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

AT THE

GLOBAL GAW STATION
CAPE POINT
SOUTH AFRICA
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Empa
Materials Science and Technology

WCC-Empa Report 21/3

Submitted to the World Meteorological Organization by

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Acknowledgements

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WCC-Empa Report 21/3

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 6th system and performance audit by WCC-Empa[1] at the global GAW station Cape Point (CPT), which is run by the South African Weather Service (SAWS), was conducted from 16 - 19 November 2021 in agreement with the WMO/GAW quality assurance system (WMO, 2017). The audit was initially planned for 2020, but had to be postponed due to the Covid-19 pandemic. A first set of travelling standards were already shipped in 2020, and they were analysed by the station staff before the on-site audit at CPT. A list of previous audits at CPT, as well as the corresponding audit reports, is available from the WCC-Empa webpage (www.empa.ch/gaw).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Dr Warren Joubert	SAWS, station manager, head of the observatory, lead scientist
Mr Casper Labuschagne	SAWS, senior scientist, greenhouse gas programme
Dr Thumeka Mkololo	SAWS, scientist, ozone programme
Dr Lynwill Martin	SAWS, senior scientist, mercury programme
Mr Ernest Mbambalala	SAWS, senior scientist, meteorology programme

This report summarises the assessment of the Cape Point GAW station in general, as well as the surface ozone, methane, carbon dioxide, and carbon monoxide in particular.

The report is distributed to the station manager of Cape Point and the responsible scientists, the national focal point for GAW in South Africa, and the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and posted on the internet (www.empa.ch/web/s503/wcc-empa).

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

Station Management and Operation

The station is operated and managed by the South African Weather Service. The offices of the station staff are located in Stellenbosch, and the station is usually visited on two days per week. The responsibility for the financial and personnel management resides with the programme manager, who is based at the headquarters of the SAWS in Pretoria.

Station Location and Access

CPT (34.3534812927°S, 18.4896831512°E, 230 m a.s.l.) is located in a nature reserve at the southern end of the Cape Peninsula, South Africa. The monitoring station is exposed to the sea on top of a cliff, and is located about 60 km south from the city of Cape Town. Since the dominant wind direction is SE - S - SW, the station is subjected to maritime air from the South Atlantic for most of the time. The location is adequate for the intended purpose. The station is accessible by road during the opening hours of the national park. More information is available from GAWSIS (https://gawsis.meteoswiss.ch).

Station Facilities and Infrastructure

The Cape Point station comprises extensive laboratory space. Basic offices, kitchen and sanitary facilities are available. Internet access is available with sufficient bandwidth. It is an ideal platform for

[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 Science and Technology (Empa). The mandate is to conduct system and performance audits at Global GAW stations based on mutual agreement.

continuous atmospheric monitoring as well as for extensive measurement campaigns. The air inlet and several pieces of meteorological equipment are mounted on a platform at the top of the flat roof.

South Africa's main energy supplier is currently not able to meet the electricity demand nationwide. As a consequence, the electrical power is turned off frequently, usually for two hour periods. The power outages are usually announced 24 hours in advance. CPT has a Diesel generator, located a few hundred meters downwind of the station, to bridge power cuts. However, the uninterruptible power supply (UPS) at the station is unable to bypass the short period between the power outage and the start of the generator, which frequently causes power outages of a few seconds.

> **Recommendation 1 (***, important, 2023)**
> *A UPS unit, which is able to bridge short power outages, needs to be installed (done December 2022).*

Measurement Programme

The CPT GAW station hosts a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured species is available from GAWSIS (https://gawsis.meteoswiss.ch/GAWSIS).

The information available from GAWSIS was reviewed as part of the audit. The last update was made in March 2022, and the information was mostly up-to-date. However, more details (e.g. instrument characteristics) should be added.

> **Recommendation 2 (**, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. Part of the reviewed information needs to be updated. The GAWSIS support should be contacted for updates which are not possible through the web interface (e.g. deletion of station contacts).*

During last decade, many of the instruments at CPT were replaced by analysers based on newer technologies. Particularly, all gas chromatographic systems (CO and GHGs) were replaced by spectroscopic instruments. As a consequence, no nitrous oxide (N2O) measurements are currently made. For a short period, a Picarro G5310 CRDS spectrometer, which is owned by a South African university, was available for CO and N_2O measurements. This instrument has been used in another project in Antarctica, and is currently not available for CPT.

> **Recommendation 3 (**, important, 2023)**
> *It is recommended to re-establish continuous N_2O measurements at CPT as the existing N_2O data constitute one of the very rare records in Africa.*

Data Submission

As of June 2022, the following CPT data of the scope of the audit has been submitted to the World Data Centres:

SAWS, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2015-2021)

SAWS, submission to World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (1983-2021), CO_2 (1993-2021), CO (1979-2021), N_2O (1994-2006)

National Oceanic and Atmospheric Administration (NOAA), submission to WDCGG:
CO_2 (2010-2020), CH_4 (2010-2020), CO (2010-2020), N_2O (2010-2020)

Data shown in this report was accessed on 27 September 2021 and on 7 June 2022. All data of the scope of the audit has been submitted with a submission delay of less than one year. Continuation of this timely submission practice is recommended.

Ozone measurements commenced in 1983 at Cape Point. Data between 1983 and 2014 is not available at WDCRG, although it was transferred from WDCGG to WDCRG. The data should again be made available.

> **Recommendation 4 (**, important, 2023)**
> *Ozone data from 1983 to 2014 needs to be made available at WDCRG. In case of issues with regard to data quality or missing metadata, re-submission of the historic time series is recommended after quality control of the data.*

Data Review

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

Documentation

All relevant information is entered in electronic log books (GHG and CO), or hand written log books (ozone). Log books are available for all instruments. The electronic note books are stored locally on the instrument PC. It was noted that no backup was available. The instrument manuals are available at the site. The reviewed information was mostly comprehensive and up-to-date.

> **Recommendation 5 (*, minor, 2023)**
> *It is recommended to change to electronic log books for all parameters, which allows better remote access and archiving. All log books need to be backed-up in regular (e.g. weekly) intervals.*

Air Inlet System

Ozone: The air inlet is located 4 m above the flat roof above the laboratory, and it is protected against rain by an upside-down stainless steel bucket. It consists of a 4.3 m long glass tube with 50 mm outer diameter inside a stainless steel tube followed by a short manifold with a length of 0.4 m and an inner diameter of 80 mm, also made of glass. The flow rate in the glass part is 1500 l/min. The instruments are connected to the manifold with short (1.5 m) ¼ inch PFA lines, and are protected by PTFE inlet filters. The residence time is approximately 2 seconds.

GHG and CO measurements: Air is sampled from the tower above the station at a sampling height of 30 m above ground. Direct ½ and ¼ inch Synflex-1300 lines flushed with approximately 12 l/min lead to the laboratory. A freezing trap (-20°C) is used to dry the sample air. The drying system will be replaced by a Nafion dryer in 2023.

The inlet systems are adequate regarding material and residence times, and no change is required.

Surface Ozone Measurements

Surface ozone measurements at CPT were established in 1982, and continuous time series are available since then.

Instrumentation. The GAW programme at CPT is currently running one ozone analyser (Thermo Scientific 49i). An additional instrument of the same type is run by the air quality division of the SAWS, which is not part of the GAW programme (https://saaqis.environment.gov.za/). Several issues were found for the CPT instruments, as detailed below. It is recommended to exchange the instrumentation.

Recommendation 6 (*, critical, 2023)**
The ozone analyser showed a non-linearity in the relevant amount fraction range, and the RS-232 communication port is not working. The analyser needs to be serviced, and replacement should be considered because the instrument has reached the end of its lifetime.
Status 2023: An instrument has been ordered and should be delivered in 2023.

Standards. An ozone calibrator (Thermo Scientific 49i-PS) is available at CPT. It was found to be not in a working condition, and clear indications of the malfunction of the instrument were not correctly interpreted by the responsible PI. The instrument was shipped to WCC-Empa after the CPT audit for repair and calibration.

Recommendation 7 (*, critical, 2023)**
The ozone calibrator was not in working condition due to a worn pump diaphragm, and leaking solenoid valves. This has been fixed at WCC-Empa after the audit, and a calibration certificate has been issued. Nevertheless, replacement of the calibrator is strongly recommended due to the age of the instrument.
Status 2023: Procurement of a new ozone standard is foreseen in 2023.

Data Acquisition. The data acquisition systems remained unchanged since the last WCC-Empa audit in 2015. The CRDS instruments acquire the data using the integrated Python based data acquisition system. Data is analysed and checked on a daily, weekly and monthly basis. Ozone is acquired on a Testpoint data acquisition system using ADAM 4017 D/A modules (Keithley) logging the analogue signals of the instruments. 1-minute and 30-minute averages are stored on the data acquisition computer. No additional instrument parameters are stored. Data back-ups are made weekly, and the data evaluation is made at the office in Stellenbosch. Acquiring analogue signals increases the overall uncertainty, and a change to an alternative solution using the digital output of the instruments is strongly recommended.

Recommendation 8 (, important, 2022)**
It is strongly recommended to replace the analogue data acquisition system by a solution that acquires the digital signal of the instrument, which allows also the storage of ancillary instrument parameter.

Recommendation 9 (, important, 2022)**
It was noted that the time of the ozone data acquisition was about 3 minutes ahead. The time setting needs to be checked / verified, and should be automatically synchronised with a time server.

Intercomparison (Performance Audit). The CPT analyser and calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system (TS and CPT calibrator), and the CPT data acquisition system (CPT analyser). 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 #1327059053 (BKG -1.1 nmol mol^{-1}, SPAN 1.100):

The initial comparison was made with the above calibration settings, and the data was treated according to the usual procedure of CPT, which involved correction of the raw data based on calibrations with the station ozone calibrator. Due to the fact that the calibrator was not in a good working condition, which has not been realised by the station staff, the correction was wrong, and a large deviation between CPT and WCC-Empa was observed.

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.67 nmol mol^{-1}) / 1.2247 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.09e-05 * $X_{O3}{}^2$) (1b)

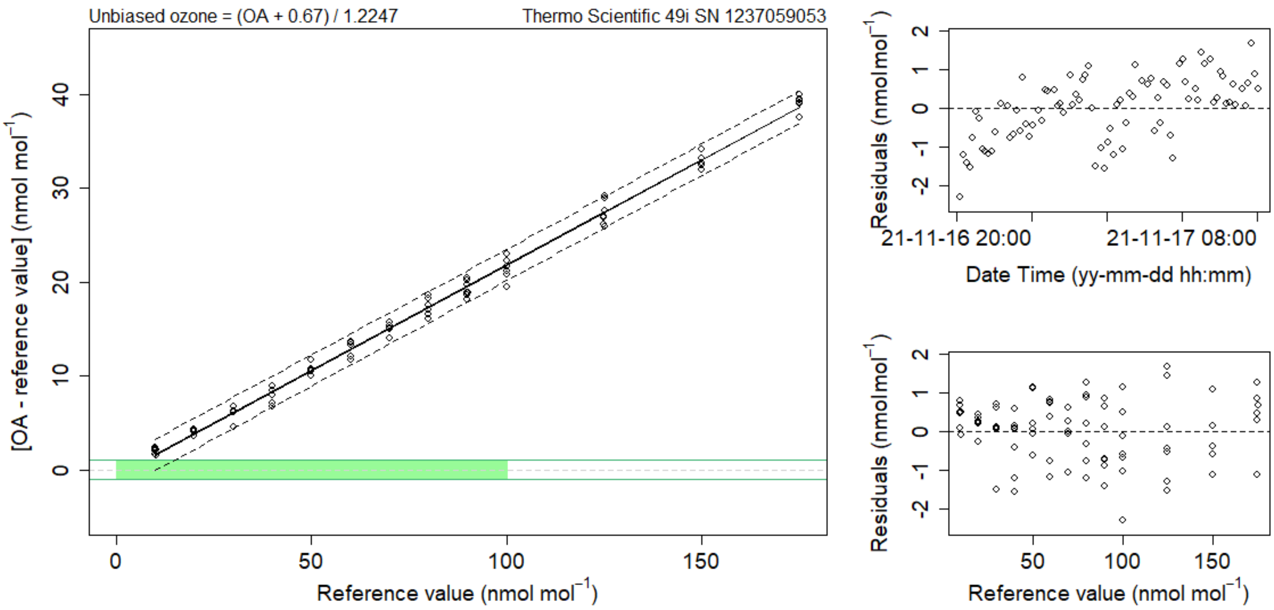

Figure 1. *Left: Bias of the CPT ozone analyser (Thermo Scientific 49i #1327059053, BKG -1.1 nmol mol^{-1}, COEF 1.100, corrected by CPT staff based on comparisons with the CPT ozone reference) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute 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 result of the initial comparisons can be summarised as follows:

A large bias was observed due to a correction of the data which based on invalid calibration data of the CPT ozone reference. To avoid this in future, the following recommendations are made:

Recommendation 10 (*, critical, 2023)**
All data that were calibrated using invalid data of the ozone calibrator need to be re-evaluated based on the last valid calibrations. In case these data have been submitted or were used otherwise, the corresponding data repositories and data users need to be informed, and the data series need to be withdrawn.
Status 2023: This process has been imitated immediately after the audit.

Recommendation 11 (*, critical, ongoing)**
The agreement between the station analyser and the calibrator should usually be within a few nmol mol^{-1}. If deviations larger than 3 nmol mol^{-1} are observed, the whole system needs to be carefully checked for potential failures, and the comparison should be repeated.

Recommendation 12 (, important, ongoing)**
Before starting a comparison, the calibrator should be used to condition the station analyser at an ozone amount fraction of 500 nmol mol^{-1}. During the conditioning, an A/B ozone check (see instrument manual) needs to be made for both the calibrator and the analyser. If the check fails (deviation between A and B larger than 3%), the reason must be identified, and the affected instrument can no longer be used until the issue is fixed.

The CPT station analyser was then calibrated using the WCC-Empa transfer standard, and the calibration settings were changed in a way that only minor post-corrections are needed. It is recommended to proceed with these settings, and no further change of the calibration settings should be made. The results with the new settings, without applying any further correction, were as follows:

Thermo Scientific 49i #1327059053 (BKG +0.6 nmol mol^{-1}, SPAN 1.054):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.00 nmol mol^{-1}) / 1.0077 (1c)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.06e-05 * X_{O3}^2) (1d)

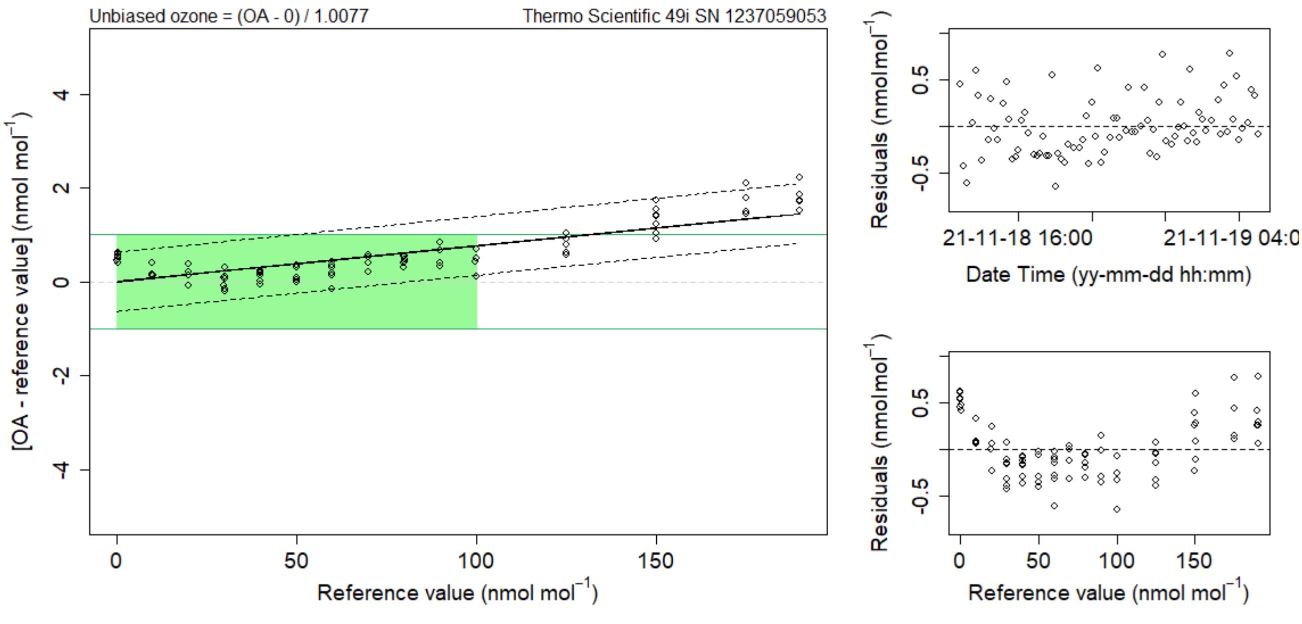

Figure 2. *Left: Bias of the CPT ozone analyser (Thermo Scientific 49i #1327059053, BKG +0.6 nmol mol^{-1}, COEF 1.054, no further data treatment) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area 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 result of the second comparisons can be summarised as follows:

Agreement within the WMO/GAW DQOs was found after the adjustment of the calibration settings. However, the setting of the span coefficient is relatively high, and the instrument showed also a small non-linearity.

