62	0.22	0.72	1.44
2020-07-02 06:28	69.93	0.04	70.93	0.23	1.00	1.43
2020-07-02 06:38	10.60	0.29	10.57	0.43	-0.03	-0.28
2020-07-02 06:48	39.92	0.10	40.35	0.46	0.43	1.08
2020-07-02 07:08	29.96	0.05	30.28	0.21	0.32	1.07
2020-07-02 07:18	0.27	0.08	0.22	0.25	-0.05	NA
2020-07-02 07:28	74.95	0.03	76.15	0.34	1.20	1.60
2020-07-02 07:38	175.05	0.07	177.66	0.13	2.61	1.49
2020-07-02 07:48	24.91	0.08	25.08	0.04	0.17	0.68
2020-07-02 07:58	124.93	0.12	126.99	0.29	2.06	1.65

Table 6. Five-minute aggregates computed from the last five of a total of ten one-minute values for the comparison of the HPB ozone calibrator (OC) Thermo Scientific 49C-PS #423807729 (initial pressure sensor settings) with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2020-06-30 15:31	0.31	0.08	0.72	0.13	0.41	NA
2020-06-30 15:41	80.00	0.08	81.63	0.09	1.63	2.04
2020-06-30 15:51	59.90	0.23	61.69	1.21	1.79	2.99
2020-06-30 16:01	89.96	0.08	91.69	0.20	1.73	1.92
2020-06-30 16:11	19.90	0.10	20.38	0.16	0.48	2.41
2020-06-30 16:21	49.93	0.10	51.18	0.39	1.25	2.50
2020-06-30 16:31	70.00	0.09	71.53	0.24	1.53	2.19
2020-06-30 16:41	10.24	0.35	10.73	0.43	0.49	4.79
2020-06-30 16:51	39.93	0.06	40.93	0.22	1.00	2.50
2020-06-30 17:11	29.93	0.03	30.50	0.14	0.57	1.90
2020-06-30 17:21	0.33	0.06	0.46	0.13	0.13	NA
2020-06-30 17:31	74.94	0.10	76.54	0.21	1.60	2.14
2020-06-30 17:41	175.03	0.07	178.40	0.16	3.37	1.93
2020-06-30 17:51	24.95	0.04	25.54	0.02	0.59	2.36
2020-06-30 18:01	125.02	0.06	127.51	0.22	2.49	1.99
2020-06-30 18:11	200.04	0.05	204.14	0.17	4.10	2.05
2020-06-30 18:21	150.02	0.08	153.10	0.21	3.08	2.05
2020-06-30 18:31	0.10	0.11	0.37	0.09	0.27	NA
2020-06-30 18:41	39.96	0.04	40.89	0.13	0.93	2.33
2020-06-30 18:51	10.53	0.66	10.71	0.56	0.18	1.71
2020-06-30 19:01	80.00	0.05	81.59	0.22	1.59	1.99
2020-06-30 19:11	19.95	0.10	20.50	0.11	0.55	2.76
2020-06-30 19:21	59.94	0.07	61.21	0.22	1.27	2.12
2020-06-30 19:31	89.91	0.13	91.82	0.21	1.91	2.12
2020-06-30 19:41	29.95	0.15	30.75	0.18	0.80	2.67
2020-06-30 19:51	69.93	0.06	71.14	0.34	1.21	1.73
2020-06-30 20:01	49.94	0.08	50.93	0.28	0.99	1.98
2020-06-30 20:11	0.21	0.11	0.34	0.10	0.13	NA
2020-06-30 20:21	79.94	0.06	81.38	0.16	1.44	1.80

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2020-06-30 20:31	59.94	0.08	60.98	0.20	1.04	1.74
2020-06-30 20:41	89.95	0.08	91.34	0.17	1.39	1.55
2020-06-30 20:51	19.92	0.10	20.35	0.17	0.43	2.16
2020-06-30 21:01	49.92	0.10	50.66	0.17	0.74	1.48
2020-06-30 21:11	69.99	0.04	71.04	0.23	1.05	1.50
2020-06-30 21:21	10.81	0.30	10.86	0.23	0.05	0.46
2020-06-30 21:31	39.94	0.04	40.68	0.28	0.74	1.85
2020-06-30 21:51	29.92	0.13	30.63	0.14	0.71	2.37
2020-06-30 22:01	0.20	0.15	0.44	0.16	0.24	NA
2020-06-30 22:11	74.96	0.06	76.21	0.11	1.25	1.67
2020-06-30 22:21	175.07	0.16	177.82	0.20	2.75	1.57
2020-06-30 22:31	24.90	0.10	25.33	0.20	0.43	1.73
2020-06-30 22:41	124.96	0.05	126.98	0.22	2.02	1.62
2020-06-30 22:51	200.11	0.04	203.42	0.34	3.31	1.65
2020-06-30 23:01	150.01	0.07	152.64	0.23	2.63	1.75
2020-06-30 23:11	0.11	0.08	0.28	0.10	0.17	NA
2020-06-30 23:21	39.91	0.07	40.87	0.23	0.96	2.41
2020-06-30 23:31	10.30	0.57	10.68	0.57	0.38	3.69
2020-06-30 23:41	79.96	0.06	81.71	0.17	1.75	2.19
2020-06-30 23:51	20.06	0.56	20.68	0.78	0.62	3.09
2020-07-01 00:01	59.95	0.11	61.08	0.28	1.13	1.88
2020-07-01 00:11	89.95	0.11	91.79	0.15	1.84	2.05
2020-07-01 00:21	29.90	0.08	30.55	0.27	0.65	2.17
2020-07-01 00:31	69.94	0.07	71.47	0.29	1.53	2.19
2020-07-01 00:41	49.94	0.09	51.05	0.20	1.11	2.22
2020-07-01 02:41	0.28	0.11	0.29	0.18	0.01	3.57
2020-07-01 02:51	74.95	0.09	76.24	0.15	1.29	1.72
2020-07-01 03:01	175.07	0.08	178.00	0.23	2.93	1.67
2020-07-01 03:11	24.89	0.08	25.30	0.24	0.41	1.65
2020-07-01 03:21	124.98	0.05	127.13	0.14	2.15	1.72
2020-07-01 03:31	200.06	0.11	203.27	0.39	3.21	1.60
2020-07-01 03:41	150.00	0.03	152.29	0.22	2.29	1.53
2020-07-01 03:51	0.26	0.17	0.32	0.22	0.06	NA
2020-07-01 04:01	39.93	0.08	40.63	0.16	0.70	1.75
2020-07-01 04:11	10.09	0.21	10.38	0.26	0.29	2.87
2020-07-01 04:21	79.92	0.05	81.40	0.17	1.48	1.85
2020-07-01 04:31	20.04	0.42	20.68	0.80	0.64	3.19
2020-07-01 04:41	59.96	0.07	61.10	0.20	1.14	1.90
2020-07-01 04:51	89.98	0.07	91.66	0.28	1.68	1.87
2020-07-01 05:01	29.92	0.08	30.48	0.29	0.56	1.87
2020-07-01 05:11	69.95	0.05	71.22	0.17	1.27	1.82
2020-07-01 05:21	49.94	0.08	50.89	0.28	0.95	1.90
2020-07-01 07:21	0.29	0.11	0.34	0.15	0.05	NA
2020-07-01 07:31	74.96	0.07	76.42	0.20	1.46	1.95
2020-07-01 07:41	175.01	0.09	178.54	0.09	3.53	2.02

