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

GLOBAL GAW STATION ZUGSPITZE-SCHNEEFERNERHAUS GERMANY SEPTEMBER 2020

Submitted to the World Meteorological Organization by

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WCC-Empa Report 20/3

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WCC-Empa Report 20/3

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CONTENTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 6th system and performance audit by WCC-Empa[1] at the global GAW station Zugspitze-Schneefernerhaus (ZSF) was conducted from 8 - 9 September 2020 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at ZSF, as well as the corresponding audit reports, is available from the WCC-Empa webpage (www.empa.ch/gaw).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Mr Cédric Couret	Zugspitze-Schneefernerhaus, station manager
Mr Ralph Sohmer	Zugspitze-Schneefernerhaus, station technician

This report summarises the assessment of the Zugspitze-Schneefernerhaus 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 Zugspitze-Schneefernerhaus, the national focal point for GAW in Germany, and the World Meteorological Organization in Geneva. The report will be posted on the internet (www.empa.ch/web/s503/wcc-empa).

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

Station Management and Operation

The Environmental Research Station Schneefernerhaus was established in 1999, and is managed by the Betriebsgesellschaft Umweltforschungsstation Schneefernerhaus (UFS) GmbH. The research at ZSF is coordinated by a consortium initiated by the Bavarian State Ministry of the Environment, Public Health and Consumer Protection, representing the Free State of Bavaria, the German Aerospace Centre, the Karlsruhe Institute of Technology (KIT/IMK-IFU), the German Research Centre for Environmental Health as well as the Federal Republic of Germany represented by the federal agencies of the German Meteorological Service (DWD) and the Federal Environment Agency (UBA). ZSF is also part of the Integrated Carbon Observation System (ICOS), and the labelling process as an ICOS class 2 station is currently on track. The measurements of the scope of the current audit are carried out by UBA. The staff responsible for the trace gas measurements is present at ZSF about four days a week.

Station Location and Access

The Environmental Research Station Zugspitze-Schneefernerhaus (ZSF) (47.4165°N, 10.97964°E, 2671 m a.s.l.) is located on the southern slope of Zugspitze, the highest mountain of the German Alps (2964 m a.s.l.). The station was moved from the Zugspitze summit (ZUG) to Schneefernerhaus during 2001/2002. It is located in southern Germany, about 90 km southwest of Munich, near the Austrian border and the town of Garmisch-Partenkirchen (720 m a.s.l.). A cable car and a cog wheel train lead directly to observatory. Measurements on the summit are partly ongoing but are no longer considered as part of the GAW programme. Further information is available from GAWSIS (https://gawsis.meteoswiss.ch/) and the station web site (https://schneefernerhaus.de/en/).

[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.

The location is adequate for the intended purpose. Year-round access to ZSF is possible by cable car, and material can be transported by the cog railway directly into the research station, which normally operates once per month.

Station Facilities

The ZSF research station offers extensive laboratory, office and conference facilities. Accommodation (45 beds) for scientists and two kitchens which may be used by scientists who stay overnight is available. During the operation times of the cable car (usually 8:00 – 15:00) it is possible to visit the restaurant "SonnAlpin" in the ski resort Zugspitzplatt. ZSF is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Measurement Programme

The ZSF station comprises a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured parameters is available from GAWSIS. The information available from GAWSIS was reviewed as part of the audit.

> **Recommendation 1 (***, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. Part of the reviewed information was not up to date and 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 May 2021, data of the scope of the audit has been submitted to the World Data Centres by ZSF:

Submission to the World Data Centre for Reactive Gases (WDCRG):

O_3 (four data sets, 1978-2011 from ZUG, and three data sets covering the period 2002-2019 from ZSF)

Submission to World Data Centre for Greenhouse Gases (WDCGG):
CO_2 (1981-1990, ZUG, submitted by IMK-IFU)
CO_2 (1995-2001, ZUG, submitted by UBA)
CO_2 (2002-2020, ZSF, submitted by UBA)
CH_4 (1995-2001, ZUG, submitted by UBA)
CH_4 (2002-2020, ZSF, submitted by UBA)
CO (1995-2001, ZUG, submitted by UBA)
CO (2008-2020, ZSF, submitted by UBA)
N_2O (2003-2020, ZSF, submitted by UBA)

Data shown in this report was accessed on 3 May 2021.

> **Recommendation 2 (***, important, ongoing)**
> *Data has been timely submitted for all parameters of the scope of the audit. 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.*
>
> **Recommendation 3 (**, important, 2020)**
> *No CO data is available from WDCGG for the period from 2002 until 2007. It recommended to submit these data if they are available and of sufficient quality.*

Data Review

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

Documentation

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

Air Inlet System

The design of the air inlet systems has not been changed since the last audit by WCC-Empa. The heated air intake is located on the terrace above the laboratory, 2.5 m above the roof. The inlet is protected against rain and snow and consists of 8 cm inner diameter glass tube which serves as a manifold. From there, instruments are connected using suitable materials (stainless steel for GHG and CO measurements, PFA for ozone measurements). The inlet systems are adequate, and no change is required.

An additional air intake was installed at the ridge above to the ZSF station at an altitude of 2825 m a.s.l. A direct Synflex 1300 line, which is flushed at a high flow rate with a flushing pump, is used to sample air which is analysed by a CRDS instrument for the comparison of CO, CO_2, and CH_4 measurements with the ZSF air intake location. These measurements are currently not considered for the submission to the data centres, but are used to studying the exposure of ZSF to local pollution events.

Surface Ozone Measurements

Surface ozone measurements from Zugspitze are available since 1978. Until 2001, the measurements were made at ZUG, and moved to ZSF in 2002. Continuous time series are available since the start of the measurements in 1978.

Instrumentation. ZSF is currently equipped with two ozone analysers (Thermo Scientific 49i and Horiba APOA-370). The Horiba instrument only serves as a short-term backup system in case the Thermo Scientific 49i fails, and it is normally not running. In case of a failure of the Thermo Scientific 49i, it will be replaced within a few days by a spare instrument from UBA.

Standards. A Thermo Scientific 49i-PS ozone standard is available. The instrument has traceability to the NIST Standard Reference Photometer (SRP) #29 maintained at UBA Langen. The last certification was done on 18 February 2020.

Data Acquisition. The GAWDAQ system, which was developed by the former station manager, has been replaced by a commercial data acquisition solution (Breitfuss GmbH). The data acquisition system is fully appropriate, and no further action is required.

Intercomparison (Performance Audit). The ZSF ozone analyser (Thermo Scientific 49i) and ozone calibrator (Thermo Scientific 49i-PS) were compared against the WCC-Empa travelling standard (TS) with traceability to a SRP#15. The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system (WCC-Empa TS) and the ZSF data acquisition system (ZFS instruments). The following equations characterise the bias of instruments and the remaining uncertainty after compensation of the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the ozone absorption cross section of 11.476x10^{-18} cm^2 molecule^{-1} (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #1173620016 (BKG -0.1 nmol mol^{-1}, SPAN 0.998):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] - 0.39 nmol mol^{-1}) / 0.9957 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.19e-05 * X_{O3}^2) (1b)

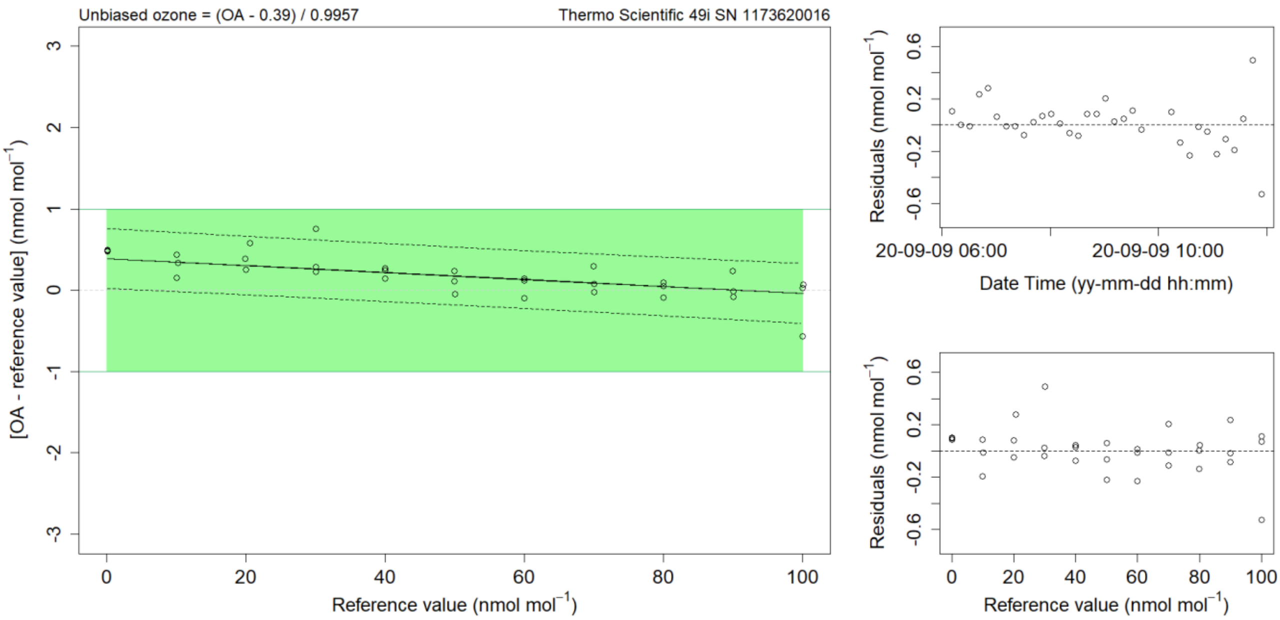

Figure 1. *Left: Bias of the ZSF ozone analyser (Thermo Scientific 49i #1173620016) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

The comparison between the WCC-Empa TS was analysed with and without applying the correction based on the certification against SRP#29 at UBA Langen. The result without correction agreed slightly better, which is shown below.

Thermo Scientific 49i-PS #1163020021 (BKG 0.0 nmol mol^{-1}, SPAN 0.994, uncorrected):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OC] - 0.07 nmol mol^{-1}) / 0.9993 (1c)

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

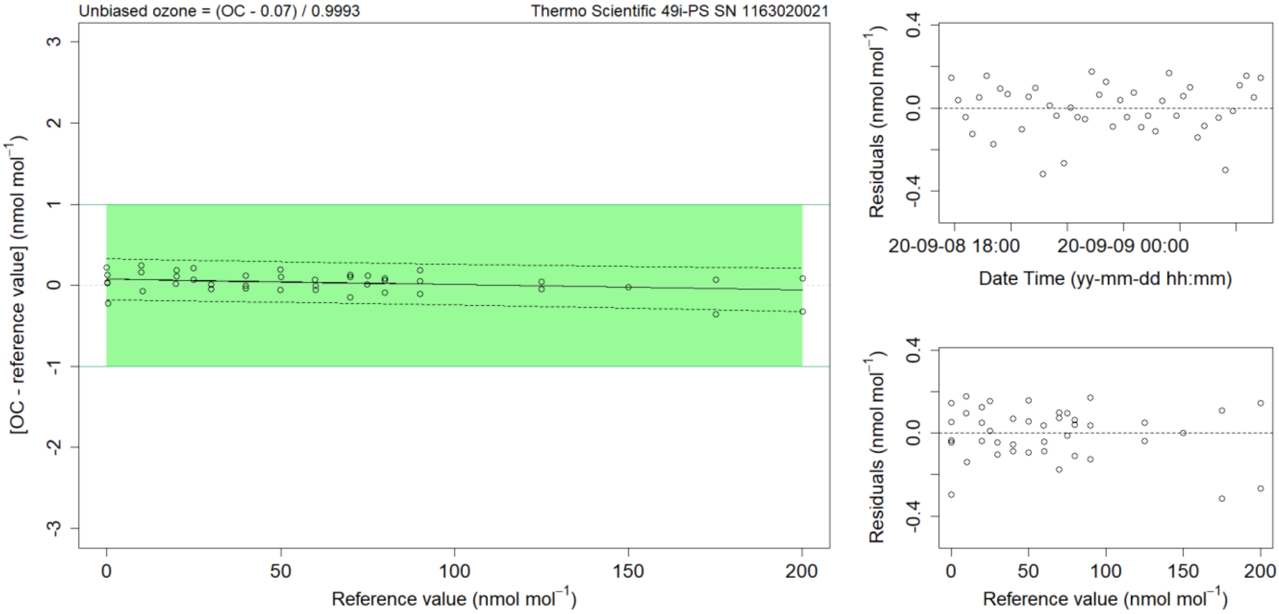

Figure 2. *Same as above for the ZSF Thermo Scientific 49i-PS #1163020021 ozone calibrator (uncorrected, data as measured by the instrument were used for the comparison).*

Thermo Scientific 49i-PS #1163020021 (BKG 0.0 nmol mol^{-1}, SPAN 0.994, data corrected based on the calibration certificate from UBA Langen from 18. February 2020):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OC] - 0.24 nmol mol^{-1}) / 0.9948 (1e)

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

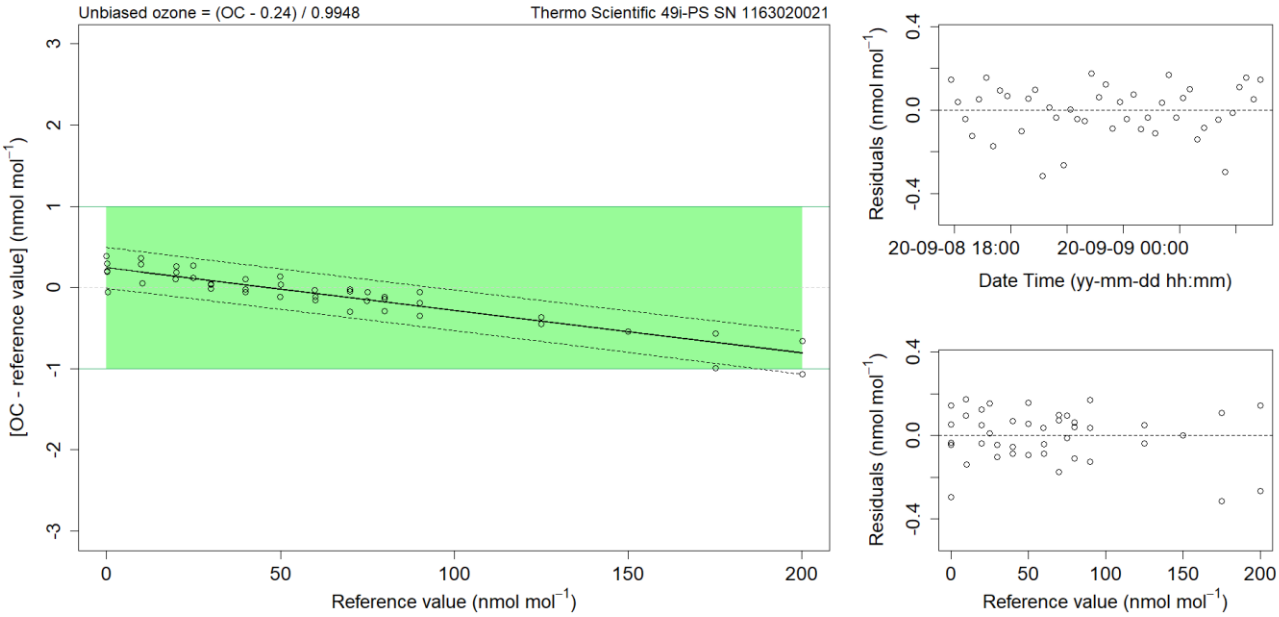

Figure 3. *Same as above for the ZSF Thermo Scientific 49i-PS #1163020021 ozone calibrator (corrected based on calibration certificate from UBA Langen from 18. February 2020).*

The results of the comparisons can be summarised as follows:

The agreement of the ZSF ozone analyser and calibrator was within the WMO/GAW DQOs for all comparisons. However, it should be noted that the agreement slightly decreased when the values based on the correction with SRP#29 were used. However, the bias was small and within the uncertainty of SRP-SRP comparisons.

Recommendation 4 (, important, 2020)**
Regular certification (at least every 3 years) of the ZSF ozone calibrator against a SRP is recommended. Due to the small difference observed during the calibrations with the WCC-Empa reference (traceable to SRP#15) and the reference of UBA Langen (SRP#29), re-calibration at UBA Langen with the next few months is recommended.