Thermo Scientific 49i-PS # 708821231 (BKG -0.1 nmol mol^{-1}, SPAN 1.019):

The CPT ozone calibrator was found to be not in a working condition due to a broken pump diaphragm, and internal leaks in the solenoid valves. The results shown below confirm the malfunction of the instrument.

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] – 2.33 nmol mol^{-1}) / 0.0998 (1e)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.06e-05 * X_{O3}^2) (1f)

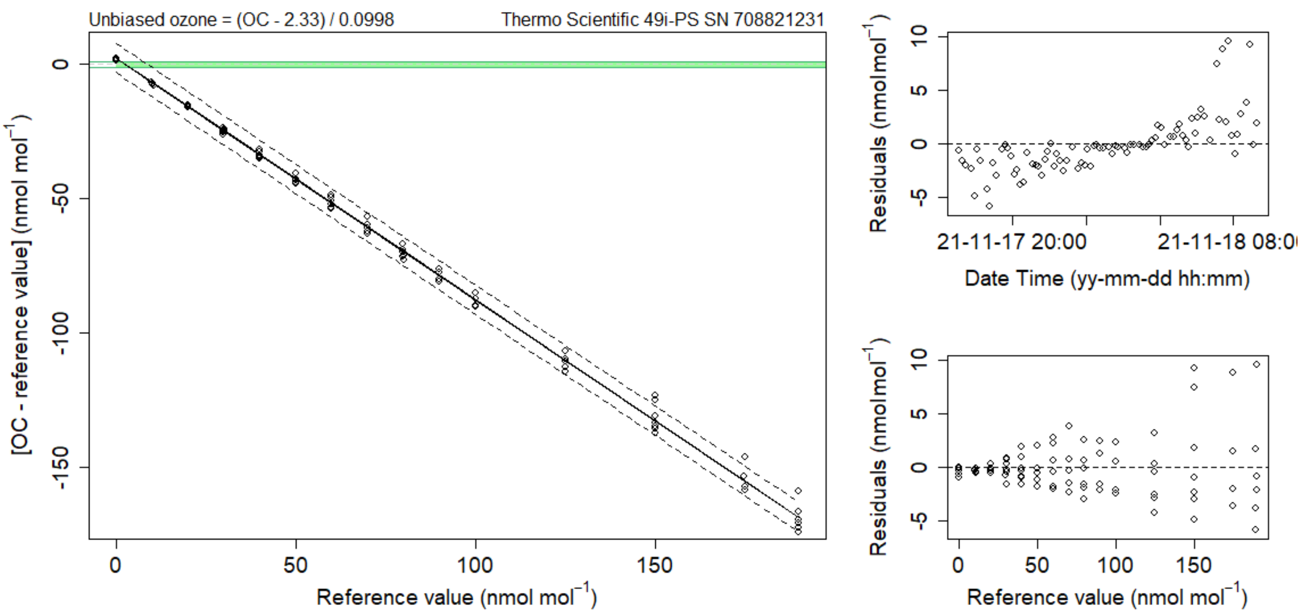

Figure 3. *Left: Bias of the CPT ozone calibrator (Thermo Scientific 49i-PS #708821231, BKG -0.1 nmol mol^{-1}, COEF 1.019, no further data treatment) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green 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).*

Due to the malfunction of the instrument, it was decided to ship the calibrator to WCC-Empa after the audit for repair and re-certification. The instrument arrived at Empa in March 2023, and a direct calibration against WCC-Empa's ozone reference (SRP#15) was made at Empa. The results were as follows:

Thermo Scientific 49i-PS # 708821231 (BKG -0.1 nmol mol^{-1}, SPAN 1.019) comparison against SRP#15 at WCC-Empa:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.07 nmol mol^{-1}) / 1.0074 (1g)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.04e-05 * X_{O3}^2) (1h)

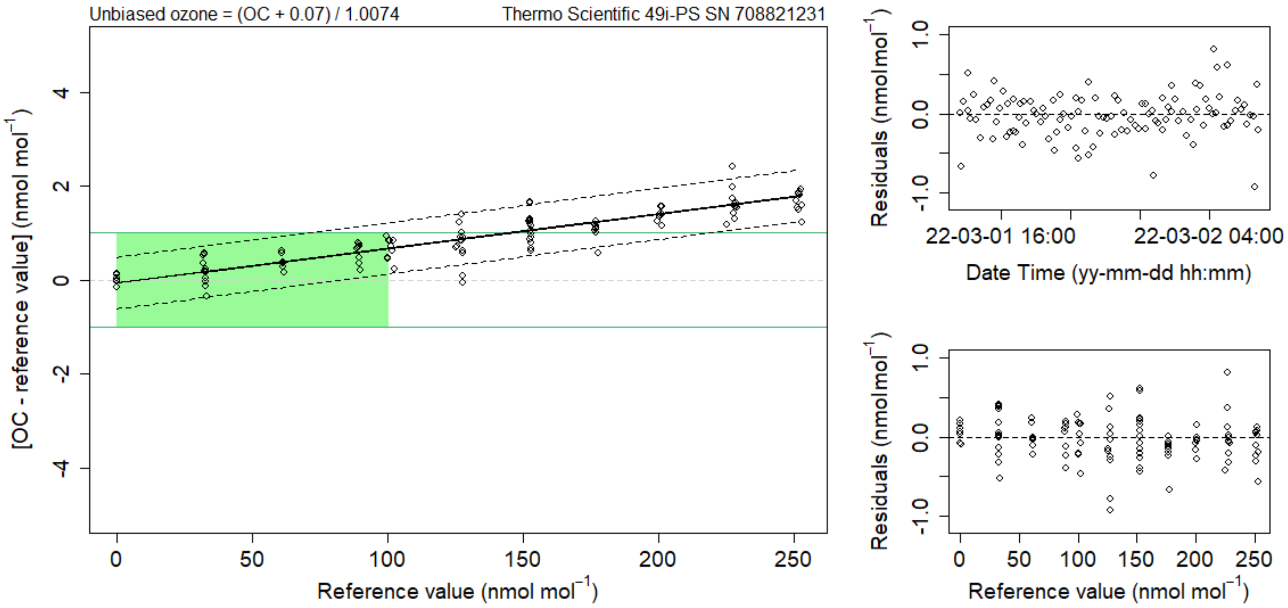

Figure 4. *Same as above, after repair at WCC-Empa.*

For the CPT calibrator, the result of the comparisons can be summarised as follows:

The calibrator was not in a working condition and reading significantly low when it was compared at CPT to the WCC-Empa reference instrument. The malfunction (leaking solenoid valves, worn pump diaphragm) was not detected by the CPT station staff. Such a malfunction can easily be identified if basic QA/QC checks are made (see recommendation 12).

The instrument was shipped to WCC-Empa, repaired, and compared against SRP#15 after the CPT audit. The results of this comparison are in good agreement with previous comparisons against the WCC-Empa reference of this instrument.

Carbon Monoxide Measurements

Continuous measurements of CO at CPT started in 1987 using gas chromatographic (GC) systems, and Cavity Ringdown Spectroscopy (CRDS) measurements started in 2012. The CPT CO time series is amongst the longest worldwide.

Instrumentation. The following instruments are currently available:
Picarro G2302 and G2401 (CRDS) with a cold trap to dry the air. The Picarro G2302 instrument was only available during the first round of TS comparison, and failed afterwards and was sent for repair.

Standards. A set of five NOAA laboratory standards is available at CPT. In addition, four working standards to track any system changes and one target tank (for quality assurance and quality control; filled with ambient CPT air) is available. An overview of available NOAA standards is shown in Table 8 in the Appendix.

Calibrations using the NOAA laboratory standards are made on a quarterly basis. A linear function is obtained and applied to the monthly 1-min data file; at the end of the year a smoothed fit through the 4 linear functions is obtained and the annual data is recalculated accordingly, before submission to the WDCGG.

The working standards are measured every 25 days to track any system changes, and the target tank is measured daily.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. Two batches of TS were analysed: one before the audit in February/March 2021, and the other during the on-site audit in November 2021.

The following equations characterise the instrument bias. The result is further illustrated in Figures 5 and 6 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #3498-CFKADS2350:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 2.55 nmol mol^{-1}) / 0.9631 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.8 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2b)

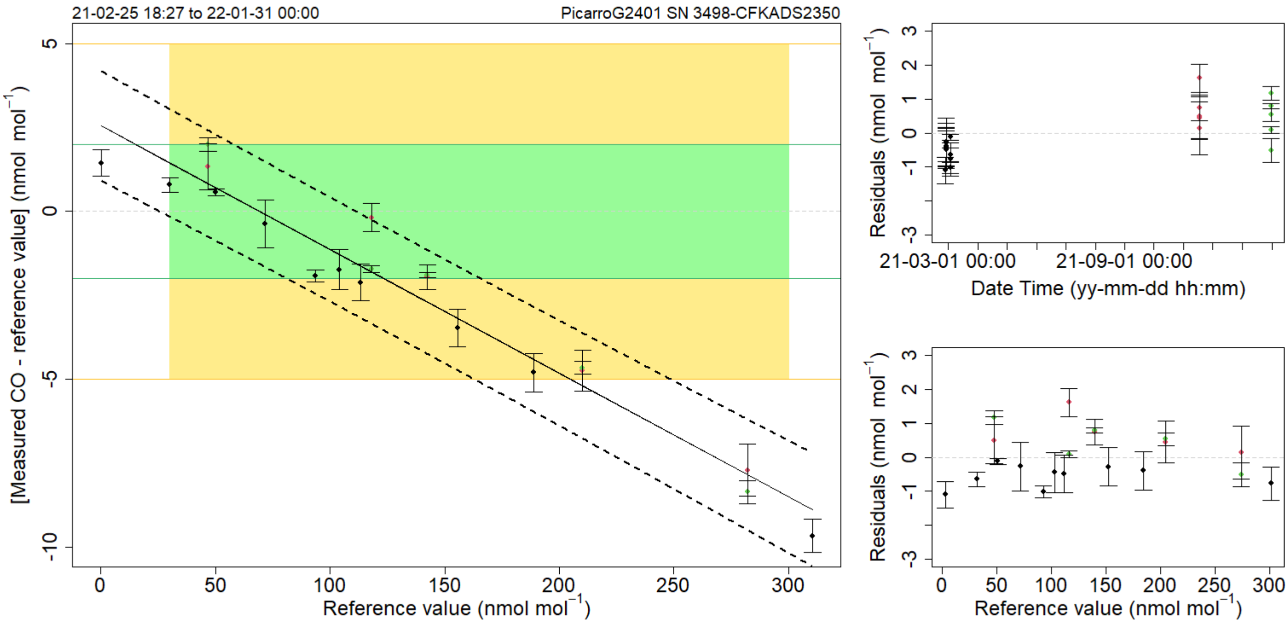

Figure 5. *Left: Bias of the CPT Picarro G2401 #3498-CFKADS2350 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point (black: TS 1st batch, purple: TS 2nd batch, green: TS 2nd batch, measured in January 2022) represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2302 #835-CKADS2026:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 9.05 nmol mol^{-1}) / 0.9060 (2c)

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

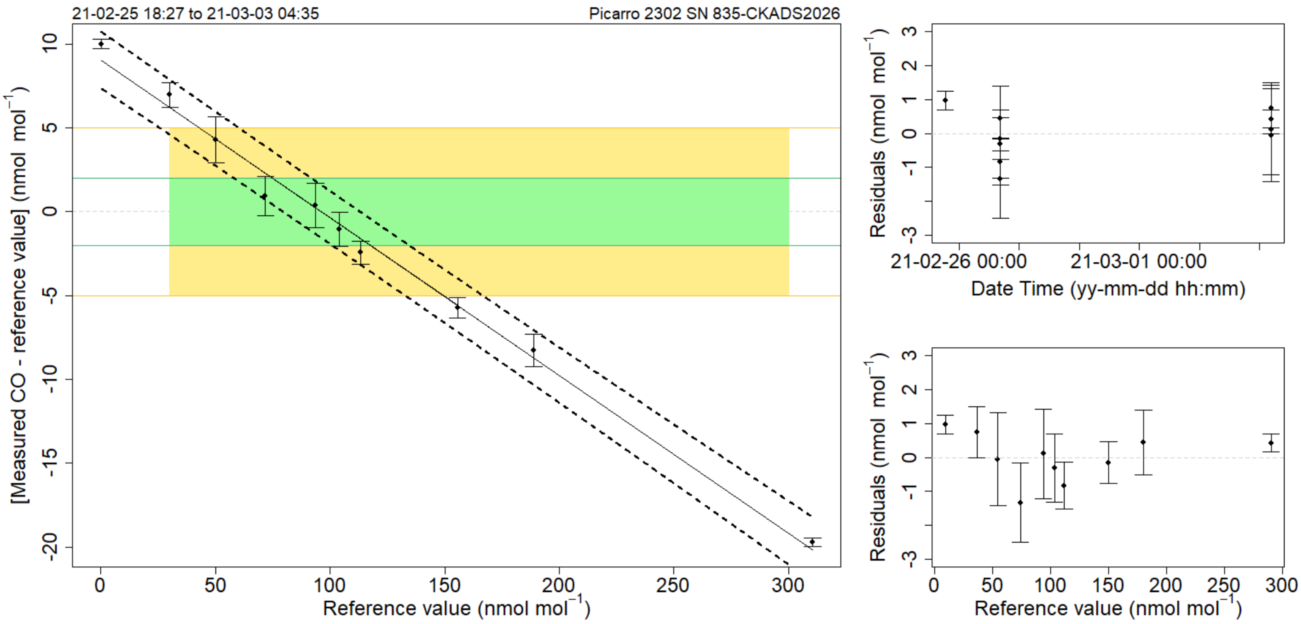

Figure 6. *Same as above, for the Picarro G2302 #835-CKADS2026 instrument. Only standards from the 1st batch could be measured due to instrument failure afterwards.*

The results of the comparisons can be summarised as follows:

A significant dependency of the bias on the CO amount fraction was observed for both instruments; it was less pronounced for the Picarro G2401 instrument, which serves as the main CO analyser. For this instrument, the bias was exceeding the extended WMO/GAW compatibility goal for amount fractions above 200 nmol mol^{-1}. The bias may to a large part be explainable with the uncertainty and the stability of the CO standards. Drift of CO in reference gases at low amount fractions remains a significant challenge, and therefore, the following recommendation is made:

Recommendation 13 (*, minor, 2023)
The CRDS measurement technique shows a linear response for CO in the amount fraction range from at least 0 to 1000 nmol mol^{-1}. To minimise the influence of standard drift, WCC-Empa recommends that the calibration strategy focuses on higher CO mole fractions (300 to 1000 nmol mol^{-1}), and also includes CO free air (or N_2 6.0) to compensate for a zero offset.

Methane Measurements

Continuous measurements of CH_4 at CPT started in 1983 using GC / flame ionization detection (FID). Since 2012 CH_4 measurements are made using CRDS technique, and the GC/FID system is no longer in operation. The CPT methane time series is one of the longest data sets of the Southern Hemisphere.

Instrumentation. The following instruments are currently available:
Picarro G2401 and Picarro G2301 (CRDS), both using a cold trap for the drying of the air.

Standards. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT instruments with randomised methane levels using WCC-Empa travelling standards. Two batches of TS were analysed: one before the audit in February/March 2021, and the other during the on-site audit in November 2021.