Table 7. Five-minute aggregates computed from the last five of a total of ten one-minute values for the comparison of the HPB ozone calibrator (OC) Thermo Scientific 49C-PS #423807729 (final pressure sensor settings) with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2020-07-01 10:48	0.27	0.15	0.19	0.03	-0.08	NA
2020-07-01 10:58	79.89	0.05	80.48	0.40	0.59	0.74
2020-07-01 11:08	59.96	0.07	60.48	0.26	0.52	0.87
2020-07-01 11:18	90.03	0.09	90.73	0.26	0.70	0.78
2020-07-01 11:28	19.91	0.11	20.12	0.26	0.21	1.05
2020-07-01 11:38	49.94	0.10	50.49	0.09	0.55	1.10
2020-07-01 11:48	69.97	0.06	70.65	0.16	0.68	0.97
2020-07-01 11:58	9.86	0.08	9.80	0.10	-0.06	-0.61
2020-07-01 12:08	39.91	0.05	40.20	0.09	0.29	0.73
2020-07-01 12:28	29.96	0.03	30.40	0.17	0.44	1.47
2020-07-01 12:38	0.26	0.14	0.23	0.15	-0.03	NA
2020-07-01 12:48	74.95	0.04	75.93	0.25	0.98	1.31
2020-07-01 12:58	175.08	0.09	177.16	0.30	2.08	1.19
2020-07-01 13:08	24.87	0.03	25.30	0.19	0.43	1.73
2020-07-01 13:18	125.04	0.11	126.69	0.14	1.65	1.32
2020-07-01 13:28	200.07	0.07	202.87	0.27	2.80	1.40
2020-07-01 13:38	150.03	0.07	152.05	0.29	2.02	1.35
2020-07-01 13:48	0.24	0.09	0.33	0.15	0.09	NA
2020-07-01 13:58	39.91	0.10	40.35	0.32	0.44	1.10
2020-07-01 14:08	10.22	0.32	10.48	0.44	0.26	2.54
2020-07-01 14:18	79.89	0.11	80.91	0.05	1.02	1.28
2020-07-01 14:28	19.95	0.09	20.23	0.12	0.28	1.40
2020-07-01 14:38	59.97	0.07	60.66	0.25	0.69	1.15
2020-07-01 14:48	89.98	0.07	91.13	0.19	1.15	1.28
2020-07-01 14:58	29.88	0.09	30.34	0.21	0.46	1.54
2020-07-01 15:08	69.94	0.04	70.80	0.22	0.86	1.23
2020-07-01 15:18	49.93	0.10	50.70	0.15	0.77	1.54
2020-07-01 15:28	0.27	0.18	0.36	0.21	0.09	NA
2020-07-01 15:38	79.92	0.06	80.93	0.13	1.01	1.26
2020-07-01 15:48	59.99	0.06	60.98	0.44	0.99	1.65
2020-07-01 15:58	89.92	0.05	91.19	0.32	1.27	1.41
2020-07-01 16:08	19.94	0.12	20.15	0.18	0.21	1.05
2020-07-01 16:18	49.92	0.07	50.28	0.12	0.36	0.72
2020-07-01 16:28	69.98	0.08	70.61	0.22	0.63	0.90
2020-07-01 16:38	9.97	0.14	9.80	0.19	-0.17	-1.71
2020-07-01 16:48	39.98	0.09	40.47	0.30	0.49	1.23
2020-07-01 17:08	29.97	0.09	30.15	0.21	0.18	0.60
2020-07-01 17:18	0.25	0.09	0.36	0.17	0.11	NA
2020-07-01 17:28	74.93	0.08	75.53	0.23	0.60	0.80
2020-07-01 17:38	175.03	0.03	176.56	0.19	1.53	0.87
2020-07-01 17:48	24.96	0.10	25.24	0.09	0.28	1.12
2020-07-01 17:58	124.99	0.06	126.17	0.22	1.18	0.94
2020-07-01 18:08	200.06	0.10	202.00	0.10	1.94	0.97
2020-07-01 18:18	149.99	0.08	151.39	0.17	1.40	0.93

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2020-07-01 18:28	0.24	0.11	0.26	0.15	0.02	NA
2020-07-01 18:38	39.94	0.08	40.41	0.23	0.47	1.18
2020-07-01 18:48	10.15	0.30	10.36	0.41	0.21	2.07
2020-07-01 18:58	79.92	0.11	80.79	0.23	0.87	1.09
2020-07-01 19:08	19.93	0.09	20.15	0.17	0.22	1.10
2020-07-01 19:18	59.94	0.08	60.67	0.36	0.73	1.22
2020-07-01 19:28	89.98	0.06	91.02	0.33	1.04	1.16
2020-07-01 19:38	29.95	0.07	30.48	0.09	0.53	1.77
2020-07-01 19:48	69.95	0.08	70.83	0.19	0.88	1.26
2020-07-01 19:58	49.94	0.09	50.61	0.24	0.67	1.34
2020-07-01 21:58	0.29	0.13	0.28	0.08	-0.01	NA
2020-07-01 22:08	74.94	0.05	75.95	0.09	1.01	1.35
2020-07-01 22:18	175.05	0.05	177.43	0.37	2.38	1.36
2020-07-01 22:28	24.95	0.09	25.06	0.22	0.11	0.44
2020-07-01 22:38	125.03	0.05	126.61	0.18	1.58	1.26
2020-07-01 22:48	200.10	0.10	202.79	0.23	2.69	1.34
2020-07-01 22:58	149.99	0.06	151.84	0.25	1.85	1.23
2020-07-01 23:08	0.25	0.10	0.19	0.11	-0.06	NA
2020-07-01 23:18	39.90	0.10	40.23	0.21	0.33	0.83
2020-07-01 23:28	10.17	0.34	10.32	0.33	0.15	1.47
2020-07-01 23:38	79.95	0.07	80.73	0.25	0.78	0.98
2020-07-01 23:48	19.91	0.09	20.16	0.21	0.25	1.26
2020-07-01 23:58	59.94	0.05	60.50	0.24	0.56	0.93
2020-07-02 00:08	89.99	0.05	90.84	0.14	0.85	0.94
2020-07-02 00:18	29.93	0.08	30.42	0.15	0.49	1.64
2020-07-02 00:28	69.94	0.08	70.61	0.24	0.67	0.96
2020-07-02 00:38	50.00	0.06	50.47	0.18	0.47	0.94
2020-07-02 02:38	0.19	0.11	0.42	0.17	0.23	NA
2020-07-02 02:48	74.95	0.12	76.01	0.22	1.06	1.41
2020-07-02 02:58	175.04	0.04	177.36	0.24	2.32	1.33
2020-07-02 03:08	24.98	0.07	25.35	0.23	0.37	1.48
2020-07-02 03:18	124.98	0.09	126.73	0.25	1.75	1.40
2020-07-02 03:28	200.06	0.07	202.66	0.17	2.60	1.30
2020-07-02 03:38	150.01	0.06	152.10	0.35	2.09	1.39
2020-07-02 03:48	0.15	0.08	0.27	0.19	0.12	NA
2020-07-02 03:58	39.86	0.12	40.42	0.33	0.56	1.40
2020-07-02 04:08	10.26	0.43	10.23	0.33	-0.03	-0.29
2020-07-02 04:18	79.92	0.10	81.07	0.28	1.15	1.44
2020-07-02 04:28	19.92	0.08	20.19	0.10	0.27	1.36
2020-07-02 04:38	59.99	0.04	60.77	0.27	0.78	1.30
2020-07-02 04:48	90.00	0.05	91.08	0.15	1.08	1.20
2020-07-02 04:58	29.95	0.11	30.33	0.17	0.38	1.27
2020-07-02 05:08	69.97	0.04	70.90	0.23	0.93	1.33
2020-07-02 05:18	49.93	0.08	50.59	0.10	0.66	1.32
2020-07-02 05:28	0.27	0.09	0.23	0.21	-0.04	NA
2020-07-02 05:38	79.94	0.08	81.02	0.19	1.08	1.35
2020-07-02 05:48	59.95	0.08	60.63	0.14	0.68	1.13
2020-07-02 05:58	89.98	0.07	90.95	0.35	0.97	1.08

