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

AT THE

GLOBAL GAW STATION ZEPPELIN MOUNTAIN SVALBARD

SEPTEMBER 2022

WCC-Empa Report 22/3

Submitted to the World Meteorological Organization by

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Acknowledgements

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WCC-Empa Report 22/3

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 5th WCC-Empa[1] system and performance audit at the Zeppelin Mountain global GAW station (ZEP) was conducted from 8 - 12 September 2022 in accordance with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at ZEP and the corresponding audit reports are available on the WCC-Empa website (www.empa.ch/gaw).

The following persons contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr Matz Hill	Empa Dübendorf, technician climate gases group / AGAGE
Mr. Ove Hermansen	NILU, Station Manager
Mrs. Anne Catharina Nielsen	NILU, Station Technician

This report summarises the evaluation of the Zeppelin Mountain GAW station in general and the measurements of surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide in particular.

The report will be distributed to the station manager of the Zeppelin Mountain GAW station, the national focal point for GAW in Norway, and the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and made available on the internet (www.empa.ch/web/s503/wcc-empa).

The recommendations found in this report are classified as minor, important and critical and are accompanied by a priority (*** indicates highest priority) and a proposed date for completion.

Management and operation of the station

The station is visited during working days by the station operators for routine work. Scientists and technicians from the Norwegian Institute for Air Research (NILU) visit the station twice per year in spring and autumn, and additional visits are made as required. All of the facilities at Ny Ålesund are managed by the company Kings Bay AS. They manage all the necessary services in the community such as the provision of food, electricity and water. Kings Bay is also responsible for the infrastructure in Ny-Ålesund and operates the settlement throughout the year. Measurements at the ZEP site are mainly coordinated by NILU, which operates ZEP in close cooperation with the Norwegian Polar Institute (NPI). NPI is responsible for the day-to-day technical maintenance of the observatory, while NILU has the scientific responsibility. More information can be found on the websites of NILU, NPI and Kings Bay:

NILU: nilu.com/facility/nilus-observatories-and-monitoring-stations/zeppelin-observatory/
NPI: npolar.no/en/zeppelin/
Kings Bay: kingsbay.no

Location and access

The Zeppelin Mountain GAW Station (78.906688°N, 11.889342°E, 475 m a.s.l.) is located south of the research village Ny-Ålesund in the European Arctic in the King's fjord on north-western Spitsbergen, which is the largest of the Svalbard islands. The station was built in 1988/89 on a small plateau east of the summit of Zeppelin Mountain. A cable car provides easy access to the station. A new and larger station was built on the same location in 1999/2000. Ny-Ålesund (78.923576°N, 11.923660°E, 9 m a.s.l.)

[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 Empa, the Swiss Federal Laboratories for Materials Science and Technology. The mandate is to conduct system and performance audits at Global GAW stations based on mutual agreement.

is permanently maintained by about 30 people, with an additional 150 scientists during the peak summer season.

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

Station facilities

Zeppelin Mountain offers adequate laboratory and office facilities with high-speed internet access. There are no sanitary facilities on site. The laboratories are air conditioned. ZEP provides an ideal platform for continuous atmospheric research. In addition to the large number of permanent measurements, limited space is available for campaign-based experiments.

Measurement Programme

ZEP hosts a comprehensive measurement programme covering all focal areas of the GAW programme. An overview of measured species is available on GAWSIS. The monitoring activities of ZEP are linked to several international programmes and research infrastructures, such as EMEP (European Monitoring and Evaluation Programme), AMAP (Arctic Monitoring and Assessment Programme), ACTRIS (The Aerosol, Clouds and Trace Gases Research Infrastructure), ICOS (Integrated Carbon Observation System), and the Advanced Global Atmospheric Gases Experiment (AGAGE).

The information available from GAWSIS was reviewed as part of the audit. The last update was made in February 2020, and the information was mostly up-to-date. However, some details on the instrumentation need to be reviewed and corrected.

> **Recommendation 1 (***, important, ongoing)**
> *It is recommended that GAWSIS be updated annually or when major changes occur. Some of the information checked needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface (e.g. deletion of station contacts).*

Data submission

As of February 2023, the following ZEP data within the scope of the audit were available at the World Data Centres:

NILU, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (two data sets, one covering the period from 1989-2022 (final data), and one covering the period from 2020-2023 (near real time data)).

NILU, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2001-2021), CO_2 (2012-2021), CO (not submitted)

Stockholm University, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CO_2 (1988-2012) (measurements stopped in 2012)

NOAA, submission to WDCGG:
CH_4 (1994-2021), CO_2 (1994-2021), CO (1994-2021)

It should be noted that GHG data from ZEP is also available from EBAS. EBAS data has not be reviewed, and only GHG and CO data submitted to WDCGG have been considered.

The data presented in this report was accessed on 17 February 2023. All data within the scope of the review were submitted with a submission delay of less than one year. The continuation of this timely submission practice is recommended.

Data review

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

Documentation

Electronic station and instrument logbooks are available at ZEP. Handwritten notes are also kept in laboratory notebooks. All instrument manuals are available at the site and the information reviewed was mostly comprehensive and up to date. However, it was not possible to identify the period during which the ozone inlet was modified (see below for details) due to missing logbook entries.

Air inlet system

Surface ozone:

Location of air intake:	Outside the building on the west side approximately 1 m from the building wall.
Inlet protection:	Protection against rain water / snow / insects.
Tubing:	Approximately 3.5 m 6 mm PFA line, flow approx. 0.8 l/min.
Inlet filter:	PTFE (Millipore LSWP 5 µm) inlet filter inside API 400E
Residence time:	Approximately 4 s

The air inlet for surface ozone has not been modified since the last WCC-Empa audit in 2012 except for a short piece of silicon tubing (~3 cm) that was inserted into the main inlet line. This modification to the inlet line was made at all surface ozone stations operated by NILU and was also made for SO_2 and NO_x measurements. The inlet line was tested for ozone loss using the WCC-Empa ozone calibrator. An ozone loss of about 1.5 nmol mol^{-1} at an ozone level of about 40 nmol mol^{-1} was found, as shown in Figure 1.

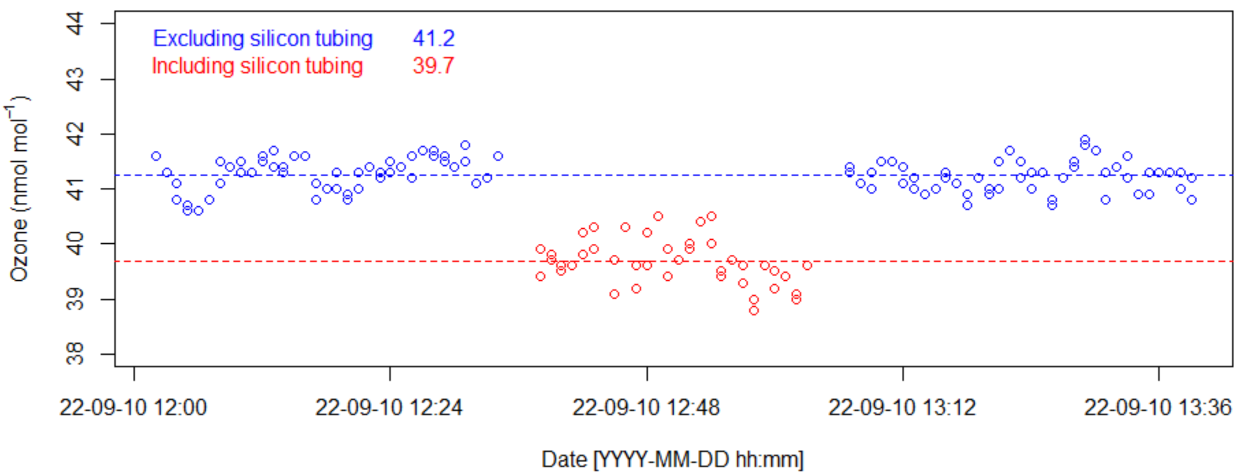

Figure 1. *Surface ozone measured with the ZEP ozone analyser including (red) and excluding (blue) the 3 cm silicon tubing in the inlet system. A constant amount fraction of ozone was generated using the WCC-Empa ozone calibrator.*

Testing of the inlet system showed that silicon tubing was unsuitable for surface ozone measurements. The inlet line was replaced with PFA tubing during the audit.

Recommendation 2 (*, critical, immediately, all stations operated by NILU)**
Silicon is an inappropriate material for surface ozone measurements and causes ozone loss when used in the air stream. The silicon tubes in the ozone air inlets must be removed from all surface ozone stations operated by NILU. It is also strongly recommended that the silicon tubing in the SO_2 and NO_x inlet systems be removed as well, as loss of these compounds is also likely. If possible, the data should be corrected for the loss of substance due to the inlet design.

Carbon monoxide, methane and carbon dioxide:

The inlet system has not been modified since the last WCC-Empa in 2012. It is fully adequate in terms of inlet design, sampling location, materials, and residence time.

Air intake location:	Top of 15 m tower, 8 m SE of the station building. Inlet tube is 1 inch heated (35°C) stainless steel. Total length approx. 20 m, flow speed maintained constant at approximately 10 m/s.
Inlet protection:	Protection against rainwater / snow / insects.
Instrument connection:	Instruments are connected directly to the 1 inch SS tube with ¼ inch Dekabon tubing
Inlet filter:	Swagelok SS-6F-60 particle filter.
Residence time:	Approximately 5 s

Surface ozone measurements

Surface ozone measurements at ZEP were established in 1989, and continuous time series have been available since then with several UV absorption O_3 analysers.

Instrumentation. ZEP is equipped with one ozone analyser (Teledyne API T400).

Standards. No standard is available at the site. The instrument is exchanged annually with an analyser that has been calibrated at NILU against a Teledyne API 400E instrument with traceability to the Stockholm University Standard Reference Photometer (SRP) #11.

Data acquisition. A custom-made data acquisition system (ADACS - Automatic Data Collection System) is used at ZEP. ADACS collects data from the ozone instrument every 10 seconds, and minute and hourly data are generated. The raw data are stored in a database at NILU. The data is released monthly after a manual quality control of the measured data. The whole system including backup policy, data transfer and evaluation is fully adequate.

Intercomparison (performance audit). The ZEP Ozone Analyser (OA) was compared to the WCC-Empa Travelling Standard (TS) with traceability to SRP#15. The internal ozone generator of the WCC-Empa transfer standard was used to generate a random sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}. The result of the comparisons is summarised below in relation to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data were acquired using the WCC-Empa data acquisition system. The data were treated in the same way as ambient air measurements, and the following correction was applied based on the last zero check, X_{O3} is the unbiased O_3 amount fraction and OA is the analyser reading:

$$X_{O3}\ (\mathrm{nmol\ mol^{-1}}) = ([\mathrm{OA}] - 1.1\ \mathrm{nmol\ mol^{-1}}) \quad (1a)$$

The following equations characterise the bias of the instrument and the remaining uncertainty after compensation of the bias. Uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). As the measurements refer to a conventionally agreed value of the ozone absorption cross section of 1.1476x10^{-17} cm^2 (Hearn, 1961), the uncertainties reported below do not include the uncertainty of the ozone absorption cross section.

Teledyne API T400 #6848 (Offset +2.5 nmol mol^{-1}, Span 0.998):

Unbiased O_3 amount fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.12 nmol mol^{-1}) / 1.0027 (1b)

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

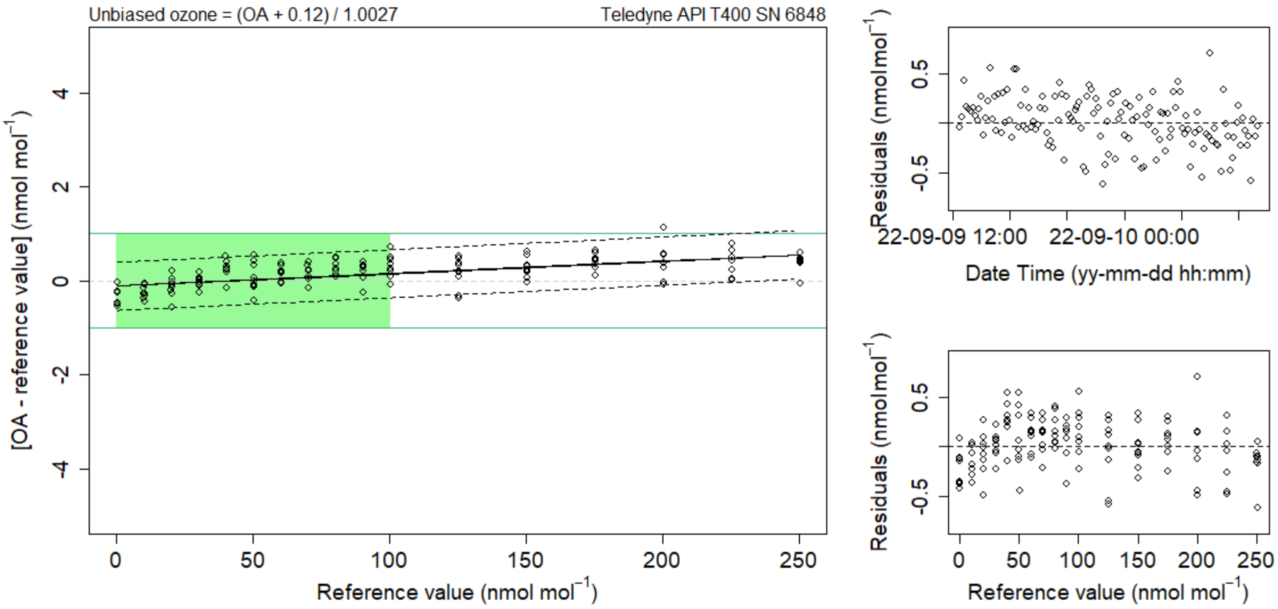

Figure 2. *Left: Bias of the ZEP ozone analyser (Teledyne API T400 #6848, offset 2.5 nmol mol^{-1}, span 0.998) with respect to the SRP as a function of amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

The results of the comparisons can be summarised as follows:

The result of the ZEP ozone analyser was within the WMO/GAW DQOs over the whole measurement range. Due to the good agreement, no further action is required.

Carbon Monoxide Measurements

Continuous measurements of CO at ZEP started in 1994 using gas chromatography (GC) / mercuric oxide reduction (RGD) detection. Continuous time series have been available since then with a few gaps. Since 2012, measurements have been made using Cavity Ring Down Spectroscopy (CRDS).

Instrumentation. The following instrumentation was available during the audit: Picarro G2401 (near-IR CRDS) with a Nafion dryer (MD-070-144S-2) to dry the sample air. Dried ambient air is used as purge gas.

Standards. Four reference standards from the ICOS Flask and Calibration Laboratory (FCL) are available at ZEP. In addition, target tanks are available for quality control. An overview of available standards is given in Table 5 in the Appendix.

Calibration. Calibrations using the four ICOS FCL standards are performed every 20 days. The tanks are run in sequence and this is repeated 4 times. The data from the first cycle is discarded to allow for stabilisation due to moisture in the Nafion dryer. At the time of the audit, a short term target was run every 49.5 hours. This was changed to every 25.5 hours at the end of October 2022. A long term target is run every 20 days, immediately after a calibration.

Data acquisition. The Picarro G2401 has an internal data acquisition, and the highest resolution (1-2 s resolution) raw data files are sent daily to ICOS ATC for processing. See Hazan et al. (2016) for details of the ATC processing.

Intercomparison (performance audit). The comparison consisted of repeated challenges of the ZEP instrument with randomly selected levels of carbon monoxide, using the WCC-Empa travelling standards.