The following equations characterise the instrument bias. The result is further illustrated in Figures 7 and 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #3498-CFKADS2350:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 3.10 nmol mol^{-1}) / 0.9987 (3a)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.5 nmol mol^{-1} + 1.30e-07 * $X_{CH4}{}^2$) (3b)

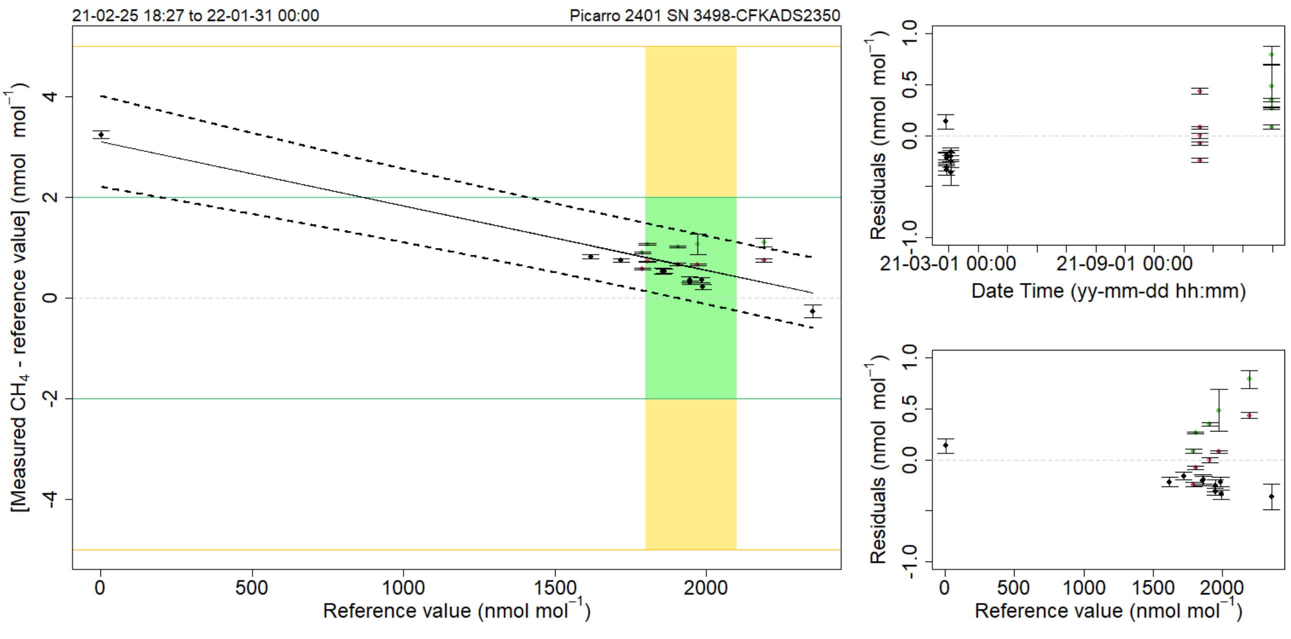

Figure 7. *Left: Bias of the Picarro G2401 #3498-CFKADS2350 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point (black: TS 1st batch, purple: TS 2nd batch, green: TS 2nd batch, measured in January 2022) represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2301 #923-CFADS2201:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 + 2.40 nmol mol^{-1}) / 1.0014 (3a)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (1.2 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (3b)

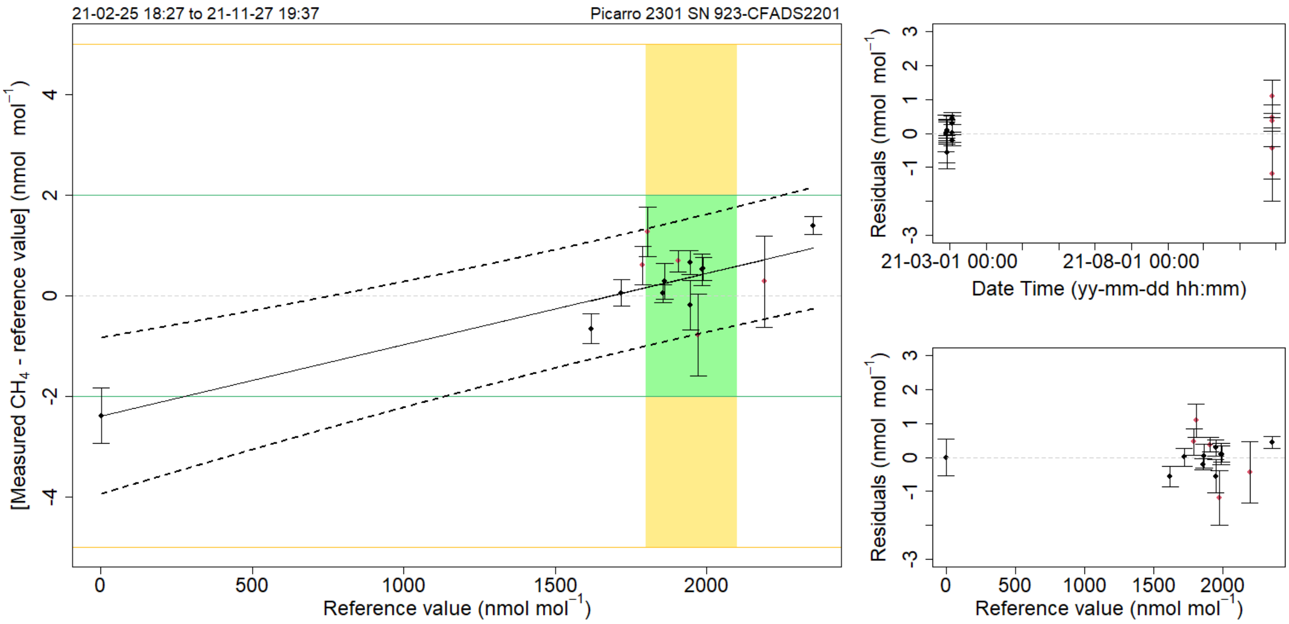

Figure 8. *Same as above, for the Picarro G2301 #923-CFADS2201.*

The result of the comparison can be summarised as follows:

Excellent agreement well with the WMO/GAW compatibility goal was found for both instruments. However, a slight dependence of the bias on the amount fraction was observed for both analysers, and the results are significantly different for the methane free TS.

Recommendation 14 (*, minor, 2023)
The CRDS measurement technique shows a linear response for CH_4 in the amount fraction range from at least 0 to 5000 nmol mol^{-1}. It should be considered to include CH_4 free air (or N_2 6.0) in the calibration scheme to compensate for a zero offset.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at CPT commenced in 1993 using NDIR technique and continuous data is available since then. Since 2012 CO_2 measurements are made using CRDS technique, and the NDIR instrument was decommissioned.

Instrumentation. The following instruments are currently available:
Picarro G2401, Picarro G2301, and Picarro G2302 (CRDS), all using a cold trap for the drying of the air. The Picarro G2302 instrument was only available during the first round of TS comparison, and failed afterwards and was sent for repair.

Standards. See Carbon Monoxide Measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT instrument with randomised CO_2 levels from travelling standards. Two batches of TS were analysed: one before the audit in February/March 2021, and the other during the on-site audit in November 2021.

The following equations characterise the instrument bias. The result is further illustrated in Figures 9 and 10 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #3498-CFKADS2350:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.15 µmol mol^{-1}) / 0.99952 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.017 µmol mol^{-1} + 3.28e-8 * $X_{CO2}{}^2$) (4b)

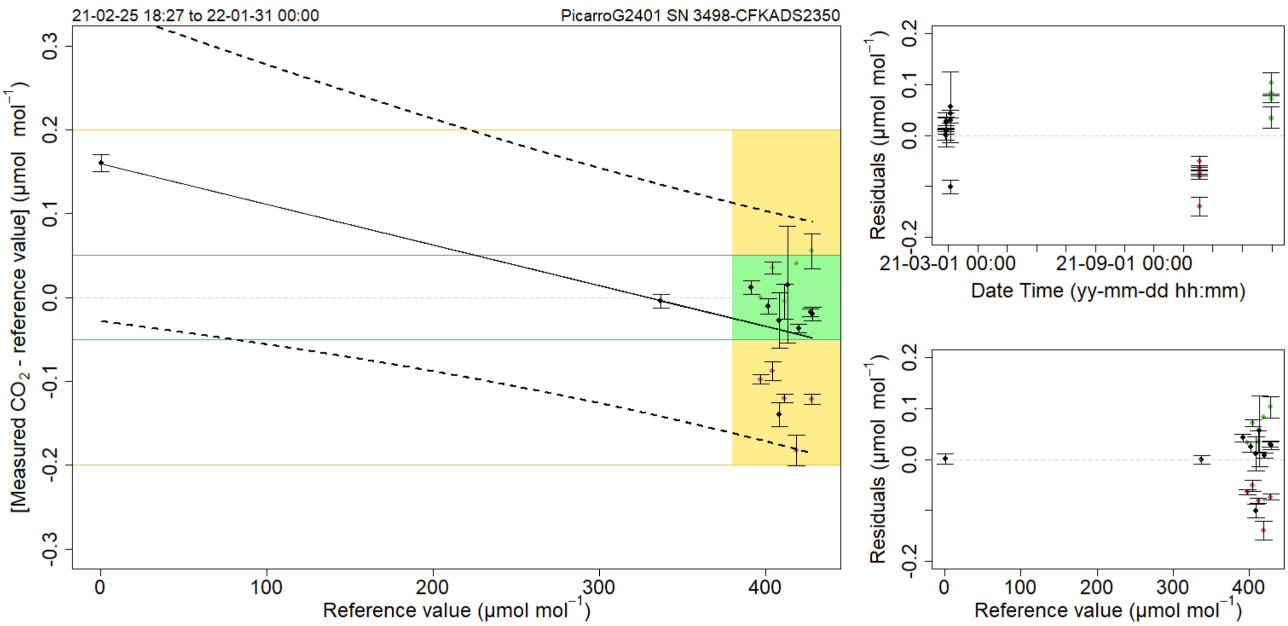

Figure 9. *Left: Bias of the Picarro G2401 #3498-CFKADS2350 CO_2 instrument with respect to the WMO-X2007 (measurements in February/March 2021) and X2019 (November 2021, January 2022) reference scale as a function of mole fraction. Each point (black: TS 1st batch, purple: TS 2nd batch, green: TS 2nd batch, measured in January 2022) represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2301 #923-CFADS2201:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 1.87 µmol mol^{-1}) / 0.99564 (4c)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.162 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4d)

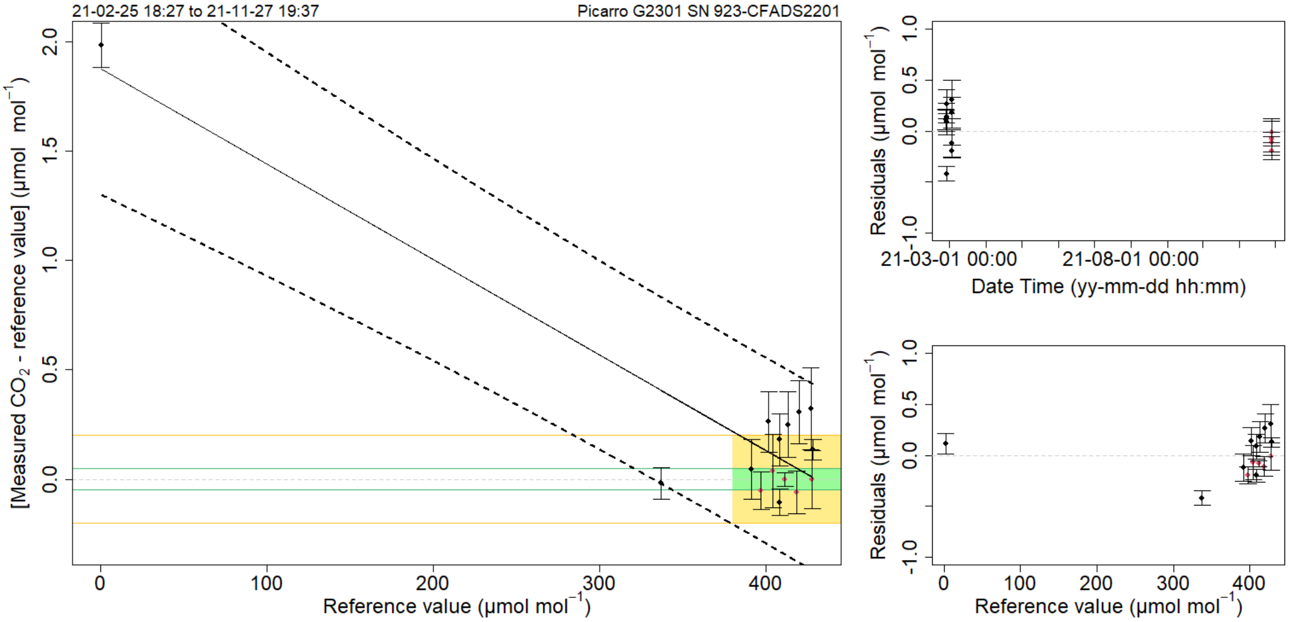

Figure 10. *Left: Bias of the Picarro G2301 #923-CFADS2201 CO_2 instrument with respect to the WMO-X2007 (measurements in February/March 2021) and X2019 (November 2021) reference scale as a function of mole fraction. Each point (black: TS 1st batch, purple: TS 2nd batch) represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2302 #835-CKADS2026:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.05 µmol mol^{-1}) / 0.99979 (4c)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.004 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4d)

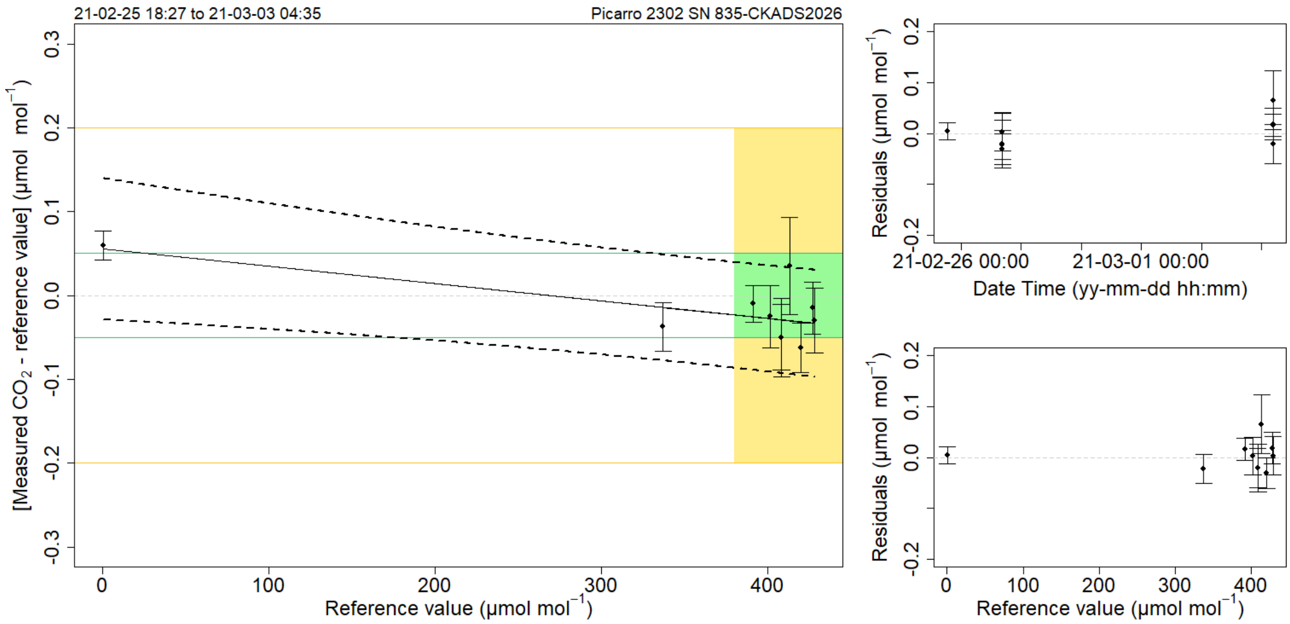

Figure 11. . *Left: Bias of the Picarro G2302 #835-CKADS2026 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for CPT. 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 Cape Point GAW CRDS instruments showed agreement within the extended WMO/GAW network compatibility goal. The best results were observed for the Picarro G2302 instrument; however, this instrument could only be assessed using the first batch of travelling standards due to later instrument failure, and it is not considered to be the main CO_2 instrument of CPT. The analysis of the TS on the main analyser (Picarro G2401) showed significantly different results for the comparisons carried out in November 2021 and January 2022. The reason could not be identified, and further assessments of the reproducibility are recommended.