Date – Time	**TS (nmol mol^{-1})**	**sdTS (nmol mol^{-1})**	**OC (nmol mol^{-1})**	**sdOC (nmol mol^{-1})**	**OC-TS (nmol mol^{-1})**	**OC-TS (%)**
2020-07-02 06:08	19.93	0.16	20.05	0.20	0.12	0.60
2020-07-02 06:18	49.90	0.09	50.50	0.23	0.60	1.20
2020-07-02 06:28	69.93	0.04	70.61	0.14	0.68	0.97
2020-07-02 06:38	10.60	0.29	10.71	0.52	0.11	1.04
2020-07-02 06:48	39.92	0.10	40.07	0.11	0.15	0.38
2020-07-02 07:08	29.96	0.05	30.20	0.16	0.24	0.80
2020-07-02 07:18	0.27	0.08	0.24	0.10	-0.03	NA
2020-07-02 07:28	74.95	0.03	75.49	0.17	0.54	0.72
2020-07-02 07:38	175.05	0.07	176.57	0.29	1.52	0.87
2020-07-02 07:48	24.91	0.08	25.34	0.23	0.43	1.73
2020-07-02 07:58	124.93	0.12	125.96	0.05	1.03	0.82

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

Table 8. Experimental details of HPB CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 21.	
Station Analyser (GAW) (CO)	
Model, S/N	Aerolaser AL5001 #142
Principle	Vacuum UV Resonance Fluorescence (VURF)
Drying system	PERMAPURE Nafion drier
Station Analyser (ICOS) (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #1670-CFKADS2120
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference
Station Analyser (ICOS) (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #2322-CFKADS2192
Principle	CRDS
Drying system	PERMAPURE MD-070-144S-4 Nafion drier
Station Analyser (ICOS) (CO, N_2O)	
Model, S/N	LGR 913-0015 #US4300160200001043
Principle	Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)
Drying system	PERMAPURE MD-070-144S-4 Nafion drier
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Table 9 Calibration standards at HPB as of July 2020.

Cylinder ID	N_2O (nmol mol^{-1})	CO (nmol mol^{-1})	CH_4 (nmol mol^{-1})	CO_2 (µmol mol^{-1})	Usage
D4NPYY1	NA	966.00	NA	NA	VURF WS
CB12279	NA	289.29	NA	NA	NOAA / VURF
CC311852	NA	348.21	NA	NA	NOAA / VURF
CB12407	NA	196.83	NA	NA	NOAA / VURF
D073410	NA	92.00	1845.36	375.14	ICOS Picarro
D073412	NA	183.52	1948.34	404.94	ICOS Picarro
D073414	NA	298.49	2048.04	434.71	ICOS Picarro
D337349	NA	153.77	1969.08	400.98	ICOS Picarro
D073410	319.98	92.00	NA	NA	ICOS LGR
D073412	334.14	183.52	NA	NA	ICOS LGR
D073414	348.92	298.72	NA	NA	ICOS LGR
D175433	334.95	180.88	NA	NA	ICOS LGR target archive
D337348	332.15	159.09	NA	NA	ICOS LGR WS
D337349	332.39	153.77	NA	NA	ICOS LGR target performance

Results

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

Table 10. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Aerolaser AL5001 #142 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(20-07-01 09:49:30)	181128_FF61487	110.8	1.8	110.6	0.1	4	-0.2	-0.2
(20-07-01 10:47:30)	171124_FA01467	140.9	0.4	140.9	0.3	4	-0.1	-0.1
(20-07-01 11:21:30)	160622_FA02474	237.5	0.6	235.8	0.2	4	-1.6	-0.7
(20-07-06 08:34:30)	171204_FA01469	103.1	0.8	104.1	0.1	4	1.0	1.0
(20-07-06 09:21:30)	180318_FF61508	355.9	0.8	353.8	0.2	4	-2.1	-0.6
(20-07-06 10:24:30)	160825_FB03887	194.5	1.2	195.0	0.2	4	0.5	0.3
(20-07-06 11:16:30)	171128_FA02476	149.4	0.6	151.1	0.1	4	1.7	1.1
(20-07-06 11:44:30)	160825_FB03365	178.2	1.0	178.0	0.2	4	-0.2	-0.1
(20-07-06 13:18:30)	171201_FA02773	0.0	0.5	0.7	0.0	4	0.7	NA

Table 11. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1670-CFKADS2120 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (nmol mol-1)	sdTS (nmol mol-1)	AL (nmol mol-1)	sdAL (nmol mol-1)	N	AL-TS (nmol mol-1)	AL-TS (%)
(20-06-30 15:36:00)	180318_FF61508	355.9	0.8	356.2	0.3	3	0.3	0.1
(20-07-02 13:07:20)	160825_FB03365	178.2	1.0	180.2	0.1	3	2.0	1.1
(20-07-01 15:20:00)	171124_FA01467	140.9	0.4	143.6	0.5	3	2.7	1.9
(20-07-01 15:50:00)	181128_FF61487	110.8	1.8	113.2	0.6	3	2.5	2.2
(20-06-30 16:06:00)	171204_FA01469	103.1	0.8	104.9	0.1	3	1.9	1.8
(20-07-02 13:41:00)	171201_FA02773	0.0	0.5	7.0	0.1	3	7.0	NA
(20-06-30 17:36:00)	160825_FB03887	194.5	1.2	195.6	0.3	3	1.1	0.5
(20-07-01 16:20:00)	160622_FA02474	237.5	0.6	239.8	0.1	3	2.3	1.0
(20-06-30 16:36:00)	171128_FA02476	149.4	0.6	151.4	0.4	3	2.0	1.4