The following equation characterises the instrument bias, and the result is further illustrated in Figure 3 with respect to the WMO GAW DQOs (WMO, 2020):

Picarro G2401 #4033-CFKADS2414:

Unbiased CO mixing ratio:	X_{CO} (nmol mol^{-1}) = (CO – 7.45 nmol mol^{-1}) / 0.9793	(2a)
Remaining standard uncertainty:	u_{CO} (nmol mol^{-1}) = sqrt (1.1 nmol mol^{-1} + 1.01e-04 * X_{CO}^2)	(2b)

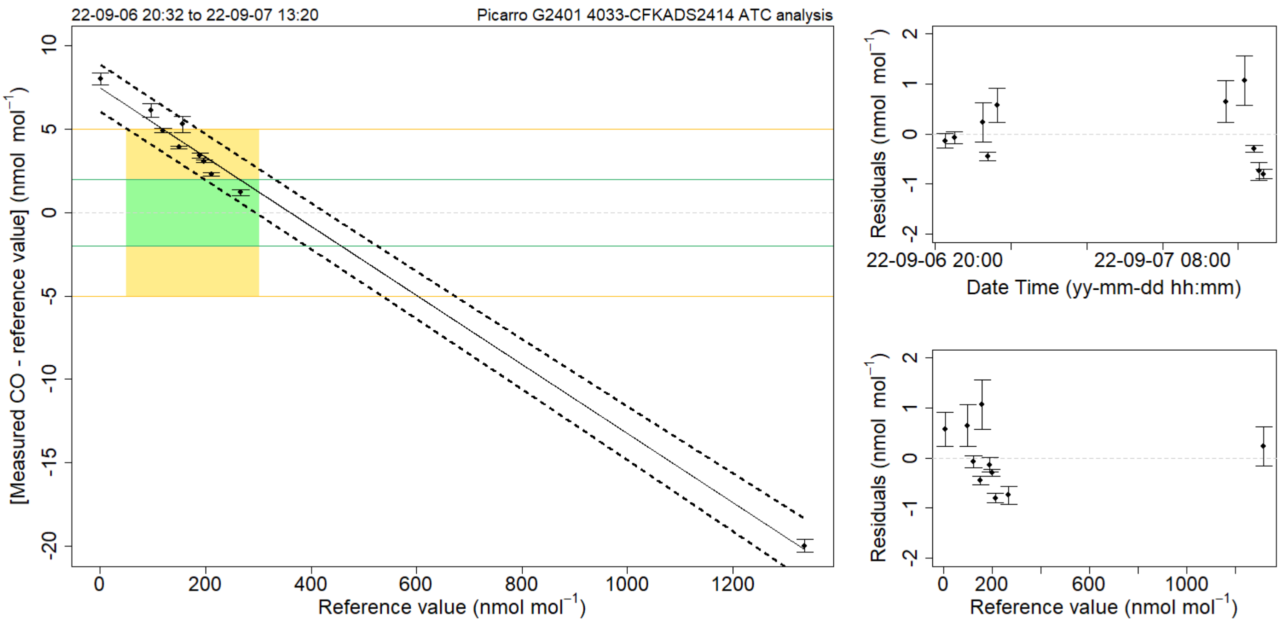

Figure 3. *Left: Bias of the ZEP Picarro G2401 #4033-CFKADS2414 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for ZEP. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

The comparison results did not meet the extended network compatibility goal of 5 nmol mol^{-1} in the relevant amount fraction range. The relationship between the ZEP and WCC-Empa values was linear, with a large zero offset of 7.5 nmol mol^{-1} and low values at higher CO amount fractions. The CO standards used at ZEP have shown high drift rate in recent years, and incorrect estimation of the drift rates for some of the cylinders may have led to the current result.

> **Recommendation 3 (***, critical, 2023)**
> *The ZEP CO standards need to be recalibrated at the ICOS Flask and Calibration Laboratory.*

In order to avoid measurement bias due to drifting standards, a calibration strategy based on standards with high CO amount fractions and zero air should be considered as an alternative.

> **Recommendation 4 (**, important, 2023)**
> *The CRDS measurement technique shows a linear response for CO in the amount fraction range at least from 0 to 4000 nmol mol^{-1}. In order to minimise the influence of standard drift, WCC-Empa recommends that the calibration strategy focuses on higher CO amount fractions, and also includes CO-free air (or N_2 6.0) to compensate for a zero offset. If standards with an amount fraction higher than 500 nmol mol^{-1} are used, the linearity of the analyser and the traceability to the CCL must be checked.*

Methane measurements

Continuous measurements of CH_4 at ZEP started in 1997 using GC / Flame Ionization Detection (FID). Since 2012, measurements have been made using Cavity Ring Down Spectroscopy (CRDS).

Instrumentation, standards and calibration. See carbon monoxide measurements.

Data Acquisition. See CO.

Intercomparison (performance audit). The comparison involved repeated challenges of the ZEP instrument with randomly selected CH_4 levels from travelling standards.

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

Picarro G2401 #4033-CFKADS2414:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.20 nmol mol^{-1}) / 0.9989 (3a)

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

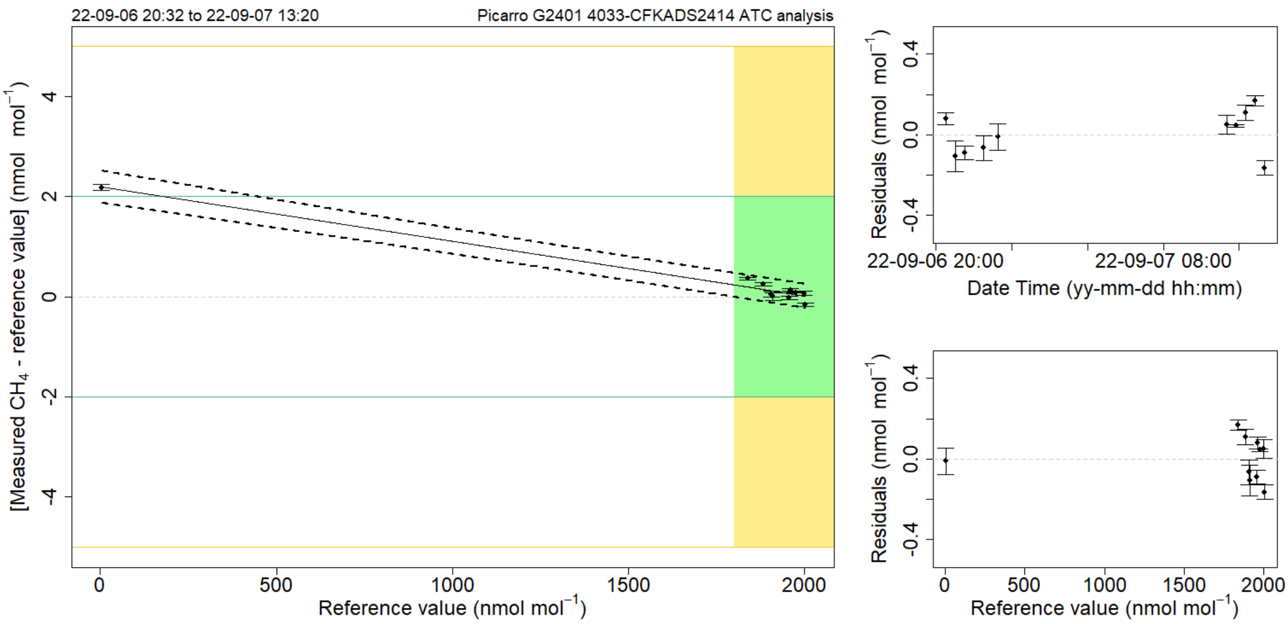

***Figure 4.** Left: Bias of the Picarro G2401 #4033-CFKADS2414 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for ZEP. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

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

Carbon dioxide measurements

Continuous measurements of CO_2 using NDIR technique, operated by the Stockholm University, started at ZEP in 1988 and continuous data have been available since then. These measurements were discontinued in 2012 after a short overlap period with the CRDS measurements that have since been carried out by NILU.

Instrumentation, standards and calibration. See carbon monoxide measurements.

Data Acquisition. See CO.

Intercomparison (performance audit). The comparison involved repeated challenges of the ZEP instrument with randomised CO_2 levels from travelling standards.

The following equation characterises the instrument bias. The result is further illustrated in Figure 5 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G2401 #4033-CFKADS2414:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.33 µmol mol^{-1}) / 0.99915 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.00 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4b)

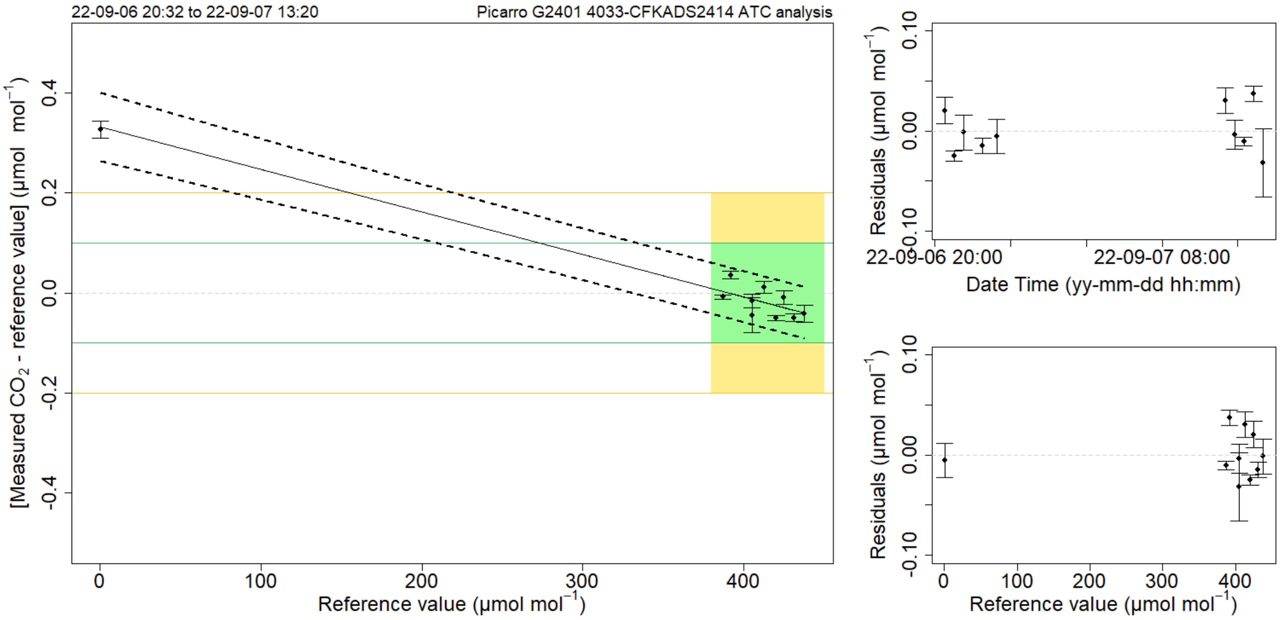

Figure 5. *Left: Bias of the Picarro G2401 #4033-CFKADS2414 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for ZEP. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

The result was within the WMO/GAW network compatibility goal in the relevant CO_2 range, and the bias showed only a small dependence on the amount fraction with an offset of about 0.3 µmol mol^{-1} at the zero point. Based on the good results, no further action is required.

ZEP PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the ZEP performance audit with other station audits conducted 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, but is also applicable to other compounds. Essentially, the bias in the middle of the relevant amount fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant amount 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 commonly found in unpolluted air masses. For surface ozone the amount fraction range of 0-100 nmol mol^{-1} was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 6 shows the bias vs. the slope of WCC-Empa performance audits by for O_3, CO, CH_4, and CO_2. The grey dots show all comparisons made during WCC-Empa audits for the main station analysers, but exclude cases with known instrumental problems. Where an adjustment was made during an audit, only the final comparison is shown. The results of the current ZEP audit are shown as coloured dots in Figure 6, and are also summarised in Table 1. The percentages of all WCC-Empa audits that met the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

Results were within the DQOs for O_3, CH_4, and CO_2. The results for CO were not within the DQOs, mainly due to a large offset at low CO amount fractions.

Table 1. *ZEP performance audit results compared to other stations. The 4th column shows whether the results of the current audit were within the DQOs (green tick mark), the extended DQO (orange tick mark) or exceeded the DQOs (red cross), while the 5th and 6th columns show the percentage of all WCC-Empa audits up to December 2022 within these criteria since 1996 (O_3), 2005 (CO and CH_4), and 2010 (CO_2).*

Compound / Instrument	Range	Unit	ZEP within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]
O_3 (Teledyne API T400 #6848)	0 -100	nmol mol^{-1}	✓	66	NA
CO (Picarro G2401 CFKADS2414, ICOS ATC analysis)	30 - 300	nmol mol^{-1}	×	18	50
CH_4 (Picarro G2401 CFKADS2414, ICOS ATC analysis)	1750 - 2100	nmol mol^{-1}	✓	76	94
CO_2 (Picarro G2401 CFKADS2414, ICOS ATC analysis)	380 - 450	µmol mol^{-1}	✓	48	73

[1] Percentage of stations within the eDQO and DQO

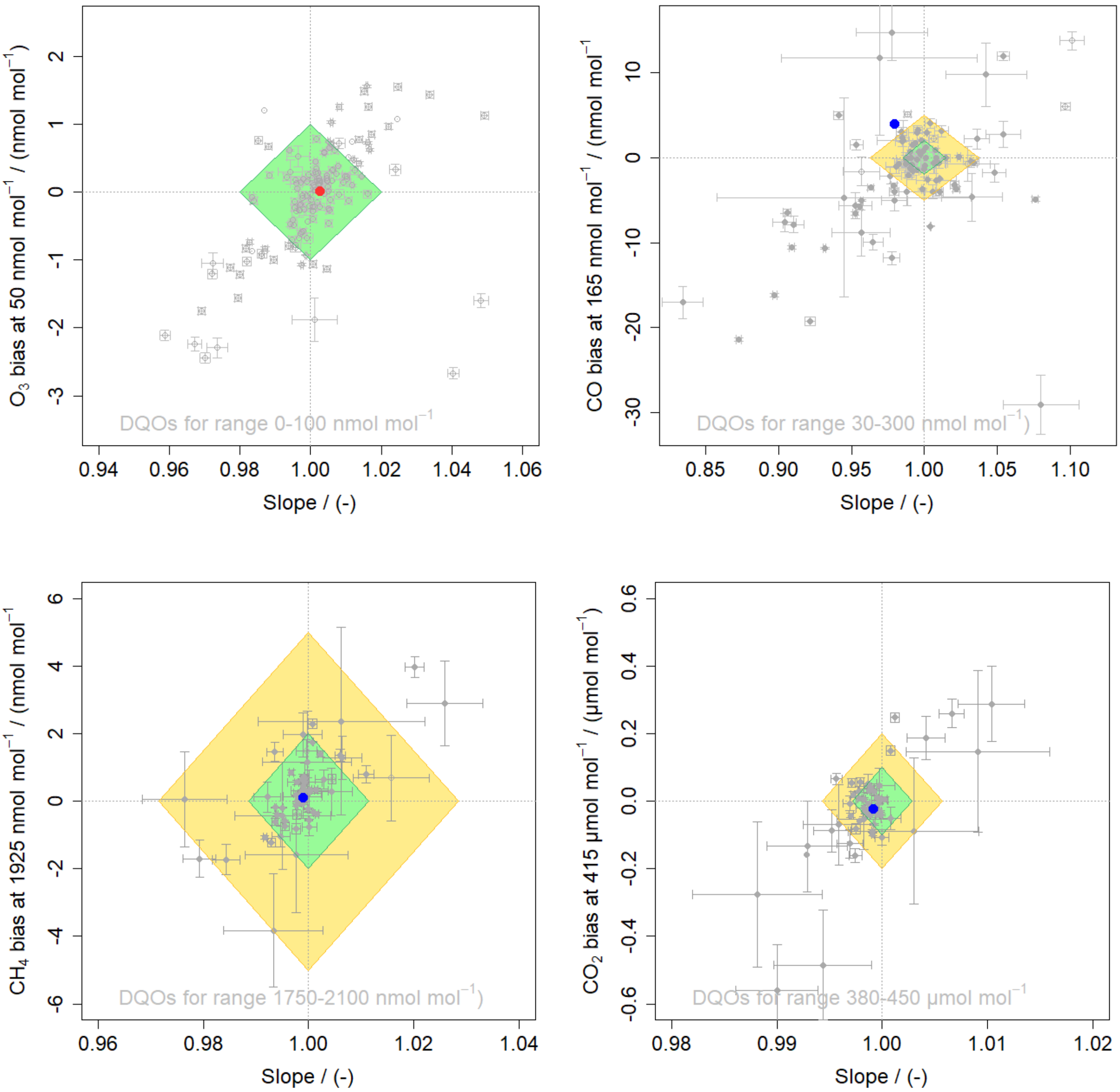

Figure 6. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show ZEP results (red: TELEDYNE API T400, blue: Picarro G2401). Filled symbols refer to a comparison with the same calibration scale at the station and at the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and the 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 operated at ZEP from 9 September to 27 October 2022. The TI was connected to a spare inlet line of the ZEP station normally used by the CO/N_2O Picarro, which was under repair during the audit. The TI sampled air using the following sequence: 1410 min ambient air followed by 45 min measurement of three standard gases, each for 15 min. For the first six days, the standards were only run for 10 minutes. The sample air was dried with a Nafion dryer (Perma Pure model PD-50T-12MPS) in reflux mode using the Picarro pump for the vacuum in the purge air stream. To account for the residual effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The ZEP data were processed by the ICOS ATC.