CPT PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the CPT 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 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 12 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, CO, CH_4, and CO_2. 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 CPT audit are shown as coloured dots in Figure 12, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

The results were within the DQOs for O_3, CH_4, CO_2 (Picarro G2401 and G2302), and the WMO/GAW network compatibility goals were not met for CO and CO_2 (Picarro G2301).

Table 1. *CPT performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5th and 6th columns show the percentage of all WCC-Empa audits until November 2021 within these criteria since 1996 (O_3), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound / Instrument	Range	Unit	CPT within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]
O_3 (Thermo 49i #1327059053 (BKG -1.1, SPAN 1.100)	0 -100	nmol mol^{-1}	✗	65	NA
O_3 (Thermo 49i #1327059053 (BKG +0.6, SPAN 1.054)	0 -100	nmol mol^{-1}	✓	65	NA
O_3 (Thermo 49i-PS #708821231 (before repair)	0 -100	nmol mol^{-1}	✗	65	NA
O_3 (Thermo 49i-PS #708821231 (after repair)	0 -100	nmol mol^{-1}	✓	65	NA
CO (Picarro G2401 #3498-CFKADS2350)	30 - 300	nmol mol^{-1}	✗	19	50
CO (Picarro G2302 #835-CKADS2026)	30 - 300	nmol mol^{-1}	✗	19	50
CH_4 (Picarro G2401 #3498-CFKADS2350)	1750 - 2100	nmol mol^{-1}	✓	74	94
CH_4 (Picarro G2301 #923-CFADS2201)	1750 - 2100	nmol mol^{-1}	✓	74	94
CO_2 (Picarro G2401 #3498-CFKADS2350)	380 - 450	µmol mol^{-1}	✓*	45	71
CO_2 (Picarro G2302 #835-CKADS2026)	380 - 450	µmol mol^{-1}	✓*	45	71
CO_2 (Picarro G2301 #923-CFADS2201)	380 - 450	µmol mol^{-1}	✗	45	71

[1] Percentage of stations within the eDQO and DQO
* Refers to Northern Hemisphere DQOs

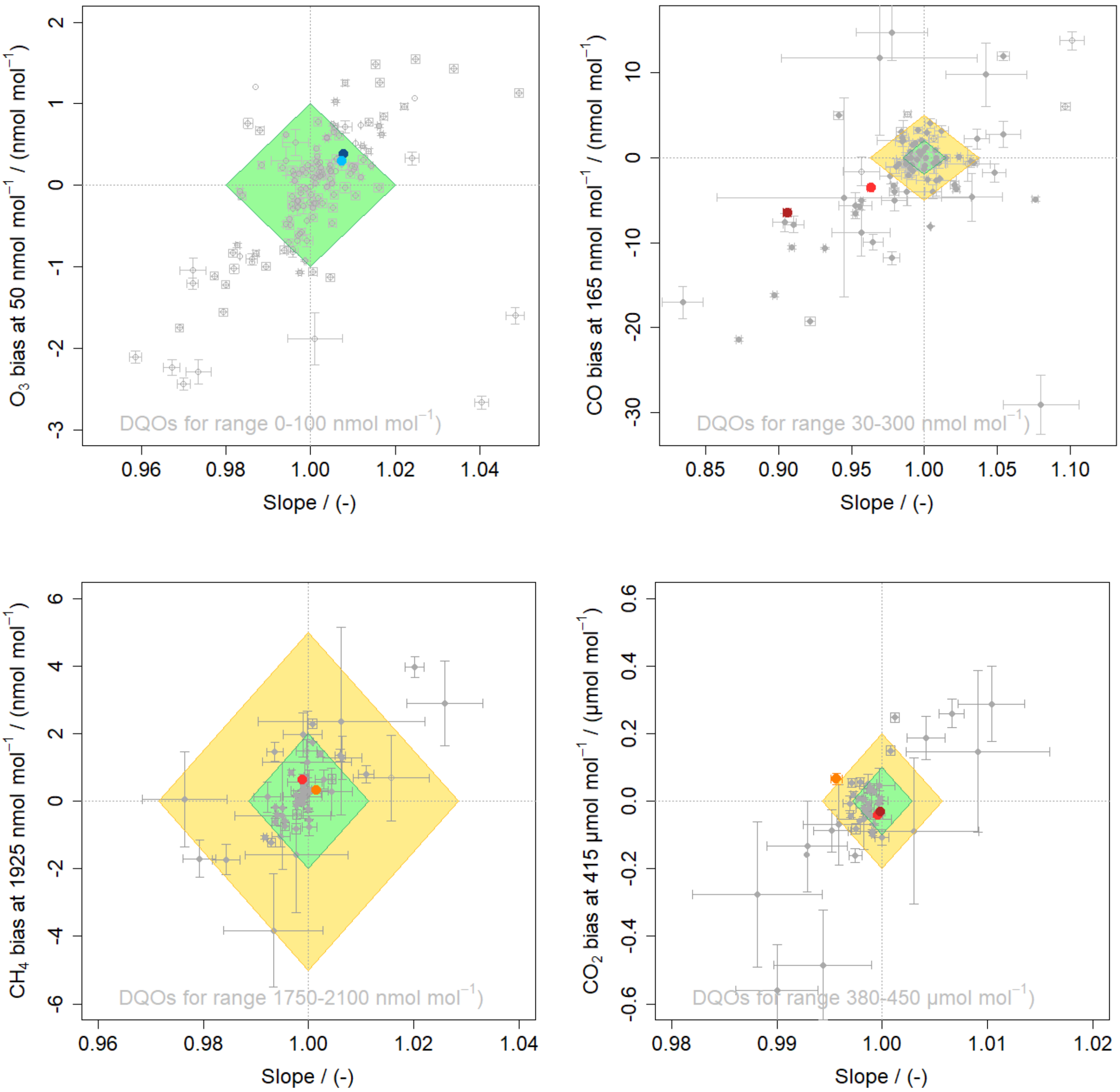

Figure 12. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show CPT results (dark blue: Thermo Scientific 49i, light blue: Thermo Scientific 49i-PS, dark red: Picarro G2302, orange: Picarro G2301, red: Picarro G2401). Filled symbols refer to a comparison with the same calibration scale at the station and the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow). The ozone comparisons refer to the calibrated / repaired instruments. Initial comparisons were outside the WMO/GAW DQOs.*

PARALLEL MEASUREMENTS OF AMBIENT AIR

The audit included parallel measurements of CO_2, CH_4 and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401). The TI was installed at CPT during the audit, and was running from 19 November 2021 through 22 May 2022. The TI was connected to a separate independent inlet line sampling from the same location on the tower as the CPT analysers. The TI was sampling air using the following sequence: 1440 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 with the CPT Picarro G2401 are presented below. The CPT data shown here was processed by CPT staff.

Carbon monoxide comparison

Figure 13 shows the comparison of hourly CO measurements between the WCC-Empa TI and the CPT analyser. The corresponding deviation histograms is shown in Figure 14.

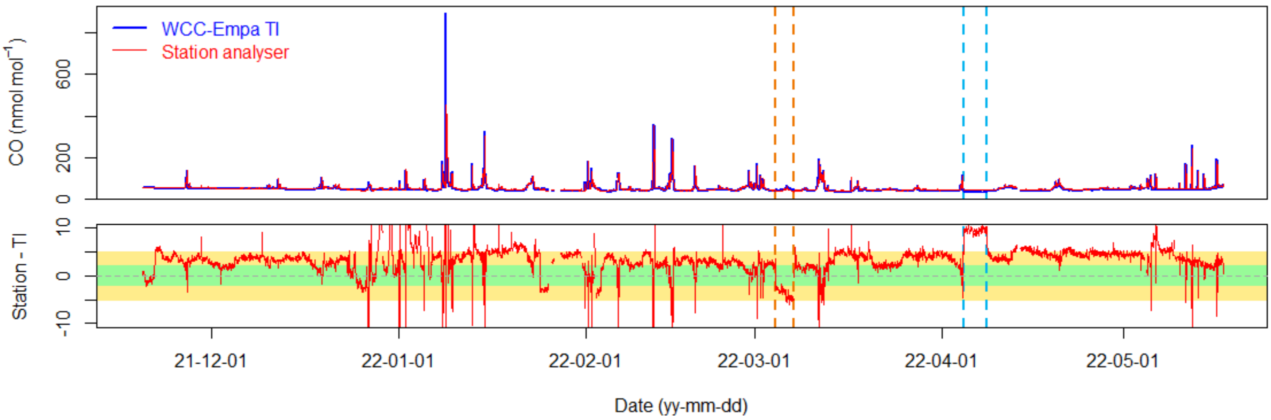

Figure 13. *Comparison of the Picarro G2401#3498-CFKADS2350 with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals. The dashed vertical lines indicate periods when the dryer was bypassed (orange: station analyser, light blue: WCC TI).*

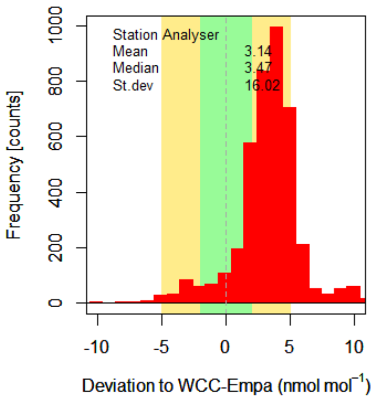

Figure 14. *CO deviation histograms for the Picarro G2401#3498-CFKADS2350.*

The bias between the CPT and the WCC-Empa measurements was highly variable, and certain periods showed a significantly higher variability of the bias. Most likely, this was caused by leakages in the CPT drying system; similar patterns were also observed for the CO_2 comparisons, which are shown further below. During two short periods, the dryers of the CPT and the TI were bypassed. This resulted also in a change of the bias due to inappropriate internal water vapour correction of the CRDS system. It is not recommended to run CO CRDS measurements without a drying system (Zellweger et al., 2019). In conclusion, the following recommendation can be made:

Recommendation 15 (*, critical, 2023)**
To avoid leakages, it is recommended to replace the cryogenic drying system by a Nafion dryer operated in reflux mode using the CRDS pump for the vacuum in the purge air.
Status 2023: Nafion dryers were ordered and will replace the cryogenic drying system in 2023.

Methane

Figure 15 shows the comparison of hourly CH_4 between the WCC-Empa TI and the CPT CRDS instrument. The corresponding deviation histogram is shown in Figure 16. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers and the WCC-Empa TI. On average, agreement within the WMO/GAW network compatibility goals was found between the TI and the CPT instrument. However, periods with larger deviations and variability were observed, which most likely are also due to temporary leakages of the CPT drying system.

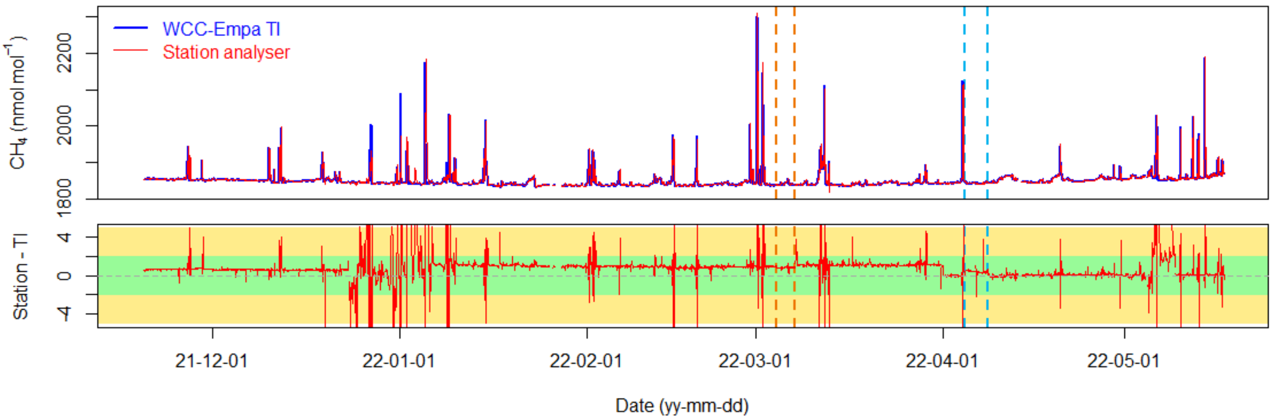

Figure 15. *Comparison of the Picarro G2401#3498-CFKADS2350 with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals. The dashed vertical lines indicate periods when the dryer was bypassed (orange: station analyser, light blue: WCC TI).*

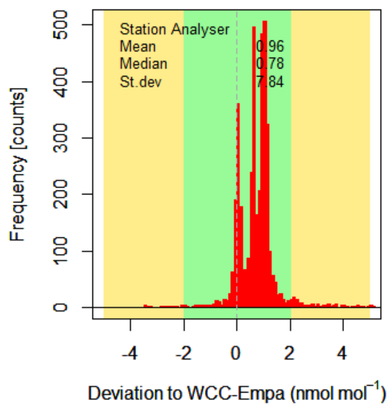

Figure 16. CH_4 deviation histograms for the Picarro G2401#3498-CFKADS2350.

Carbon dioxide

Figure 17 shows the comparison of hourly CO_2 between the WCC-Empa TI and the CPT CRDS instrument. The corresponding deviation histograms is shown in Figure 16. Hourly averages were calculated based on 1 min data with concurrent data availability of the station analysers and the WCC-Empa TI. The median bias was within the WMO/GAW compatibility goal of 0.05 µmol mol^{-1}. However, the potential leakage of the CPT drying system affected the CO_2 measurements more than CO and CH_4, due to higher indoor air CO_2 levels. Furthermore, the bias showed a distinct diurnal cycle, which also might be the result of leakage in the inlet system. It is strongly recommended to replace the current drying system by a Nafion dryer.

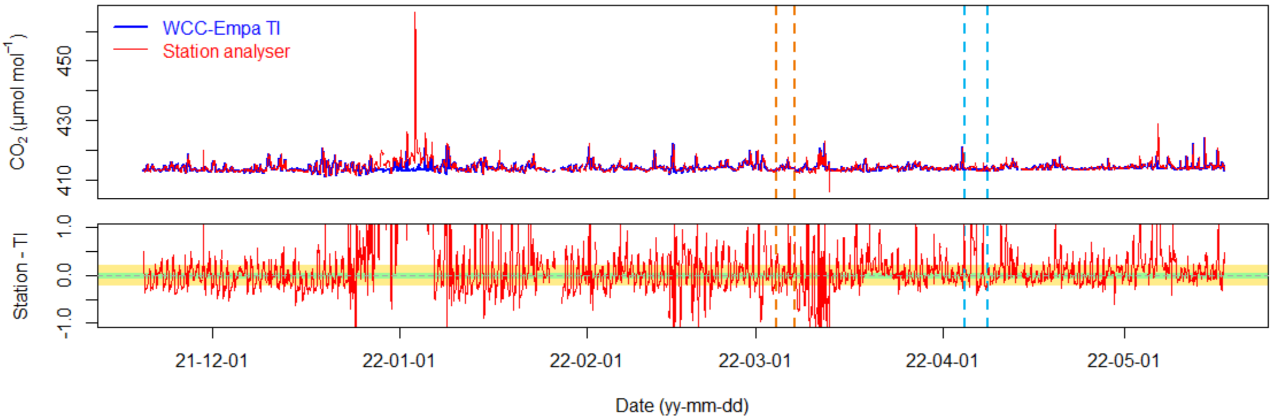

***Figure 17.** Comparison of the Picarro G2401#3498-CFKADS2350 with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals. The dashed vertical lines indicate periods when the dryer was bypassed (orange: station analyser, light blue: WCC TI).*

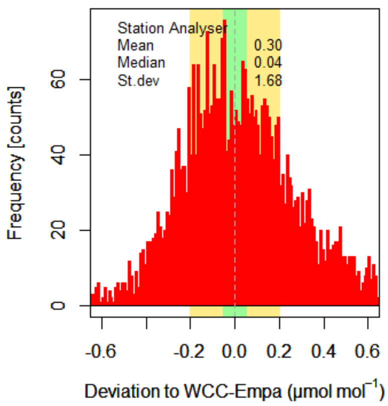

***Figure 18.** CO_2 deviation histograms for the Picarro G2401#3498-CFKADS2350.*

CONCLUSIONS

The global GAW station Cape Point offers extensive laboratory space, and hosts a large number of long-term observations in all WMO/GAW focal areas as well as research projects. Furthermore, the location of CPT enables studies on remote southern hemispheric air masses as well as emissions from nearby Cape Town and surrounding areas, makes it a very significant contribution to the GAW programme.