Carbon Monoxide Measurements

Carbon monoxide measurements at Zugspitze commenced in 1995. Until 2001, the measurements were made at ZUG, and moved to ZSF in 2002. Continuous time series are available for the period 1995 – 2001 from ZUG, and since 2008 from ZSF.

Instrumentation. Zugspitze-Schneefernerhaus is equipped with a Cavity Ring-Down Spectroscopy (CRDS) analyser (Picarro G2401) and an Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument (LGR 913-0015-1000).

Standards. The station is equipped with four laboratory standards from NOAA. In addition, working and target standards are available. The NOAA standard are used every two months to calibrate two working standards. These two WS are then used every three days to calibrate another WS, which then is used to apply a calibration every 8 hours. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the ZSF instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figures 4 and 5 with respect to the WMO GAW DQOs (WMO, 2014):

LGR 913-0015-1000 #14-0066:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 6.6) / 1.020 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.6 + 1.01e-04 * X_{CO}^2) (2b)

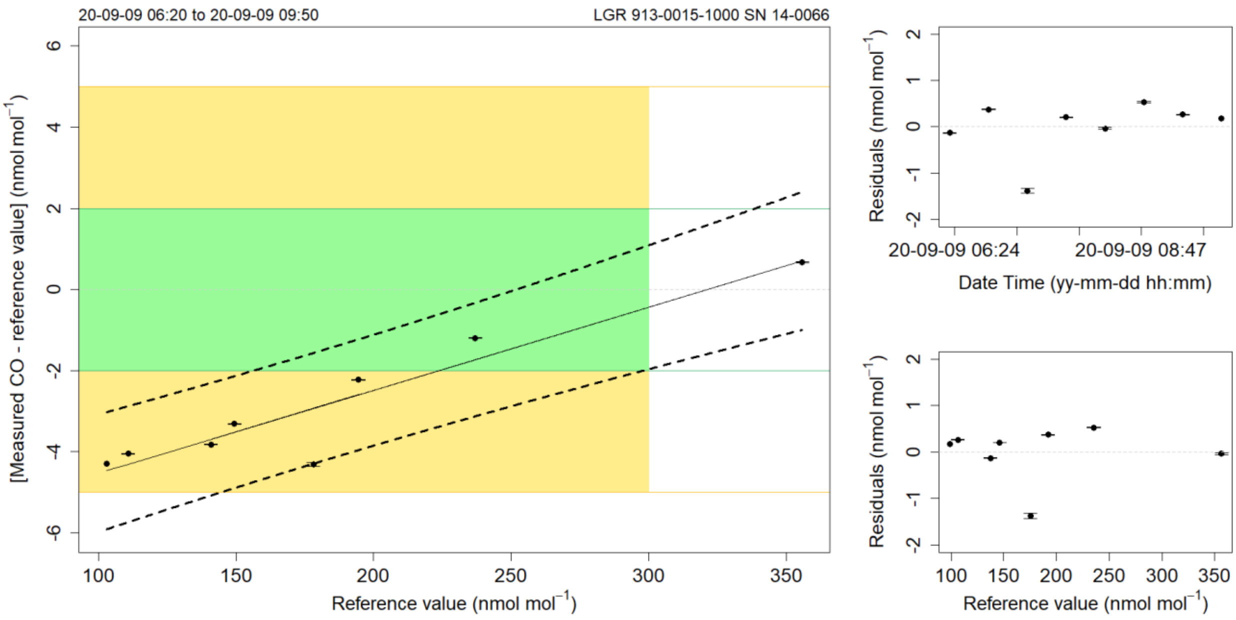

Figure 4. *Left: Bias of the ZSF LGR 913-0015-1000 #14-0066 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for ZSF. 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 #2663-CFKADS2243:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 7.3) / 1.022 (2c)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.7 + 1.01e-04 * X_{CO}^2) (2d)

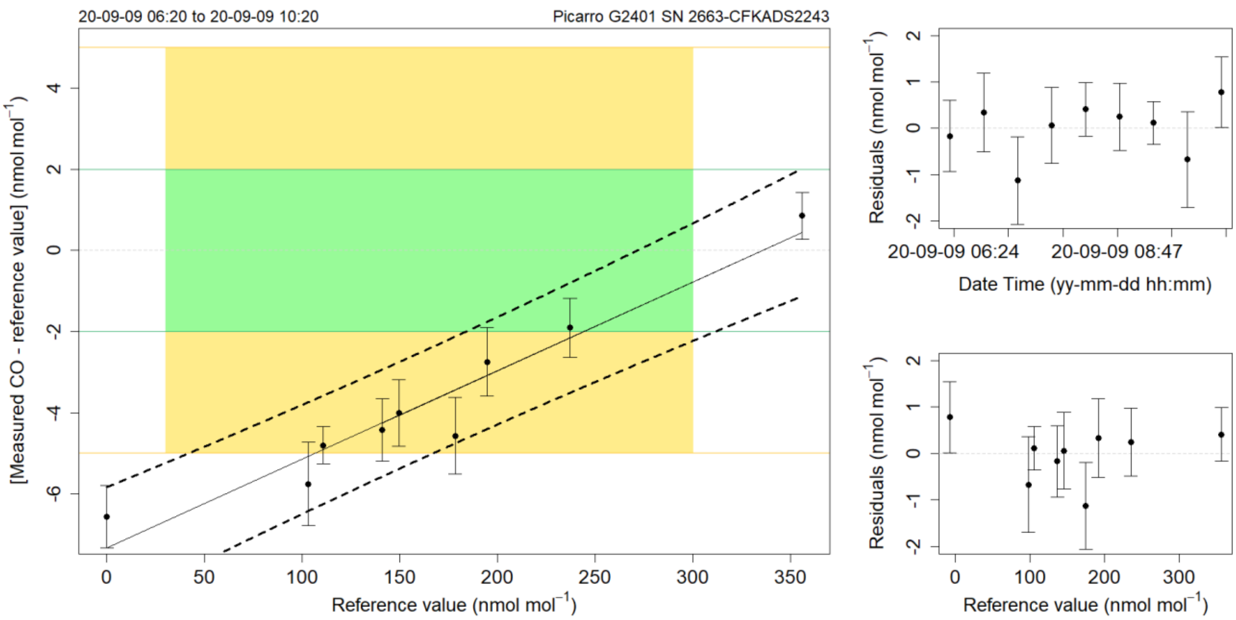

Figure 5. *Same as above, for the Picarro G2401 #2663-CFKADS2243 instrument.*

The results of the comparisons can be summarised as follows:

Significant deviations were observed for both the LGR 913 and the Picarro G2401 instrument. Both instruments showed agreement at higher mole fractions within the WMO/GAW network compatibility goals, but both instruments were measuring low at lower mole fractions. The deviations were characterised by good linearity, and can most likely be explained by drift of the ZSF laboratory standards. In January 2021, ZSF received a set of standards from the ICOS Flask and Calibration Laboratory (FCL), and measurements of ZSF confirmed the differences found by the current audit. Interestingly, the deviation was not observed by the comparison of ambient air with the travelling instrument (see further below). The reason is probably the fact that only one working standard at ~175 nmol mol^{-1} was used to calibrated the station analyser during the ambient air comparison, whereas the full suite of standards was used for the measurements of the WCC-Empa TS.

Recommendation 5 (, important, 2021)**
The reason for the bias between ZSF CO measurements the WCC-Empa CO values needs to be identified. Most likely, drift of the ZSF NOAA standards caused the bias. Recalibration of the standards at NOAA and/or purchase of additional standards is recommended.

Recommendation 6 (, important, 2021)**
Drift is a serious issue for CO standards, especially at low mole fractions. WCC-Empa therefore recommends to carefully assess the linearity of all CO analyser, and use in case of proven linearity CO free zero air and standards with higher CO amount fractions (>500 nmol mol^{-1}) for calibrations.

Methane Measurements

Methane measurements at Zugspitze commenced in 1995. Until 2001, the measurements were made at ZUG, and moved to ZSF in 2002. Continuous time series are available since the start of the measurements in 1995.

Instrumentation. ZSF is equipped with two CDRS methane analysers (Picarro G2301 and G2401). The Picarro G2301 instrument is sampling air from the main ZSF inlet system, and the Picarro G2401 is used to sample air from the mountain ridge above the Schneefernerhaus. This is done to compare the values between the two different inlet locations.

Standards. The station is equipped with four laboratory standards from NOAA. In addition, working and target standards are available. The calibration strategy is identical as described for CO. A list of available standards is given in the Appendix.

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

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

Picarro G2301 #2043-CFADS2378:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.8 nmol mol^{-1}) / 0.9986 (3a)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.2 + 1.30e-07 * X_{CH4}^2) (3b)

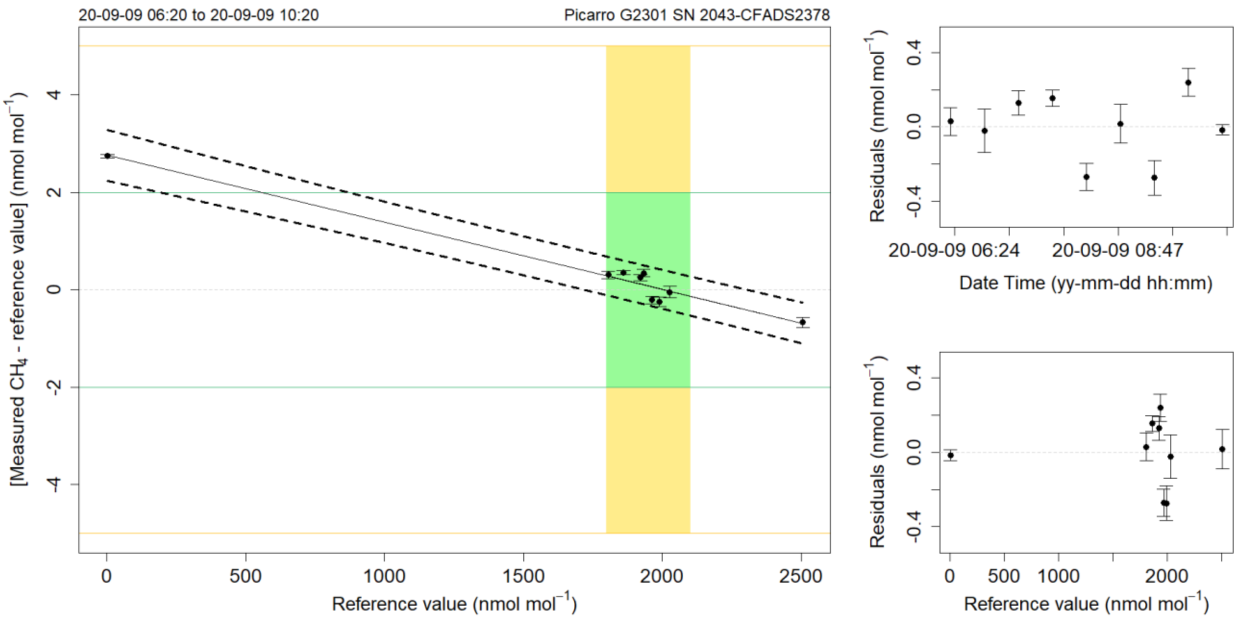

Figure 6. *Left: Bias of the Picarro G2301 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for ZSF. 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 #2663-CFKADS2243:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.0 nmol mol^{-1}) / 0.9991 (3e)

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

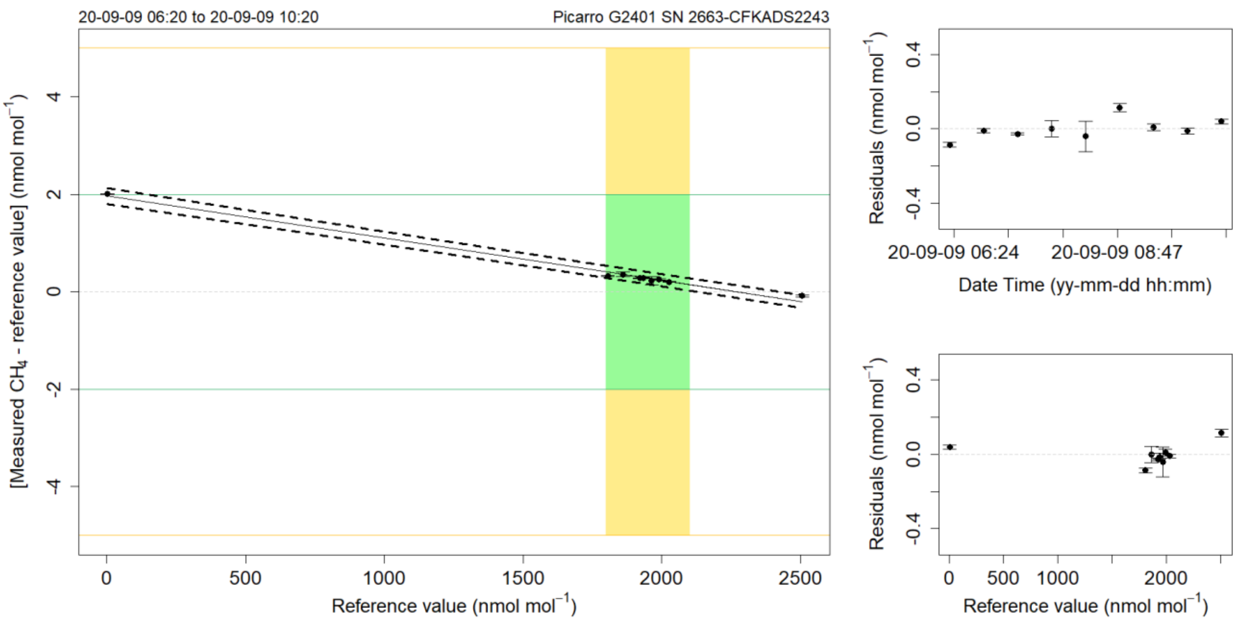

Figure 7. *Same as above, for the Picarro G2401 methane analyser*

The result of the comparison can be summarised as follows:

Excellent agreement well within the WMO/GAW compatibility goal was found for both CRDS instruments. However, the 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

Carbon Dioxide measurements at Zugspitze commenced in 1981. Until 2001, the measurements were made at ZUG using NDIR technique (URAS instruments), and moved to ZSF in 2002. Until 2010, measurements at ZSF were made with a GC/FID/methaniser system, which was succeeded by the CRDS technique. Continuous time series are available since the start of the measurements in 1981, except for the period from 1991-1994.

Instrumentation. ZSF is equipped with two CDRS methane analysers (Picarro G2301 and G2401). The Picarro G2301 instrument is sampling air from the main ZSF inlet system, and the Picarro G2401 is used to sample air from the mountain ridge above the Schneefernerhaus. This is done to compare the values between the two different inlet locations.

Standards. The station is equipped with four laboratory standards from NOAA. In addition, working and target standards are available. The calibration strategy is identical as described for CO. A list of available standards is given in the Appendix.