Figures 7 to 9 show the comparison of hourly CO, CH_4, and CO_2 measurements between the WCC-Empa TI and the ZEP Picarro G2401 analyser. Hourly averages were calculated based on 1 minute data with simultaneous data availability from the station analysers and the WCC-Empa TI.

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

Carbon Monoxide

ZEP measured higher CO amount fractions than WCC-Empa, which is consistent with the results of the TS comparison. The largest deviations were found during the first days of the comparison. During this period, the CO measurements of the WCC-Empa TI suddenly dropped by about 5 nmol mol^{-1}, which was not observed by the ZEP instrument. The TI data for this period were not invalidated as no indication of instrument malfunction was found in the TI ancillary measurement data. Overall, the observed results confirm the results of the travelling standard comparison.

Methane

Excellent agreement within the WMO/GAW network compatibility goals was found between the TI and the ZEP instrument, confirming the results of the travelling standard performance check. The temporal variation was well captured by both instruments and the deviation between the two instruments was very small.

Carbon dioxide

The temporal variability was well captured by both instruments, and no significant dependence of the bias on the amount fraction was observed. On average, the agreement was within the extended WMO/GAW network compatibility goal, confirming the results of the travelling standard comparison.

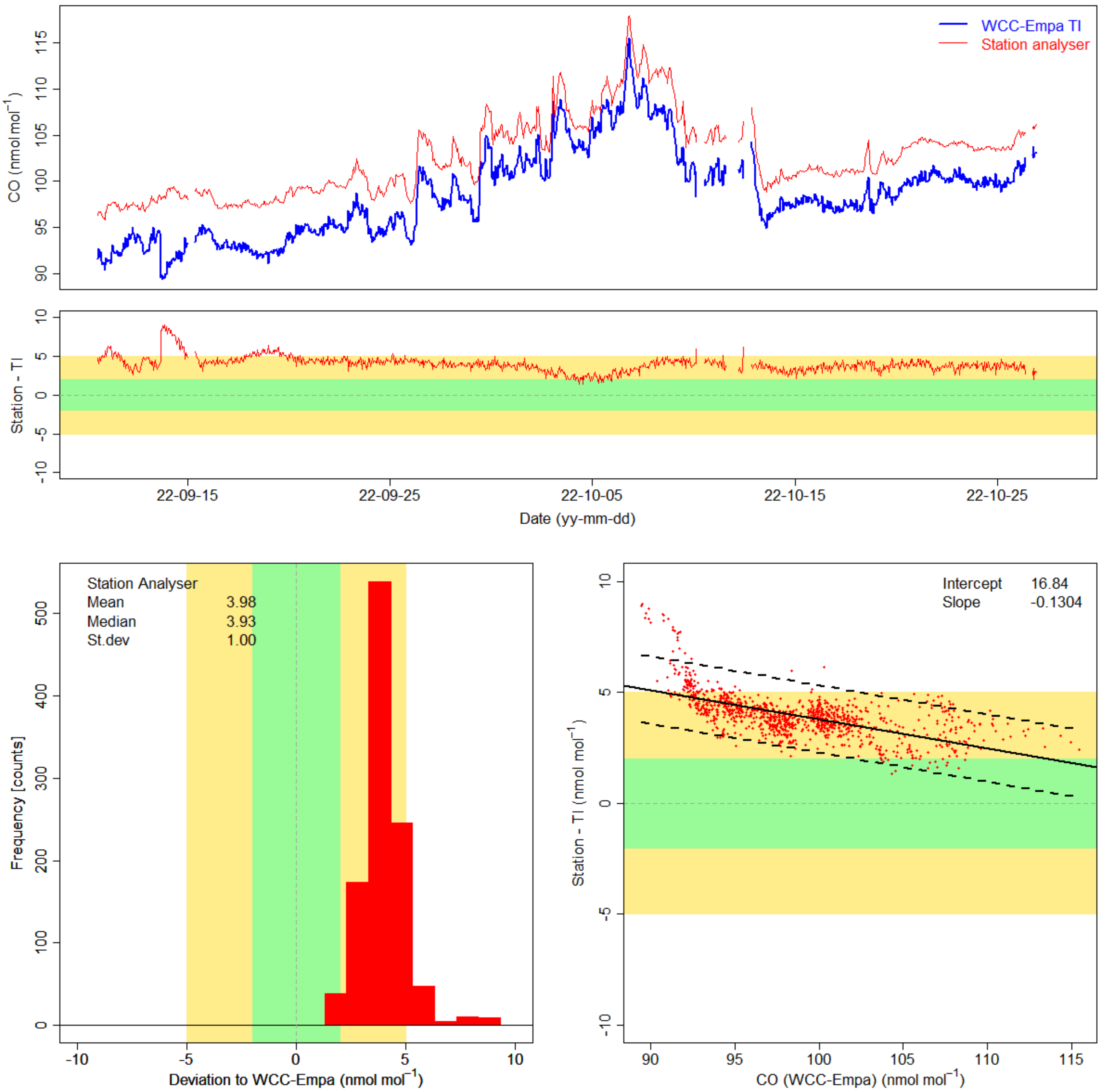

Figure 7. *Top: Comparison of the Picarro G2401#4033-CFKADS2414 with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G2401#4033-CFKADS2414 analyser compared to the WCC-Empa TI. Bottom right: ZEP instrument bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

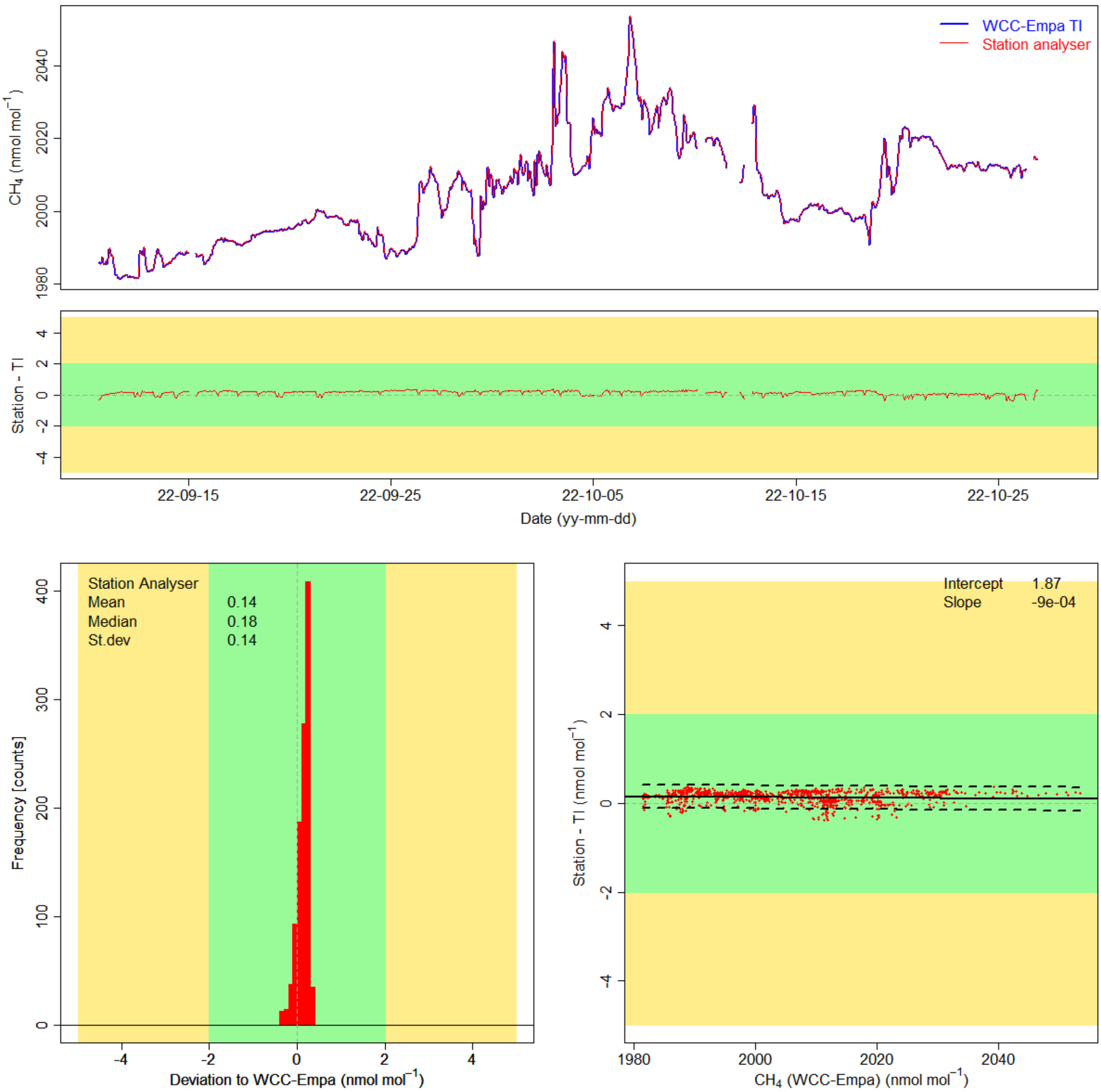

Figure 8. *Top: Comparison of the Picarro G2401#4033-CFKADS2414 with the WCC-Empa travelling instrument for* CH_4*. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left:* CH_4 *deviation histograms for the Picarro G2401#4033-CFKADS2414 analyser compared to the WCC-Empa TI. Bottom right: ZEP instrument bias as a function of the* CH_4 *amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

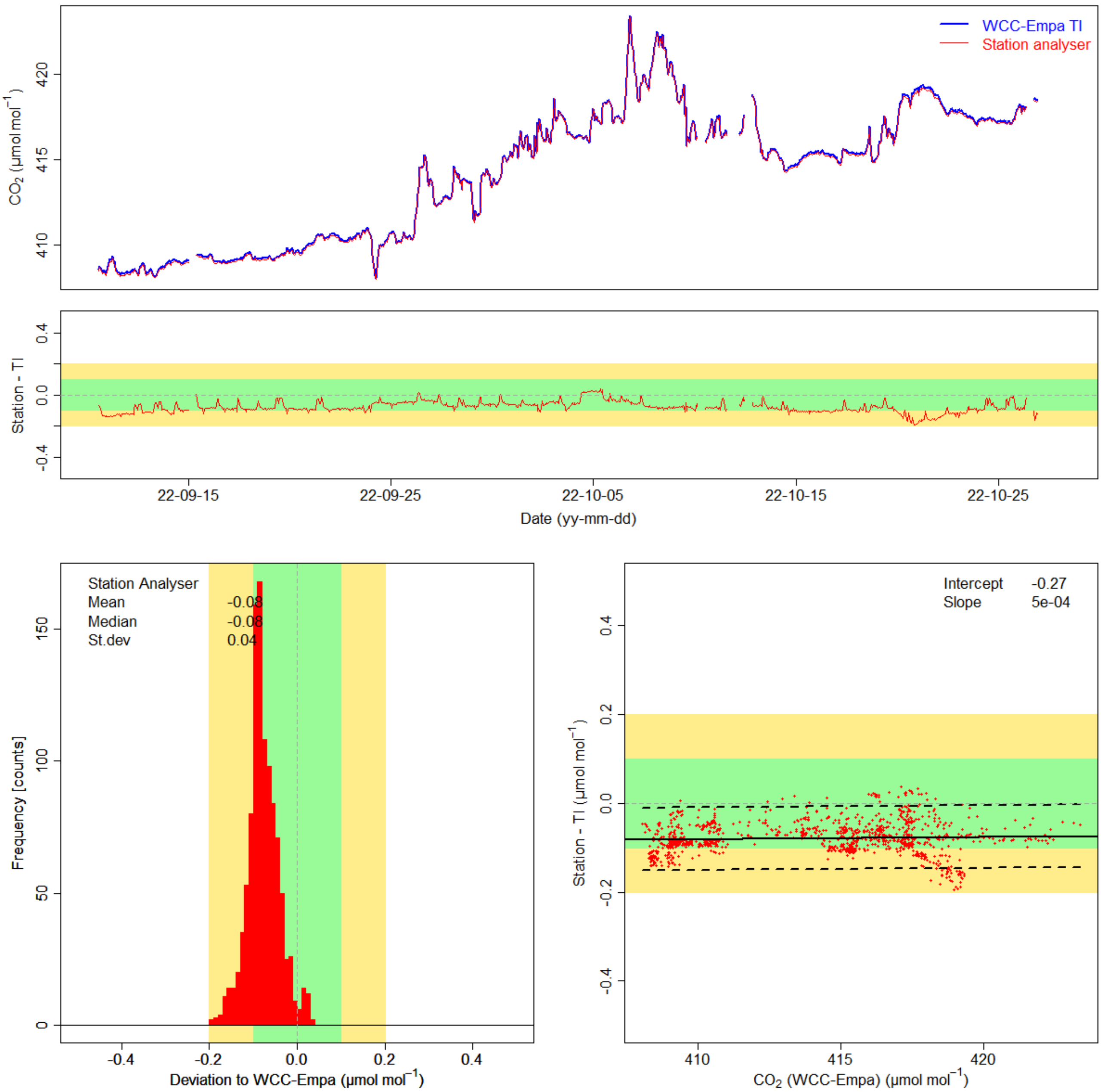

Figure 9. *Top: Comparison of the Picarro G2401#4033-CFKADS2414 with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO_2 deviation histograms for the Picarro G2401#4033-CFKADS2414 analyser compared to the WCC-Empa TI. Bottom right: ZEP instrument bias as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

CONCLUSIONS

The Zeppelin Mountain Global GAW Station provides extensive research facilities. It hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects. The GAW activities at ZEP are well embedded in the national and international research landscape, making it a very important contributor to the WMO/GAW programme. Therefore, the continuation of the Zeppelin Mountain measurement series is very important for GAW. The large number of atmospheric constituents measured, combined with the high data quality, allows state-of-the-art research.

Most of the measurements evaluated were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant range of amount fractions. Only the CO measurements showed a relatively high bias, which may be due to the drift of the CO standards available at ZEP. The audit also identified a problem with the ozone inlet system. This was corrected immediately during the audit, but the data prior to the current audit should be corrected for the loss of substance due to the inlet design.

Table 2 summarises the results of the performance audit and the ambient air comparison against the WMO/GAW compatibility goals. It should be noted that Table 2 refers only to the amount fractions relevant to ZEP, whereas Table 1 further above covers a wider range of amount fractions.