The assessed greenhouse gas measurements were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant mole fraction range. However, the observed bias in the surface ozone and CO measurements needs further attention, and more internal quality assessments are required.

The continuation of the Cape Point measurement series is highly important for GAW, and continued investments are needed to ensure high data quality.

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 CPT, 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 (before audit)	O_3 (after audit)	CO Picarro G2401 CFKADS2350	CO Picarro G2302 CKADS2026	CH_4 Picarro G2401 CFKADS2350	CH_4 Picarro G2301 CFADS2201	CO_2 Picarro G2401 CFKADS2350	CO_2 Picarro G2302 CKADS2026	CO_2 Picarro G2301 CFADS2201
Audit with TS	✗	✓	(✓)	(✓)	✓	✓	✓	✓	✓
Ambient air	NA	NA	✓	NA	✓	NA	✓	NA	NA

NA no ambient air comparisons were made

SUMMARY RANKING OF THE CAPE POINT GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(4)	Comprehensive programme, some parameters (e.g. N_2O) discontinued.
Access	(5)	Year round access.
Facilities		
Laboratory and office space	(5)	Fully adequate, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(4)	Available, temperature variations
Power supply	(3)	Frequent (short, a few seconds) power outages
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(4)	Skilled staff, ongoing training recommended
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(3)	Instruments need service, replacement recommended due to age.
CH_4/CO_2 (Picarro G2401/2301)	(5)	State of the art instrumentation
CO (Picarro G2401/2302)	(4)	Adequate system
Standards		
O_3	(3)	Available, not working during audit, replacement recommended.
CO, CO_2, CH_4	(5)	Full traceability to the GAW reference, standards from the CCL
Data Management		
Data acquisition	(3)	Adequate system (CO, CO_2, CH_4), only analogue signal (O_3)
Data processing	(4)	Skilled staff, appropriate procedures
Data submission	(5)	All data submitted, usually within one year

#0: inadequate thru 5: adequate.

Dübendorf, June 2023

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WCC-Empa

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QA/SAC Switzerland

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Head of Department

APPENDIX

Data Review

The following figures show summary plots of CPT data accessed on 27 September 2021 from WDCRG, and on 7 June 2022 from WDCGG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

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

Surface ozone:

One data set is available from WDCRG, which is shown in the figure below.

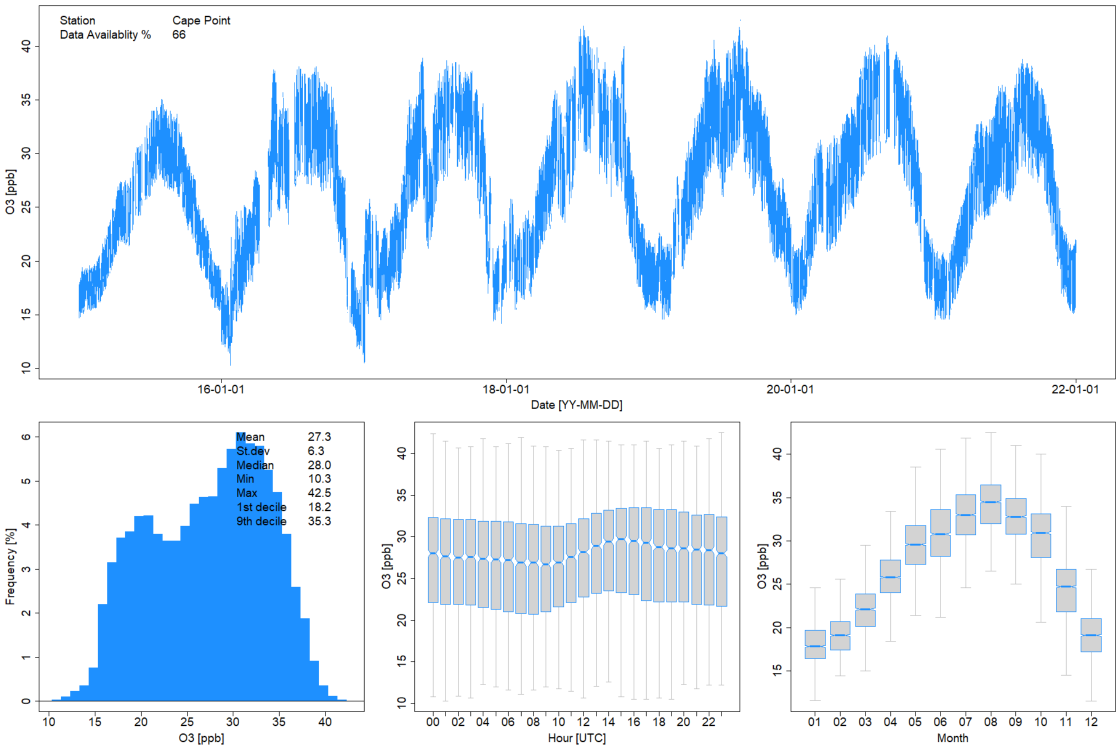

Figure 19. *O_3 data for the period from 2015 to 2021 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data look sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Ozone measurements commenced in 1983 at Cape Point. This data until 2015 is not accessible from WDCRG. It is strongly recommended to make this data available again.

Carbon monoxide:

SAWS submitted CO data as unfiltered (all valid data) and filtered (only background conditions) data sets, which are shown below.

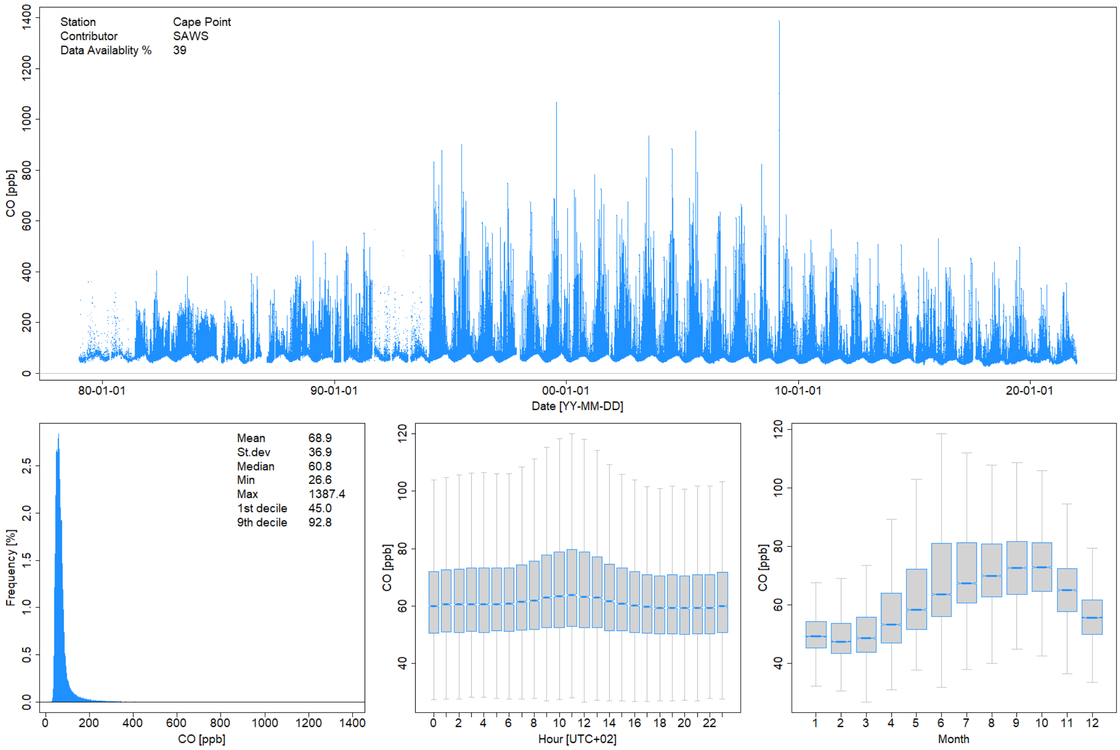

Figure 20. *Cape Point in-situ CO data (1979-2021) submitted by SAWS. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

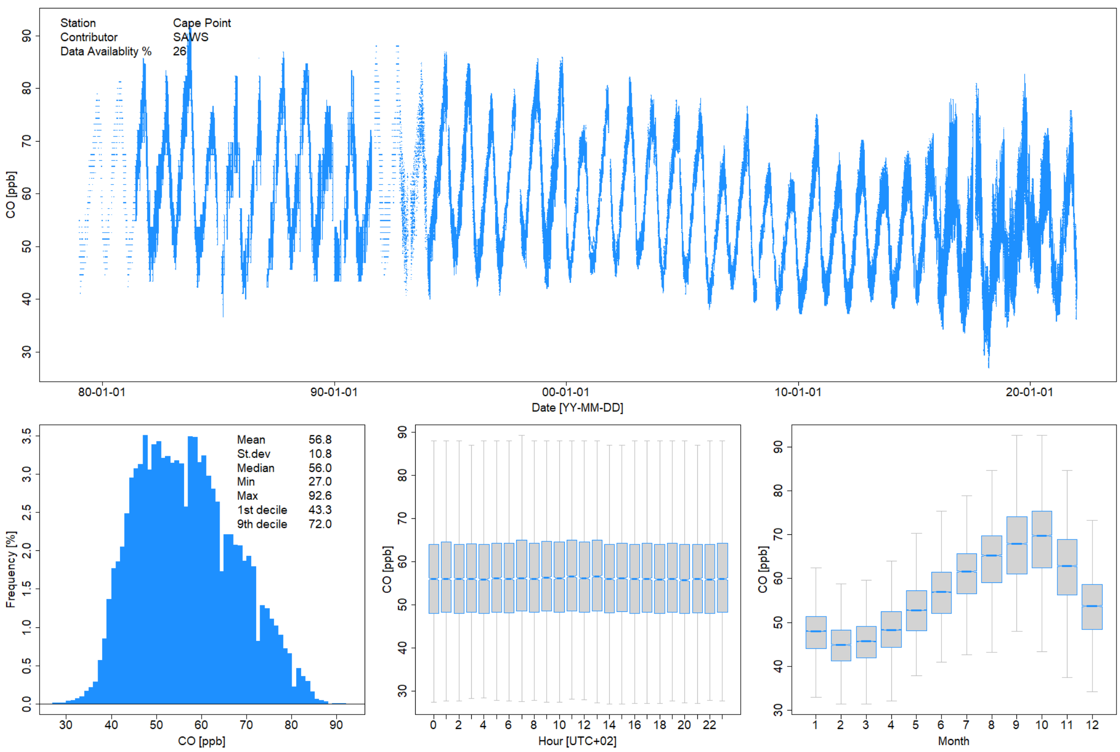

Figure 21. *Same as above, but for the filtered data set (background conditions).*

NOAA submitted flask data from 2010 to 2020, as illustrated below.

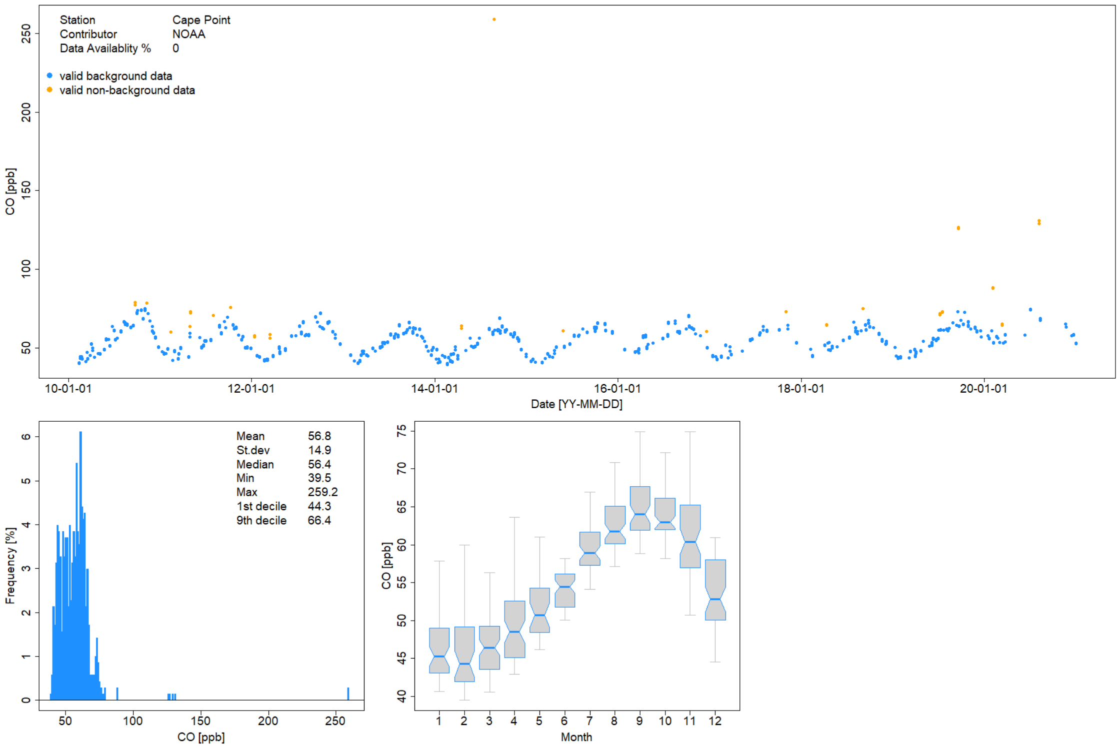

Figure 22. *NOAA CO flask data submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The SAWS and NOAA data sets look sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Only few flask data is available in 2020 due to the Covid-19 pandemic.

Methane:

SAWS submitted CH_4 data as unfiltered (all valid data) and filtered (only background conditions) data sets, which are shown below.