Table 12. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2322-CFKADS2192 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (nmol mol-1)	sdTS (nmol mol-1)	AL (nmol mol-1)	sdAL (nmol mol-1)	N	AL-TS (nmol mol-1)	AL-TS (%)
(20-06-30 14:21:00)	180318_FF61508	355.9	0.8	356.2	0.1	2	0.3	0.1
(20-07-01 22:25:40)	160825_FB03365	178.2	1.0	178.6	0.2	3	0.4	0.2
(20-07-01 22:27:00)	171124_FA01467	140.9	0.4	142.5	0.3	3	1.6	1.1
(20-07-01 15:40:00)	181128_FF61487	110.8	1.8	112.1	0.1	3	1.3	1.2
(20-06-30 23:40:40)	171204_FA01469	103.1	0.8	105.2	0.8	3	2.1	2.1
(20-07-01 22:59:20)	171201_FA02773	0.0	0.5	6.7	0.1	3	6.7	NA
(20-07-01 07:47:40)	160825_FB03887	194.5	1.2	196.0	0.2	3	1.5	0.8
(20-07-01 09:05:20)	160622_FA02474	237.5	0.6	238.6	0.7	3	1.1	0.5
(20-07-01 00:10:40)	171128_FA02476	149.4	0.6	151.8	0.5	3	2.4	1.6

Table 13. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015 #US4300160200001043 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (nmol mol-1)	sdTS (nmol mol-1)	AL (nmol mol-1)	sdAL (nmol mol-1)	N	AL-TS (nmol mol-1)	AL-TS (%)
(20-06-30 15:36:00)	180318_FF61508	355.9	0.8	356.0	0.1	3	0.1	0.0
(20-07-02 13:07:20)	160825_FB03365	178.2	1.0	178.9	0.2	3	0.7	0.4
(20-07-01 15:20:00)	171124_FA01467	140.9	0.4	142.7	0.0	3	1.8	1.2
(20-07-01 15:50:00)	181128_FF61487	110.8	1.8	112.6	0.0	3	1.8	1.6
(20-06-30 16:06:00)	171204_FA01469	103.1	0.8	105.5	0.0	3	2.5	2.4
(20-07-02 13:41:00)	171201_FA02773	0.0	0.5	2.7	0.1	3	2.7	NA
(20-06-30 17:36:00)	160825_FB03887	194.5	1.2	195.8	0.0	3	1.3	0.7
(20-07-01 16:20:00)	160622_FA02474	237.5	0.6	238.3	0.0	3	0.8	0.3
(20-06-30 16:36:00)	171128_FA02476	149.4	0.6	151.4	0.0	3	2.0	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 8 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 HPB data acquisition system. The standards used for the calibration of the HPB 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 14. CH4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1670-CFKADS2120 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH4 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 (%)
(20-06-30 15:36:00)	180318_FF61508	1963.75	0.02	1963.63	0.10	3	-0.12	-0.01
(20-06-30 16:06:00)	171204_FA01469	1933.18	0.04	1933.02	0.10	3	-0.16	-0.01
(20-06-30 16:36:00)	171128_FA02476	1860.12	0.03	1860.24	0.27	3	0.12	0.01
(20-06-30 17:36:00)	160825_FB03887	2027.36	0.04	2027.06	0.23	3	-0.30	-0.01
(20-07-01 15:20:00)	171124_FA01467	1805.72	0.02	1805.66	0.17	3	-0.06	0.00
(20-07-01 15:50:00)	181128_FF61487	1990.63	0.02	1990.32	0.15	3	-0.31	-0.02
(20-07-01 16:20:00)	160622_FA02474	2506.81	0.02	2506.03	0.07	3	-0.78	-0.03
(20-07-02 13:07:20)	160825_FB03365	1921.02	0.01	1921.41	0.04	3	0.39	0.02
(20-07-02 13:41:00)	171201_FA02773	1.36	0.07	3.25	0.01	3	1.89	NA

Table 15. CH4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2322-CFKADS2192 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH4 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 (%)
(20-06-30 15:36:00)	180318_FF61508	1963.75	0.02	1963.85	0.04	3	0.10	0.01
(20-06-30 16:06:00)	171204_FA01469	1933.18	0.04	1933.37	0.10	3	0.19	0.01
(20-06-30 16:36:00)	171128_FA02476	1860.12	0.03	1860.38	0.10	3	0.26	0.01
(20-06-30 17:36:00)	160825_FB03887	2027.36	0.04	2027.45	0.11	3	0.09	0.00
(20-07-01 15:20:00)	171124_FA01467	1805.72	0.02	1805.90	0.04	3	0.18	0.01
(20-07-01 15:50:00)	181128_FF61487	1990.63	0.02	1990.66	0.04	3	0.03	0.00
(20-07-01 16:20:00)	160622_FA02474	2506.81	0.02	2506.36	0.06	3	-0.45	-0.02
(20-07-02 13:07:20)	160825_FB03365	1921.02	0.01	1921.11	0.08	3	0.09	0.00
(20-07-02 13:41:00)	171201_FA02773	1.36	0.07	3.04	0.01	3	1.68	NA

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 8 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 HPB data acquisition system. The standards used for the calibration of the HPB 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 16. CO2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LSCE Picarro G2401 #1670-CFKADS2120 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO2 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 (%)
(20-06-30 15:36:00)	180318_FF61508	417.30	0.05	417.26	0.01	3	-0.04	-0.01
(20-06-30 16:06:00)	171204_FA01469	406.78	0.03	406.76	0.01	3	-0.02	0.00
(20-06-30 16:36:00)	171128_FA02476	418.29	0.02	418.24	0.02	3	-0.06	-0.01
(20-06-30 17:36:00)	160825_FB03887	457.74	0.01	457.62	0.02	3	-0.12	-0.03
(20-07-01 15:20:00)	171124_FA01467	397.02	0.01	396.96	0.01	3	-0.06	-0.02
(20-07-01 15:50:00)	181128_FF61487	398.14	0.09	398.03	0.01	3	-0.11	-0.03
(20-07-01 16:20:00)	160622_FA02474	421.29	0.01	421.22	0.01	3	-0.07	-0.02
(20-07-02 13:07:20)	160825_FB03365	412.94	0.01	412.86	0.01	3	-0.08	-0.02
(20-07-02 13:41:00)	171201_FA02773	0.29	0.03	0.54	0.00	3	0.26	NA

Table 17. CO2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LSCE Picarro G2401 #2322-CFKADS2192 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO2 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 (%)
(20-06-30 15:36:00)	180318_FF61508	417.30	0.05	417.23	0.01	3	-0.07	-0.02
(20-06-30 16:06:00)	171204_FA01469	406.78	0.03	406.74	0.01	3	-0.04	-0.01
(20-06-30 16:36:00)	171128_FA02476	418.29	0.02	418.21	0.02	3	-0.08	-0.02
(20-06-30 17:36:00)	160825_FB03887	457.74	0.01	457.60	0.02	3	-0.14	-0.03
(20-07-01 15:20:00)	171124_FA01467	397.02	0.01	396.93	0.00	3	-0.09	-0.02
(20-07-01 15:50:00)	181128_FF61487	398.14	0.09	398.01	0.01	3	-0.13	-0.03
(20-07-01 16:20:00)	160622_FA02474	421.29	0.01	421.19	0.01	3	-0.10	-0.02
(20-07-02 13:07:20)	160825_FB03365	412.94	0.01	412.79	0.00	3	-0.15	-0.04
(20-07-02 13:41:00)	171201_FA02773	0.29	0.03	0.57	0.00	3	0.28	NA

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 8 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 HPB data acquisition system. The standards used for the calibration of the HPB 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 Table.