Table 2. *Synthesis of the performance audit results for the TS and ambient air comparisons. A tick mark indicates that the compatibility goal (green) or the extended compatibility goal (orange) was achieved on average. Tick marks in brackets indicate that the goal was only partially met in the relevant amount fraction range (performance audit only), and ✗ indicates results outside the compatibility goals.*

Comparison type	O_3 Teledyne API T400	CO Picarro G2401 ICOS ATC analysis	CH_4 Picarro G2401 ICOS ATC analysis	CO_2 Picarro G2401 ICOS ATC analysis
TS	✓	(✓)	✓	✓
Air	NA	✓	✓	✓

NA: no comparison was made

SUMMARY RANKING OF THE ZEPPELIN MOUNTAIN GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme
Access	(5)	Year round access
Facilities		
Laboratory and office space	(4)	Adequate, with limited space for additional research campaigns
Internet access	(5)	Wired high-speed connection (glass fibre, no wireless devices permitted)
Air Conditioning	(4)	Air conditioned, temperature fluctuations of a few degrees (<5°C)
Power supply	(5)	Reliable and stable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(4)	Issue with ozone inlet rectified during audit
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2 Picarro G2401	(5)	State of the art instrumentation
CO Picarro G2401	(4)	Adequate instrument
Standards		
O_3	(4)	No standard on-site, calibration with NIST traceable instrument at NILU
CO, CO_2, CH_4	(5)	Full traceability to the GAW reference through ICOS FCL
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(3)	Skilled staff, appropriate procedures
Data submission WDCRG	(5)	Timely submission of all parameters, NRT data available
Data submission WDCGG	(3)	CO has not been submitted

#0: inadequate thru 5: adequate.

Dübendorf, March 2023

Dr C. Zellweger
WCC-Empa

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Dr B. Buchmann
Head of Department

APPENDIX

Data review

The following figures show summary plots of ZEP data obtained from WDCRG and WDCGG on 17 February 2023. The plots show time series of hourly data, frequency distribution and diurnal and seasonal variations.

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

Surface ozone:

Two data sets are available from the WDCRG. The plots below show the final revised data for the period from 1989 to 2022, and more recent data for the period from 2020 to 2023.

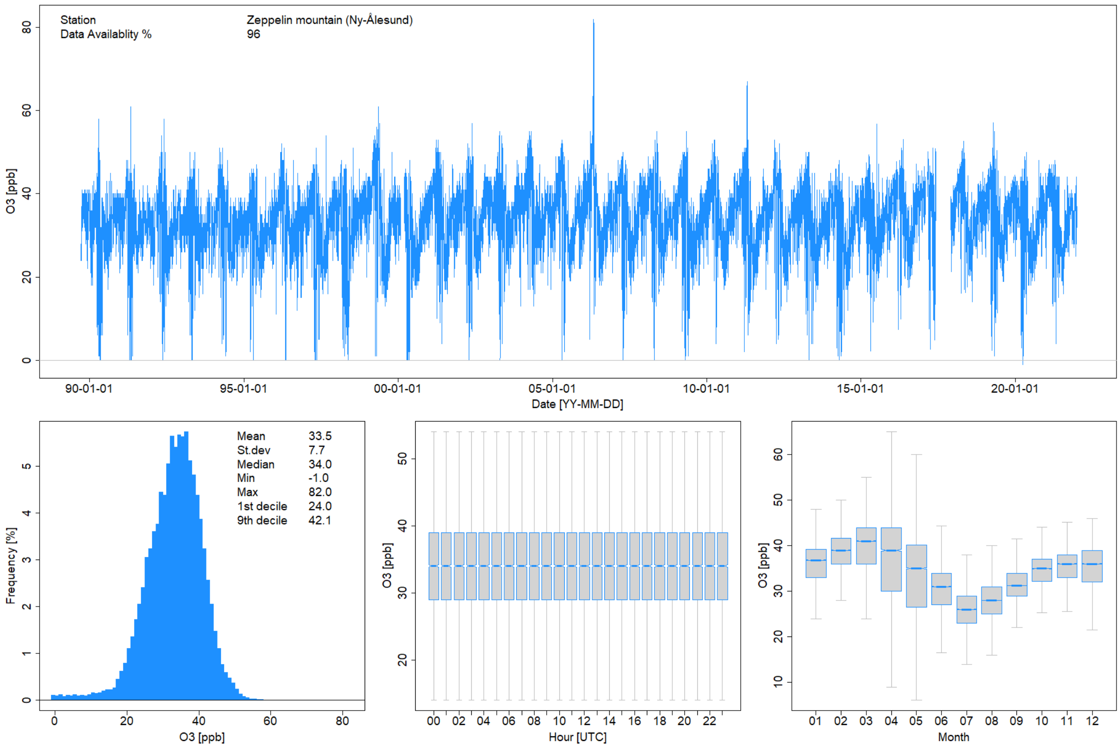

Figure 10. *WDCRG O_3 data for the period from 1989 to 2022. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range. This dataset shows the final revised data.*

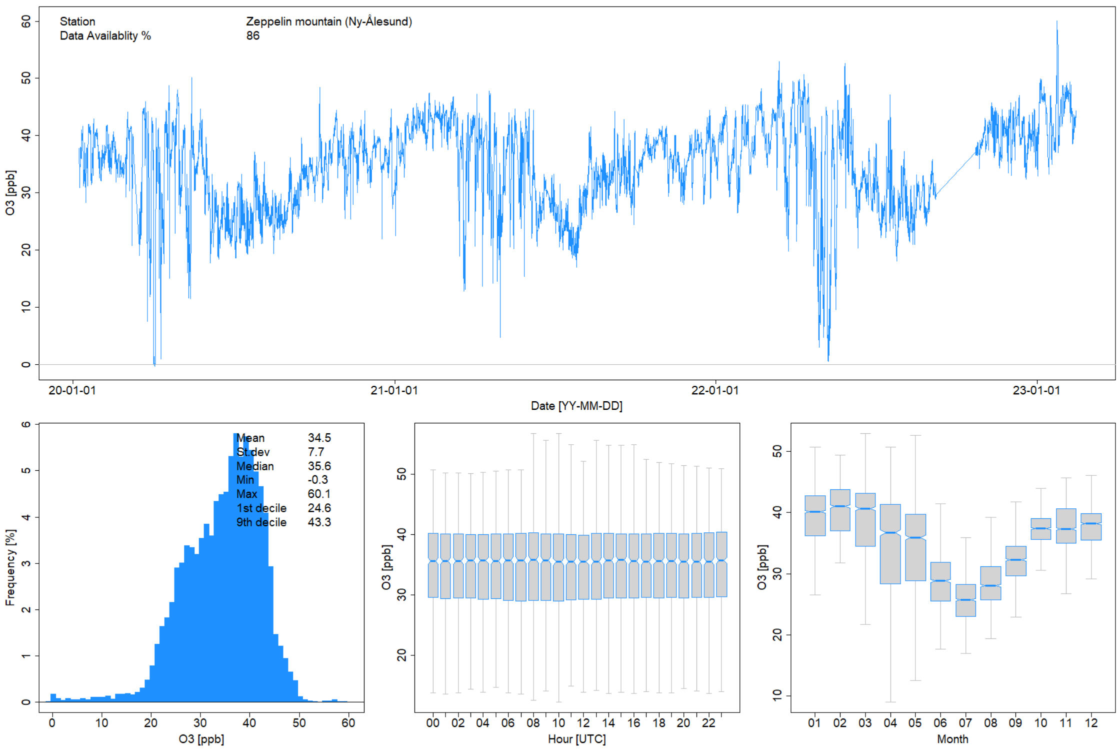

Figure 11. *WDCRG O_3 data for the period from 2020 to 2023. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range. This dataset shows initially revised data.*

- The datasets look good in terms of amount fraction, trend, seasonal and diurnal variation.
- The resolution is only 1 nmol mol^{-1} for the final revised data, but 0.1 nmol mol^{-1} for preliminary data.

Carbon monoxide:

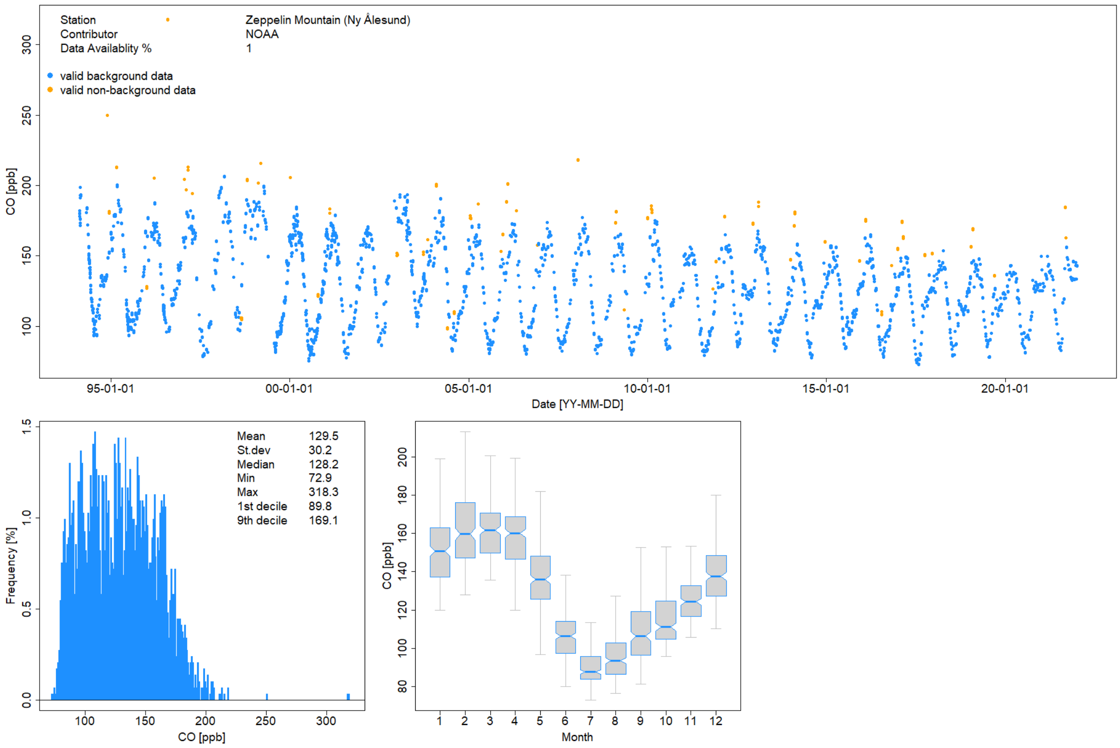

Figure 12. *ZEP CO flask data (1994-2021) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- For CO, only NOAA flask data have been submitted to the WDCGG.
- The NOAA ZEP CO data set looks good in terms of amount fraction, trend, seasonal and diurnal variation.

Methane:

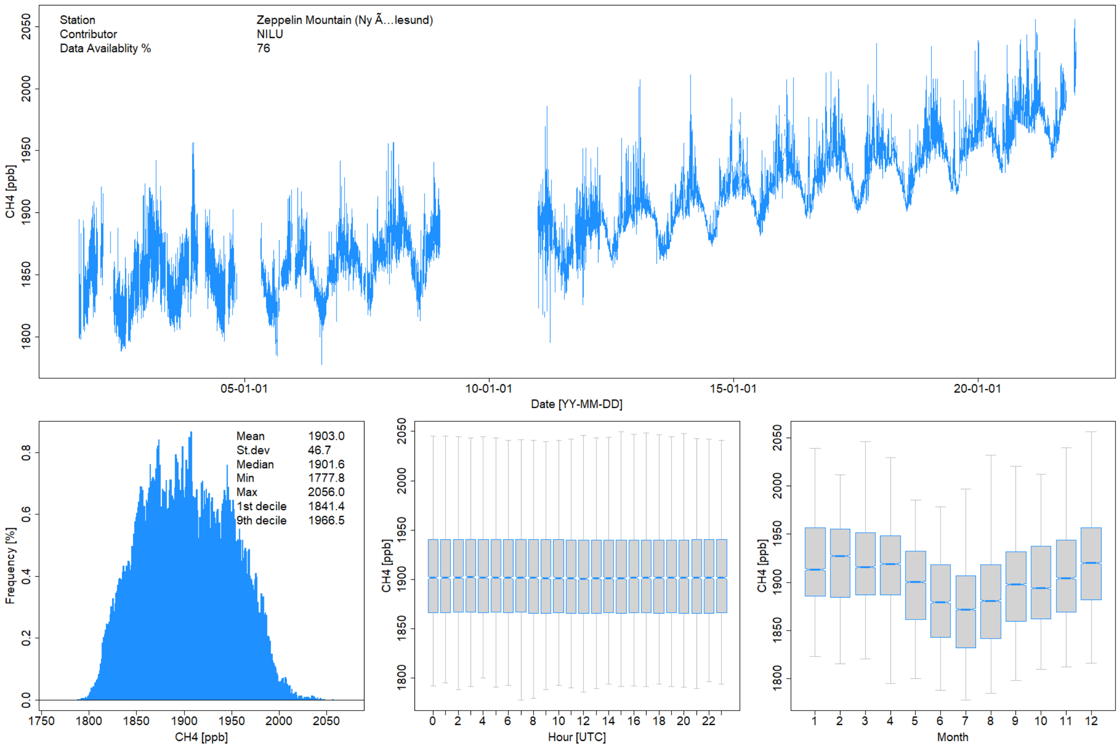

Figure 13. *ZEP in-situ CH_4 data (2001-2021) provided by NILU. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

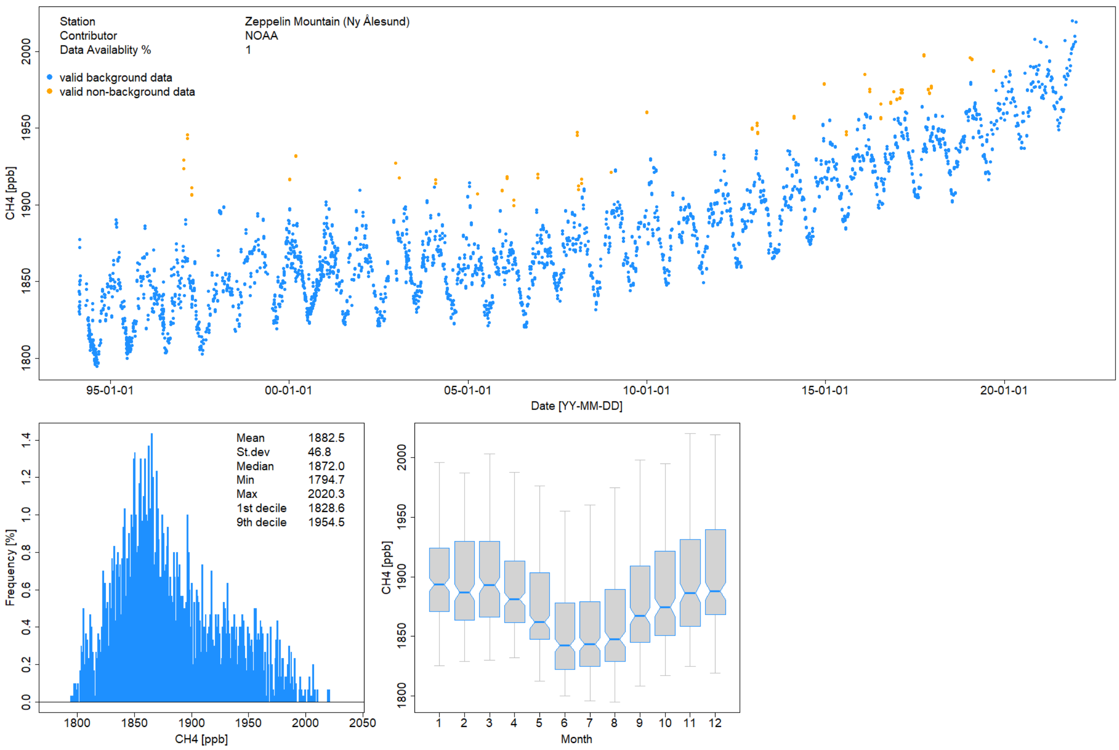

Figure 14. *ZEP CH_4 flask data (1994-2021) provided by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

Submission by NILU

- The NILU ZEP CH_4 dataset looks mostly good with respect to amount fraction, trend, seasonal and diurnal variations.
- In-situ CH_4 data for the years 2009 and 2010 are missing. Reason?
- An unusually large variability with higher occurrence of low CH_4 values compared to other years was observed in 2011, which needs further attention.