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

The following equation characterises the instrument bias. The result is further illustrated in Figure 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2301 #2043-CFADS2378:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.16 µmol mol^{-1}) / 0.99952 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.005 + 3.28e-08 * $X_{CO2}{}^2$) (4b)

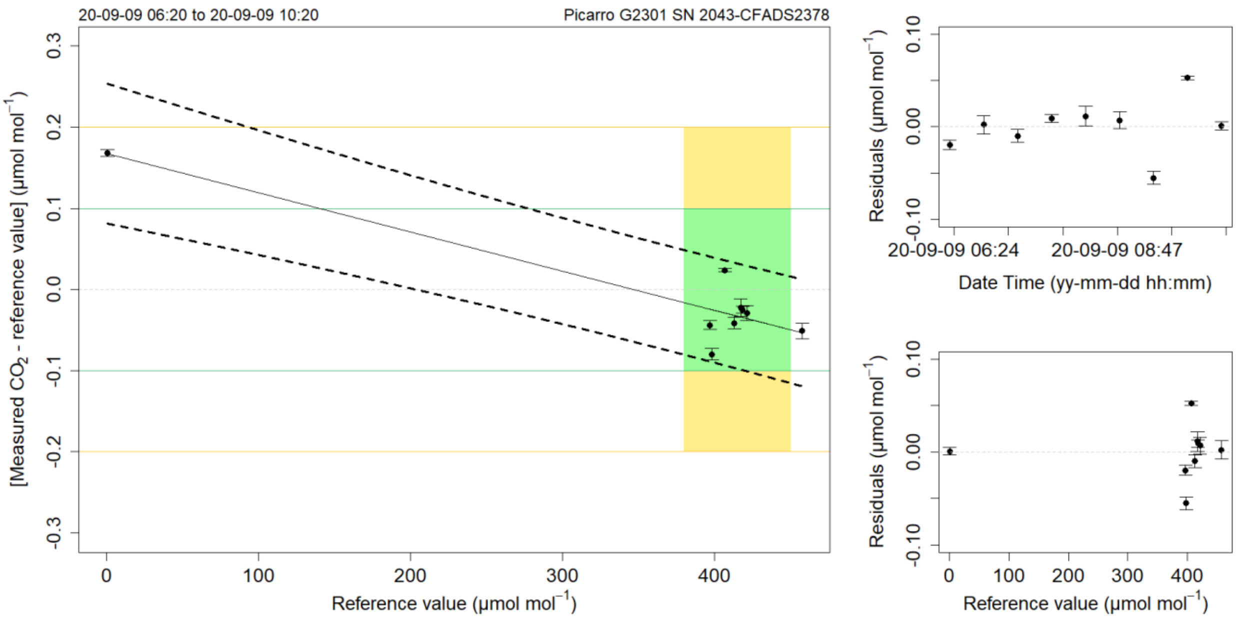

Figure 8. *Left: Bias of the Picarro G2301 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for ZSF. 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 #2663-CFKADS2243:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.14 µmol mol^{-1}) / 0.99966 (4c)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.005 + 3.28e-08 * X_{CO2}^2) (4d)

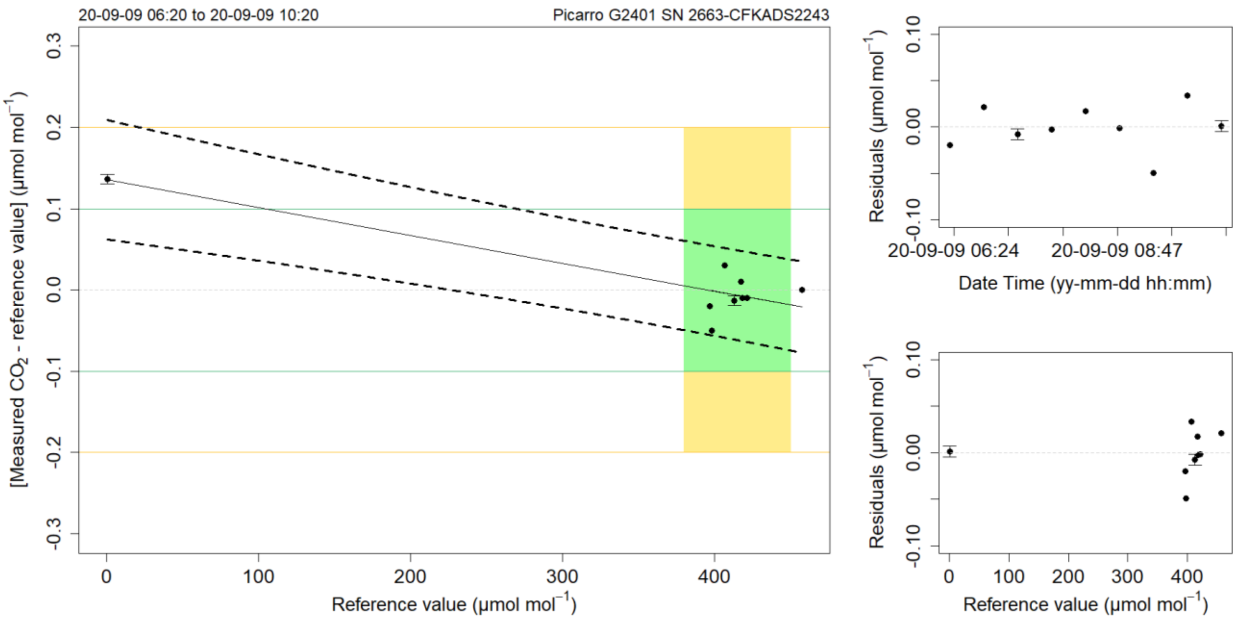

Figure 9. *Same as above, for the Picarro G2401 carbon dioxide analyser.*

The result of the comparison can be summarised as follows:

Both ZSF CRDS instruments showed excellent agreement within the WMO/GAW compatibility goals in the relevant mole fraction range. The bias depended slightly on the mole fraction with a zero offset. The reason for this is most likely the different calibration strategy between WCC-Empa (calibrations are done with a set four reference standards and CO_2 free air), and ZSF (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 7 (, important, 2021)**
It is recommended to update the data to the WMO-X2019 CO_2 calibration scale. (This task was already completed in April 2021).

Nitrous Oxide Measurements

Nitrous oxide measurements at Zugspitze commenced in 2000 using a GC/ECD system, which was in operation until 2015. Starting in 2016, measurements have been made using the OA-ICOS technique. Continuous time series are available since 2003.

Instrumentation. Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument (LGR 913-0015-1000).

Standards. The station is equipped with four laboratory standards from NOAA. In addition, working and target standards are available. The calibration strategy is identical as described for CO. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the ZSF instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 10 with respect to the WMO GAW DQOs (WMO, 2020):

LGR 913-0015-1000 #14-0066:

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 5.98) / 1.0182 (5a)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.06 + 1.01e-07 * X_{N2O}^2) (5b)

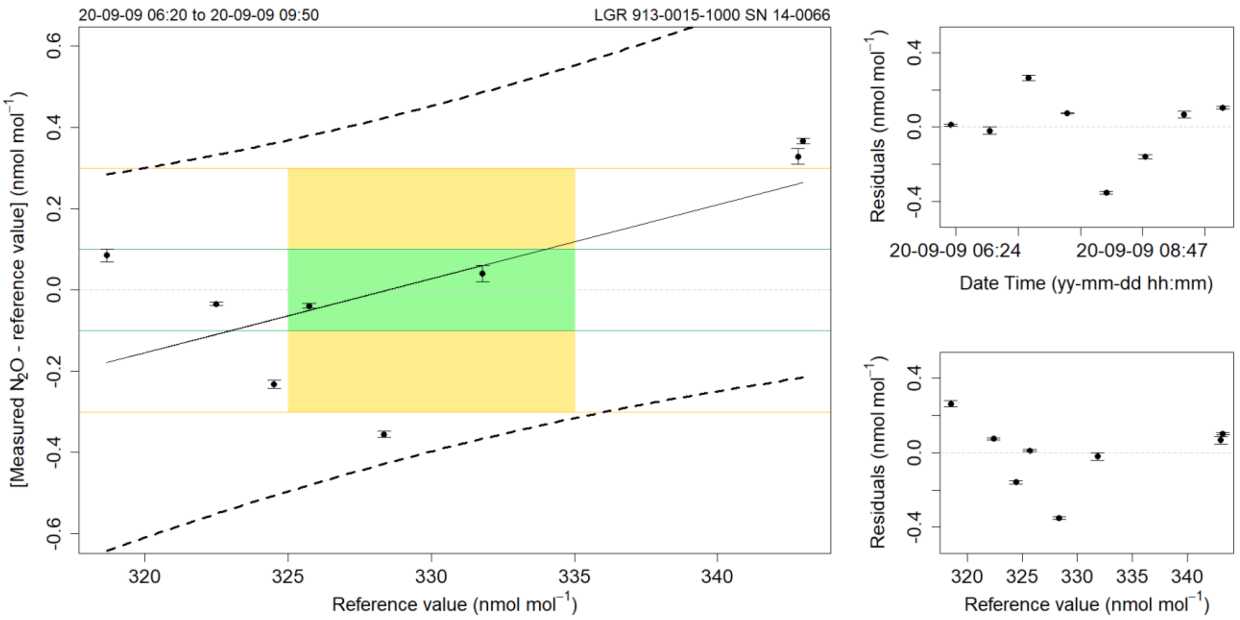

Figure 10. *Left: Bias of the LGR 913 N_2O analyser with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for ZSF. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The average agreement between ZSF and WCC-Empa was within the extended WMO/GAW network compatibility goals. The individual uncertainties of the ZSF measurements were small, but the consistency was rather poor. Considering the uncertainty of the reference standards, which is larger than the WMO/GAW network compatibility goal of 0.1 nmol mol^{-1}, the results are as good as it can be expected for a fully adequate analytical system. The limiting factor for further improving the results is currently the uncertainty of the reference standards. Therefore, the system of ZSF is fully adequate, and no further action is required.

ZSF PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the ZSF 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 11 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 12. 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 ZSF audit are shown as coloured dots in Figure 11 and 12, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also given in Table 1.

The results were within the DQOs for O_3, CH_4 and CO_2, and the extended WMO/GAW network compatibility goals was reached for N_2O. The DQOs were not met for CO, which needs further attention, especially as this has not been confirmed by the ambient air comparison where good agreement was observed.

Table 1. *ZSF performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5-7th columns show the percentage of all WCC-Empa and WCC-N_2O audits 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**	**ZSF within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**
O_3 (Thermo Scientific 49i #1173620016)	0 -100	nmol mol^{-1}	✓	64	NA
O_3 (Thermo Scientific 49i-PS #1163020021, uncorrected)	0 -100	nmol mol^{-1}	✓	64	NA
O_3 (Thermo Scientific 49i-PS #1163020021, corrected)	0 -100	nmol mol^{-1}	✓	64	NA
CO (LGR 913-0015-1000 #14-0066)	30 - 300	nmol mol^{-1}	✗	20	49
CO (Picarro G2401 #2663-CFKADS2243)	30 - 300	nmol mol^{-1}	✗	20	49
CH_4 (Picarro G2301 #2043-CFADS2378)	1750 - 2100	nmol mol^{-1}	✓	71	93
CH_4 (Picarro G2401 #2663-CFKADS2243)	1750 - 2100	nmol mol^{-1}	✓	71	93
CO_2 (Picarro G2301 #2043-CFADS2378)	380 - 450	µmol mol^{-1}	✓	43	69
CO_2 (Picarro G2401 #2663-CFKADS2243)	380 - 450	µmol mol^{-1}	✓	43	69
N_2O (LGR 913-0015-1000 #14-0066)	325 - 335	nmol mol^{-1}	✓	2	40

[1] Percentage of stations within the eDQO and DQO

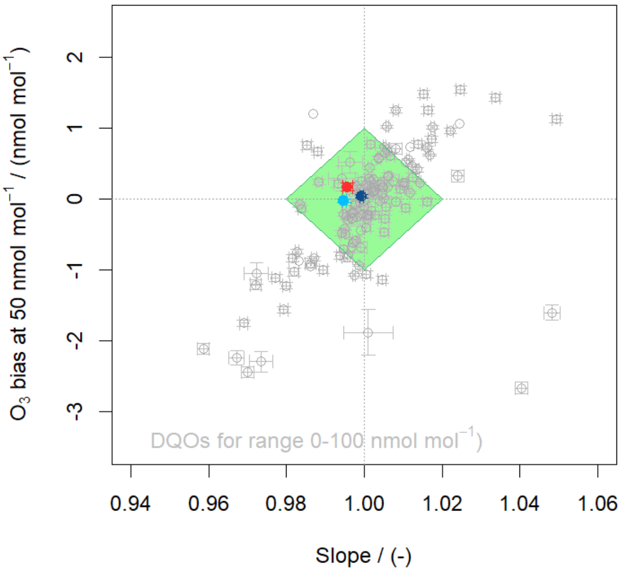

Figure 11. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the results of the ZSF instruments (red: Thermo Scientific 49i #1173620016, dark blue: Thermo Scientific 49i-PS #116302002 uncorrected, light blue: Thermo Scientific 49i-PS #116302002 corrected). The green area corresponds to the WMO/GAW DQO for surface ozone.*

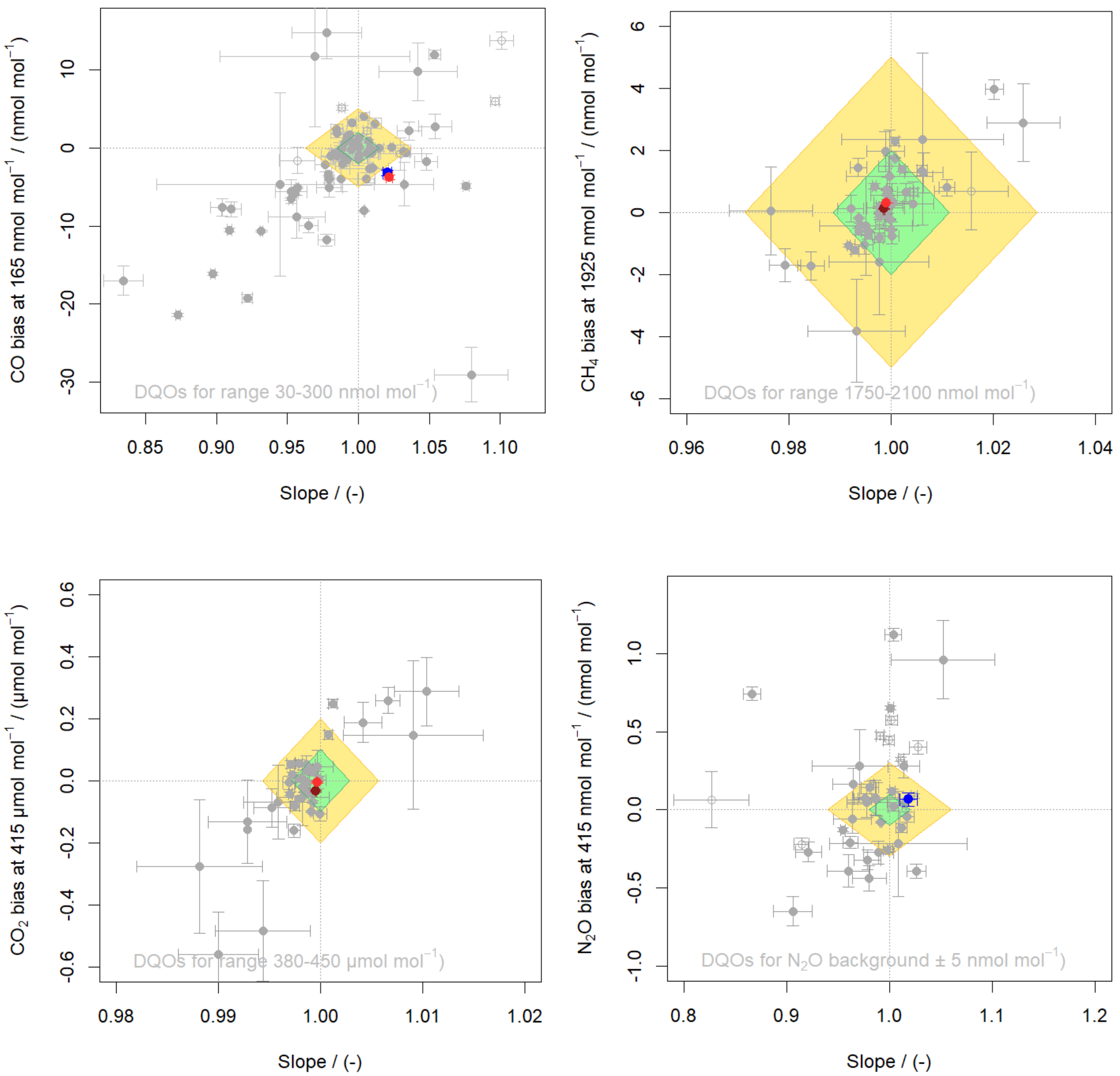

Figure 12. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show ZSF results (blue: LGR 913-0015-1000 #14-0066, red: Picarro G2401 #2663-CFKADS2243, dark red: Picarro G2301 #2043-CFADS2378). 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 an independent travelling instrument (TI) (Picarro G2401). The TI of WCC-Empa was installed during the audit, but a leak was discovered after the comparison of the first data. The leak was inside the TI downstream of the internal filter, and it could not be fixed. It was decided to use the ZSF Picarro G2401 #2663-CFKADS2243A as the travelling instrument. This instrument was disconnected from the inlet to the ridge and was connected to the WCC-Empa calibration system, which was completely independent from the ZSF setup. The TI was running from 5 October 2020 through 9 November 2020. The TI was connected to a separate independent inlet line sampling from the same location as the ZSF analyser. 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 ZSF data shown here were processed by the ZSF station manager.

Carbon monoxide

Figure 13 shows the comparison of hourly CO between the travelling instrument and the ZSF LGR 913-0015-1000 analyser. The corresponding deviation histograms are shown in Figure 14.

The LGR 913-0015-1000 analyser captured the temporal variability of CO well, and showed agreement within the WMO/GAW network compatibility goals compared to the TI. This contradicts the findings of the performance audit with travelling standards, where larger deviations were found. As discussed above, this most likely is due to the fact that that only one working standard was used for calibration of the ambient air data while all NOAA tanks were used for determination of the CO mole fraction in the travelling standards.