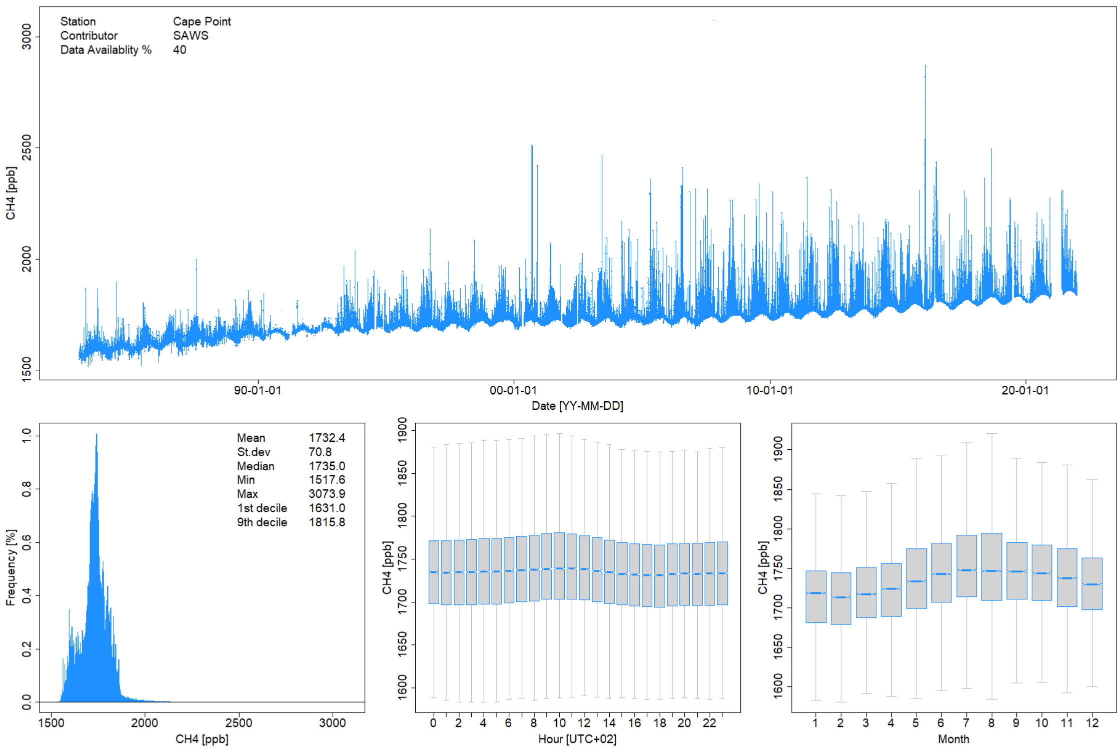

Figure 23. *Cape Point in-situ CH_4 data (1983-2021) submitted by SAWS. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

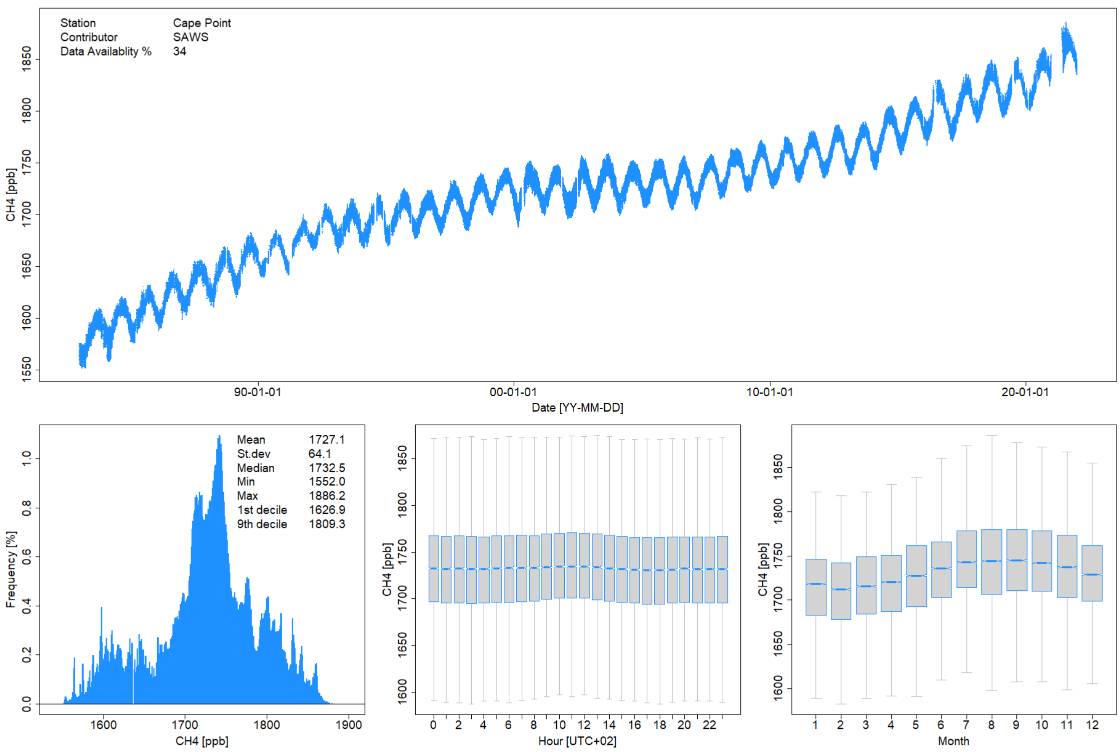

Figure 24. *Same as above, but for the filtered data set (background conditions).*

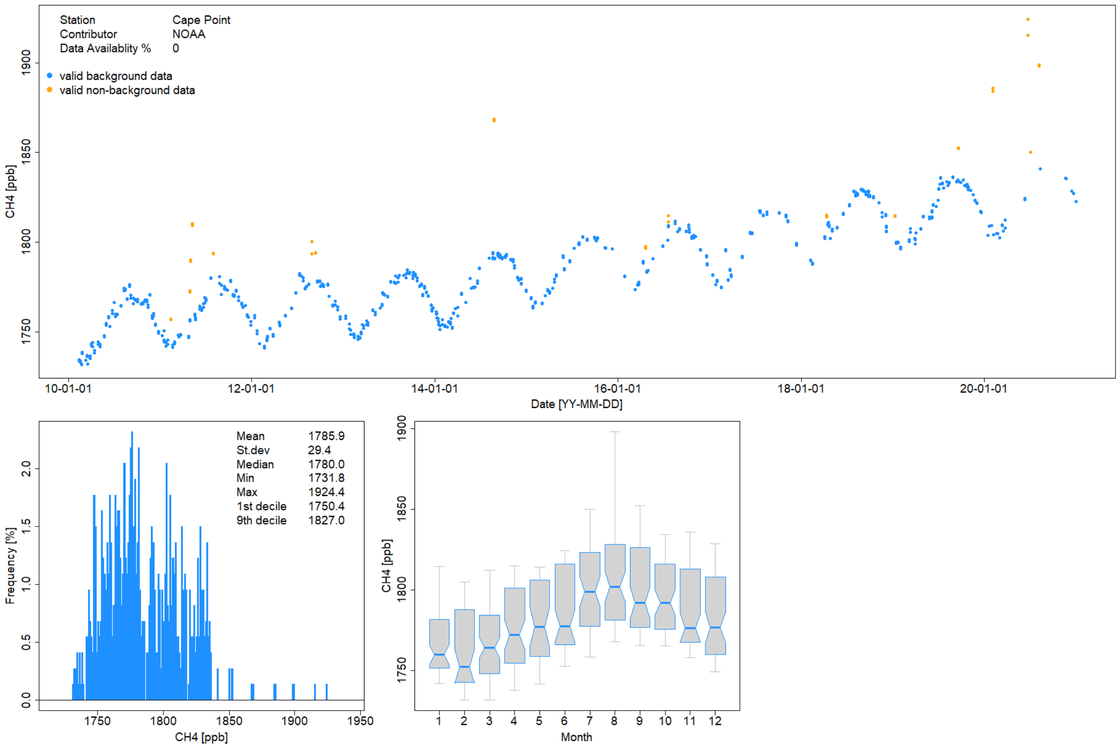

Figure 25. *NOAA flask CO data of Cape Point (2010-2020) submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The SAWS and NOAA data sets look sound with respect to mole fraction, trend, seasonal and diurnal variation. Continued comparisons of the NOAA and SAWS data series is encouraged.
- Only few flask data is available in 2020 due to the Covid-19 pandemic.
- The unfiltered SAWS data for years 1992 and 1993 look different compared to other years. Different filtering method?

Carbon dioxide:

SAWS submitted CO_2 data as unfiltered (all valid data) and filtered (only background conditions) data sets, which are shown below.

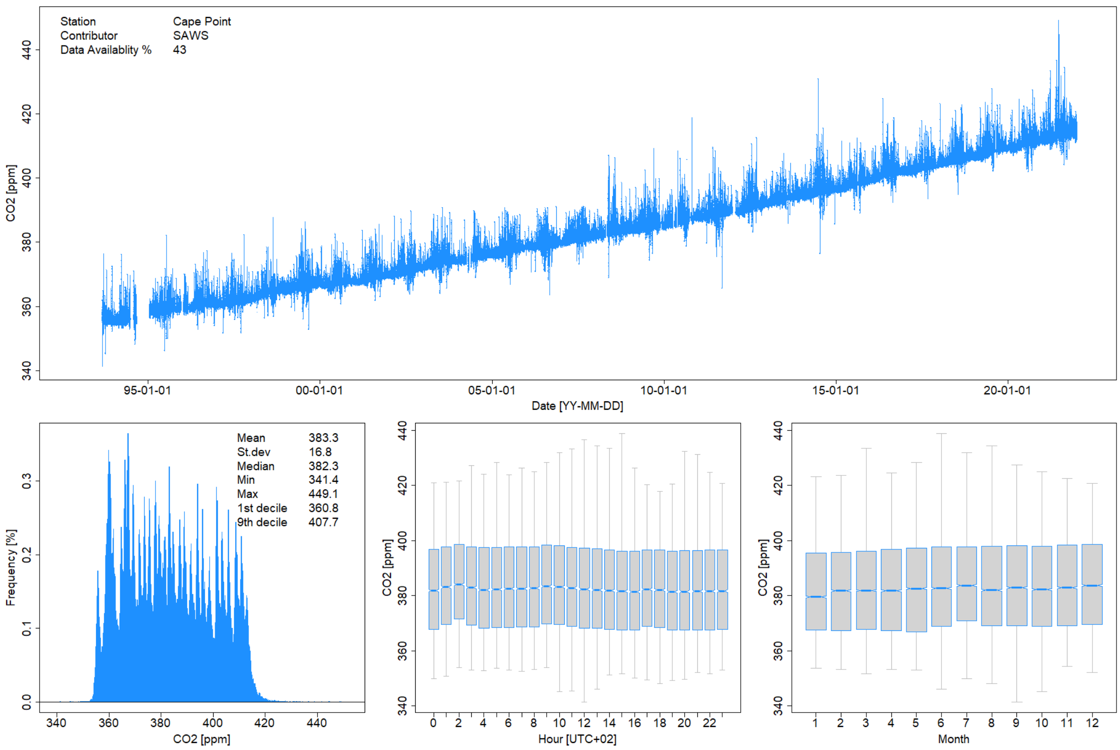

Figure 26. *Cape Point in-situ CO_2 data (1993-2021) submitted by SAWS. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

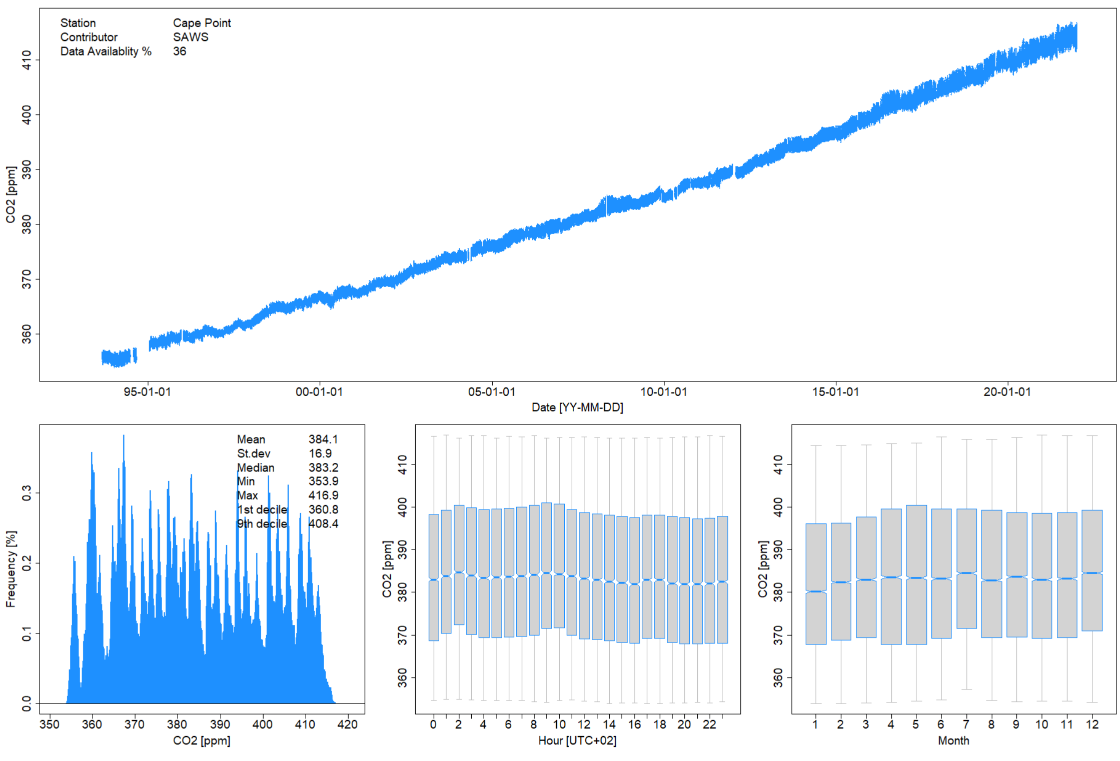

Figure 27. *Same as above, but for the filtered data set (background conditions).*

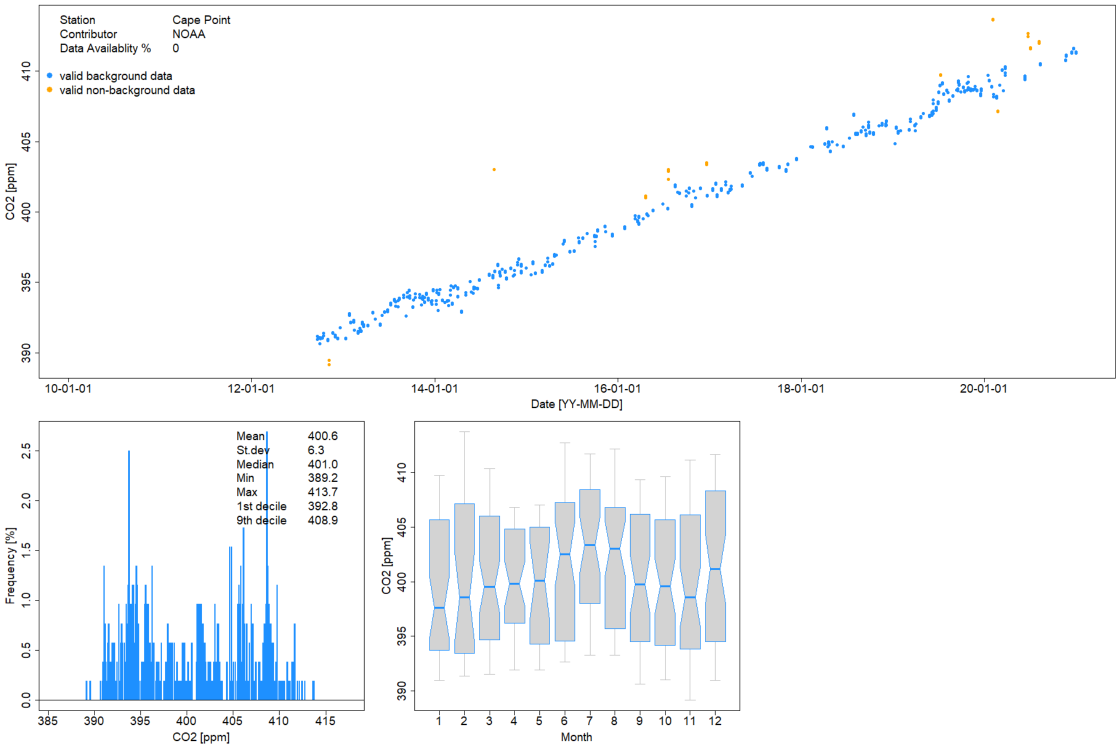

Figure 28. *Flask CO_2 data (2012-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The SAWS and NOAA data sets look sound with respect to mole fraction, trend, seasonal and diurnal variation. Continued comparisons of the NOAA and SAWS data series is encouraged.
- Only few flask data is available in 2020 due to the Covid-19 pandemic.
- It was noticed that all flask data was flagged as invalid for the years 2010 and 2011, and partly for 2012.

Nitrous oxide:

SAWS submitted CO_2 data as unfiltered (all valid data) and filtered (only background conditions) data sets, which are shown below.