Submission by NOAA

- The NOAA ZEP CO dataset looks good in terms of amount fraction, trend, seasonal and diurnal variability.

Carbon dioxide:

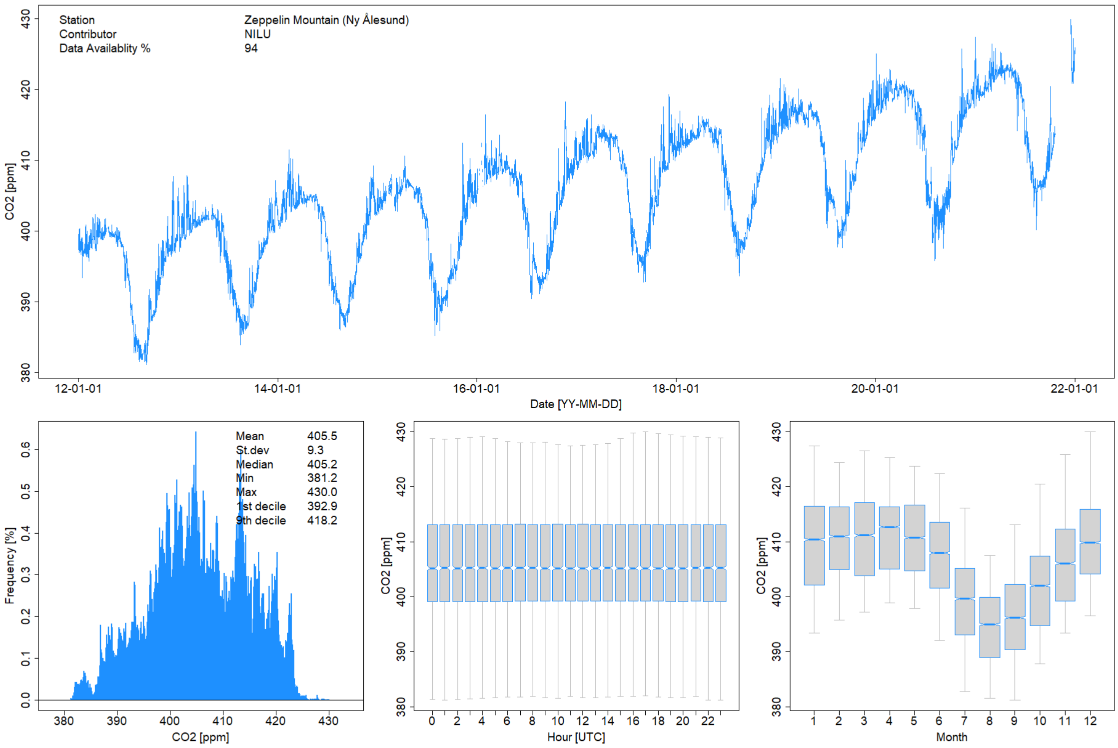

Figure 15. *ZEP in-situ CO_2 data (2012-2021) submitted by NILU. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

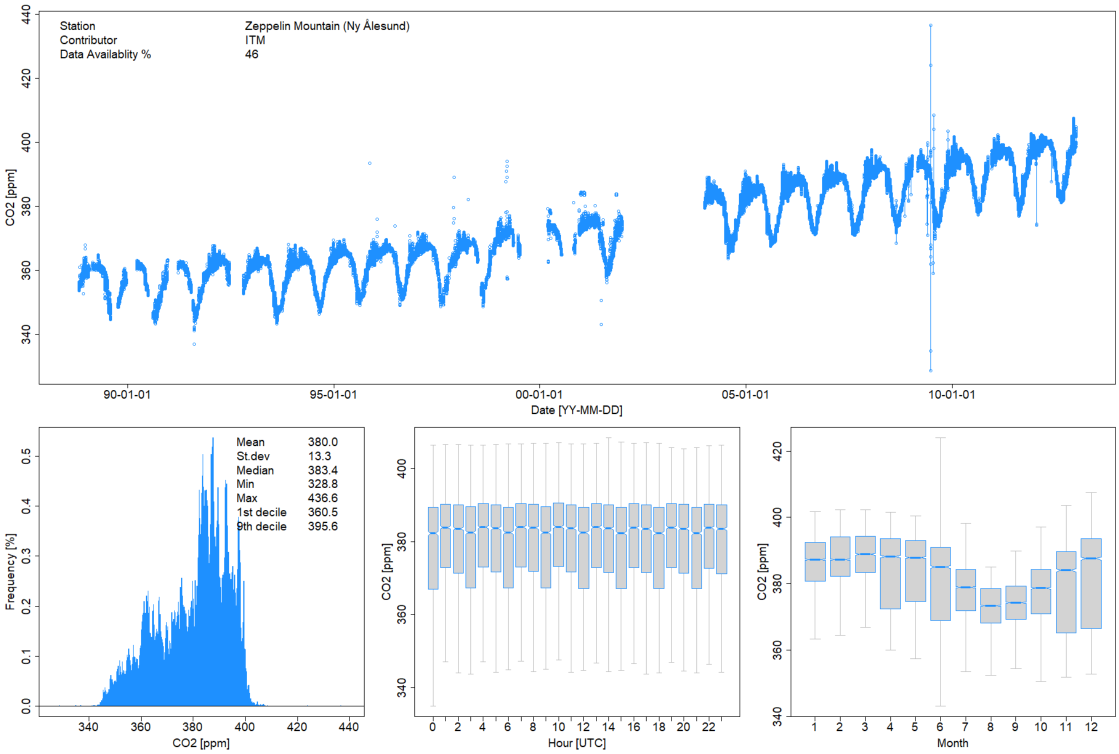

Figure 16. *ZEP in-situ CO_2 data (1988-2012) submitted by the University of Stockholm. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

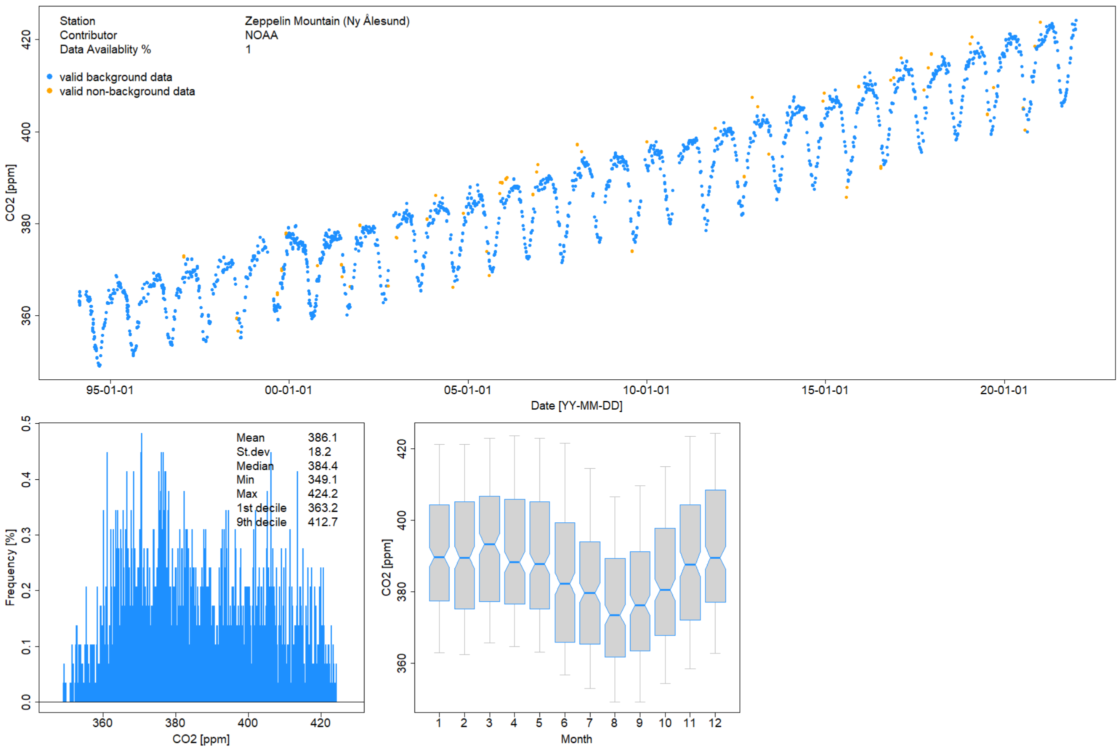

Figure 17. *ZEP CO_2 flask data (1994-2021) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

Submission by NILU

- The NILU ZEP CO_2 dataset looks good in terms of amount fraction, trend, seasonal and diurnal variation.

Submission by the University of Stockholm (ITM)

- The ITM ZEP CO_2 dataset looks mostly sound with respect to amount fraction, trend, seasonal and diurnal variation.
- Measurements were made using the Non-Dispersive Infrared technique (NDIR), and have been discontinued since 2013.
- An unusually high variability was observed in 2009, with a higher frequency of high and low CO_2 values compared to other years.

Submission by NOAA

- The NOAA ZEP CO_2 dataset looks good in terms of amount fraction, trend, seasonal and diurnal variation.

Surface Ozone Comparisons

All procedures were carried out 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 analyser comparison.

The internal ozone generator of the WCC-Empa transfer standard was used to generate a randomised sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (Nafion dryer, Purafil, activated charcoal). The TS was connected to the station analyser using approximately 1.5 m of PFA tubing. Table 3 details the experimental setup for the travelling standard and the station analyser comparisons. The data used for the evaluation were recorded by the WCC-Empa and ZEP data acquisition systems.

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

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #CM22117101 (WCC-Empa)
Settings	BKG +0.0 COEF 1.009
Pressure readings (hPa)	Ambient 953.0; TS 952.2, (no adjustment was made)
ZEP analyser (OA)	
Model, S/N	Teledyne API T400 #6848
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	Offset 2.5 nmol mol^{-1}, Span 0.998
Pressure readings (hPa)	No adjustments was made, system was running

Results

Each ozone level was measured for approximately ten minutes, and the last ten 40 s averages were aggregated. These aggregates were used to evaluate the comparison. All results are valid for the calibration factors as given in Table 3 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment was applied as for the ambient air analysis.
The results of the assessment are shown in the following table (individual measurement points) and are also presented in the Executive Summary.

Table 4. *Comparison of the ZEP ozone analyser (OA) Teledyne API T400* #6848 (*offset 2.5 nmol mol^{-1}, span 0.998*) *with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-09-09 12:30	225.42	0.12	225.86	0.25	0.44	0.20
2022-09-09 12:39	50.33	0.10	50.40	0.32	0.07	0.14
2022-09-09 12:47	40.31	0.11	40.72	0.36	0.41	1.02
2022-09-09 12:56	60.34	0.12	60.55	0.22	0.21	0.35
2022-09-09 13:07	200.38	0.27	200.94	0.35	0.56	0.28
2022-09-09 13:15	125.29	0.19	125.63	0.28	0.34	0.27
2022-09-09 13:24	90.38	0.09	90.65	0.33	0.27	0.30
2022-09-09 13:35	175.40	0.24	175.82	0.23	0.42	0.24
2022-09-09 13:44	150.43	0.12	150.74	0.42	0.31	0.21
2022-09-09 13:52	70.36	0.08	70.57	0.28	0.21	0.30
2022-09-09 14:01	80.34	0.08	80.70	0.28	0.36	0.45
2022-09-09 14:10	0.60	0.11	0.35	0.19	-0.25	NA
2022-09-09 14:21	250.38	0.24	250.97	0.34	0.59	0.24
2022-09-09 14:30	30.30	0.10	30.49	0.53	0.19	0.63
2022-09-09 14:38	100.36	0.10	101.07	0.32	0.71	0.71
2022-09-09 14:47	10.31	0.17	10.25	0.24	-0.06	-0.58
2022-09-09 14:55	20.36	0.11	20.56	0.30	0.20	0.98
2022-09-09 15:04	20.38	0.14	20.24	0.18	-0.14	-0.69
2022-09-09 15:13	60.38	0.17	60.71	0.39	0.33	0.55
2022-09-09 15:24	250.39	0.24	250.84	0.22	0.45	0.18
2022-09-09 15:32	175.39	0.45	176.04	0.86	0.65	0.37
2022-09-09 15:41	125.28	0.21	125.50	0.38	0.22	0.18
2022-09-09 15:49	150.41	0.27	151.03	0.72	0.62	0.41
2022-09-09 16:01	225.31	0.14	225.82	0.21	0.51	0.23
2022-09-09 16:10	0.47	0.14	0.21	0.27	-0.26	NA
2022-09-09 16:19	40.26	0.11	40.79	0.29	0.53	1.32
2022-09-09 16:27	50.35	0.11	50.90	0.37	0.55	1.09
2022-09-09 16:38	200.41	0.14	200.78	0.37	0.37	0.18
2022-09-09 16:47	90.35	0.11	90.64	0.34	0.29	0.32
2022-09-09 16:55	70.34	0.13	70.38	0.19	0.04	0.06
2022-09-09 17:04	100.38	0.14	100.87	0.28	0.49	0.49
2022-09-09 17:12	10.29	0.10	10.13	0.48	-0.16	-1.55
2022-09-09 17:21	80.44	0.12	80.69	0.26	0.25	0.31
2022-09-09 17:29	30.33	0.10	30.25	0.35	-0.08	-0.26
2022-09-09 17:38	30.34	0.27	30.31	0.36	-0.03	-0.10
2022-09-09 17:49	250.32	0.14	250.81	0.34	0.49	0.20
2022-09-09 17:58	125.41	0.20	125.61	0.37	0.20	0.16