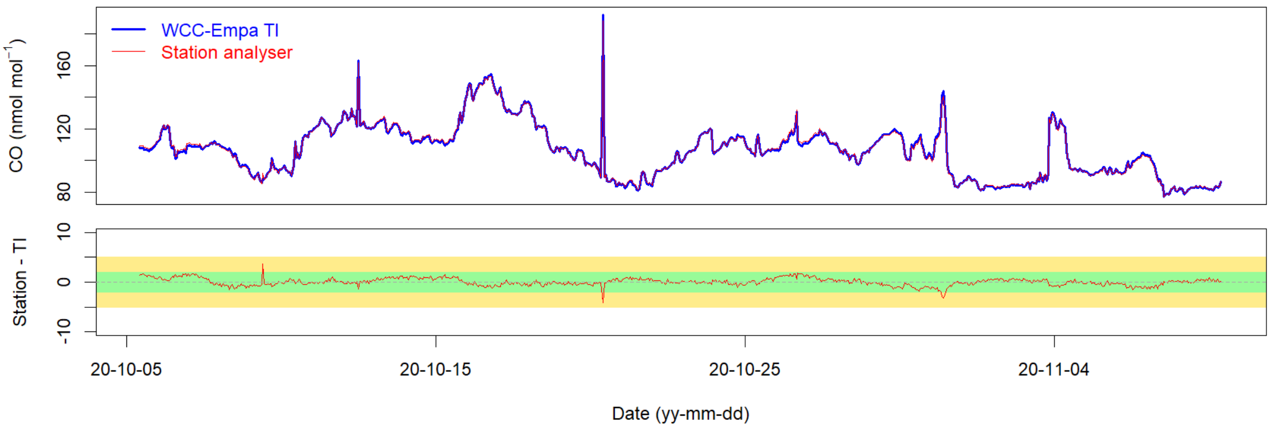

Figure 13. *Comparison of the LGR 913-0015-1000 analyser with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

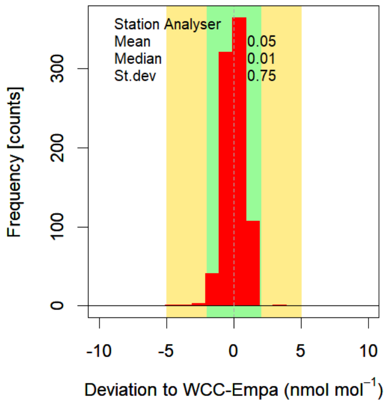

Figure 14. *Carbon monoxide deviation histograms for the ZSF LGR 913-0015-1000 analyser.*

Methane

Figure 15 shows the comparison of hourly CH_4 between the TI and the ZSF Picarro G2301. The corresponding deviation histograms are shown in Figure 16. Excellent agreement within the WMO/GAW network compatibility goals was found between the TI and the ZSF instrument, which confirms the results of the performance audit using traveling standards. The temporal variation was well captured by both instruments.

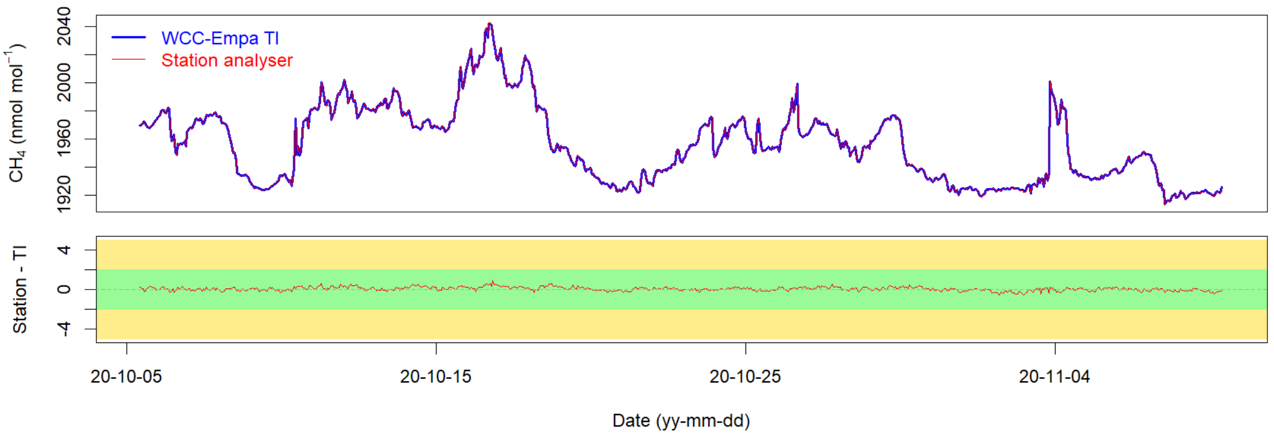

Figure 15. *Comparison of the ZSF Picarro G2301 with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

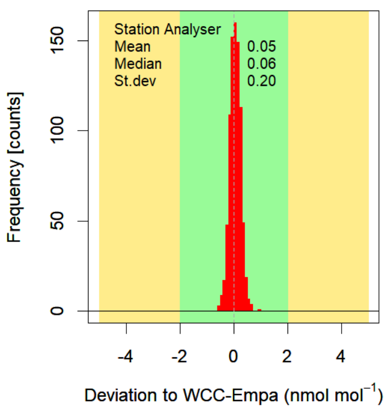

Figure 16. *Methane deviation histogram for the ZSF Picarro G2301.*

Carbon dioxide

Figure 17 shows the comparison of hourly CO_2 between the TI and the ZSF Picarro G2301, and Figure 18 shows the corresponding deviation histogram. The temporal variability was well captured by both instruments, and no dependency of the bias on the amount fraction was observed. The agreement was on average within the WMO/GAW network compatibility goals, which confirms the results of the performance audit using traveling standards. Towards the end of the comparison, the deviation became larger. This finding was discussed with the ZSF station manager, and the change started after an adjustment of the calibration gas output pressures. Most likely, it is an adsorption effect on the pressure regulators, which needs further attention.

> **Recommendation 8 (**, important, 2021)**
> *It is recommended to further investigate the dependency of the CO_2 measurements on the output pressure of the pressure regulators. In case significant adsorption/desorption of CO2 occurs, change of the pressure regulator model is recommended.*

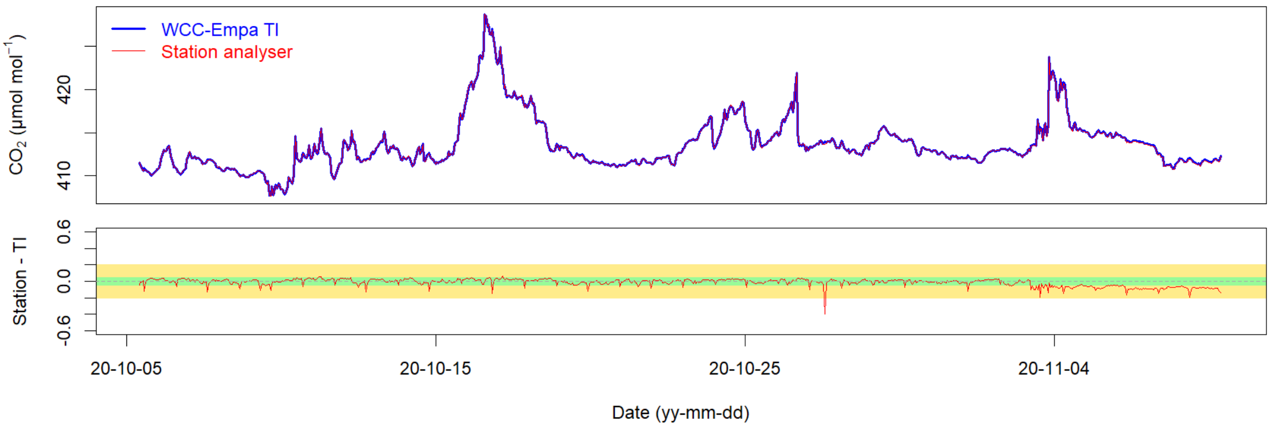

Figure 17. *Comparison of the ZSF Picarro G2301 with the travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

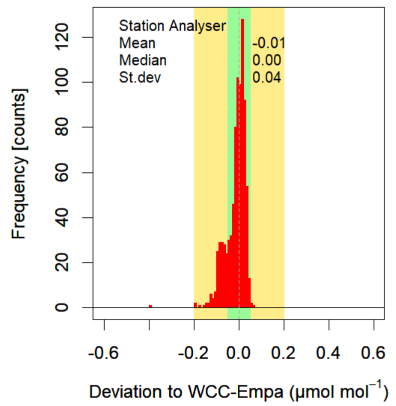

Figure 18. *Carbon dioxide deviation histogram of the ZSF Picarro G2301 compared to WCC-Empa.*

The good results of the ambient air comparison demonstrates that the entire system, including instruments, calibration, inlet system, and data processing is fully appropriate.

CONCLUSIONS

The global GAW station Zugspitze-Schneefernerhaus provides extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects, which makes it a very significant contribution to the GAW programme.

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, an issue with the calibration of the CO instruments needs further attention. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Please note that Table 2 refers only to the mole fractions relevant to ZSF, 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 LGR 913	CO Picarro G2401	CH_4 Picarro G2301	CH_4 Picarro G2401	CO_2 Picarro G2301	CO_2 Picarro G2401	N_2O LGR 913
Audit with TS	✓	✓	(✓)	✓	✓	✓	✓	(✓)
Ambient air comparison	NA	✓	NA	✓	NA	✓	NA	NA

NA no ambient air comparisons were made for O_3 and N_2O; the ZSF Picarro G2401 was used as the TI.

The continuation of the Zugspitze-Schneefernerhaus 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 ZSF GAW STATION

System Audit Aspect	Adequacy[#]	Comment
Measurement programme	(5)	Comprehensive programme
Access	(5)	Year round access
Facilities		
Laboratory and office space	(5)	Large and adequate laboratories, space for additional campaigns
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(5)	Fully adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2	(5)	State of the art instrumentation
CO	(5)	State of the art instrumentation
N_2O	(5)	State of the art instrumentation
Standards		
O_3	(4)	Adequate standard, small difference between WCC and UBA calibration
CO, CO_2, CH_4, N_2O	(5)	Standards from the CCL
Data Management		
Data acquisition	(5)	Fully adequate system
Data processing	(5)	Skilled staff, appropriate procedures
Data submission	(4)	Timely submission for all parameter, part of the CO data missing

[#]0: inadequate thru 5: adequate.

Dübendorf, May 2021



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APPENDIX

Data Review

The following figures show summary plots of ZSF data accessed on 4 May 2021 from WDCRG and WDCRG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

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

Surface ozone:

Several data sets are available for ozone from WDCRG. The three sets of ZSF ozone data were made using different instruments.

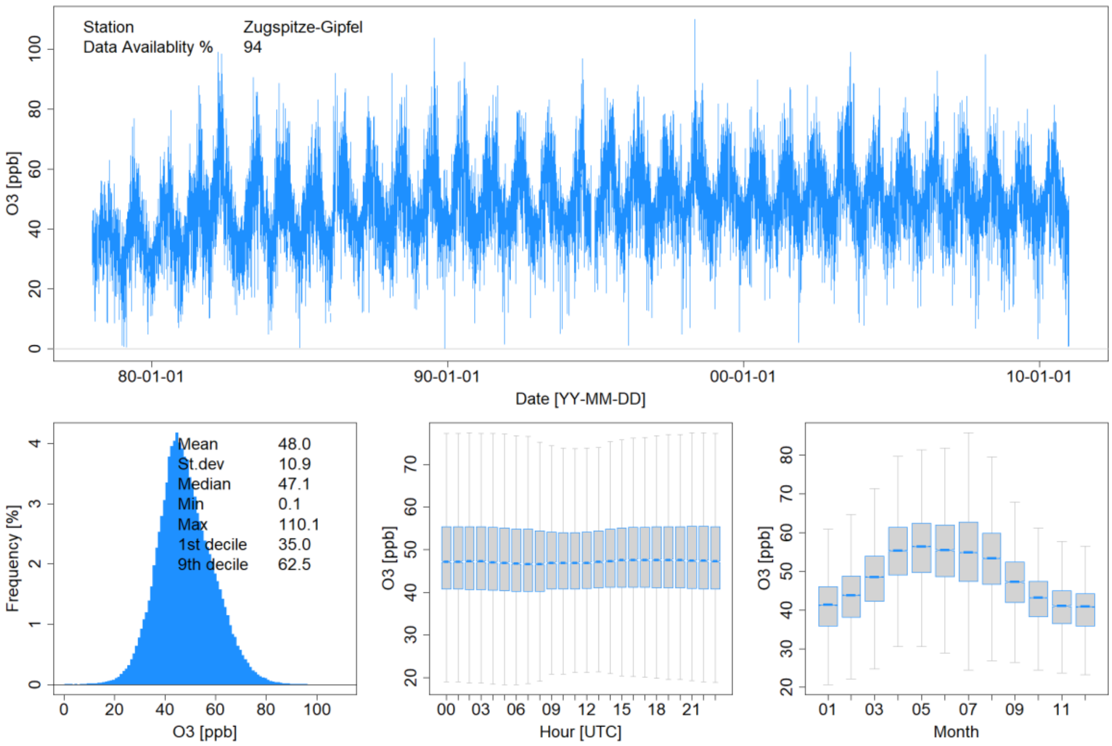

Figure 19. *O_3 data (ZUG) for the period from 1978 to 2011 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