Table 18. N2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015 instrument (AL) with the WCC-Empa TS (WMO-X2006A N2O 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 (%)
(20-06-30 15:36:00)	180318_FF61508	328.35	0.03	327.97	0.02	3	-0.38	-0.12
(20-06-30 16:06:00)	171204_FA01469	342.99	0.06	343.21	0.03	3	0.22	0.06
(20-06-30 16:36:00)	171128_FA02476	322.49	0.04	322.35	0.01	3	-0.14	-0.04
(20-06-30 17:36:00)	160825_FB03887	331.79	0.11	331.69	0.02	3	-0.10	-0.03
(20-07-01 15:20:00)	171124_FA01467	325.73	0.06	325.59	0.02	3	-0.14	-0.04
(20-07-01 15:50:00)	181128_FF61487	342.81	0.05	343.01	0.02	3	0.20	0.06
(20-07-01 16:20:00)	160622_FA02474	324.50	0.01	324.20	0.01	3	-0.30	-0.09
(20-07-02 13:07:20)	160825_FB03365	318.67	0.01	318.61	0.04	3	-0.06	-0.02

WCC-Empa Travelling Standards

Ozone

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

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

WCC-Empa TS: Thermo Scientific 49C-PS #1171430027, BKG -0.3, COEF 0.991

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 19. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 44). 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)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] - 0.05\ \text{nmol mol}^{-1}) / 0.9992 \quad (6a)$$

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

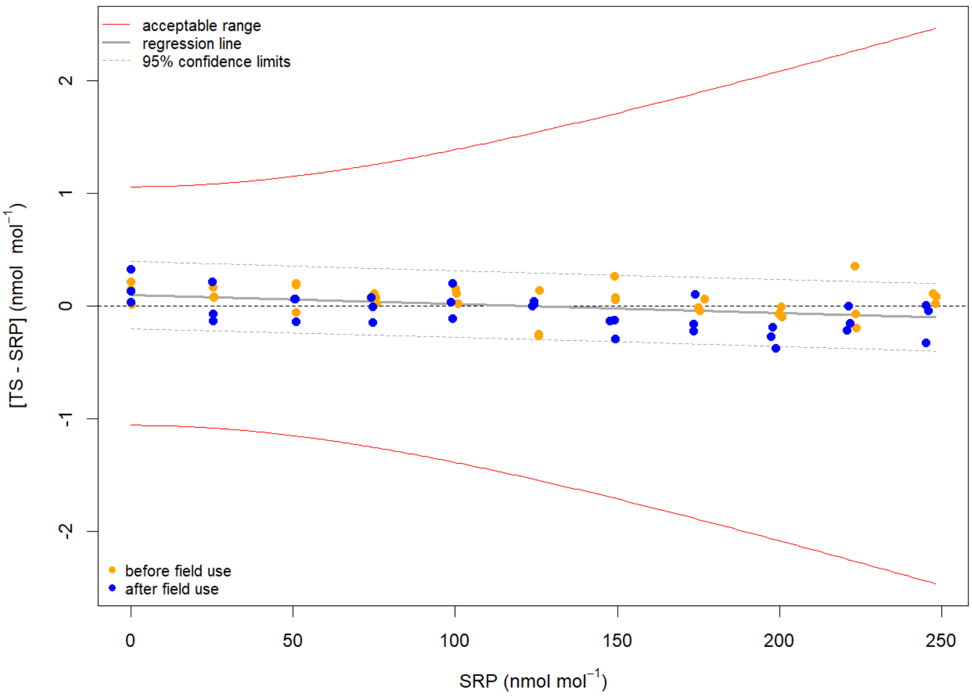

Figure 44. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 19. Five-minute aggregates computed from ten valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard (TS).

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2020-01-24	1	25	25.52	0.26	25.60	0.09
2020-01-24	1	0	0.00	0.25	0.15	0.12
2020-01-24	1	75	75.86	0.27	75.89	0.08
2020-01-24	1	125	125.89	0.35	126.03	0.15
2020-01-24	1	100	100.80	0.39	100.82	0.14
2020-01-24	1	175	175.42	0.18	175.39	0.10
2020-01-24	1	200	200.67	0.20	200.58	0.18
2020-01-24	1	150	149.19	0.17	149.46	0.13
2020-01-24	1	225	223.54	0.34	223.47	0.15
2020-01-24	1	50	50.99	0.40	50.94	0.13
2020-01-24	1	250	248.23	0.49	248.31	0.20
2020-01-24	2	150	149.30	0.16	149.38	0.14
2020-01-24	2	0	-0.01	0.26	0.21	0.09
2020-01-24	2	175	176.79	0.44	176.85	0.35
2020-01-24	2	100	100.45	0.20	100.56	0.12
2020-01-24	2	200	200.58	0.36	200.57	0.17
2020-01-24	2	25	25.38	0.20	25.55	0.11
2020-01-24	2	75	75.57	0.28	75.65	0.07
2020-01-24	2	125	125.68	0.26	125.42	0.13
2020-01-24	2	50	50.98	0.28	51.17	0.15
2020-01-24	2	225	223.73	0.31	223.53	0.17
2020-01-24	2	250	248.13	0.26	248.14	0.27
2020-01-24	3	25	25.54	0.29	25.62	0.08
2020-01-24	3	125	125.71	0.38	125.46	0.16
2020-01-24	3	175	174.92	0.28	174.91	0.18
2020-01-24	3	75	75.02	0.32	75.13	0.15
2020-01-24	3	0	0.14	0.29	0.16	0.07
2020-01-24	3	225	223.32	0.38	223.67	0.42
2020-01-24	3	150	149.26	0.23	149.32	0.14
2020-01-24	3	50	50.89	0.25	51.09	0.10
2020-01-24	3	100	100.04	0.20	100.19	0.13
2020-01-24	3	200	199.89	0.37	199.82	0.15
2020-01-24	3	245	247.37	0.29	247.48	0.29
2020-12-02	4	25	25.21	0.37	25.43	0.14
2020-12-02	4	175	173.45	0.29	173.29	0.11
2020-12-02	4	125	124.37	0.25	124.41	0.07
2020-12-02	4	0	0.02	0.37	0.15	0.11
2020-12-02	4	150	149.39	0.31	149.09	0.18
2020-12-02	4	75	74.68	0.24	74.67	0.10
2020-12-02	4	220	221.82	0.45	221.66	0.10
2020-12-02	4	100	99.14	0.28	99.33	0.09
2020-12-02	4	200	198.77	0.33	198.40	0.19
2020-12-02	4	50	50.67	0.31	50.73	0.06
2020-12-02	4	245	245.94	0.24	245.90	0.25
2020-12-02	5	175	173.40	0.31	173.17	0.11