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-09-09 18:09	200.35	0.13	200.92	0.45	0.57	0.28
2022-09-09 18:18	40.33	0.15	40.59	0.42	0.26	0.64
2022-09-09 18:26	60.36	0.10	60.55	0.39	0.19	0.31
2022-09-09 18:35	50.34	0.11	50.25	0.34	-0.09	-0.18
2022-09-09 18:43	20.33	0.20	20.04	0.31	-0.29	-1.43
2022-09-09 18:52	10.30	0.23	10.02	0.27	-0.28	-2.72
2022-09-09 19:03	175.45	0.20	175.55	0.40	0.10	0.06
2022-09-09 19:12	70.26	0.12	70.59	0.31	0.33	0.47
2022-09-09 19:23	225.40	0.08	225.91	0.35	0.51	0.23
2022-09-09 19:31	80.34	0.10	80.84	0.37	0.50	0.62
2022-09-09 19:40	100.35	0.13	100.79	0.21	0.44	0.44
2022-09-09 19:49	0.56	0.11	0.07	0.13	-0.49	NA
2022-09-09 20:00	150.37	0.10	150.92	0.28	0.55	0.37
2022-09-09 20:09	90.38	0.13	90.58	0.21	0.20	0.22
2022-09-09 20:18	100.40	0.12	100.60	0.22	0.20	0.20
2022-09-09 20:26	10.33	0.21	10.25	0.21	-0.08	-0.77
2022-09-09 20:35	175.41	0.30	175.89	0.83	0.48	0.27
2022-09-09 20:43	70.34	0.09	70.57	0.21	0.23	0.33
2022-09-09 20:52	90.37	0.09	90.70	0.40	0.33	0.37
2022-09-09 21:00	150.28	0.29	150.50	1.14	0.22	0.15
2022-09-09 21:09	200.44	0.28	200.41	0.78	-0.03	-0.01
2022-09-09 21:17	20.37	0.16	19.81	0.32	-0.56	-2.75
2022-09-09 21:26	125.33	0.15	125.82	0.35	0.49	0.39
2022-09-09 21:34	80.36	0.10	80.84	0.25	0.48	0.60
2022-09-09 21:43	60.37	0.10	60.75	0.22	0.38	0.63
2022-09-09 21:51	30.35	0.12	30.41	0.20	0.06	0.20
2022-09-09 22:00	40.38	0.15	40.61	0.41	0.23	0.57
2022-09-09 22:11	225.39	0.09	226.03	0.25	0.64	0.28
2022-09-09 22:20	50.30	0.12	50.18	0.27	-0.12	-0.24
2022-09-09 22:31	250.42	0.25	250.35	0.31	-0.07	-0.03
2022-09-09 22:40	0.52	0.22	-0.03	0.27	-0.55	NA
2022-09-09 22:49	70.35	0.12	70.43	0.18	0.08	0.11
2022-09-09 22:57	150.40	0.18	150.36	0.74	-0.04	-0.03
2022-09-09 23:06	40.30	0.18	40.49	0.21	0.19	0.47
2022-09-09 23:14	90.33	0.09	90.74	0.42	0.41	0.45
2022-09-09 23:23	10.37	0.08	9.92	0.23	-0.45	-4.34
2022-09-09 23:31	50.36	0.15	50.69	0.47	0.33	0.66
2022-09-09 23:40	80.39	0.12	80.53	0.43	0.14	0.17
2022-09-09 23:48	60.37	0.10	60.52	0.35	0.15	0.25
2022-09-10 00:00	200.42	0.20	200.71	0.41	0.29	0.14
2022-09-10 00:08	100.32	0.16	100.67	0.29	0.35	0.35
2022-09-10 00:20	250.35	0.19	250.74	0.30	0.39	0.16
2022-09-10 00:28	125.41	0.24	125.79	0.96	0.38	0.30
2022-09-10 00:37	20.31	0.21	20.27	0.19	-0.04	-0.20
2022-09-10 00:46	0.62	0.13	0.14	0.37	-0.48	NA
2022-09-10 00:54	30.43	0.14	30.45	0.25	0.02	0.07
2022-09-10 01:03	175.26	0.49	175.86	1.17	0.60	0.34
2022-09-10 01:14	225.42	0.11	225.45	0.28	0.03	0.01

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-09-10 01:23	200.40	0.25	200.37	0.16	-0.03	-0.01
2022-09-10 01:32	0.56	0.17	0.52	0.40	-0.04	NA
2022-09-10 01:41	80.39	0.12	80.46	0.64	0.07	0.09
2022-09-10 01:49	70.32	0.10	70.54	0.42	0.22	0.31
2022-09-10 02:00	225.36	0.15	226.16	0.47	0.80	0.35
2022-09-10 02:09	150.32	0.15	150.51	0.63	0.19	0.13
2022-09-10 02:17	90.32	0.12	90.06	0.44	-0.26	-0.29
2022-09-10 02:29	250.41	0.19	250.79	0.28	0.38	0.15
2022-09-10 02:37	175.39	0.25	175.85	0.68	0.46	0.26
2022-09-10 02:46	20.33	0.15	20.36	0.43	0.03	0.15
2022-09-10 02:54	10.29	0.16	9.91	0.46	-0.38	-3.69
2022-09-10 03:03	100.36	0.16	100.61	0.23	0.25	0.25
2022-09-10 03:11	40.32	0.11	40.17	0.37	-0.15	-0.37
2022-09-10 03:20	30.39	0.10	30.28	0.18	-0.11	-0.36
2022-09-10 03:28	125.34	0.25	125.88	0.36	0.54	0.43
2022-09-10 03:37	60.30	0.12	60.50	0.18	0.20	0.33
2022-09-10 03:45	50.37	0.13	50.80	0.22	0.43	0.85
2022-09-10 03:54	40.32	0.15	40.62	0.26	0.30	0.74
2022-09-10 04:05	175.41	0.14	175.70	0.33	0.29	0.17
2022-09-10 04:14	60.30	0.15	60.23	0.20	-0.07	-0.12
2022-09-10 04:22	30.29	0.13	30.32	0.37	0.03	0.10
2022-09-10 04:31	90.33	0.12	90.38	0.21	0.05	0.06
2022-09-10 04:39	50.42	0.16	49.99	0.27	-0.43	-0.85
2022-09-10 04:48	70.33	0.11	70.18	0.63	-0.15	-0.21
2022-09-10 04:59	250.30	0.22	250.76	0.48	0.46	0.18
2022-09-10 05:08	80.37	0.13	80.58	0.49	0.21	0.26
2022-09-10 05:16	150.33	0.22	150.54	0.54	0.21	0.14
2022-09-10 05:25	125.45	0.21	125.12	0.28	-0.33	-0.26
2022-09-10 05:36	225.39	0.19	225.62	0.28	0.23	0.10
2022-09-10 05:45	0.47	0.13	0.24	0.21	-0.23	NA
2022-09-10 05:54	20.29	0.14	20.08	0.14	-0.21	-1.03
2022-09-10 06:02	200.51	0.54	201.63	0.90	1.12	0.56
2022-09-10 06:11	10.25	0.19	9.98	0.34	-0.27	-2.63
2022-09-10 06:19	100.34	0.10	100.43	0.26	0.09	0.09
2022-09-10 06:28	150.39	0.18	150.45	0.63	0.06	0.04
2022-09-10 06:36	30.35	0.11	30.09	0.17	-0.26	-0.86
2022-09-10 06:48	200.37	0.19	200.30	0.54	-0.07	-0.03
2022-09-10 06:56	70.28	0.15	70.68	0.25	0.40	0.57
2022-09-10 07:05	20.38	0.13	20.30	0.20	-0.08	-0.39
2022-09-10 07:16	250.38	0.19	250.79	0.50	0.41	0.16
2022-09-10 07:25	225.36	0.33	225.37	0.26	0.01	0.00
2022-09-10 07:34	0.40	0.20	-0.08	0.32	-0.48	NA
2022-09-10 07:42	40.39	0.13	40.23	0.49	-0.16	-0.40
2022-09-10 07:54	175.37	0.17	175.72	0.50	0.35	0.20
2022-09-10 08:02	90.35	0.14	90.65	0.54	0.30	0.33
2022-09-10 08:11	10.31	0.14	9.99	0.11	-0.32	-3.10
2022-09-10 08:19	80.37	0.10	80.51	0.28	0.14	0.17
2022-09-10 08:28	60.33	0.14	60.30	0.43	-0.03	-0.05

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-09-10 08:36	100.40	0.18	100.32	0.21	-0.08	-0.08
2022-09-10 08:45	50.31	0.12	50.19	0.38	-0.12	-0.24
2022-09-10 08:53	125.32	0.23	124.96	0.49	-0.36	-0.29
2022-09-10 09:02	150.30	0.26	150.62	0.67	0.32	0.21
2022-09-10 09:10	125.32	0.18	125.41	0.45	0.09	0.07
2022-09-10 09:19	50.33	0.11	50.32	0.35	-0.01	-0.02

Calibration Standards for CO, CH_4, CO_2 and N_2O

Table 5 provides an overview the standard gases for available for calibration of the CO, CH_4, CO_2 and N_2O instruments. The standards are provided by the ICOS FCL with full traceability to the CCL.

Table 5 *ZEP calibration standards as of September 2022.*

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
D477531	318.458	72.36	1799.67	379.68	Picarro G2401, ICOS FCL standard
D477537	328.681	109.94	1898.77	399.97	Picarro G2401, ICOS FCL standard
D477539	333.878	186.03	1998.47	420.01	Picarro G2401, ICOS FCL standard
D477541	338.856	260.33	2096.92	451.16	Picarro G2401, ICOS FCL standard

Due to drift, the CO values were linearly extrapolated from two calibrations in 2016 and 2019 at the ICOS FCL, as shown in the table below.

Table 6 *CO calibration results of the ICOS FCL from 2016 and 2019.*

Cylinder ID	2016-10-28 CO (X2014A) (nmol mol^{-1})	2019-12-11 CO (X2014A) (nmol mol^{-1})
D477531	62.45	67.52
D477537	102.44	106.28
D477539	177.65	181.94
D477541	252.57	256.54

Carbon Monoxide Comparisons

All procedures were carried out in accordance with 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 7 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation were recorded by the ZEP data acquisition system.

Table 7. Experimental details of the ZEP comparison.

Travelling standard (TS)	
WCC-Empa travelling standards (6 l aluminium cylinders containing a mixture of natural and synthetic air), assigned values and standard uncertainties are given in Tables 13 and 14.	
Station analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #4033-CFKADS2414
Principle	Near-IR CRDS
Drying system	Nafion dryer
Comparison procedure	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

The result of the evaluation is shown in the Executive Summary, and the individual measurements of the TS are shown in the following table.

Table 8. *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #4033-CFKADS2414 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 (%)
(22-09-06 22:47:00)	210420_FB03382	149.2	1.2	153.1	0.1	3	3.9	2.6
(22-09-07 12:20:00)	130819_FB03870	156.1	1.6	161.4	0.5	4	5.3	3.4
(22-09-06 23:17:00)	220124_FA02773	0.4	0.6	8.4	0.3	3	8.0	NA
(22-09-07 13:05:00)	140514_FB03899	266.5	0.3	267.7	0.2	3	1.2	0.5
(22-09-06 20:32:00)	210422_FA02466	188.9	0.6	192.3	0.1	4	3.4	1.8
(22-09-06 22:32:00)	150601_FA02482	1336.8	0.5	1316.8	0.4	4	-20.0	-1.5
(22-09-07 12:50:00)	180318_FA02782	197.0	0.4	200.1	0.1	4	3.1	1.6
(22-09-07 11:20:00)	181129_FB03853	95.7	1.1	101.8	0.4	4	6.1	6.4
(22-09-06 21:02:00)	210420_FB03348	119.2	1.2	124.1	0.1	4	4.9	4.1
(22-09-07 13:20:00)	140514_FB03904	211.0	0.1	213.3	0.1	4	2.3	1.1

Methane comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the WCC-Empa travelling standards before and after the audit. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA are given below.

Table 7 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation was recorded by the ZEP data acquisition system. The standards used for the calibration of the ZEP instruments are listed in Table 5.

Results

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

Table 9. *CH_4 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #4033-CFKADS2414 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-09-06 21:32:00)	210420_FB03382	1956.67	0.05	1956.64	0.03	4	-0.03	0.00
(22-09-07 12:20:00)	130819_FB03870	1883.45	0.06	1883.70	0.04	4	0.25	0.01
(22-09-06 23:17:00)	220124_FA02773	3.05	0.02	5.23	0.07	3	2.18	NA
(22-09-07 11:50:00)	140514_FB03899	1974.80	0.06	1974.89	0.01	4	0.09	0.00
(22-09-06 20:32:00)	210422_FA02466	1959.87	0.03	1960.01	0.03	4	0.14	0.01
(22-09-06 22:32:00)	150601_FA02482	1906.04	0.02	1906.09	0.06	4	0.05	0.00
(22-09-07 12:50:00)	180318_FA02782	1838.78	0.03	1839.14	0.03	4	0.36	0.02
(22-09-07 11:20:00)	181129_FB03853	1998.93	0.06	1998.99	0.05	4	0.06	0.00
(22-09-06 21:02:00)	210420_FB03348	1910.64	0.03	1910.64	0.08	4	0.00	0.00
(22-09-07 13:20:00)	140514_FB03904	2003.31	0.12	2003.15	0.04	4	-0.15	-0.01

Carbon dioxide comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the WCC-Empa travelling standards 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 7 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation were recorded by the ZEP data acquisition system. The standards used to calibrate the ZEP instrument are shown in Table 5.

Results

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

Table 10. *CO_2 aggregates calculated from individual analyses (mean and standard deviation of the mean)for* each level during the comparison of the Picarro G2401 #4033-CFKADS2414 instrument (AL) with the WCC-Empa TS (WMO-X2007 CO_2 scale).

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(22-09-06 21:32:00)	210420_FB03382	437.89	0.00	437.85	0.02	4	-0.04	-0.01
(22-09-07 12:20:00)	130819_FB03870	387.14	0.00	387.13	0.00	4	-0.01	0.00
(22-09-06 23:17:00)	220124_FA02773	0.10	0.01	0.43	0.02	3	0.33	NA
(22-09-07 11:50:00)	140514_FB03899	405.25	0.01	405.23	0.01	4	-0.02	0.00
(22-09-06 20:32:00)	210422_FA02466	425.10	0.01	425.09	0.01	4	-0.01	0.00
(22-09-06 22:32:00)	150601_FA02482	431.29	0.03	431.24	0.01	4	-0.05	-0.01
(22-09-07 12:50:00)	180318_FA02782	391.84	0.03	391.88	0.01	4	0.04	0.01
(22-09-07 11:20:00)	181129_FB03853	412.67	0.02	412.68	0.01	4	0.01	0.00
(22-09-06 21:02:00)	210420_FB03348	420.19	0.02	420.14	0.01	4	-0.05	-0.01
(22-09-07 13:20:00)	140514_FB03904	405.04	0.02	405.00	0.03	4	-0.04	-0.02

WCC-Empa Traveling Standards

Ozone

The WCC-Empa Travelling Standard (TS) was compared with the standard reference photometer before and after the audit. The instruments used were

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

WCC-Empa TS: Thermo Scientific 49i-PS #CM22117101, BKG 0.0, COEF 1.009

Zero air source: Compressed air - Dryer - Breitfuss zero air generator – Purafil – Charcoal –Filter

The results of the TS calibration before and after the audit are shown in Table 11. The TS passed the pre-audit evaluation criteria defined for maximum acceptable bias (Klausen et al., 2003) (see Figure 18). The data were pooled and evaluated by linear regression analysis, taking into account the uncertainties of both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be calculated (equation 6a). The uncertainty of the TS (Equation 6b) was previously estimated (see equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([\text{TS}] + 0.34\ \text{nmol mol}^{-1}) / 0.9999 \quad (6a)$$

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

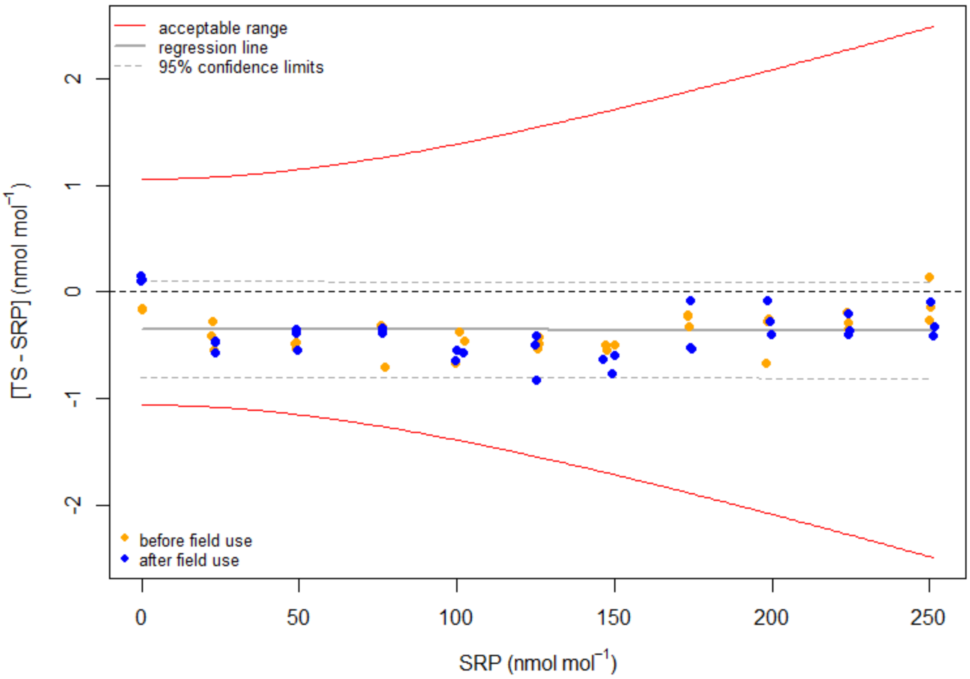

Figure 18. *Deviations between Traveling Standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS in the field.*