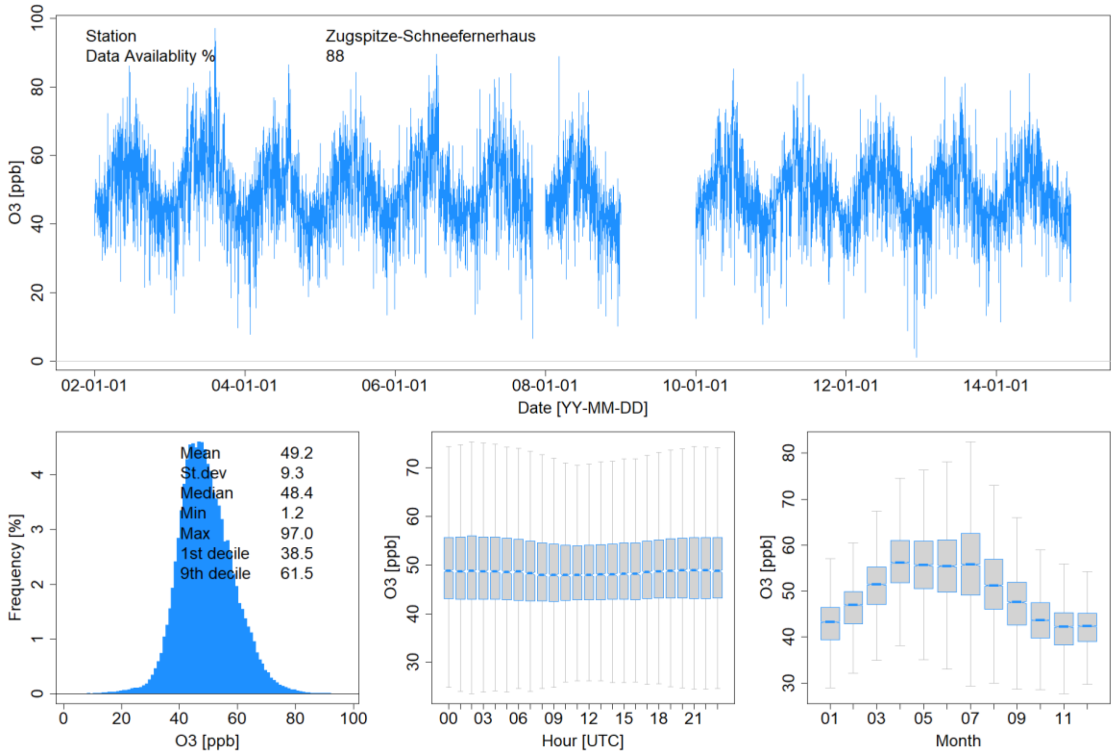

Figure 20. *Same as above for the period from 2002 to 2014 at ZSF.*

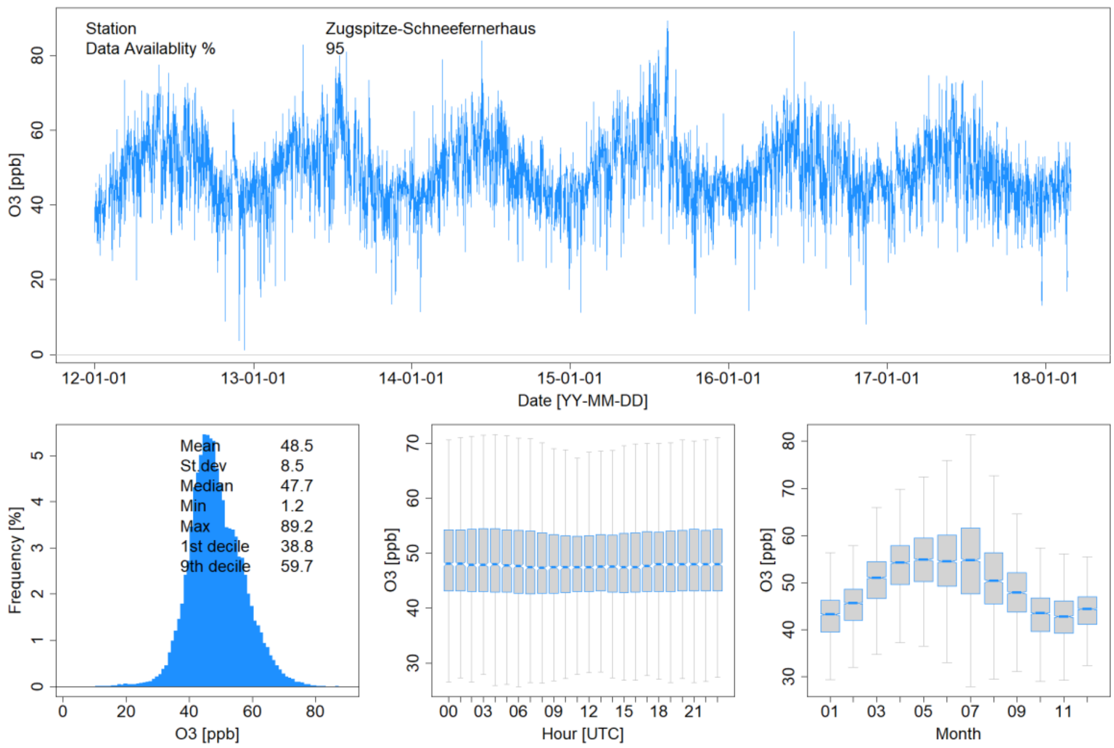

Figure 21. *Same as above for the period from 2012 to 2018 at ZSF.*

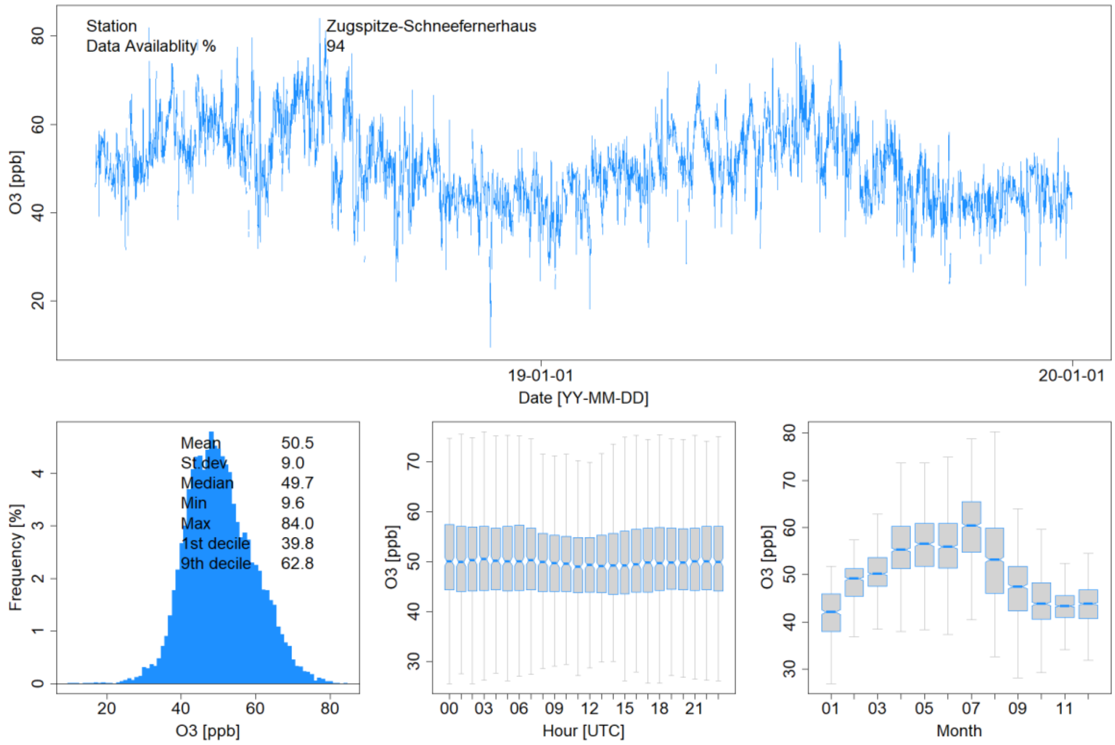

Figure 22. *Same as above for the period from 2018 to 2019 at ZSF.*

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

Carbon monoxide:

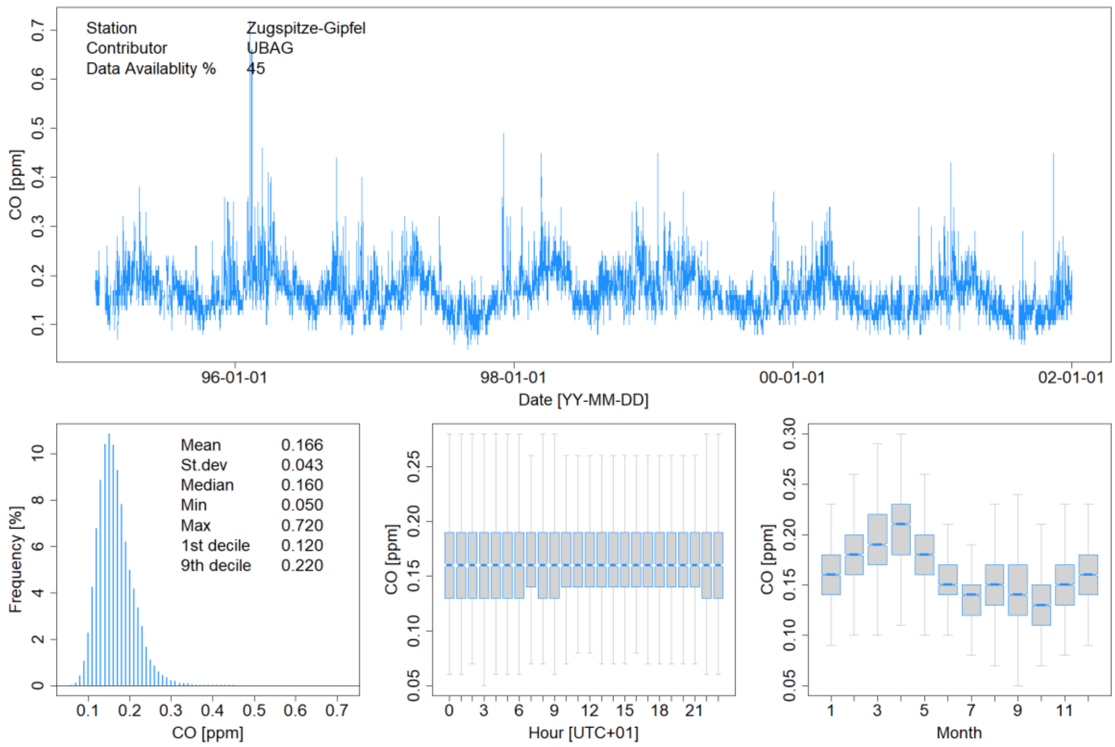

Figure 23. *In-situ CO data for ZUG submitted by UBA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

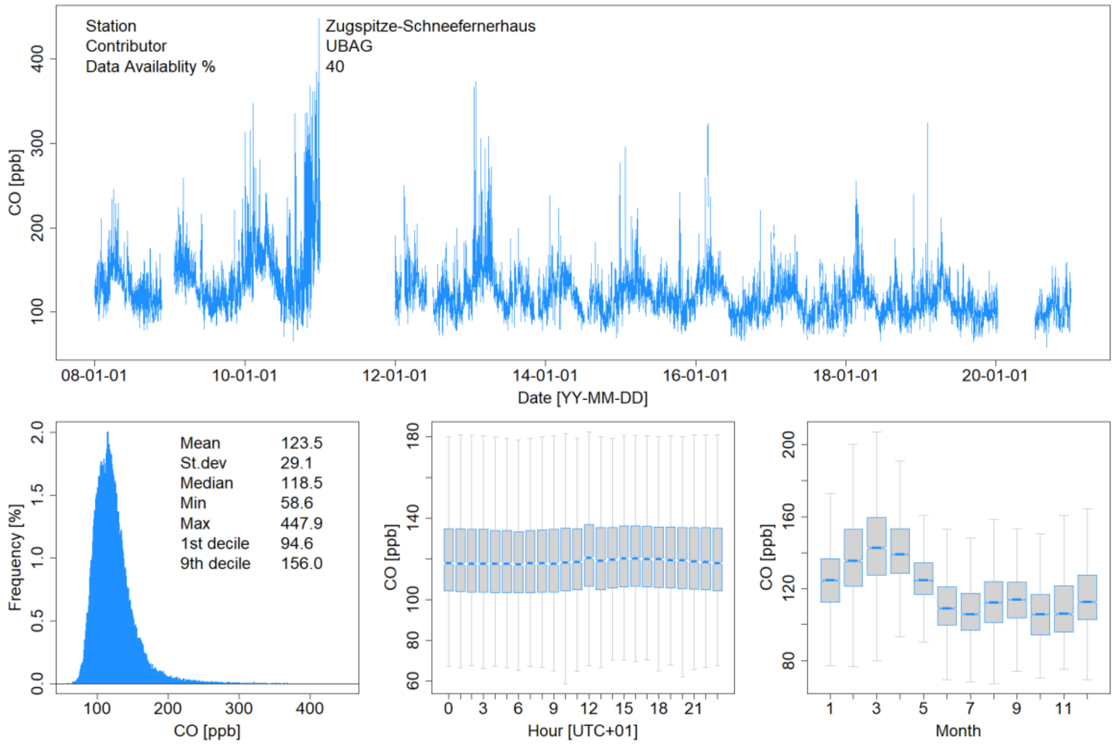

Figure 24. *In-situ CO data for ZSF submitted by UBA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data sets looks generally sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Early data from ZUG (until 2001) was reported in ppm, and the maximum resolution was 0.01 ppm, which corresponds to 10 ppb. This is not sufficient to detect e.g. diurnal variation.
- The entire year 2011 of ZSF data is missing. Data at the end of 2010 is higher compared to the rest of the time series, and a re-evaluation of this period might be considered.

Methane:

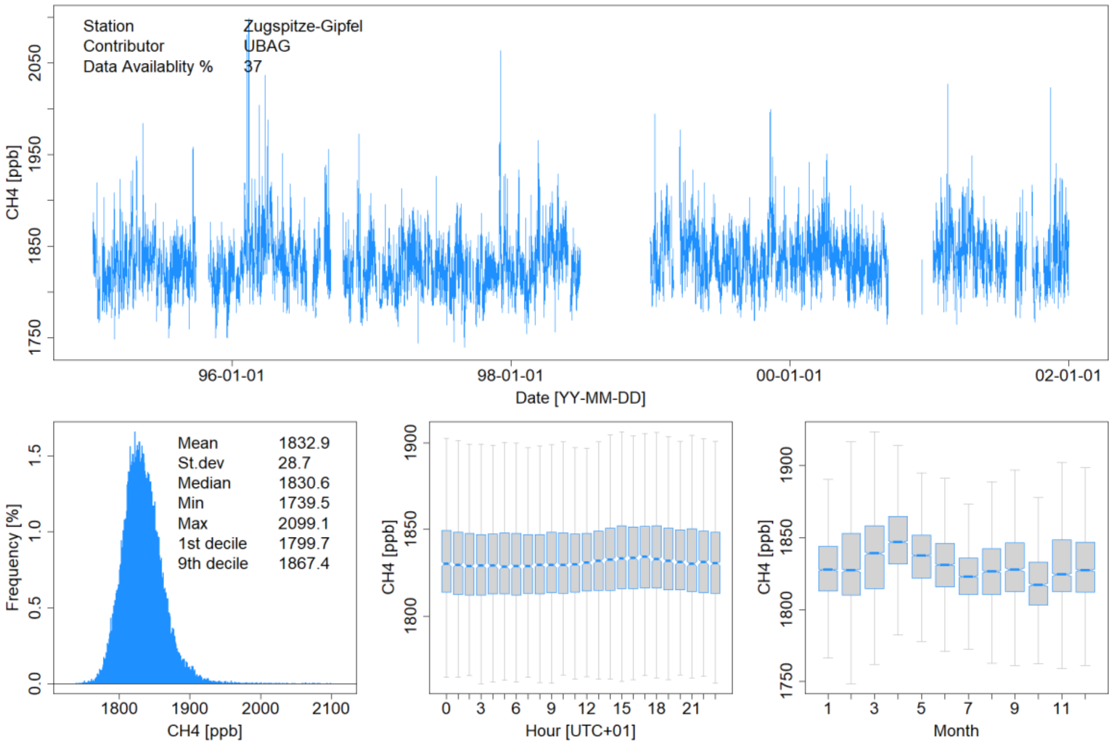

Figure 25. *In-situ CH_4 data for ZUG submitted by UBA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

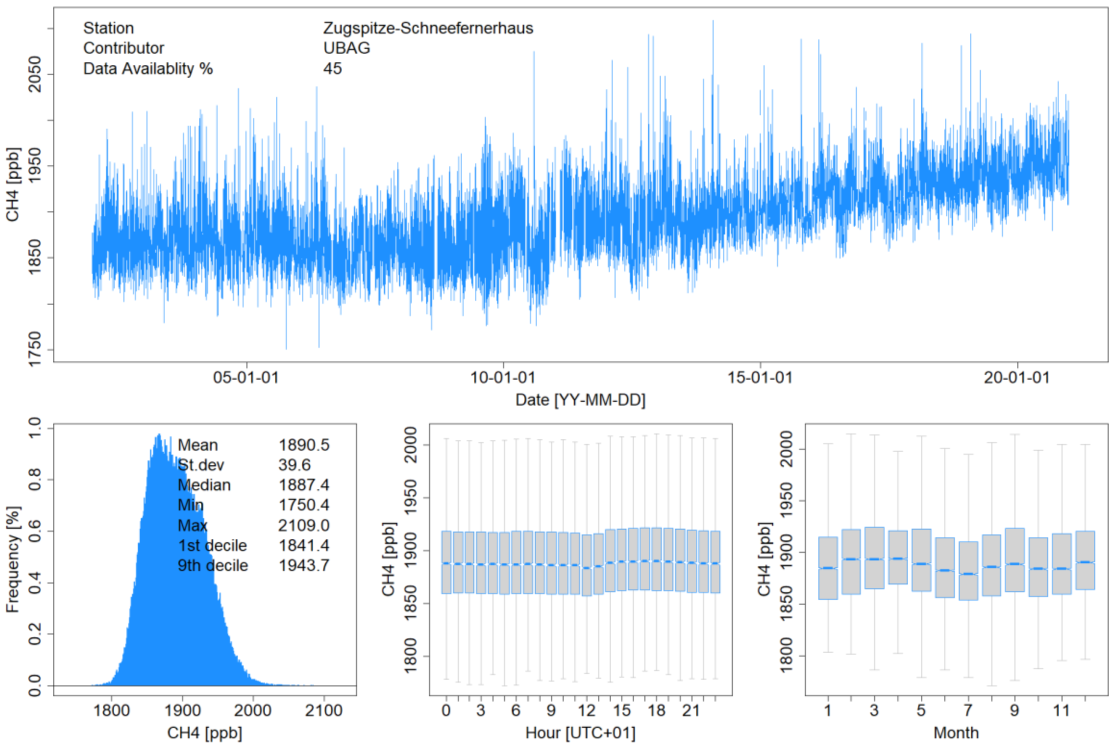

Figure 26. *Same as above for ZSF data.*

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

Carbon dioxide:

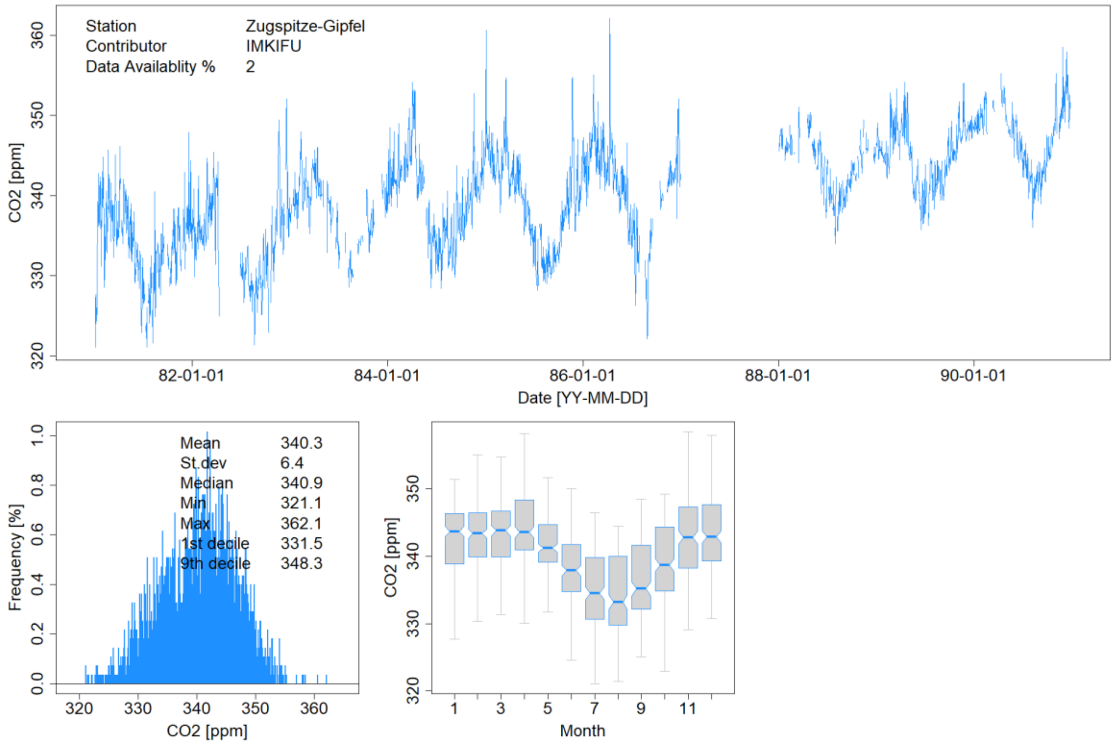

Figure 27. *Daily in-situ CO_2 data for ZUG submitted by IMK-IFU. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

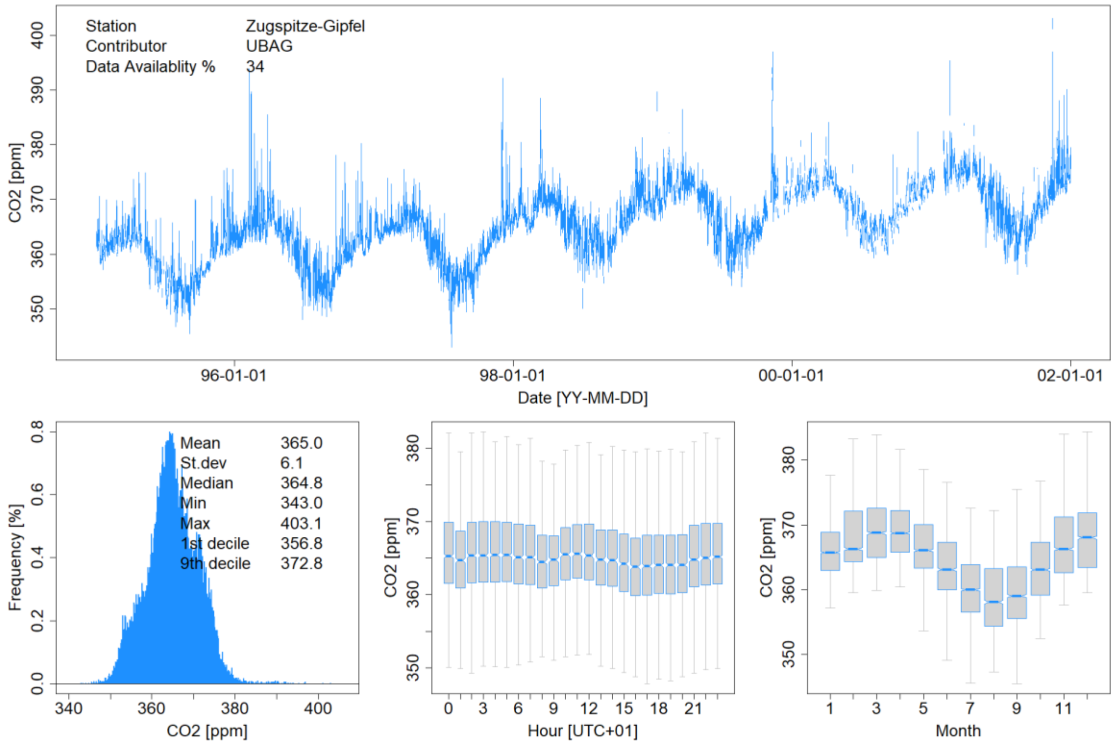

Figure 28. *Hourly in-situ CO_2 data for ZUG submitted by UBA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

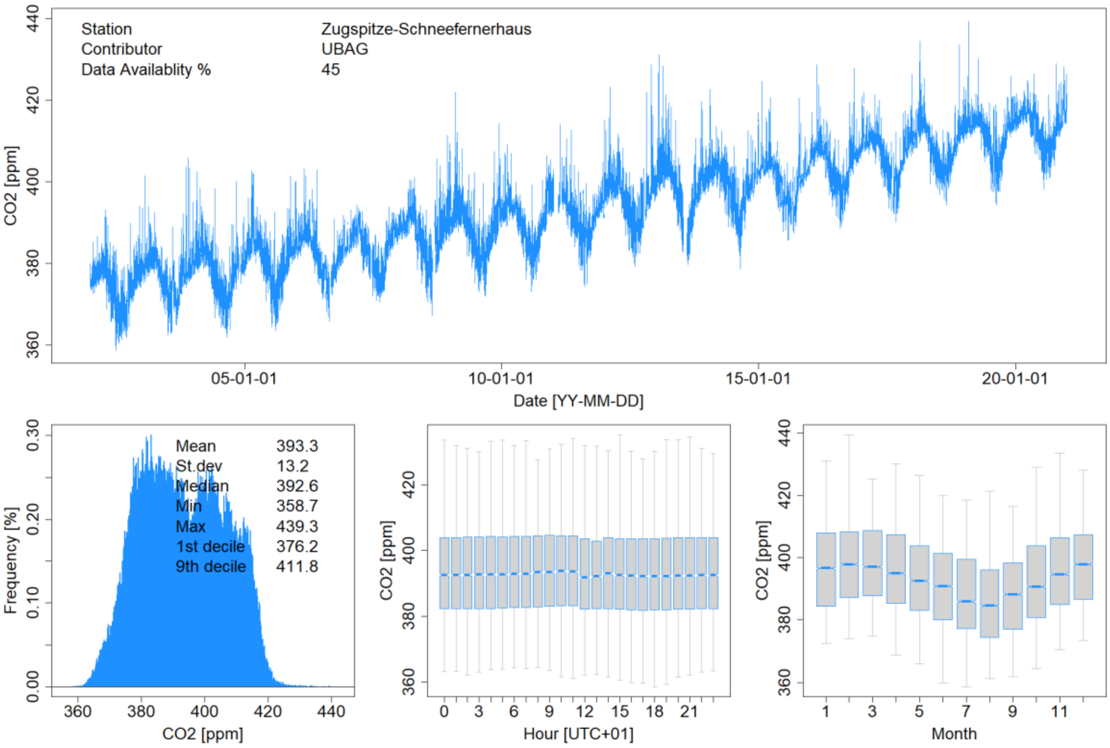

Figure 29. *Same as above for ZSF data.*

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

Nitrous oxide:

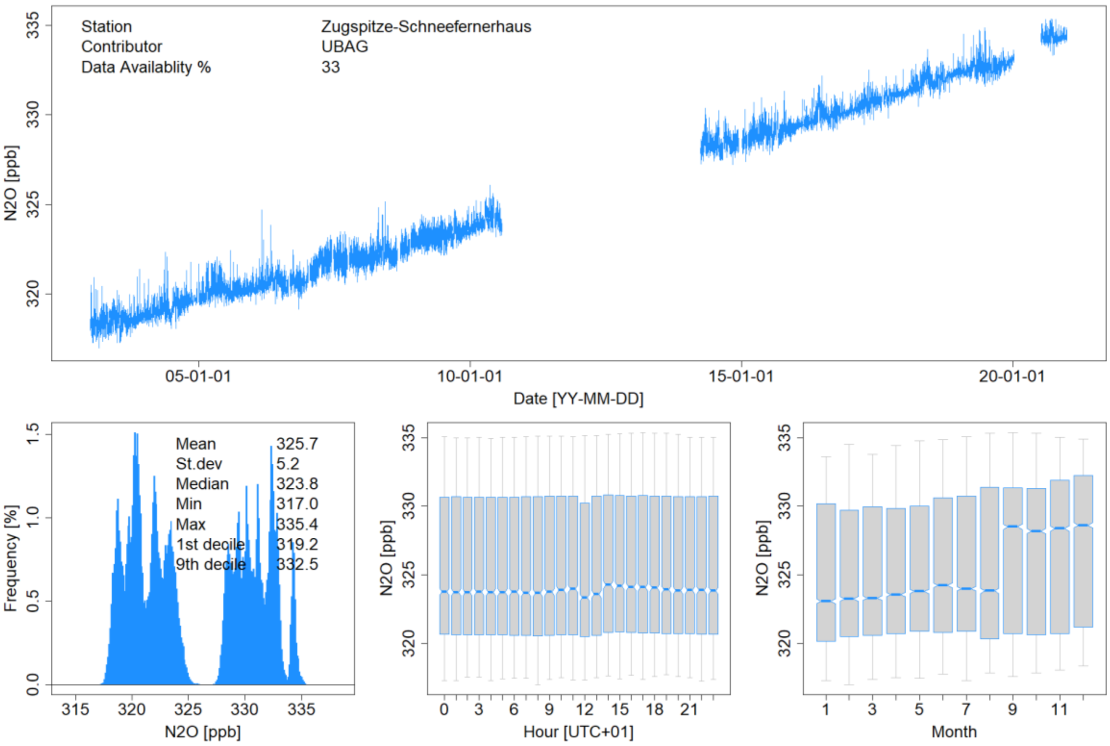

Figure 30. *In-situ N_2O data for ZSF submitted by UBA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data sets looks mostly sound with respect to mole fraction and trend.
- The seasonal cycle in the above plot are likely biased due to periods of missing data. The plot shown above might not be appropriate to assess the quality of the data.

Surface Ozone Comparisons

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal) for the comparison of the ZSF ozone calibrator. The zero air system of ZSF was used for the comparison of the ZSF analyser with the WCC-Empa TS (Breitfuss NBS). 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 ZSF 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 748.1;TS 749.0, (no adjustment was made)
ZSF station analyser (OA)	
Model, S/N	Thermo Scientific 49i #1173620016
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.1 nmol mol^{-1}, COEF 0.998
Pressure readings (hPa)	Ambient 748.1; OA 743.4 (no adjustment was made)
ZSF backup station calibrator (OC)	
Model, S/N	Thermo Scientific 49i-PS #1163020021
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG 0.0 nmol mol^{-1}, COEF 0.994
Pressure readings (hPa)	Ambient 748.1; OC 749.9 (no adjustment was made)

Results

Each ozone level was applied for 10 (OA) or 15 (OC) minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser values.

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

Table 4. *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the ZSF ozone analyser (OA) Thermo Scientific 49i #1173620016 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 (%)
2020-09-09 06:11	0.03	0.10	0.52	0.21	0.49	NA
2020-09-09 06:21	79.91	0.06	79.96	0.34	0.05	0.06
2020-09-09 06:31	59.95	0.12	60.07	0.28	0.12	0.20
2020-09-09 06:41	89.92	0.07	90.16	0.21	0.24	0.27
2020-09-09 06:51	20.58	0.98	21.15	1.05	0.57	2.77
2020-09-09 07:01	49.94	0.06	50.18	0.14	0.24	0.48
2020-09-09 07:11	69.99	0.06	70.07	0.11	0.08	0.11
2020-09-09 07:21	10.23	0.35	10.57	0.36	0.34	3.32
2020-09-09 07:31	39.91	0.08	40.06	0.25	0.15	0.38
2020-09-09 07:41	29.98	0.12	30.26	0.18	0.28	0.93
2020-09-09 07:51	99.96	0.08	99.99	0.40	0.03	0.03
2020-09-09 08:01	0.10	0.19	0.58	0.11	0.48	NA
2020-09-09 08:11	59.93	0.05	60.07	0.32	0.14	0.23
2020-09-09 08:21	49.93	0.08	50.05	0.11	0.12	0.24
2020-09-09 08:31	89.99	0.08	89.91	0.25	-0.08	-0.09
2020-09-09 08:41	19.90	0.14	20.29	0.09	0.39	1.96
2020-09-09 08:51	9.99	0.21	10.42	0.26	0.43	4.30
2020-09-09 09:01	69.93	0.04	70.22	0.17	0.29	0.41
2020-09-09 09:11	39.94	0.11	40.19	0.28	0.25	0.63
2020-09-09 09:21	79.99	0.14	80.08	0.17	0.09	0.11
2020-09-09 09:31	100.02	0.09	100.09	0.13	0.07	0.07
2020-09-09 09:41	29.96	0.10	30.18	0.30	0.22	0.73
2020-09-09 10:14	0.04	0.12	0.52	0.20	0.48	NA
2020-09-09 10:24	79.95	0.07	79.86	0.10	-0.09	-0.11
2020-09-09 10:34	59.94	0.03	59.84	0.33	-0.10	-0.17
2020-09-09 10:44	89.97	0.05	89.95	0.13	-0.02	-0.02
2020-09-09 10:54	19.92	0.05	20.17	0.17	0.25	1.26
2020-09-09 11:04	49.97	0.12	49.93	0.30	-0.04	-0.08
2020-09-09 11:14	69.96	0.09	69.94	0.17	-0.02	-0.03
2020-09-09 11:24	9.96	0.13	10.12	0.09	0.16	1.61
2020-09-09 11:34	39.93	0.10	40.20	0.19	0.27	0.68
2020-09-09 11:44	29.98	0.06	30.74	0.45	0.76	2.54
2020-09-09 11:54	99.96	0.05	99.39	0.80	-0.57	-0.57