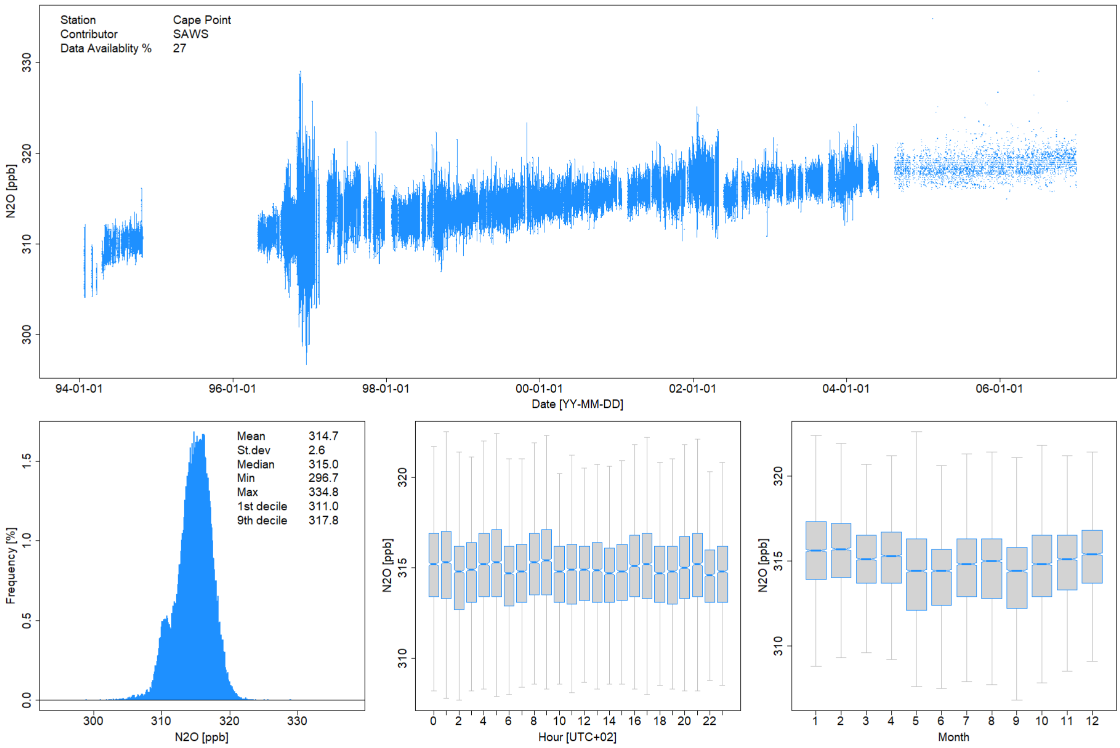

Figure 29. *Cape Point in-situ N_2O data (1994-2006) submitted by SAWS. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

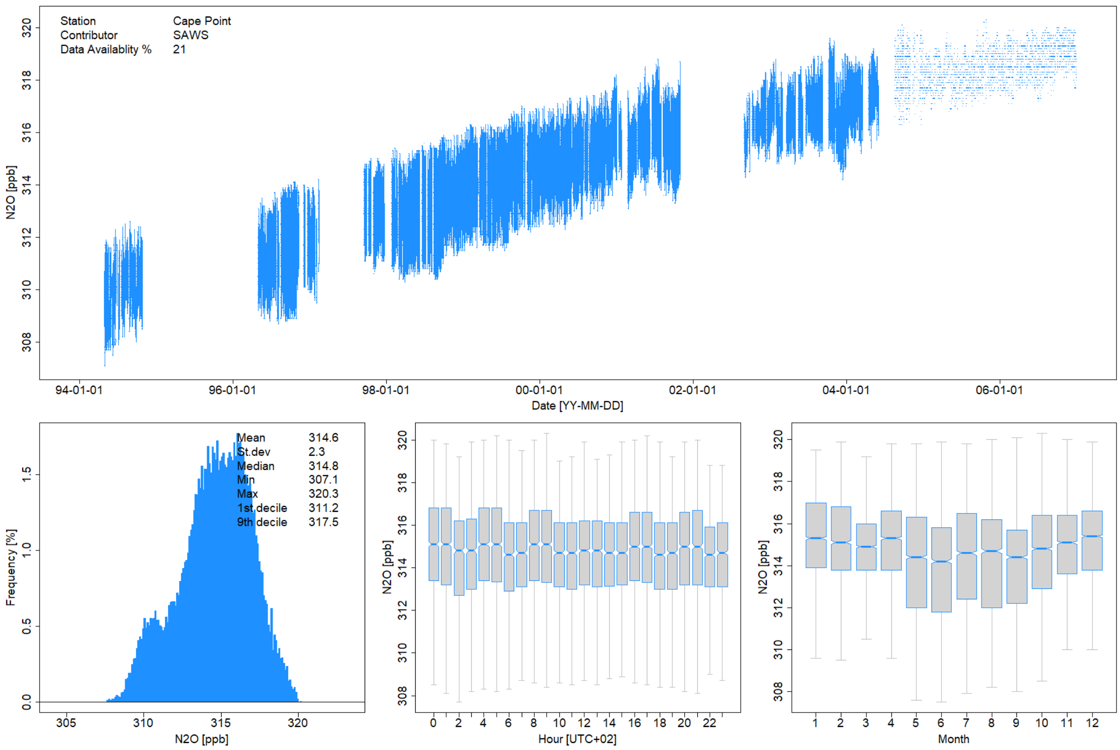

Figure 30. *Same as above, but for the filtered data set (background conditions).*

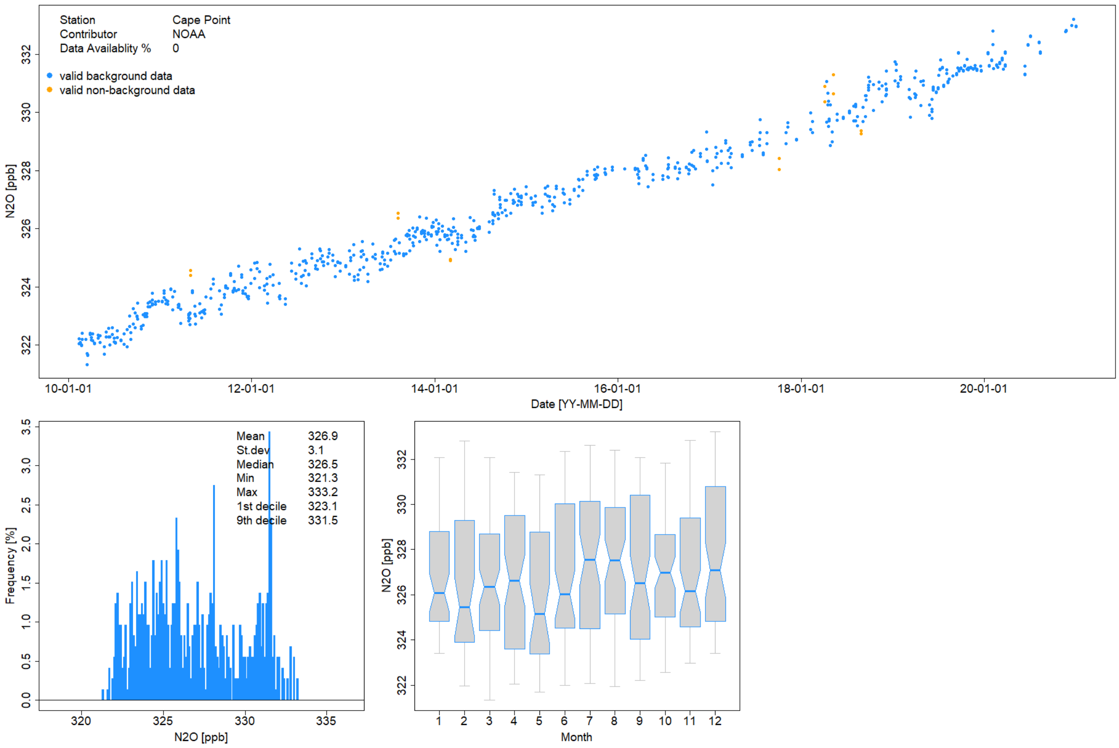

Figure 31. *Flask N_2O data (2010-2020) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The NOAA flask data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.
- SAWS data looks mostly sound; however, the uncertainty associated with the data is large, and periods with unusually high variability were observed. Most likely, these episodes are due to analytical issues.
- The sampling frequency of the SAWS measurements drastically decreased after 2005. Reason?
- In-situ N_2O measurements are discontinued.

Surface Ozone Comparisons

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

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa and CPT 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 0.0, COEF 0.991
Pressure readings (hPa)	Ambient 989.0;TS 989.0, (no adjustment was made)
CPT analyser (OA)	
Model, S/N	Thermo Scientific 49i #1327059053
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	Initial: BKG -1.1 nmol mol^{-1}, COEF 1.100 Final: BKG +0.6 nmol mol^{-1}, COEF 1.054
Pressure readings (hPa)	Ambient 983.9; OA 983.9 (no adjustment was made)
CPT calibrator (OA)	
Model, S/N	Thermo Scientific 49i #1327059053
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.1 nmol mol^{-1}, COEF 1.019
Pressure readings (hPa)	Ambient 989.0; OA 989.1 (no adjustment was made)

Results

Each ozone level was applied for 10 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment as for ambient air analysis was applied.
The results of the assessment is shown in the following Table (individual measurement points) and further presented in the Executive Summary.

Table 4. *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CPT ozone analyser (OA) Thermo Scientific 49i #1327059053 (BKG -1.1 nmol mol^{-1}, COEF 1.100) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2021-11-16 20:11	99.99	0.04	119.48	0.08	19.49	19.49
2021-11-16 20:21	39.98	0.06	47.10	0.21	7.12	17.81
2021-11-16 20:31	89.98	0.09	108.12	0.24	18.14	20.16
2021-11-16 20:41	124.99	0.03	150.88	0.13	25.89	20.71
2021-11-16 20:51	80.02	0.06	96.56	0.26	16.54	20.67
2021-11-16 21:01	10.23	0.37	11.76	0.11	1.53	14.96
2021-11-16 21:11	20.00	0.11	23.56	0.27	3.56	17.80
2021-11-16 21:21	69.98	0.01	84.00	0.31	14.02	20.03
2021-11-16 21:31	149.95	0.09	181.86	0.44	31.91	21.28
2021-11-16 21:41	60.02	0.05	71.66	0.38	11.64	19.39
2021-11-16 21:51	175.00	0.07	212.54	0.61	37.54	21.45
2021-11-16 22:01	49.97	0.03	59.92	0.61	9.95	19.91
2021-11-16 22:21	29.97	0.12	36.16	0.23	6.19	20.65
2021-11-16 22:41	30.00	0.02	36.14	0.54	6.14	20.47
2021-11-16 22:51	59.99	0.06	72.06	0.83	12.07	20.12
2021-11-16 23:01	99.98	0.07	121.10	0.89	21.12	21.12
2021-11-16 23:11	69.98	0.05	84.98	0.71	15.00	21.43
2021-11-16 23:21	150.01	0.06	182.48	0.31	32.47	21.65
2021-11-16 23:31	9.98	0.10	12.36	0.57	2.38	23.85
2021-11-16 23:41	39.97	0.08	47.88	0.15	7.91	19.79
2021-11-16 23:51	90.01	0.05	108.84	0.50	18.83	20.92
2021-11-17 00:01	124.99	0.05	151.96	0.21	26.97	21.58
2021-11-17 00:21	50.01	0.06	60.54	0.09	10.53	21.06
2021-11-17 00:31	79.97	0.07	96.96	0.11	16.99	21.25
2021-11-17 00:41	174.97	0.04	214.08	0.28	39.11	22.35
2021-11-17 00:51	20.02	0.09	24.30	0.08	4.28	21.38
2021-11-17 01:11	9.98	0.07	12.04	0.17	2.06	20.64
2021-11-17 01:21	49.94	0.06	60.56	0.41	10.62	21.27
2021-11-17 01:31	125.02	0.09	152.58	0.44	27.56	22.04
2021-11-17 01:41	100.04	0.03	121.72	0.13	21.68	21.67
2021-11-17 02:01	174.96	0.06	214.46	0.15	39.50	22.58
2021-11-17 02:11	40.00	0.04	48.40	0.28	8.40	21.00
2021-11-17 02:21	20.03	0.07	24.22	0.27	4.19	20.92
2021-11-17 02:31	80.07	0.08	97.62	0.23	17.55	21.92
2021-11-17 02:41	60.02	0.04	73.60	0.28	13.58	22.63
2021-11-17 02:51	89.95	0.05	110.36	0.32	20.41	22.69
2021-11-17 03:01	149.99	0.09	184.10	0.67	34.11	22.74
2021-11-17 03:11	69.99	0.04	85.06	0.72	15.07	21.53
2021-11-17 03:21	30.01	0.07	34.60	0.48	4.59	15.29
2021-11-17 03:41	99.96	0.08	120.74	0.15	20.78	20.79
2021-11-17 03:51	39.97	0.03	46.72	0.15	6.75	16.89
2021-11-17 04:01	90.00	0.03	108.68	0.16	18.68	20.76
2021-11-17 04:11	124.99	0.04	151.88	0.29	26.89	21.51
2021-11-17 04:21	79.98	0.08	96.08	0.58	16.10	20.13
2021-11-17 04:31	10.00	0.12	11.68	0.22	1.68	16.80
2021-11-17 04:41	20.02	0.06	24.06	0.27	4.04	20.18
2021-11-17 04:51	70.00	0.05	84.00	0.76	14.00	20.00
2021-11-17 05:01	150.02	0.08	182.68	0.11	32.66	21.77

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2021-11-17 05:11	60.02	0.06	73.24	0.29	13.22	22.03
2021-11-17 05:21	174.98	0.06	213.92	0.26	38.94	22.25
2021-11-17 05:31	49.96	0.07	61.64	0.33	11.68	23.38
2021-11-17 05:51	30.02	0.10	36.80	0.07	6.78	22.58
2021-11-17 06:11	30.03	0.10	36.74	0.19	6.71	22.34
2021-11-17 06:21	59.98	0.06	73.56	0.25	13.58	22.64
2021-11-17 06:31	99.99	0.06	121.20	0.56	21.21	21.21
2021-11-17 06:41	70.00	0.06	85.32	0.31	15.32	21.89
2021-11-17 06:51	149.99	0.05	182.66	0.53	32.67	21.78
2021-11-17 07:01	10.02	0.16	12.30	0.20	2.28	22.75
2021-11-17 07:11	40.00	0.11	48.92	0.45	8.92	22.30
2021-11-17 07:21	89.98	0.05	108.82	0.85	18.84	20.94
2021-11-17 07:31	124.98	0.07	151.10	0.73	26.12	20.90
2021-11-17 07:51	50.04	0.12	61.76	0.54	11.72	23.42
2021-11-17 08:01	80.03	0.07	98.62	0.33	18.59	23.23
2021-11-17 08:11	175.07	0.06	214.42	0.56	39.35	22.48
2021-11-17 08:21	19.99	0.08	24.06	0.05	4.07	20.36
2021-11-17 08:41	10.01	0.13	12.08	0.69	2.07	20.68
2021-11-17 08:51	49.94	0.02	60.72	0.71	10.78	21.59
2021-11-17 09:01	125.04	0.04	153.92	0.58	28.88	23.10
2021-11-17 09:11	99.98	0.07	122.92	0.36	22.94	22.94
2021-11-17 09:31	175.02	0.07	214.96	0.38	39.94	22.82
2021-11-17 09:41	40.00	0.10	48.48	0.16	8.48	21.20
2021-11-17 09:51	20.01	0.11	24.12	0.13	4.11	20.54
2021-11-17 10:01	79.99	0.07	98.24	0.18	18.25	22.82
2021-11-17 10:11	60.03	0.03	73.68	0.23	13.65	22.74
2021-11-17 10:21	89.98	0.03	109.66	0.21	19.68	21.87
2021-11-17 10:31	150.00	0.05	183.18	1.01	33.18	22.12
2021-11-17 10:41	70.04	0.03	85.72	0.26	15.68	22.39
2021-11-17 10:51	30.01	0.11	36.18	0.08	6.17	20.56
2021-11-17 11:11	99.99	0.06	122.30	0.26	22.31	22.31
2021-11-17 11:21	40.04	0.03	48.44	0.25	8.40	20.98
2021-11-17 11:31	89.98	0.06	110.18	0.16	20.20	22.45
2021-11-17 11:41	125.01	0.06	154.12	0.04	29.11	23.29
2021-11-17 11:51	80.00	0.09	98.20	0.20	18.20	22.75
2021-11-17 12:01	10.31	0.34	12.46	0.43	2.15	20.85
2021-11-16 20:11	99.99	0.04	119.48	0.08	19.49	19.49
2021-11-16 20:21	39.98	0.06	47.10	0.21	7.12	17.81
2021-11-16 20:31	89.98	0.09	108.12	0.24	18.14	20.16
2021-11-16 20:41	124.99	0.03	150.88	0.13	25.89	20.71
2021-11-16 20:51	80.02	0.06	96.56	0.26	16.54	20.67
2021-11-16 21:01	10.23	0.37	11.76	0.11	1.53	14.96
2021-11-16 21:11	20.00	0.11	23.56	0.27	3.56	17.80
2021-11-16 21:21	69.98	0.01	84.00	0.31	14.02	20.03
2021-11-16 21:31	149.95	0.09	181.86	0.44	31.91	21.28
2021-11-16 21:41	60.02	0.05	71.66	0.38	11.64	19.39
2021-11-16 21:51	175.00	0.07	212.54	0.61	37.54	21.45
2021-11-16 22:01	49.97	0.03	59.92	0.61	9.95	19.91