Date	Run	Level#	SRP (nmol mol-1)	sdSRP (nmol mol-1)	TS (nmol mol-1)	sdTS (nmol mol-1)
2020-12-02	5	0	0.12	0.17	0.16	0.08
2020-12-02	5	150	149.08	0.30	148.95	0.31
2020-12-02	5	50	50.82	0.20	50.68	0.09
2020-12-02	5	100	99.08	0.29	98.97	0.16
2020-12-02	5	25	25.45	0.23	25.32	0.10
2020-12-02	5	220	221.28	0.27	221.28	0.19
2020-12-02	5	125	124.18	0.29	124.19	0.12
2020-12-02	5	200	197.95	0.27	197.76	0.19
2020-12-02	5	75	74.62	0.31	74.47	0.10
2020-12-02	5	245	245.14	0.25	245.15	0.23
2020-12-02	6	100	98.76	0.27	98.80	0.09
2020-12-02	6	75	74.22	0.38	74.29	0.09
2020-12-02	6	220	220.71	0.20	220.49	0.17
2020-12-02	6	0	-0.10	0.49	0.23	0.09
2020-12-02	6	175	173.99	0.52	174.09	0.47
2020-12-02	6	125	123.82	0.18	123.82	0.16
2020-12-02	6	25	25.35	0.41	25.28	0.18
2020-12-02	6	50	50.46	0.44	50.53	0.17
2020-12-02	6	195	197.44	0.40	197.17	0.14
2020-12-02	6	150	147.61	0.37	147.48	0.08
2020-12-02	6	245	245.25	0.36	244.93	0.22

#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-X2007 scale (Zhao and Tans, 2006)
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, CO_2 and CH_4: Picarro G2401 (Cavity Ring-Down Spectroscopy).

Table 20 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 21, and Figures 45 and 46 show the analysis of the TS over time.

Table 20. NOAA 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	484.39
CB11499#	141.03	1933.77	329.15	407.33
CB11485#	110.88	1844.78	328.46	394.30
CA02789*	448.67	2097.48	342.18	495.85
190618_CC703041*	3244.00	2258.07	NA	419.61

used for calibrations of CO_2, CH_4 and N_2O
* used for calibrations of CO

Table 21. Calibration summary of the WCC-Empa travelling standards. CO (A) refers to CO measurements on the Aerodyne instrument, and CO (P) to measurements on the Picarro instrument.

TS	Press. (psi)	CH_4 (nmol mol^{-1})	sd	CO_2 (µmol mol^{-1})	sd	N_2O (nmol mol^{-1})	sd	CO (A) (nmol mol^{-1})	sd	CO (P) (nmol mol^{-1})	sd
160622_FA02474	1400	2506.81	0.02	421.29	0.01	324.50	0.01	236.82	0.32	237.47	0.64
160825_FB03365	830	1921.02	0.01	412.94	0.01	318.67	0.01	177.48	0.90	178.17	0.99
160825_FB03887	200	2027.36	0.04	457.74	0.01	331.79	0.11	193.95	0.21	194.50	1.20
171124_FA01467	1210	1805.72	0.02	397.02	0.01	325.73	0.06	140.18	0.66	140.93	0.35
171128_FA02476	1410	1860.12	0.03	418.29	0.02	322.49	0.04	148.79	0.31	149.43	0.55
171201_FA02773	360	1.36	0.07	0.29	0.03	0.55	0.19	0.72	0.60	-0.05	0.46
171204_FA01469	1000	1933.18	0.04	406.78	0.03	342.99	0.06	101.92	0.24	103.08	0.79
180318_FF61508	1010	1963.75	0.02	417.30	0.05	328.35	0.03	355.29	0.22	355.90	0.84
181128_FF61487	1550	1990.63	0.02	398.14	0.09	342.81	0.05	109.66	0.79	110.76	1.76

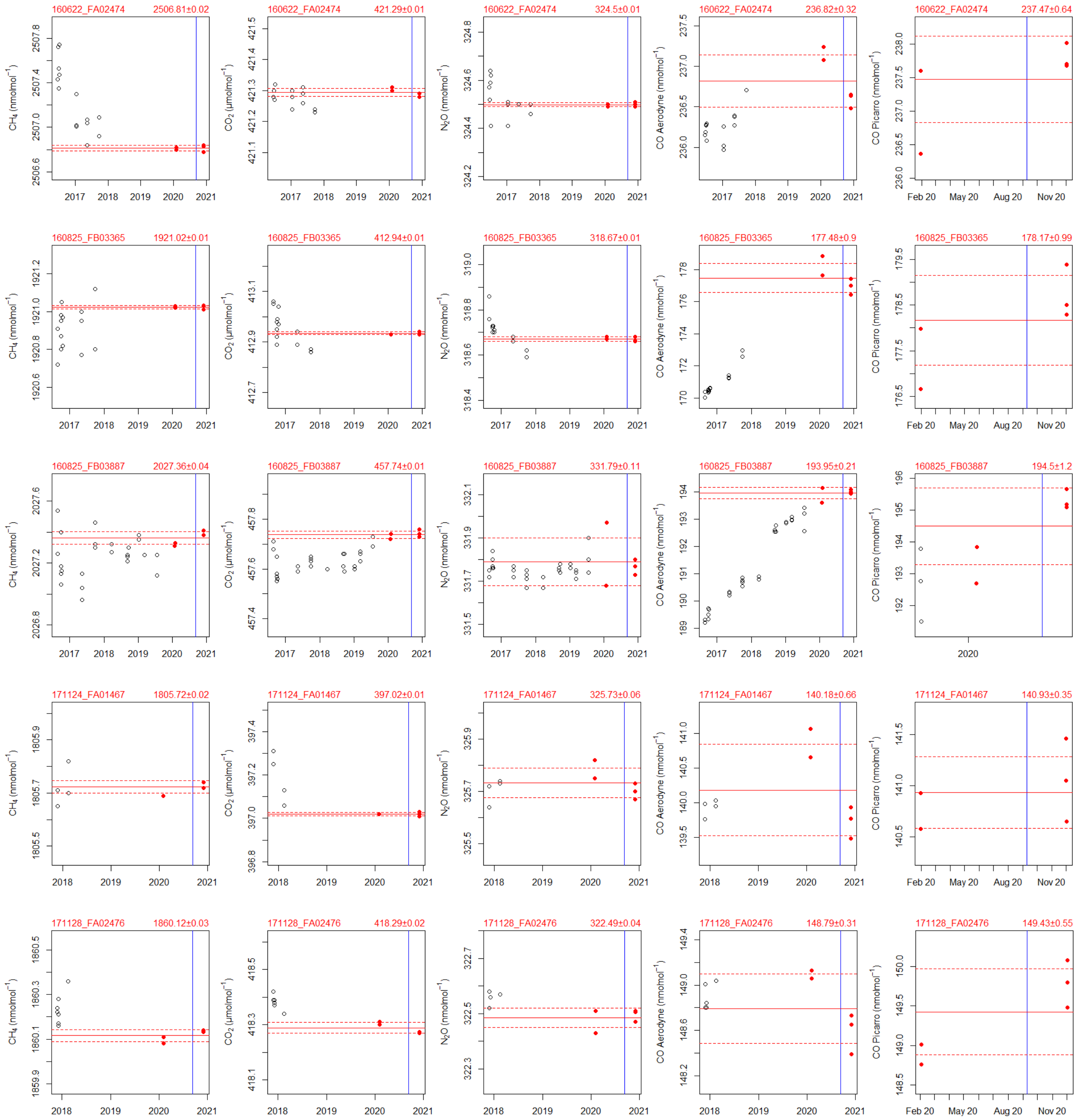

Figure 45. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.