Table 5. *Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the ZSF ozone calibrator (OC) Thermo Scientific 49i-PS #1163020021 (uncorrected data) 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 (%)**
2020-09-08 17:52	0.00	0.18	0.22	0.07	0.22	NA
2020-09-08 18:07	79.94	0.03	80.00	0.26	0.06	0.08
2020-09-08 18:22	59.95	0.05	59.95	0.19	0.00	0.00
2020-09-08 18:37	89.98	0.09	89.87	0.09	-0.11	-0.12
2020-09-08 18:52	19.94	0.13	20.05	0.16	0.11	0.55
2020-09-08 19:07	49.93	0.06	50.12	0.21	0.19	0.38
2020-09-08 19:22	69.99	0.08	69.84	0.26	-0.15	-0.21
2020-09-08 19:37	9.92	0.14	10.08	0.20	0.16	1.61
2020-09-08 19:52	39.95	0.08	40.07	0.21	0.12	0.30
2020-09-08 20:22	29.93	0.09	29.88	0.19	-0.05	-0.17
2020-09-08 20:37	0.07	0.06	0.19	0.20	0.12	NA
2020-09-08 20:52	74.96	0.10	75.08	0.23	0.12	0.16
2020-09-08 21:07	175.08	0.05	174.72	0.27	-0.36	-0.21
2020-09-08 21:22	24.92	0.04	24.98	0.09	0.06	0.24
2020-09-08 21:37	125.03	0.08	124.98	0.28	-0.05	-0.04
2020-09-08 21:52	200.05	0.05	199.72	0.15	-0.33	-0.16
2020-09-08 22:07	150.00	0.03	149.97	0.31	-0.03	-0.02
2020-09-08 22:22	0.08	0.05	0.11	0.16	0.03	NA
2020-09-08 22:37	39.94	0.12	39.93	0.22	-0.01	-0.03
2020-09-08 22:52	9.91	0.10	10.15	0.18	0.24	2.42
2020-09-08 23:07	79.96	0.09	80.04	0.32	0.08	0.10
2020-09-08 23:22	19.93	0.12	20.11	0.12	0.18	0.90
2020-09-08 23:37	59.95	0.08	59.90	0.09	-0.05	-0.08
2020-09-08 23:52	90.00	0.07	90.05	0.33	0.05	0.06
2020-09-09 00:07	29.99	0.14	29.99	0.31	0.00	0.00
2020-09-09 00:22	69.90	0.05	70.00	0.09	0.10	0.14
2020-09-09 00:37	49.93	0.15	49.87	0.31	-0.06	-0.12
2020-09-09 00:52	0.14	0.14	0.18	0.11	0.04	NA
2020-09-09 01:07	79.95	0.09	79.86	0.17	-0.09	-0.11
2020-09-09 01:22	59.90	0.10	59.97	0.20	0.07	0.12
2020-09-09 01:37	90.00	0.07	90.18	0.24	0.18	0.20
2020-09-09 01:52	19.91	0.05	19.93	0.13	0.02	0.10
2020-09-09 02:07	49.99	0.05	50.09	0.15	0.10	0.20
2020-09-09 02:22	69.95	0.09	70.08	0.32	0.13	0.19
2020-09-09 02:37	10.19	0.47	10.11	0.27	-0.08	-0.79
2020-09-09 02:52	39.89	0.11	39.85	0.27	-0.04	-0.10
2020-09-09 03:22	29.95	0.08	29.95	0.06	0.00	0.00
2020-09-09 03:37	0.22	0.18	0.00	0.14	-0.22	NA
2020-09-09 03:52	74.93	0.03	74.94	0.26	0.01	0.01
2020-09-09 04:07	175.05	0.07	175.11	0.21	0.06	0.03
2020-09-09 04:22	24.95	0.15	25.16	0.36	0.21	0.84
2020-09-09 04:37	125.04	0.06	125.08	0.23	0.04	0.03
2020-09-09 04:52	200.13	0.10	200.22	0.02	0.09	0.04

Table 6. *Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the ZSF ozone calibrator (OC) Thermo Scientific 49i-PS #1163020021 (corrected data) 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 (%)**
2020-09-08 17:52	0.00	0.18	0.38	0.07	0.38	NA
2020-09-08 18:07	79.94	0.03	79.80	0.26	-0.14	-0.18
2020-09-08 18:22	59.95	0.05	59.84	0.19	-0.11	-0.18
2020-09-08 18:37	89.98	0.09	89.63	0.08	-0.35	-0.39
2020-09-08 18:52	19.94	0.13	20.13	0.15	0.19	0.95
2020-09-08 19:07	49.93	0.06	50.06	0.21	0.13	0.26
2020-09-08 19:22	69.99	0.08	69.69	0.26	-0.30	-0.43
2020-09-08 19:37	9.92	0.14	10.21	0.20	0.29	2.92
2020-09-08 19:52	39.95	0.08	40.05	0.21	0.10	0.25
2020-09-08 20:22	29.93	0.09	29.91	0.19	-0.02	-0.07
2020-09-08 20:37	0.07	0.06	0.36	0.20	0.29	NA
2020-09-08 20:52	74.96	0.10	74.90	0.23	-0.06	-0.08
2020-09-08 21:07	175.08	0.05	174.08	0.27	-1.00	-0.57
2020-09-08 21:22	24.92	0.04	25.04	0.09	0.12	0.48
2020-09-08 21:37	125.03	0.08	124.57	0.28	-0.46	-0.37
2020-09-08 21:52	200.05	0.05	198.97	0.15	-1.08	-0.54
2020-09-08 22:07	150.00	0.03	149.46	0.31	-0.54	-0.36
2020-09-08 22:22	0.08	0.05	0.27	0.16	0.19	NA
2020-09-08 22:37	39.94	0.12	39.91	0.22	-0.03	-0.08
2020-09-08 22:52	9.91	0.10	10.27	0.17	0.36	3.63
2020-09-08 23:07	79.96	0.09	79.84	0.32	-0.12	-0.15
2020-09-08 23:22	19.93	0.12	20.19	0.12	0.26	1.30
2020-09-08 23:37	59.95	0.08	59.79	0.09	-0.16	-0.27
2020-09-08 23:52	90.00	0.07	89.81	0.33	-0.19	-0.21
2020-09-09 00:07	29.99	0.14	30.03	0.31	0.04	0.13
2020-09-09 00:22	69.90	0.05	69.85	0.09	-0.05	-0.07
2020-09-09 00:37	49.93	0.15	49.82	0.31	-0.11	-0.22
2020-09-09 00:52	0.14	0.14	0.34	0.11	0.20	NA
2020-09-09 01:07	79.95	0.09	79.66	0.17	-0.29	-0.36
2020-09-09 01:22	59.90	0.10	59.87	0.20	-0.03	-0.05
2020-09-09 01:37	90.00	0.07	89.94	0.24	-0.06	-0.07
2020-09-09 01:52	19.91	0.05	20.01	0.13	0.10	0.50
2020-09-09 02:07	49.99	0.05	50.03	0.15	0.04	0.08
2020-09-09 02:22	69.95	0.09	69.92	0.32	-0.03	-0.04
2020-09-09 02:37	10.19	0.47	10.23	0.27	0.04	0.39
2020-09-09 02:52	39.89	0.11	39.84	0.27	-0.05	-0.13
2020-09-09 03:22	29.95	0.08	29.98	0.06	0.03	0.10
2020-09-09 03:37	0.22	0.18	0.17	0.14	-0.05	NA
2020-09-09 03:52	74.93	0.03	74.76	0.26	-0.17	-0.23
2020-09-09 04:07	175.05	0.07	174.48	0.21	-0.57	-0.33
2020-09-09 04:22	24.95	0.15	25.22	0.35	0.27	1.08
2020-09-09 04:37	125.04	0.06	124.67	0.23	-0.37	-0.30
2020-09-09 04:52	200.13	0.10	199.47	0.02	-0.66	-0.33

Carbon Monoxide Comparisons

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

Table 7 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 ZSF data acquisition system. The standards used for the calibration of the ZSF instruments are shown in Table 8.

Table 7. Experimental details of ZSF 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	
Model, S/N	LGR 913-0015-1000 #14-0066
Principle	OA-ICOS
Drying system	Cold trap
Station Analyser	
Model, S/N	Picarro G2401 #2663-CFKADS2243
Principle	CRDS
Drying system	Cold trap
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Table 8 *Calibration standards at ZSF as of September 2020.*

Cylinder ID	**N_2O X2006A (nmol mol^{-1})**	**CO X2014A (nmol mol^{-1})**	**CH_4 X2004A (nmol mol^{-1})**	**CO_2 X2007 (µmol mol^{-1})**	**Usage**
ND56764	319.99	124.18	1834.73	378.60	NOAA / LGR and Picarro
CB12417	344.05	257.20	2118.99	429.52	NOAA / LGR and Picarro
ND56757	337.11	154.13	1940.25	399.02	NOAA / LGR and Picarro
ND56763	335.25	267.63	1962.06	413.45	NOAA / LGR and Picarro
Deuste 6000142	331.70	75.37	1794.73	386.93	WS (low) / LGR and Picarro
Deuste 6000138	341.64	174.56	1985.49	426.78	WS (high) / LGR and Picarro
Deuste 6000151	344.19	174.10	1982.80	423.81	WS / LGR and Picarro

Results

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

Table 9. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015-1000 #14-0066 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 (%)
(20-09-09 06:20:00)	171124_FA01467	140.9	0.4	137.1	0.0	3	-3.8	-2.7
(20-09-09 06:50:00)	160825_FB03887	194.5	1.2	192.3	0.0	3	-2.2	-1.1
(20-09-09 07:20:00)	160825_FB03365	178.2	1.0	173.9	0.1	3	-4.3	-2.4
(20-09-09 07:50:00)	171128_FA02476	149.4	0.6	146.1	0.0	3	-3.3	-2.2
(20-09-09 08:20:00)	180318_FF61508	355.9	0.8	356.6	0.0	3	0.7	0.2
(20-09-09 08:50:00)	160622_FA02474	237.0	0.9	235.8	0.0	3	-1.2	-0.5
(20-09-09 09:20:00)	181128_FF61487	110.8	1.8	106.7	0.0	3	-4.1	-3.7
(20-09-09 09:50:00)	171204_FA01469	103.1	0.8	98.8	0.0	3	-4.3	-4.2

Table 10. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2663-CFKADS2243 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 (%)
(20-09-09 06:20:00)	171124_FA01467	140.9	0.4	136.5	0.8	3	-4.4	-3.1
(20-09-09 06:50:00)	160825_FB03887	194.5	1.2	191.8	0.9	3	-2.8	-1.4
(20-09-09 07:20:00)	160825_FB03365	178.2	1.0	173.6	0.9	3	-4.6	-2.6
(20-09-09 07:50:00)	171128_FA02476	149.4	0.6	145.4	0.8	3	-4.0	-2.7
(20-09-09 08:20:00)	180318_FF61508	355.9	0.8	356.8	0.6	3	0.9	0.2
(20-09-09 08:50:00)	160622_FA02474	237.0	0.9	235.1	0.7	3	-1.9	-0.8
(20-09-09 09:20:00)	181128_FF61487	110.8	1.8	106.0	0.5	3	-4.8	-4.3
(20-09-09 09:50:00)	171204_FA01469	103.1	0.8	97.3	1.0	3	-5.8	-5.6
(20-09-09 10:20:00)	171201_FA02773	-0.1	0.5	-6.6	0.8	3	-6.6	NA

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 8, and Table 11 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

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

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 21.	
Station Analyser	
Model, S/N	Picarro G2301 #2043-CFADS2378
Principle	CRDS
Drying system	Cold trap
Station Analyser	
Model, S/N	Picarro G2401 #2663-CFKADS2243
Principle	CRDS
Drying system	Cold trap
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 12. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2301 #2043-CFADS2378 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(20-09-09 06:20:00)	171124_FA01467	1805.72	0.02	1806.02	0.08	3	0.30	0.02
(20-09-09 06:50:00)	160825_FB03887	2027.36	0.04	2027.31	0.12	3	-0.05	0.00
(20-09-09 07:20:00)	160825_FB03365	1921.02	0.01	1921.27	0.07	3	0.25	0.01
(20-09-09 07:50:00)	171128_FA02476	1860.12	0.03	1860.48	0.04	3	0.36	0.02
(20-09-09 08:20:00)	180318_FF61508	1963.75	0.02	1963.54	0.07	3	-0.21	-0.01
(20-09-09 08:50:00)	160622_FA02474	2506.81	0.02	2506.14	0.10	3	-0.67	-0.03
(20-09-09 09:20:00)	181128_FF61487	1990.63	0.02	1990.38	0.09	3	-0.25	-0.01
(20-09-09 09:50:00)	171204_FA01469	1933.18	0.04	1933.52	0.07	3	0.34	0.02
(20-09-09 10:20:00)	171201_FA02773	1.36	0.07	4.10	0.03	3	2.74	NA

Table 13. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2663-CFKADS2243 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(20-09-09 06:20:00)	171124_FA01467	1805.72	0.02	1806.04	0.01	3	0.32	0.02
(20-09-09 06:50:00)	160825_FB03887	2027.36	0.04	2027.56	0.01	3	0.20	0.01
(20-09-09 07:20:00)	160825_FB03365	1921.02	0.01	1921.30	0.01	3	0.28	0.01
(20-09-09 07:50:00)	171128_FA02476	1860.12	0.03	1860.48	0.04	3	0.36	0.02
(20-09-09 08:20:00)	180318_FF61508	1963.75	0.02	1963.98	0.08	3	0.23	0.01
(20-09-09 08:50:00)	160622_FA02474	2506.81	0.02	2506.72	0.02	3	-0.09	0.00
(20-09-09 09:20:00)	181128_FF61487	1990.63	0.02	1990.88	0.02	3	0.25	0.01
(20-09-09 09:50:00)	171204_FA01469	1933.18	0.04	1933.46	0.02	3	0.28	0.01
(20-09-09 10:20:00)	171201_FA02773	1.36	0.07	3.36	0.01	3	2.00	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 the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 8, and Table 14 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 14. *Experimental details of ZSF CO_2 comparison.*

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 21.	
Station Analyser	
Model, S/N	Picarro G2301 #2043-CFADS2378
Principle	CRDS
Drying system	Cold trap
Station Analyser	
Model, S/N	Picarro G2401 #2663-CFKADS2243
Principle	CRDS
Drying system	Cold trap
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 15. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2301 # 2043-CFADS2378 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(20-09-09 06:20:00)	171124_FA01467	397.02	0.01	396.98	0.01	3	-0.04	-0.01
(20-09-09 06:50:00)	160825_FB03887	457.74	0.01	457.69	0.01	3	-0.05	-0.01
(20-09-09 07:20:00)	160825_FB03365	412.94	0.01	412.90	0.01	3	-0.04	-0.01
(20-09-09 07:50:00)	171128_FA02476	418.29	0.02	418.26	0.00	3	-0.03	-0.01
(20-09-09 08:20:00)	180318_FF61508	417.30	0.05	417.28	0.01	3	-0.02	0.00
(20-09-09 08:50:00)	160622_FA02474	421.29	0.01	421.26	0.01	3	-0.03	-0.01
(20-09-09 09:20:00)	181128_FF61487	398.14	0.09	398.06	0.01	3	-0.08	-0.02
(20-09-09 09:50:00)	171204_FA01469	406.78	0.03	406.80	0.00	3	0.02	0.00
(20-09-09 10:20:00)	171201_FA02773	0.29	0.03	0.46	0.00	3	0.17	NA

Table 16. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2401 #2663-CFKADS2243 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(20-09-09 06:20:00)	171124_FA01467	397.02	0.01	397.00	0.00	3	-0.02	-0.01
(20-09-09 06:50:00)	160825_FB03887	457.74	0.01	457.74	0.00	3	0.00	0.00
(20-09-09 07:20:00)	160825_FB03365	412.94	0.01	412.93	0.01	3	-0.01	0.00
(20-09-09 07:50:00)	171128_FA02476	418.29	0.02	418.28	0.00	3	-0.01	0.00
(20-09-09 08:20:00)	180318_FF61508	417.30	0.05	417.31	0.00	3	0.01	0.00
(20-09-09 08:50:00)	160622_FA02474	421.29	0.01	421.28	0.00	3	-0.01	0.00
(20-09-09 09:20:00)	181128_FF61487	398.14	0.09	398.09	0.00	3	-0.05	-0.01
(20-09-09 09:50:00)	171204_FA01469	406.78	0.03	406.81	0.00	3	0.03	0.01
(20-09-09 10:20:00)	171201_FA02773	0.29	0.03	0.43	0.01	3	0.14	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 the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 8, and Table 14 shows details of the experimental setup during the comparison of the transfer standards and the station analyser.