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

Date	Run	Level#	SRP (nmol mol-1)	sdSRP (nmol mol-1)	TS (nmol mol-1)	sdTS (nmol mol-1)
2022-07-28	1	50	48.78	0.29	48.32	0.14
2022-07-28	1	20	22.33	0.27	22.06	0.15
2022-07-28	1	200	198.22	0.25	197.56	0.18
2022-07-28	1	125	125.59	0.41	125.06	0.24
2022-07-28	1	75	75.99	0.39	75.68	0.23
2022-07-28	1	175	173.70	0.26	173.37	0.22
2022-07-28	1	145	147.23	0.34	146.73	0.16
2022-07-28	1	0	0.04	0.20	-0.11	0.19
2022-07-28	1	250	250.03	0.44	249.76	0.28
2022-07-28	1	105	102.51	0.37	102.06	0.28
2022-07-28	1	225	224.38	0.48	224.03	0.18
2022-07-28	2	20	22.09	0.37	21.68	0.22
2022-07-28	2	75	76.33	0.26	76.00	0.13
2022-07-28	2	200	198.69	0.25	198.42	0.08
2022-07-28	2	100	100.60	0.24	100.23	0.21
2022-07-28	2	50	48.67	0.41	48.19	0.20
2022-07-28	2	175	173.06	0.35	172.85	0.17
2022-07-28	2	150	150.23	0.35	149.73	0.08
2022-07-28	2	250	250.27	0.14	250.13	0.17
2022-07-28	2	0	-0.17	0.34	-0.01	0.10
2022-07-28	2	225	223.80	0.39	223.61	0.19
2022-07-28	2	125	125.90	0.20	125.48	0.23
2022-07-28	3	50	48.77	0.28	48.24	0.15
2022-07-28	3	100	99.69	0.22	99.02	0.19
2022-07-28	3	225	224.32	0.13	224.03	0.19
2022-07-28	3	0	0.05	0.22	-0.11	0.15
2022-07-28	3	25	22.78	0.29	22.24	0.13
2022-07-28	3	75	76.94	0.43	76.24	0.13
2022-07-28	3	150	147.64	0.51	147.09	0.17
2022-07-28	3	125	125.98	0.20	125.49	0.09
2022-07-28	3	175	173.41	0.19	173.18	0.10
2022-07-28	3	200	198.75	0.35	198.50	0.18
2022-07-28	3	250	250.05	0.38	250.19	0.21
2022-12-22	4	25	23.30	0.28	22.83	0.21
2022-12-22	4	250	250.19	0.26	250.09	0.21
2022-12-22	4	0	-0.15	0.39	-0.05	0.07
2022-12-22	4	175	174.67	0.23	174.14	0.15
2022-12-22	4	225	224.11	0.49	223.71	0.13
2022-12-22	4	100	102.06	0.38	101.50	0.16
2022-12-22	4	75	76.19	0.34	75.81	0.21
2022-12-22	4	145	146.23	0.34	145.60	0.19
2022-12-22	4	200	198.63	0.37	198.55	0.14
2022-12-22	4	125	124.73	0.28	124.24	0.19
2022-12-22	4	50	49.24	0.56	48.69	0.18

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-12-22	5	100	99.80	0.34	99.25	0.20
2022-12-22	5	25	23.17	0.41	22.71	0.20
2022-12-22	5	125	125.36	0.40	124.53	0.32
2022-12-22	5	250	250.90	0.37	250.49	0.20
2022-12-22	5	200	199.55	0.36	199.15	0.23
2022-12-22	5	175	173.96	0.17	173.44	0.16
2022-12-22	5	150	150.07	0.32	149.47	0.24
2022-12-22	5	50	48.94	0.43	48.56	0.15
2022-12-22	5	75	76.31	0.14	75.96	0.17
2022-12-22	5	0	-0.14	0.30	0.02	0.17
2022-12-22	5	225	224.65	0.25	224.28	0.16
2022-12-22	6	250	251.54	0.37	251.21	0.25
2022-12-22	6	175	174.01	0.35	173.93	0.09
2022-12-22	6	25	23.29	0.12	22.73	0.18
2022-12-22	6	125	125.37	0.46	124.96	0.37
2022-12-22	6	150	149.36	0.35	148.59	0.10
2022-12-22	6	225	224.33	0.36	224.13	0.22
2022-12-22	6	75	76.20	0.46	75.86	0.21
2022-12-22	6	0	-0.03	0.23	0.09	0.14
2022-12-22	6	200	199.39	0.23	199.12	0.15
2022-12-22	6	50	49.12	0.33	48.78	0.24
2022-12-22	6	100	99.50	0.15	98.86	0.37

#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 has been designated by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL, which are regularly compared with the CCL by means of travelling standards and the addition of new laboratory standards from the CCL. The following calibration scales have been used to assign the volume fractions to the TS:

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

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

CO and N_2O:	Aerodyne mini-cw	(mid-IR spectroscopy).
CO and N_2O:	LGR 913-0015	(mid-IR spectroscopy).
CO, CO_2 and CH_4:	Picarro G2401	(cavity ring-down spectroscopy).

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

For N_2O, data from the LGR 913-0015 was used, because this instrument has less cross-sensitivity to CO than the Aerodyne mini-cw.

Table 12 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including standard deviations of the WCC-Empa TS are given in Tables 13 and 14, and Figures 19 to 22 show the analysis of the TS over time.

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

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

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

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

TS	Press. (psi)	CH_4 (P) (nmol mol^{-1})	sd	CO_2(P) (µmol mol^{-1})	sd	N_2O (A) (nmol mol^{-1})	sd	N_2O (L) (nmol mol^{-1})	sd
130819_FB03870	700	1883.45	0.06	387.14	0	318.87	0.04	318.94	0.08
140514_FB03899	320	1974.8	0.06	405.25	0.01	328.63	0.04	328.56	0.06
140514_FB03904	1410	2003.31	0.12	405.04	0.05	328.4	0.09	328.38	0.04
150601_FA02482	1000	1906.04	0.02	431.29	0.03	327.02	0.04	326.52	0.07
180318_FA02782	1680	1838.78	0.03	391.84	0.03	312.02	0.08	312.07	0.01
181129_FB03853	1110	1998.93	0.06	412.67	0.02	330.08	0.04	330.14	0.05
210420_FB03348	1970	1910.64	0.03	420.19	0.02	337.21	0.03	337.24	0.02
210420_FB03382	1400	1956.67	0.05	437.89	0	343.34	0.05	343.34	0.05
210422_FA02466	1990	1959.87	0.03	425.1	0.01	341.1	0.03	341.1	0.04
220124_FA02773	1410	3.05	0.02	0.1	0.01	NA	NA	11.65	1.32

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

TS	Press. (psi)	CO (P) (nmol mol^{-1})	sd	CO (A) (nmol mol^{-1})	sd	CO (L) (nmol mol^{-1})	sd
130819_FB03870	700	156.13	1.56	153.46	0.11	153.16	0.38
140514_FB03899	320	266.5	0.34	258.76	0.05	261.87	0.01
140514_FB03904	1410	211.02	0.12	203.76	1.77	206.54	0
150601_FA02482	1000	1336.81	0.5	1331.87	1.17	1338.52	1.04
180318_FA02782	1680	196.98	0.38	193.62	0.18	192.68	0.02
181129_FB03853	1110	95.73	1.11	92.29	0.28	93.4	0.37
210420_FB03348	1970	119.21	1.19	115.1	0.32	115.83	0.56
210420_FB03382	1400	149.16	1.17	144.91	0.24	145.38	0.03
210422_FA02466	1990	188.93	0.57	185.96	0.23	185.03	0.01
220124_FA02773	1410	0.35	0.57	NA	NA	0.1	0.07

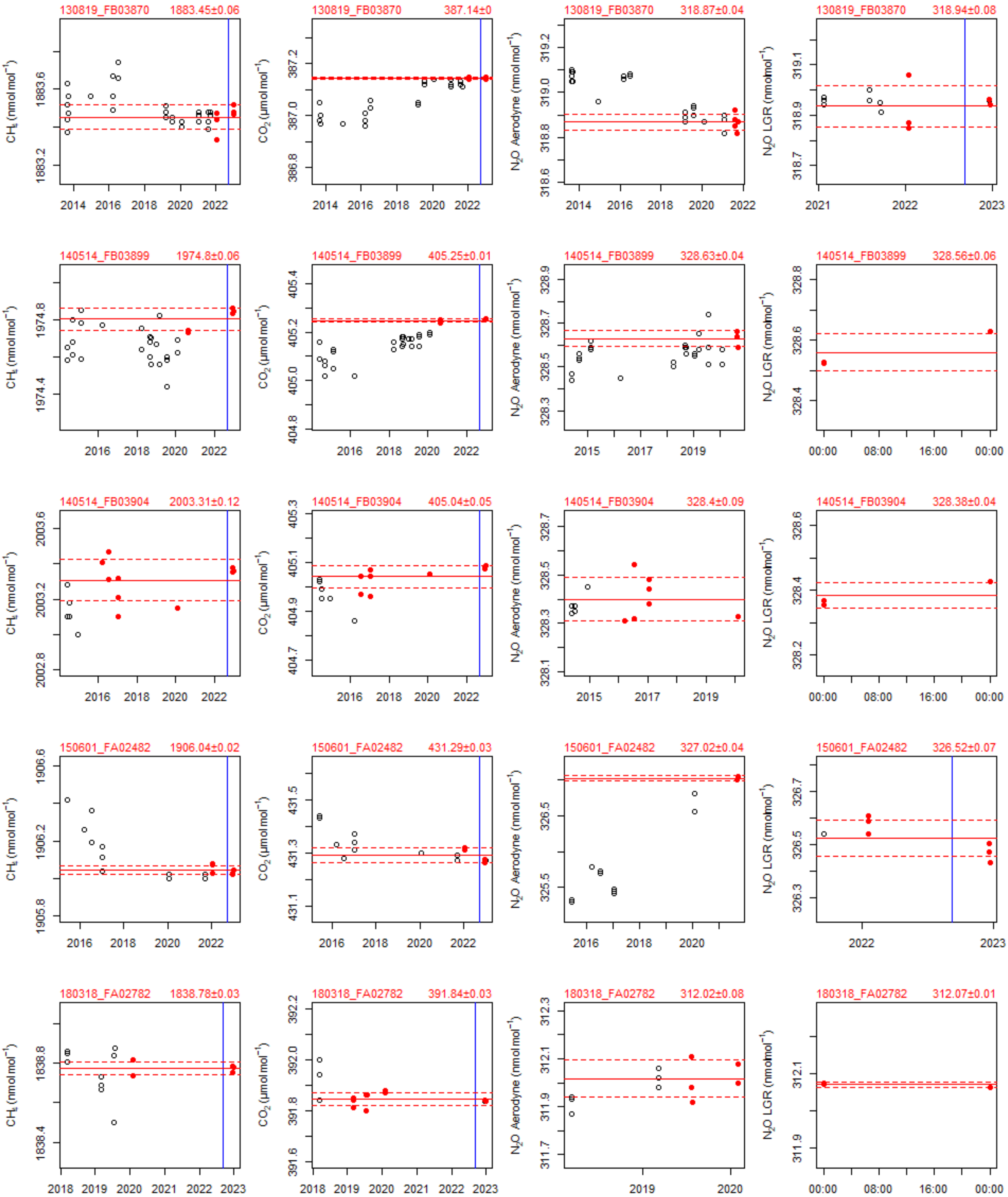

Figure 19. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points used to assign the values; the red dashed line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

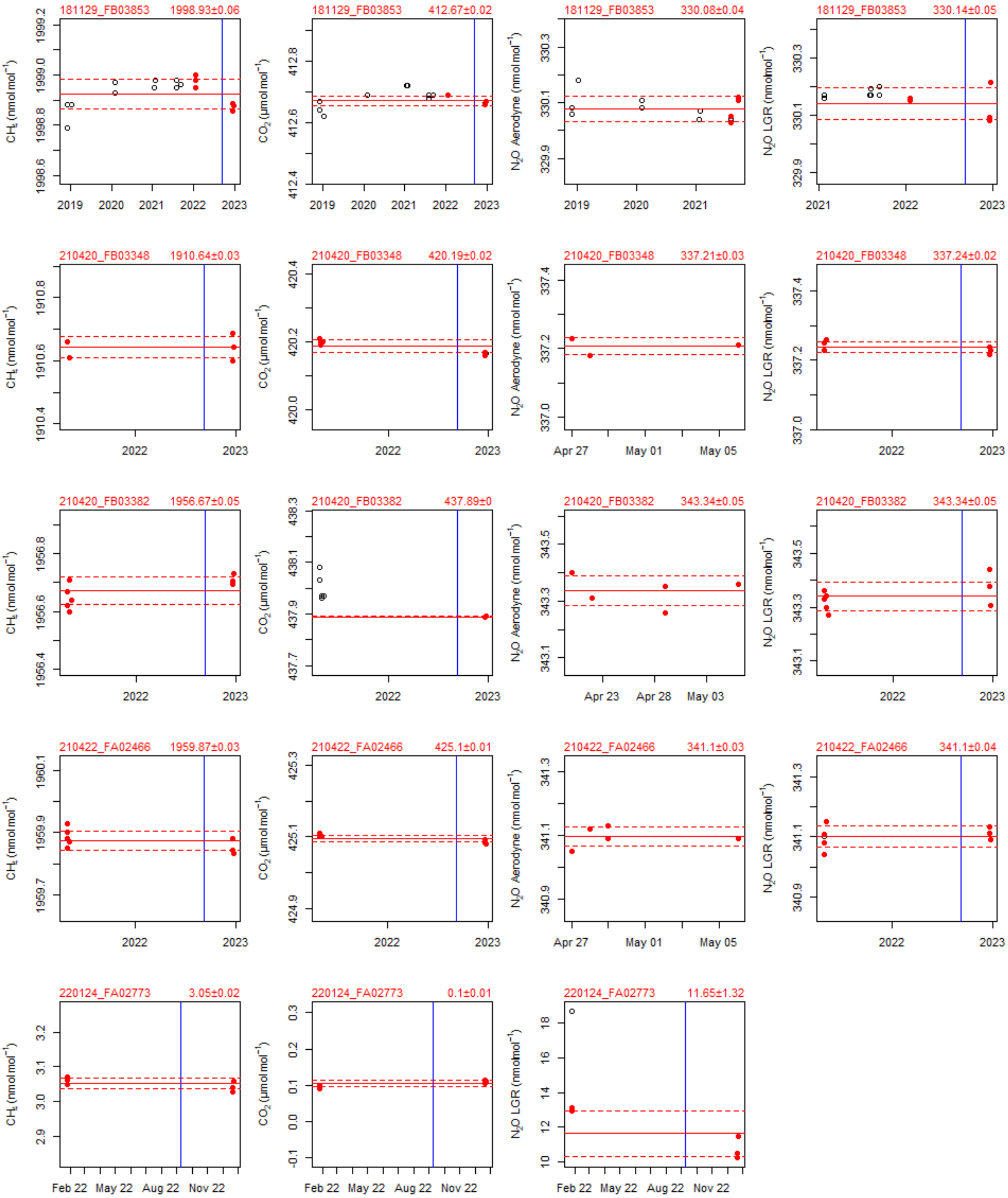

Figure 20. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points used to assign the values; the red dashed line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