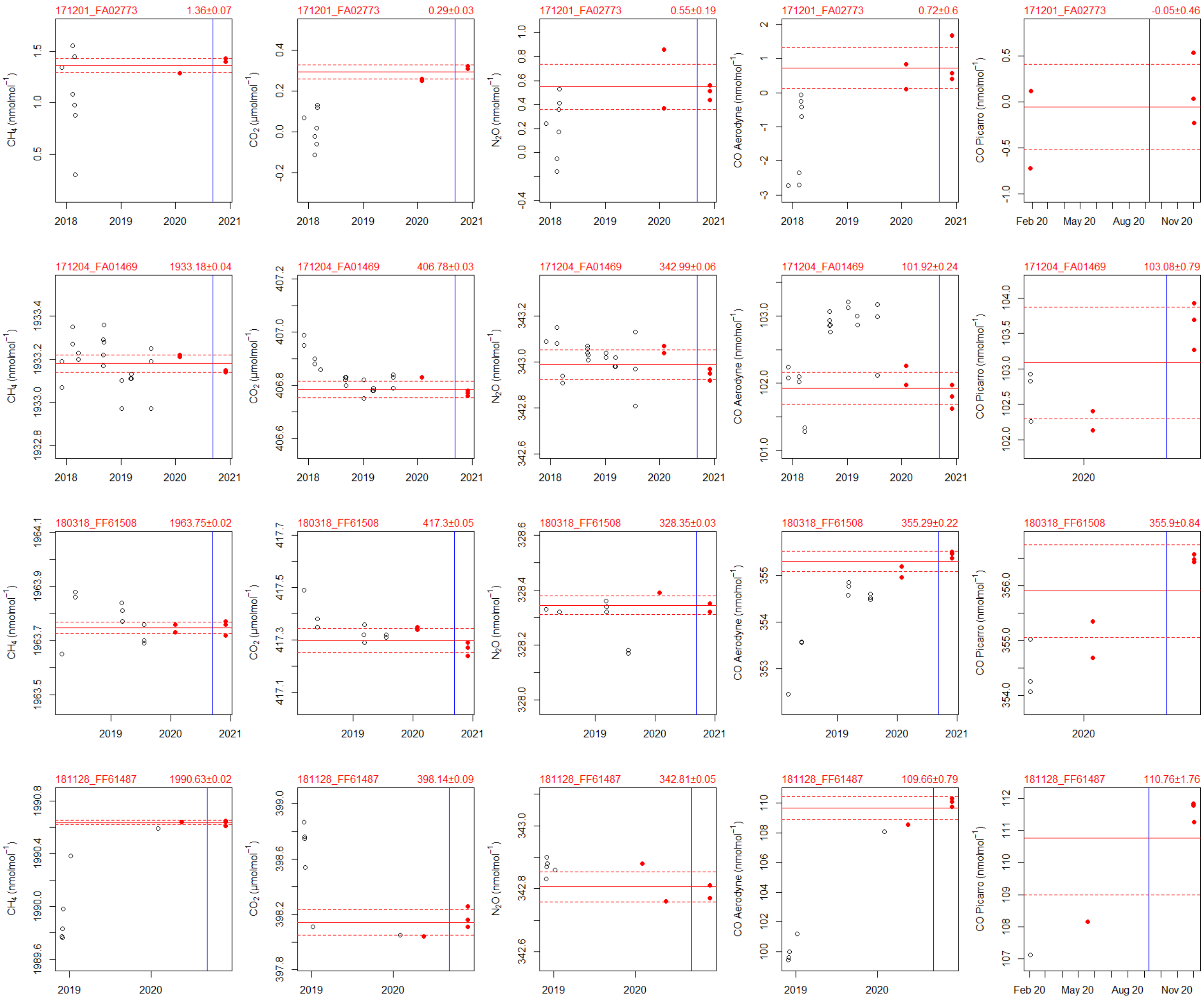

Figure 46. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.

Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH_4 and CO_2, the Picarro G2401 SN #617-CFKADS2001 was calibrated every 1445 min using one WCC-Empa TS as a working standard, and two TS as target tanks. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 0.1 ppb for CH_4 and 0.04 ppm for CO_2. With the exception of the first measurement, both target cylinders were within half of the WMO GAW compatibility goals.