Table 17. *Experimental details of ZSF N_2O comparison.*

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 21.	
Station Analyser	
Model, S/N	LGR 913-0015-1000 #14-0066
Principle	OA-ICOS
Drying system	Cold trap
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 18. *N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015-1000 #14-0066 instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(20-09-09 06:20:00)	171124_FA01467	325.73	0.06	325.69	0.01	3	-0.04	-0.01
(20-09-09 06:50:00)	160825_FB03887	331.79	0.11	331.83	0.02	3	0.04	0.01
(20-09-09 07:20:00)	160825_FB03365	318.67	0.01	318.76	0.02	3	0.09	0.03
(20-09-09 07:50:00)	171128_FA02476	322.49	0.04	322.46	0.00	3	-0.03	-0.01
(20-09-09 08:20:00)	180318_FF61508	328.35	0.03	327.99	0.01	3	-0.36	-0.11
(20-09-09 08:50:00)	160622_FA02474	324.50	0.01	324.27	0.01	3	-0.23	-0.07
(20-09-09 09:20:00)	181128_FF61487	342.81	0.05	343.14	0.02	3	0.33	0.10
(20-09-09 09:50:00)	171204_FA01469	342.99	0.06	343.36	0.01	3	0.37	0.11

WCC-Empa Traveling Standards

Ozone

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

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

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

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 19. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 31). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] - 0.10\ \text{nmol mol}^{-1}) / 0.9992 \qquad (6a)$$

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

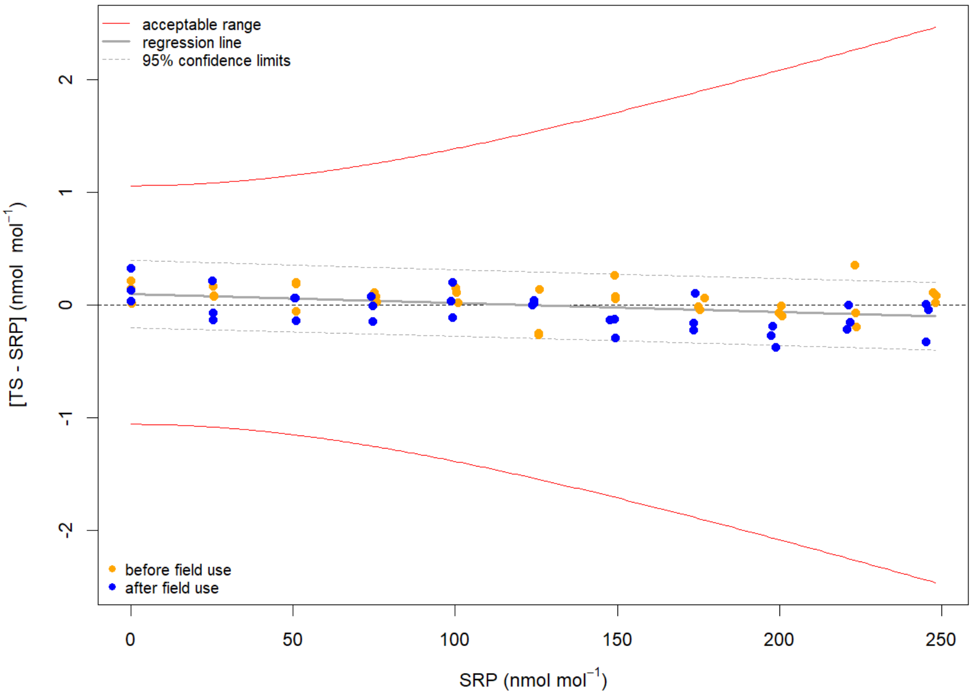

Figure 31. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 19. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level[#]	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2020-01-24	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
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

Date	Run	Level#	SRP (nmol mol-1)	sdSRP (nmol mol-1)	TS (nmol mol-1)	sdTS (nmol mol-1)
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/ESRL was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL 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 (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

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

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy).
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 Figure 32 shows the analysis of the TS over time.

Table 20. *NOAA/ESRL 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
120307_CB08963§	485.76	2470.72	322.91	363.64

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

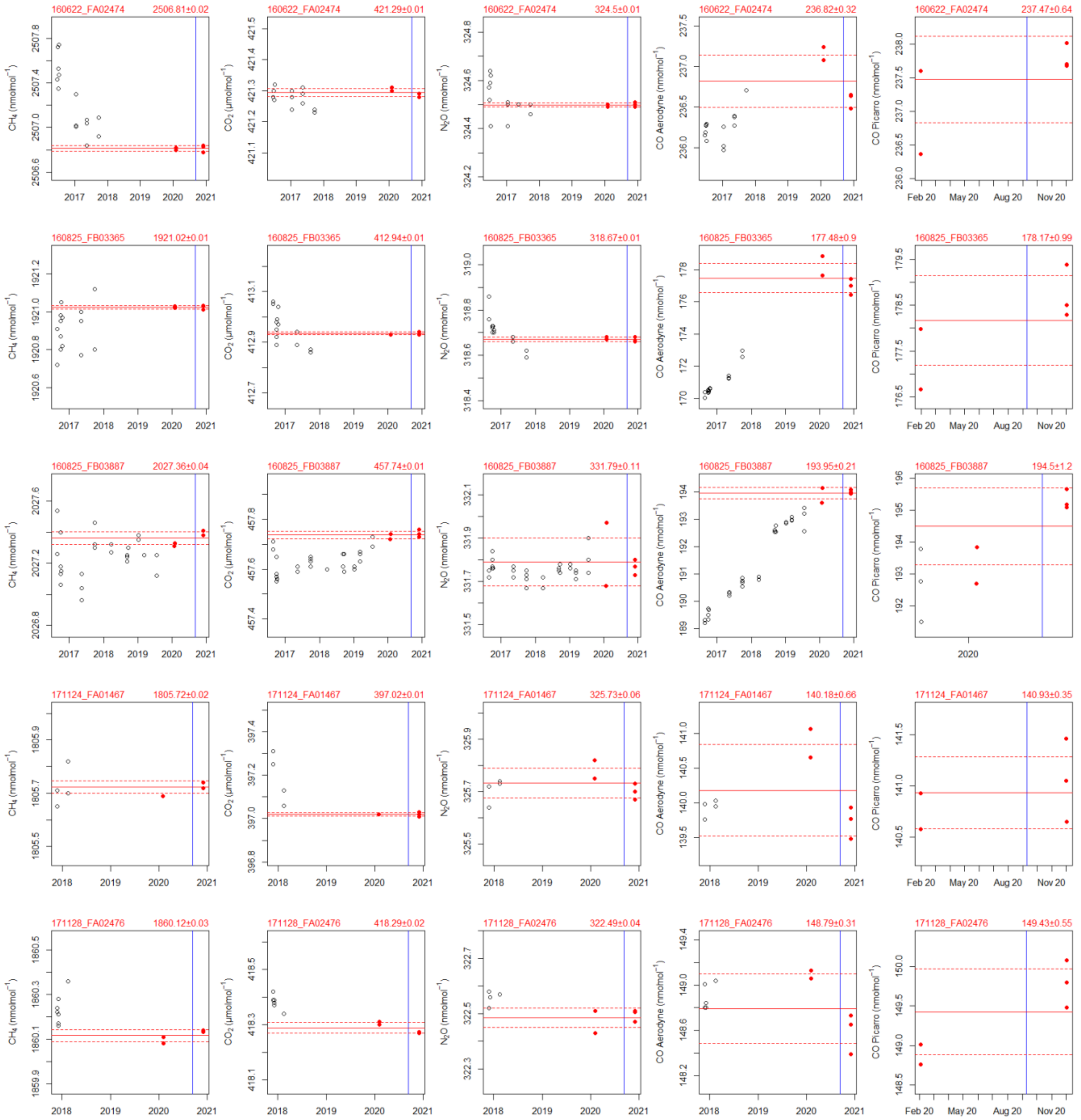

Figure 32. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

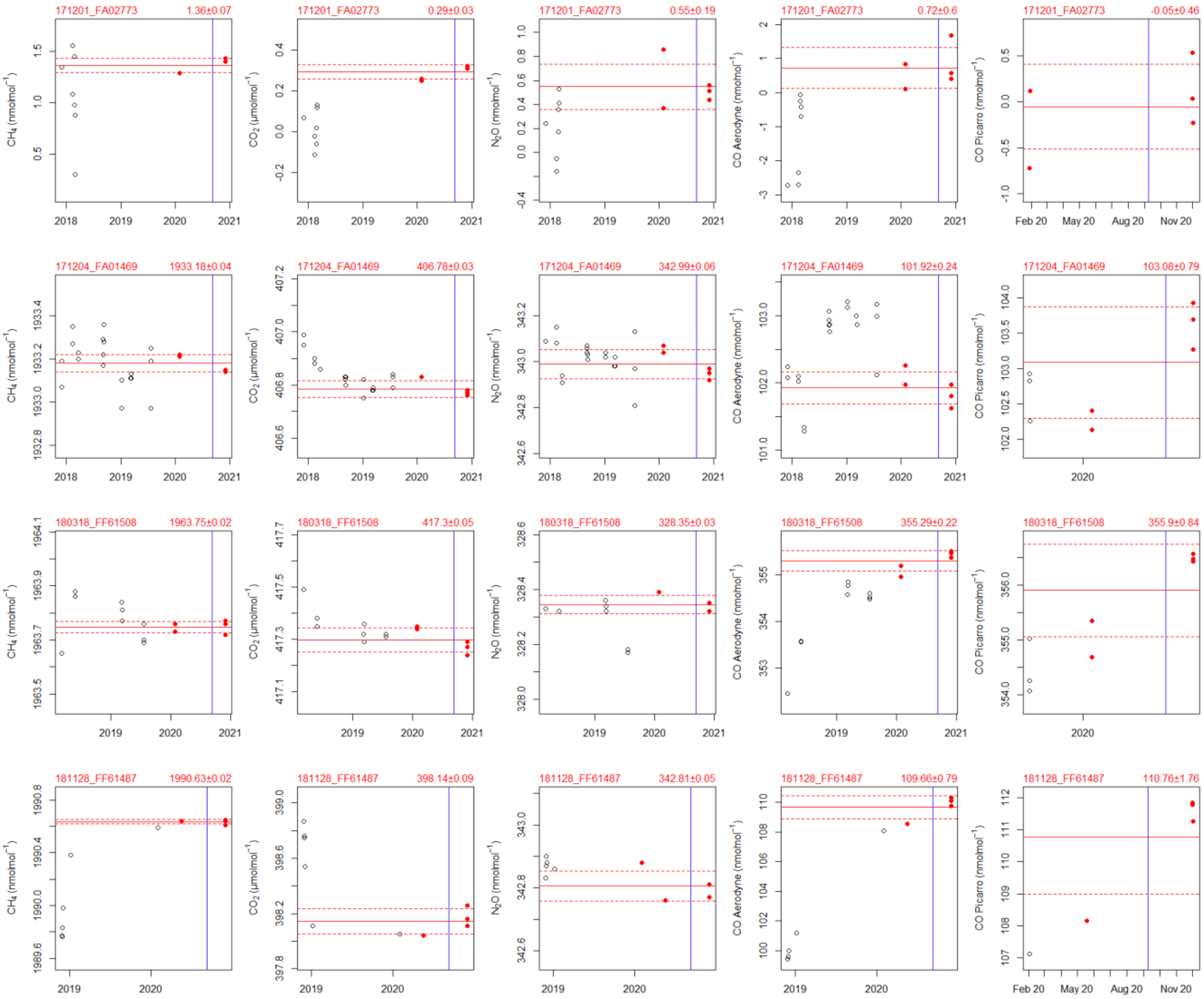

Figure 33. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

Calibration of the instrument used for the ambient air comparison

The calibration of the instrument used for the ambient air comparison (Picarro G2401 #2663-CFKADS2243) is shown in the following figures. For CO, the Picarro G2401 was calibrated every 1445 min with three WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

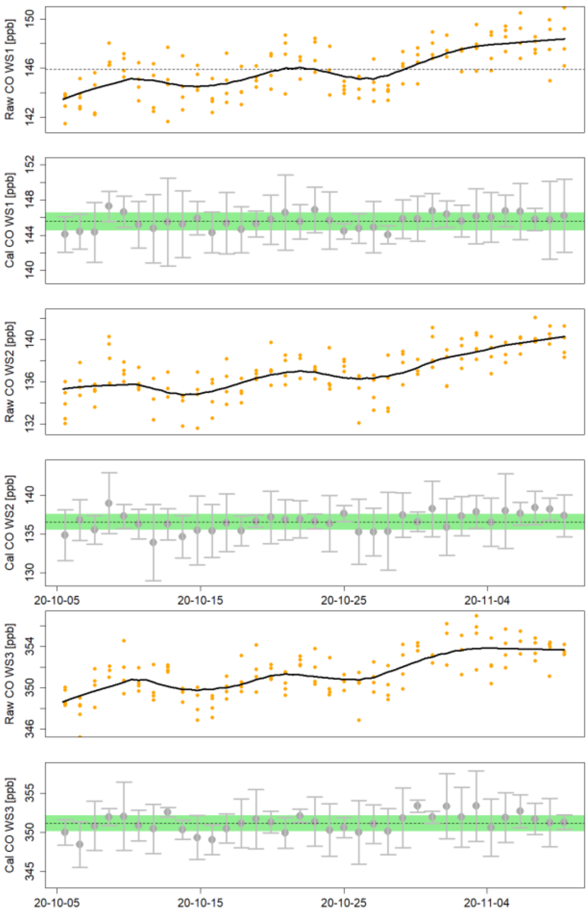

Figure 34. *CO calibrations of the instrument used for the ambient air. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual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

For CH_4 and CO_2, the analyser 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 less than 0.1 ppb for CH_4 and less than 0.02 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

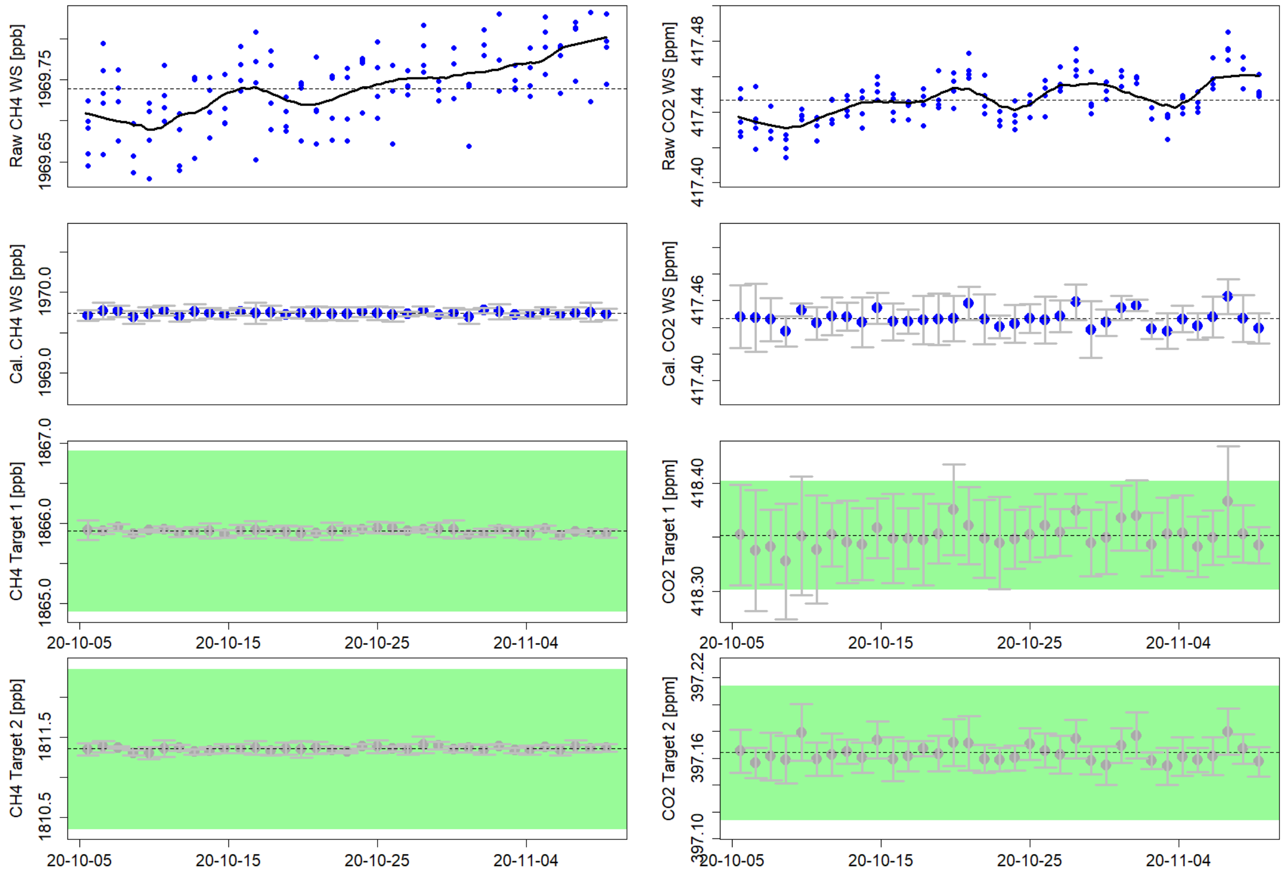

Figure 35. *CH_4 (left panel) and CO_2 (right panel) calibrations of the instrument used for the ambient air comparisons. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

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LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
DWD	Deutscher Wetterdienst (German Meteorological Service)
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
FCL	ICOS Flask and Calibration Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PI	Principle Investigator
OA	Ozone Analyser
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
OC	Ozone Calibrator
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
UBA	Umweltbundesamt (Federal Environment Agency)
UFS	Umweltforschungsstation Schneefernerhaus
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
ZSF	Zugspitze-Schneefernerhaus GAW Station
ZUG	Zugspitze-Gipfel GAW Station