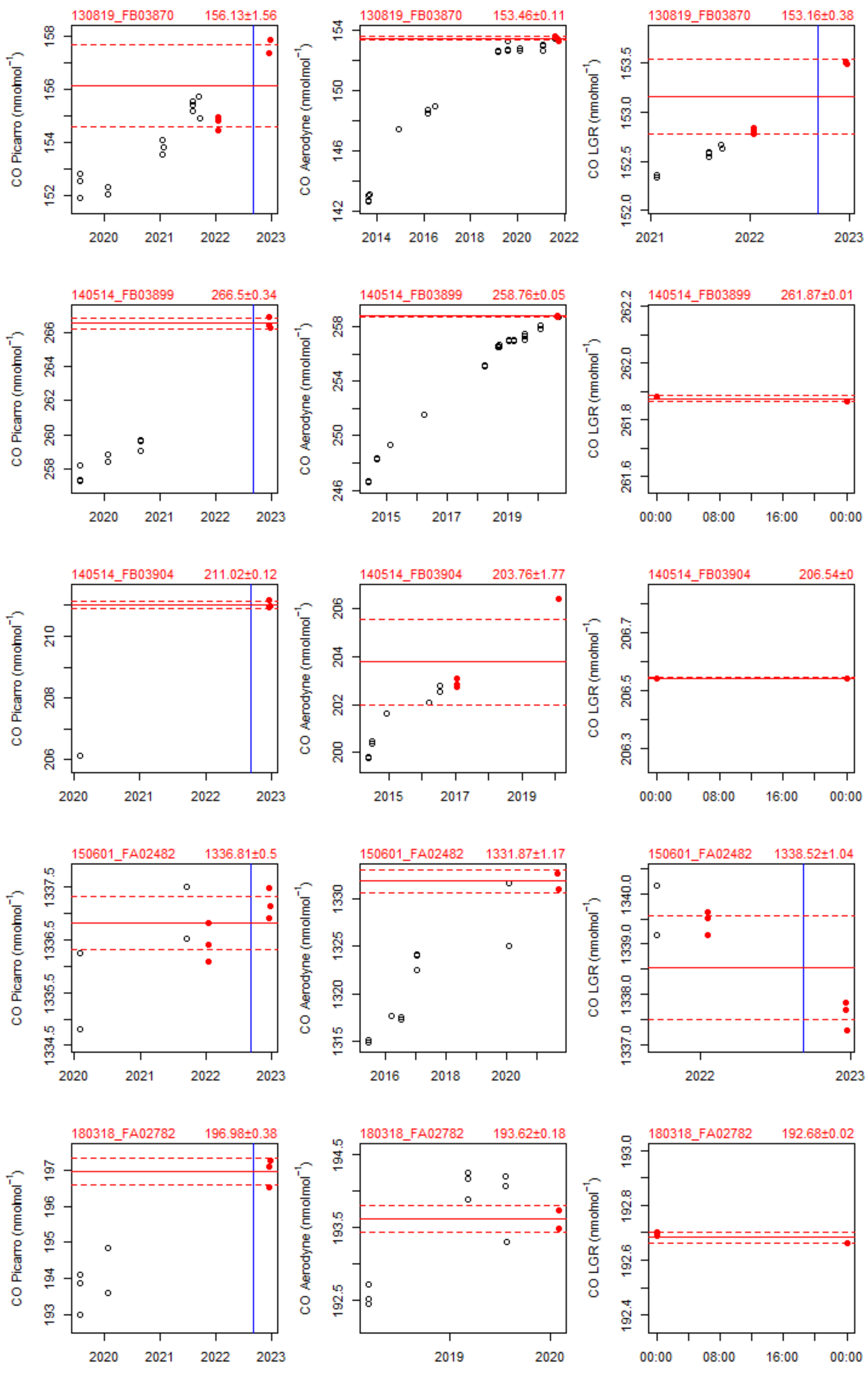

Figure 21. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that used to assign the values; the red dashes line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

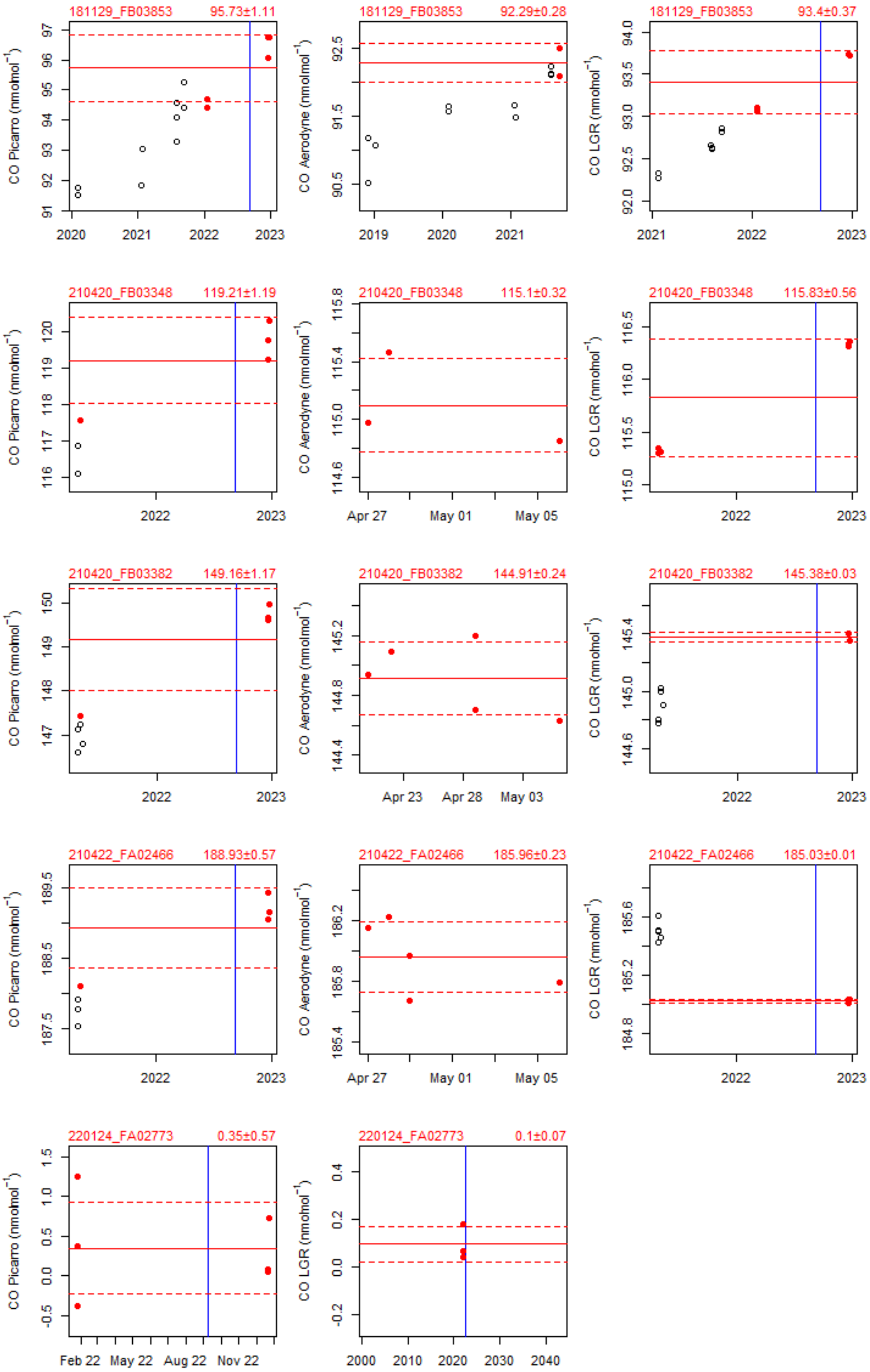

Figure 22. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that used to assign the values; the red dashes line corresponds to the standard deviation of the measurement. The blue vertical 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 1410 min using one WCC-Empa TS as a working standard, and two TS as target tanks. Based on the working standard measurements, a loess fit drift correction was applied to the data as shown in the figure below. The maximum drift between two WS measurements was approximately 0.1 nmol mol^{-1} for CH_4 and 0.1 µmol mol^{-1} for CO_2. Most of the target cylinder measurements were within half of the WMO GAW compatibility goals.

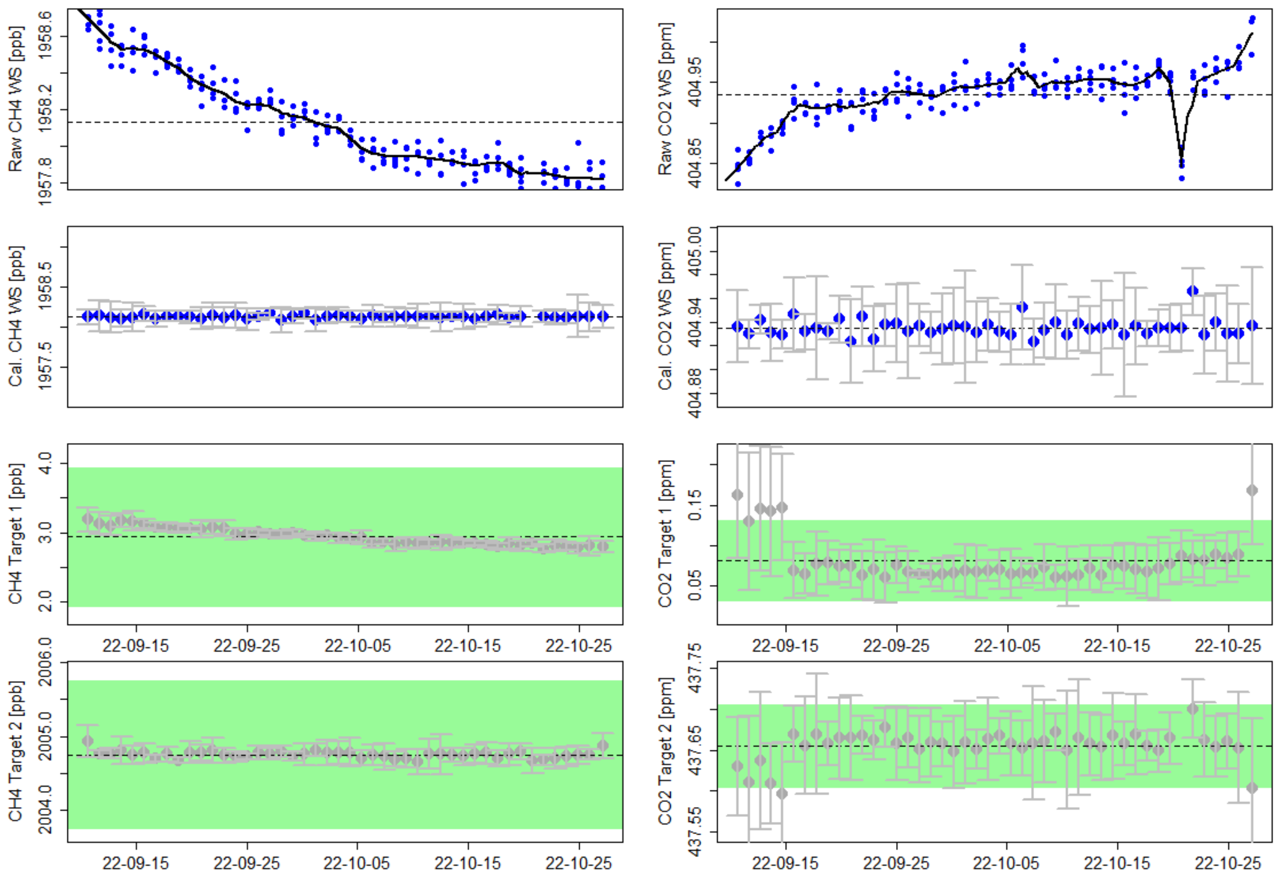

Figure 23. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The top panel shows the raw 1 min values of the working standard and the loess fit (black line) used to account for the drift. The second panel shows the variation of the WS after application of the drift correction. The bottom panel shows the results from the two target cylinders. Individual points in the three lower panels are 5 minute 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 1410 minutes using three WCC-Empa TS as a working standards. Based on the working standard measurements, a loess fit drift correction using was first applied to the data, as shown in the figure below.

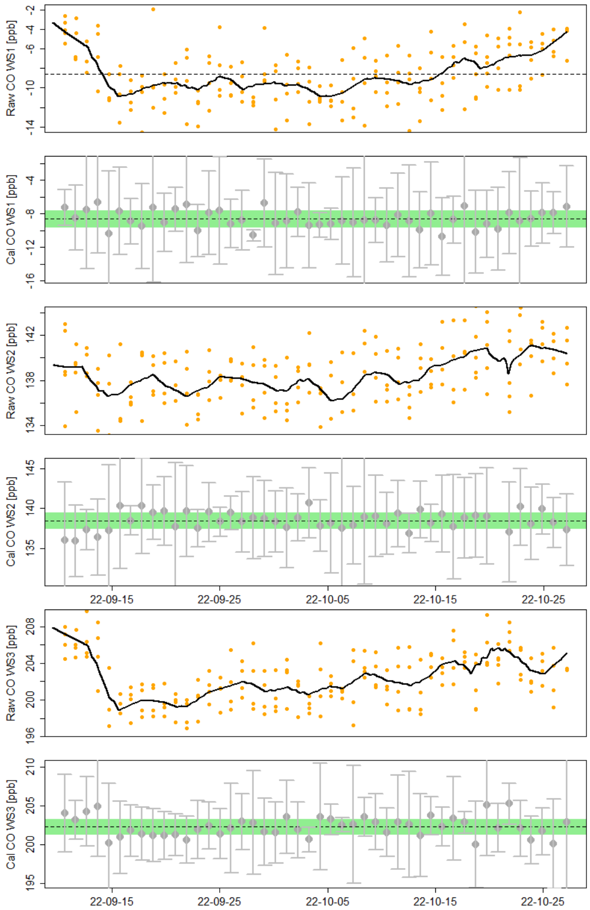

Figure 24. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show the raw 1 min values of the working standards and the loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in these panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

A linear function of the drift-corrected working standard data of then was then used to calculate calibrated CO data, which is shown in the figure below.

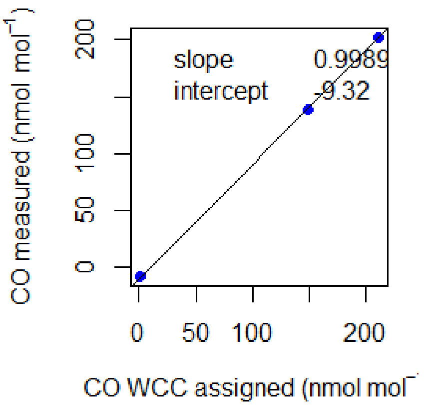

Figure 25. *CO calibration function based on the average values of the drift corrected working standard measurements.*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

LIST OF ABBREVIATIONS

a.s.l	above sea level
ACTRIS	Aerosol, Clouds and Trace Gases Research Infrastructure
ADACS	Automatic Data Collection System
AGAGE	Advanced Global Atmospheric Gases Experiment
AMAP	Arctic Monitoring and Assessment Programme
ATC	Atmosphere Thematic Centre
BKG	Background
CCL	Central Calibration Laboratory
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
eDQO	Extended Data Quality Objective
EMEP	European Monitoring and Evaluation Programme
FCL	Flask and Calibration Laboratory
FID	Flame Ionization Detection
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
IR	Infrared
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NRT	Near-real time
NILU	Norwegian Institute for Air Research
NOAA	National Oceanic and Atmospheric Administration
NPI	Norwegian Polar Institute
SOP	Standard Operating Procedure
SN	Serial Number
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization
WS	Working Standard
ZEP	Zeppelin Mountain GAW Station