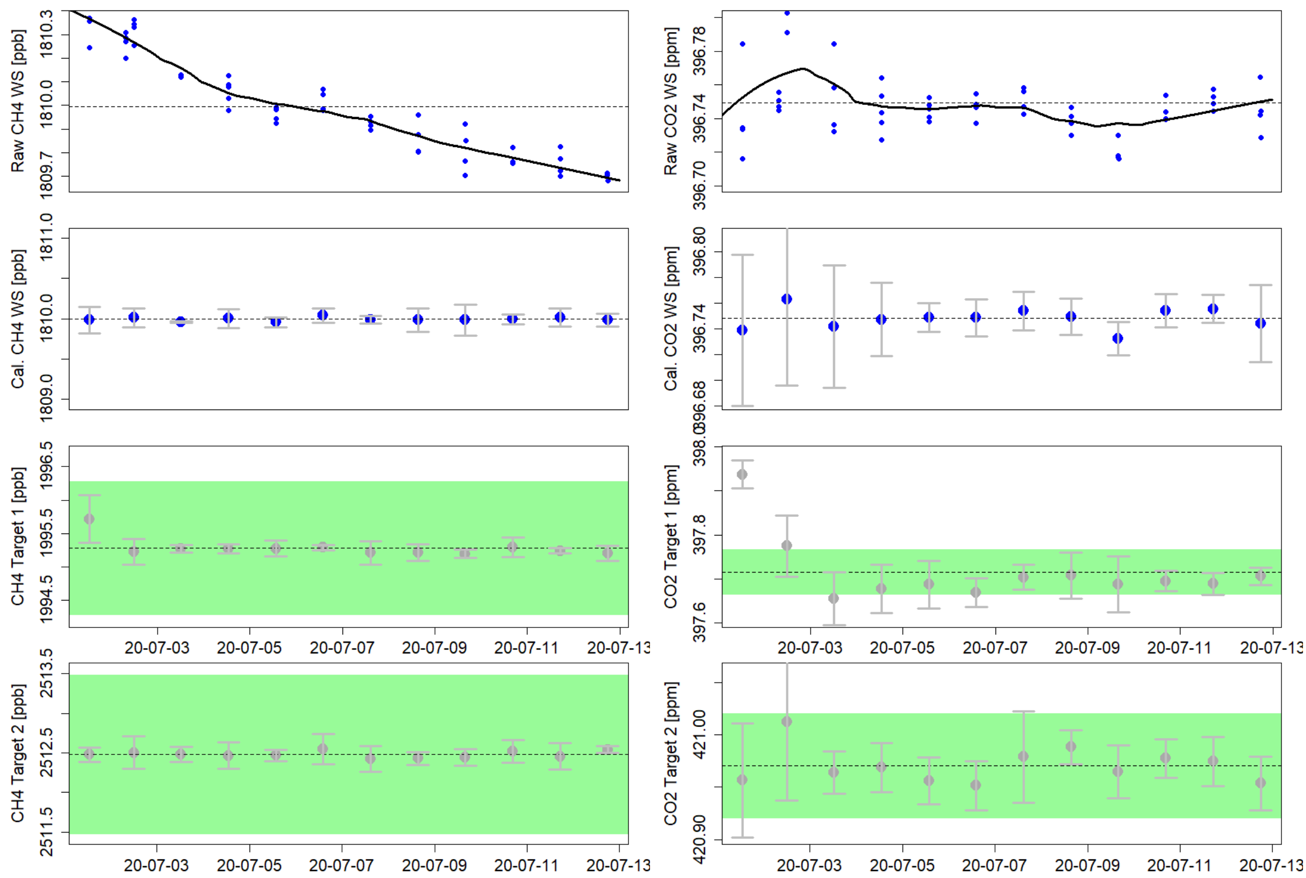

Figure 47. CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel show the results of the two target cylinders. Individual points in the three lower panels are five min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

For CO, the Picarro G2401 was calibrated every 1445 min with three WCC-Empa TS as 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.

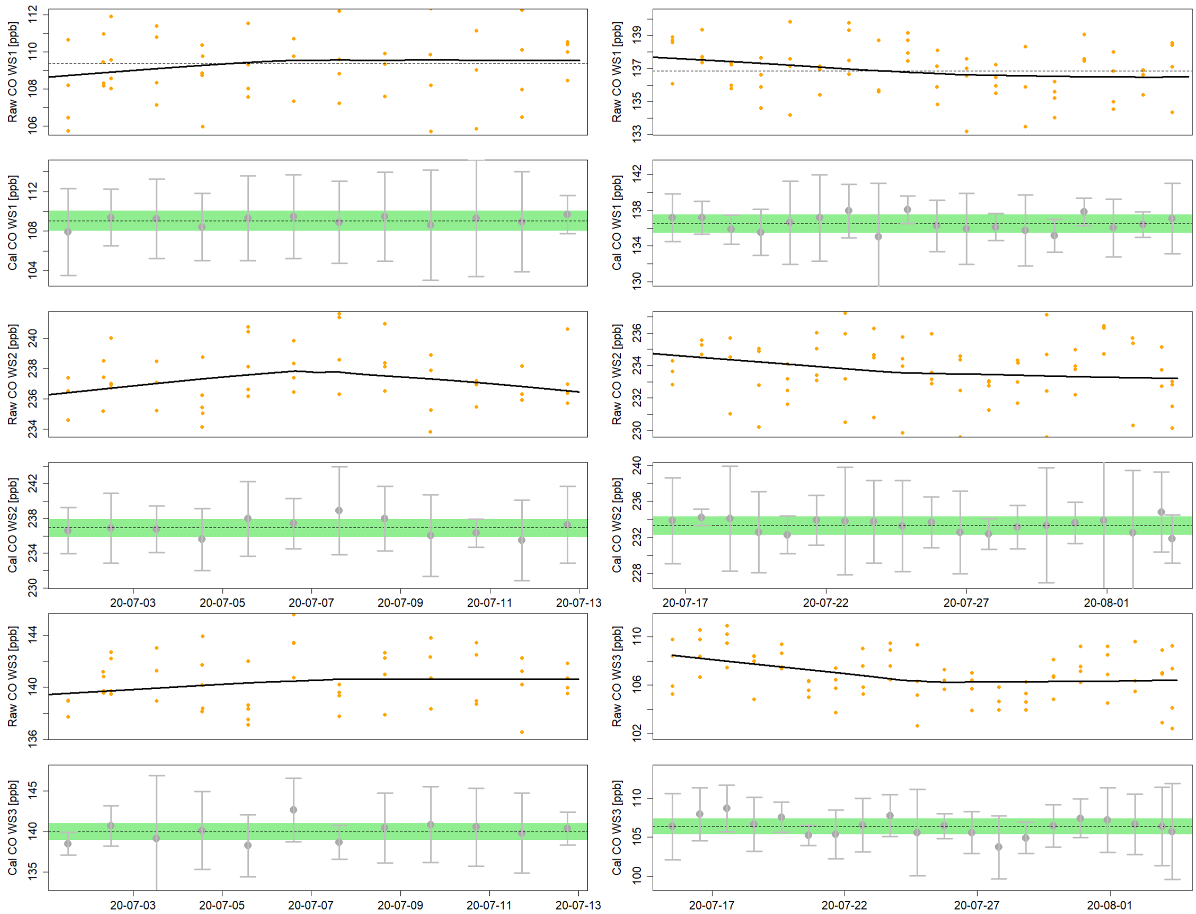

Figure 48. CO calibrations of the WCC-Empa-TI (Left: at the ICOS station. Right: at the GAW laboratory). The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are five min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

REFERENCES

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

Empa: Standard Operating Procedure (SOP), Messunsicherheit von Ozonnormalen und Ozonmessgeräten, 7. Ausgabe vom 13. Februar 2014., 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 WMO/GAW CO2 Calibration Scale, Atmos. Meas. Tech. Discuss., 2020, 1-33, 2020.

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.

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 World Meteorological Organization, Geneva, Switzerland, 2017.

Yver-Kwok, C., Philippon, C., Bergamaschi, P., Biermann, T., Calzolari, F., Chen, H., Conil, S., Cristofanelli, P., Delmotte, M., Hatakka, J., Heliasz, M., Hermansen, O., Komínková, K., Kubistin, D., Kumps, N., Laurent, O., Laurila, T., Lehner, I., Levula, J., Lindauer, M., Lopez, M., Mammarella, I., Manca, G., Marklund, P., Metzger, J. M., Mölder, M., Platt, S. M., Ramonet, M., Rivier, L., Scheeren, B., Sha, M. K., Smith, P., Steinbacher, M., Vítková, G., and Wyss, S.: Evaluation and optimization of ICOS atmosphere station data as part of the labeling process, Atmos. Meas. Tech., 14, 89-116, 2021.

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

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

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

Zhao, C. L. and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, Journal of Geophysical Research-Atmospheres, 111, 2006.

LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
FCL	Flask and Calibration Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
HPB	Hohenpeissenberg GAW Station
ICOS	Integrated Carbon Observation System
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
PI	Principle Investigator
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SN	Serial Number
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Travelling Standard
VURF	Vacuum UV Resonance Fluorescence
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

For more information, please contact:

World Meteorological Organization

Science and Innovation Department

7 bis, avenue de la Paix – P.O. Box 2300 – CH 1211 Geneva 2 – Switzerland

Tel.: +41 (0) 22 730 81 11 – Fax: +41 (0) 22 730 81 81

Email: GAW@wmo.int

Website: https://public.wmo.int/en/programmes/global-atmosphere-watch-programme

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