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2021-11-16 22:21	29.97	0.12	36.16	0.23	6.19	20.65
2021-11-16 22:41	30.00	0.02	36.14	0.54	6.14	20.47
2021-11-16 22:51	59.99	0.06	72.06	0.83	12.07	20.12
2021-11-16 23:01	99.98	0.07	121.10	0.89	21.12	21.12
2021-11-16 23:11	69.98	0.05	84.98	0.71	15.00	21.43
2021-11-16 23:21	150.01	0.06	182.48	0.31	32.47	21.65
2021-11-16 23:31	9.98	0.10	12.36	0.57	2.38	23.85
2021-11-16 23:41	39.97	0.08	47.88	0.15	7.91	19.79
2021-11-16 23:51	90.01	0.05	108.84	0.50	18.83	20.92
2021-11-17 00:01	124.99	0.05	151.96	0.21	26.97	21.58
2021-11-17 00:21	50.01	0.06	60.54	0.09	10.53	21.06
2021-11-17 00:31	79.97	0.07	96.96	0.11	16.99	21.25
2021-11-17 00:41	174.97	0.04	214.08	0.28	39.11	22.35
2021-11-17 00:51	20.02	0.09	24.30	0.08	4.28	21.38
2021-11-17 01:11	9.98	0.07	12.04	0.17	2.06	20.64
2021-11-17 01:21	49.94	0.06	60.56	0.41	10.62	21.27
2021-11-17 01:31	125.02	0.09	152.58	0.44	27.56	22.04
2021-11-17 01:41	100.04	0.03	121.72	0.13	21.68	21.67
2021-11-17 02:01	174.96	0.06	214.46	0.15	39.50	22.58
2021-11-17 02:11	40.00	0.04	48.40	0.28	8.40	21.00
2021-11-17 02:21	20.03	0.07	24.22	0.27	4.19	20.92
2021-11-17 02:31	80.07	0.08	97.62	0.23	17.55	21.92
2021-11-17 02:41	60.02	0.04	73.60	0.28	13.58	22.63
2021-11-17 02:51	89.95	0.05	110.36	0.32	20.41	22.69
2021-11-17 03:01	149.99	0.09	184.10	0.67	34.11	22.74
2021-11-17 03:11	69.99	0.04	85.06	0.72	15.07	21.53
2021-11-17 03:21	30.01	0.07	34.60	0.48	4.59	15.29
2021-11-17 03:41	99.96	0.08	120.74	0.15	20.78	20.79
2021-11-17 03:51	39.97	0.03	46.72	0.15	6.75	16.89
2021-11-17 04:01	90.00	0.03	108.68	0.16	18.68	20.76
2021-11-17 04:11	124.99	0.04	151.88	0.29	26.89	21.51
2021-11-17 04:21	79.98	0.08	96.08	0.58	16.10	20.13
2021-11-17 04:31	10.00	0.12	11.68	0.22	1.68	16.80
2021-11-17 04:41	20.02	0.06	24.06	0.27	4.04	20.18
2021-11-17 04:51	70.00	0.05	84.00	0.76	14.00	20.00
2021-11-17 05:01	150.02	0.08	182.68	0.11	32.66	21.77
2021-11-17 05:11	60.02	0.06	73.24	0.29	13.22	22.03
2021-11-17 05:21	174.98	0.06	213.92	0.26	38.94	22.25
2021-11-17 05:31	49.96	0.07	61.64	0.33	11.68	23.38
2021-11-17 05:51	30.02	0.10	36.80	0.07	6.78	22.58
2021-11-17 06:11	30.03	0.10	36.74	0.19	6.71	22.34
2021-11-17 06:21	59.98	0.06	73.56	0.25	13.58	22.64
2021-11-17 06:31	99.99	0.06	121.20	0.56	21.21	21.21
2021-11-17 06:41	70.00	0.06	85.32	0.31	15.32	21.89
2021-11-17 06:51	149.99	0.05	182.66	0.53	32.67	21.78
2021-11-17 07:01	10.02	0.16	12.30	0.20	2.28	22.75
2021-11-17 07:11	40.00	0.11	48.92	0.45	8.92	22.30
2021-11-17 07:21	89.98	0.05	108.82	0.85	18.84	20.94

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2021-11-17 07:31	124.98	0.07	151.10	0.73	26.12	20.90
2021-11-17 07:51	50.04	0.12	61.76	0.54	11.72	23.42
2021-11-17 08:01	80.03	0.07	98.62	0.33	18.59	23.23
2021-11-17 08:11	175.07	0.06	214.42	0.56	39.35	22.48
2021-11-17 08:21	19.99	0.08	24.06	0.05	4.07	20.36
2021-11-17 08:41	10.01	0.13	12.08	0.69	2.07	20.68
2021-11-17 08:51	49.94	0.02	60.72	0.71	10.78	21.59
2021-11-17 09:01	125.04	0.04	153.92	0.58	28.88	23.10
2021-11-17 09:11	99.98	0.07	122.92	0.36	22.94	22.94
2021-11-17 09:31	175.02	0.07	214.96	0.38	39.94	22.82
2021-11-17 09:41	40.00	0.10	48.48	0.16	8.48	21.20
2021-11-17 09:51	20.01	0.11	24.12	0.13	4.11	20.54
2021-11-17 10:01	79.99	0.07	98.24	0.18	18.25	22.82
2021-11-17 10:11	60.03	0.03	73.68	0.23	13.65	22.74
2021-11-17 10:21	89.98	0.03	109.66	0.21	19.68	21.87
2021-11-17 10:31	150.00	0.05	183.18	1.01	33.18	22.12
2021-11-17 10:41	70.04	0.03	85.72	0.26	15.68	22.39
2021-11-17 10:51	30.01	0.11	36.18	0.08	6.17	20.56
2021-11-17 11:11	99.99	0.06	122.30	0.26	22.31	22.31
2021-11-17 11:21	40.04	0.03	48.44	0.25	8.40	20.98
2021-11-17 11:31	89.98	0.06	110.18	0.16	20.20	22.45
2021-11-17 11:41	125.01	0.06	154.12	0.04	29.11	23.29
2021-11-17 11:51	80.00	0.09	98.20	0.20	18.20	22.75
2021-11-17 12:01	10.31	0.34	12.46	0.43	2.15	20.85

Table 5. *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CPT ozone analyser (OA) Thermo Scientific 49i #1327059053 (BKG +0.6 nmol mol^{-1}, COEF 1.054) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2021-11-18 12:51	0.18	0.15	0.63	0.09	0.45	NA
2021-11-18 13:01	29.99	0.08	29.79	0.13	-0.20	-0.67
2021-11-18 13:11	60.01	0.01	59.86	0.19	-0.15	-0.25
2021-11-18 13:31	70.01	0.05	70.57	0.11	0.56	0.80
2021-11-18 13:41	150.07	0.05	151.80	0.15	1.73	1.15
2021-11-18 13:51	9.98	0.09	10.38	0.17	0.40	4.01
2021-11-18 14:01	40.01	0.07	39.95	0.12	-0.06	-0.15
2021-11-18 14:21	124.97	0.10	125.77	0.20	0.80	0.64
2021-11-18 14:31	190.01	0.04	191.75	0.13	1.74	0.92
2021-11-18 14:41	49.95	0.07	50.30	0.04	0.35	0.70
2021-11-18 14:51	80.00	0.03	80.46	0.13	0.46	0.57
2021-11-18 15:11	20.05	0.08	20.43	0.11	0.38	1.90
2021-11-18 15:21	0.36	0.11	0.83	0.23	0.47	NA
2021-11-18 15:31	10.03	0.08	10.17	0.12	0.14	1.40
2021-11-18 15:41	50.00	0.13	50.03	0.15	0.03	0.06
2021-11-18 15:51	124.99	0.05	125.61	0.23	0.62	0.50

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2021-11-18 16:01	99.97	0.09	100.48	0.14	0.51	0.51
2021-11-18 16:11	190.00	0.09	191.51	0.27	1.51	0.79
2021-11-18 16:21	175.01	0.05	176.50	0.15	1.49	0.85
2021-11-18 16:31	40.06	0.10	40.29	0.17	0.23	0.57
2021-11-18 16:51	79.98	0.04	80.29	0.19	0.31	0.39
2021-11-18 17:01	59.99	0.13	60.13	0.21	0.14	0.23
2021-11-18 17:11	90.01	0.09	90.41	0.16	0.40	0.44
2021-11-18 17:21	150.03	0.05	151.07	0.14	1.04	0.69
2021-11-18 17:31	70.02	0.03	70.24	0.09	0.22	0.31
2021-11-18 17:41	29.97	0.06	29.88	0.14	-0.09	-0.30
2021-11-18 17:51	0.34	0.05	0.89	0.04	0.55	NA
2021-11-18 18:01	99.97	0.05	100.09	0.14	0.12	0.12
2021-11-18 18:11	39.99	0.12	40.00	0.30	0.01	0.03
2021-11-18 18:21	90.02	0.05	90.36	0.05	0.34	0.38
2021-11-18 18:31	125.03	0.03	125.60	0.11	0.57	0.46
2021-11-18 18:41	80.01	0.02	80.43	0.16	0.42	0.52
2021-11-18 19:01	19.99	0.10	19.91	0.15	-0.08	-0.40
2021-11-18 19:21	150.00	0.06	150.92	0.19	0.92	0.61
2021-11-18 19:31	60.02	0.09	60.34	0.24	0.32	0.53
2021-11-18 19:41	175.03	0.11	176.47	0.17	1.44	0.82
2021-11-18 19:51	50.03	0.08	50.00	0.09	-0.03	-0.06
2021-11-18 20:01	190.02	0.07	191.73	0.26	1.71	0.90
2021-11-18 20:11	30.03	0.11	30.15	0.21	0.12	0.40
2021-11-18 20:21	0.30	0.07	0.92	0.09	0.62	NA
2021-11-18 20:31	30.02	0.04	29.86	0.08	-0.16	-0.53
2021-11-18 20:41	60.01	0.08	60.18	0.11	0.17	0.28
2021-11-18 21:01	69.97	0.08	70.38	0.17	0.41	0.59
2021-11-18 21:11	150.06	0.03	151.29	0.08	1.23	0.82
2021-11-18 21:21	10.03	0.06	10.19	0.14	0.16	1.60
2021-11-18 21:31	40.02	0.03	40.20	0.13	0.18	0.45
2021-11-18 21:51	125.04	0.08	125.94	0.23	0.90	0.72
2021-11-18 22:01	189.98	0.09	191.85	0.16	1.87	0.98
2021-11-18 22:11	50.04	0.05	50.35	0.14	0.31	0.62
2021-11-18 22:21	79.99	0.07	80.54	0.10	0.55	0.69
2021-11-18 22:41	19.96	0.06	20.11	0.13	0.15	0.75
2021-11-18 22:51	0.41	0.08	0.82	0.11	0.41	NA
2021-11-18 23:01	10.04	0.19	10.18	0.23	0.14	1.39
2021-11-18 23:11	49.95	0.06	50.04	0.06	0.09	0.18
2021-11-18 23:21	125.02	0.03	125.93	0.17	0.91	0.73
2021-11-18 23:31	99.93	0.04	100.37	0.14	0.44	0.44
2021-11-18 23:41	189.97	0.01	191.68	0.16	1.71	0.90
2021-11-18 23:51	175.05	0.09	177.15	0.17	2.10	1.20
2021-11-19 00:01	40.03	0.11	40.17	0.15	0.14	0.35
2021-11-19 00:21	79.97	0.07	80.38	0.20	0.41	0.51
2021-11-19 00:31	59.97	0.03	60.31	0.21	0.34	0.57
2021-11-19 00:41	90.02	0.06	90.69	0.25	0.67	0.74
2021-11-19 00:51	149.99	0.08	151.38	0.16	1.39	0.93
2021-11-19 01:01	70.00	0.10	70.53	0.12	0.53	0.76

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2021-11-19 01:11	30.01	0.07	30.08	0.22	0.07	0.23
2021-11-19 01:21	0.33	0.16	0.93	0.07	0.60	NA
2021-11-19 01:31	99.96	0.12	100.65	0.15	0.69	0.69
2021-11-19 01:41	39.99	0.13	40.13	0.25	0.14	0.35
2021-11-19 01:51	89.99	0.06	90.82	0.21	0.83	0.92
2021-11-19 02:01	125.01	0.07	126.03	0.17	1.02	0.82
2021-11-19 02:11	80.00	0.11	80.55	0.25	0.55	0.69
2021-11-19 02:31	19.98	0.08	20.19	0.08	0.21	1.05
2021-11-19 02:51	150.04	0.03	151.47	0.06	1.43	0.95
2021-11-19 03:01	60.03	0.10	60.39	0.15	0.36	0.60
2021-11-19 03:11	175.05	0.23	176.82	0.07	1.77	1.01
2021-11-19 03:21	49.97	0.03	50.29	0.04	0.32	0.64
2021-11-19 03:31	190.03	0.07	192.25	0.19	2.22	1.17
2021-11-19 03:41	30.01	0.05	30.30	0.19	0.29	0.97
2021-11-19 03:51	0.33	0.03	0.86	0.13	0.53	NA
2021-11-19 04:01	29.95	0.04	30.03	0.19	0.08	0.27
2021-11-19 04:11	60.02	0.12	60.45	0.23	0.43	0.72
2021-11-19 04:31	69.99	0.04	70.56	0.08	0.57	0.81
2021-11-19 04:41	149.96	0.09	151.49	0.14	1.53	1.02
2021-11-19 04:51	10.02	0.07	10.42	0.11	0.40	3.99
2021-11-19 05:01	40.02	0.08	40.23	0.13	0.21	0.52

Table 6. *Five-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CPT ozone calibrator (OC) Thermo Scientific 49i-PS #708821231 (BKG -0.1 nmol mol^{-1}, COEF 1.019) 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 (%)
2021-11-17 17:05	-0.08	0.12	1.73	0.24	1.81	-2262.50
2021-11-17 17:15	29.95	0.04	3.70	0.20	-26.25	-87.65
2021-11-17 17:25	59.94	0.06	6.25	0.23	-53.69	-89.57
2021-11-17 17:45	69.95	0.05	6.96	0.25	-62.99	-90.05
2021-11-17 17:55	150.01	0.07	12.37	0.20	-137.64	-91.75
2021-11-17 18:05	10.66	0.34	2.85	0.16	-7.81	-73.26
2021-11-17 18:15	39.99	0.05	4.73	0.22	-35.26	-88.17
2021-11-17 18:35	124.96	0.04	10.58	0.31	-114.38	-91.53
2021-11-17 18:45	189.94	0.07	15.39	0.52	-174.55	-91.90
2021-11-17 18:55	50.03	0.06	5.47	0.16	-44.56	-89.07
2021-11-17 19:05	80.04	0.13	7.30	0.19	-72.74	-90.88
2021-11-17 19:25	19.99	0.11	3.82	0.06	-16.17	-80.89
2021-11-17 19:35	0.00	0.08	2.26	0.13	2.26	NA
2021-11-17 19:45	10.35	0.32	2.99	0.09	-7.36	-71.11
2021-11-17 19:55	49.99	0.10	6.10	0.17	-43.89	-87.80
2021-11-17 20:05	124.96	0.05	11.98	0.24	-112.98	-90.41
2021-11-17 20:15	100.00	0.04	9.88	0.12	-90.12	-90.12
2021-11-17 20:25	189.95	0.06	17.47	0.26	-172.48	-90.80
2021-11-17 20:35	175.00	0.10	16.17	0.31	-158.83	-90.76

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 (%)
2021-11-17 20:45	40.00	0.06	5.50	0.13	-34.50	-86.25
2021-11-17 21:05	79.97	0.05	8.44	0.10	-71.53	-89.45
2021-11-17 21:15	60.00	0.02	6.33	0.37	-53.67	-89.45
2021-11-17 21:25	90.03	0.06	9.17	0.47	-80.86	-89.81
2021-11-17 21:35	149.99	0.07	14.32	0.14	-135.67	-90.45
2021-11-17 21:45	69.98	0.02	7.86	0.16	-62.12	-88.77
2021-11-17 21:55	29.92	0.10	4.61	0.16	-25.31	-84.59
2021-11-17 22:05	0.04	0.05	2.37	0.13	2.33	NA
2021-11-17 22:15	99.97	0.05	10.18	0.22	-89.79	-89.82
2021-11-17 22:25	40.08	0.06	5.43	0.28	-34.65	-86.45
2021-11-17 22:35	89.99	0.04	9.69	0.23	-80.30	-89.23
2021-11-17 22:45	125.00	0.06	12.25	0.08	-112.75	-90.20
2021-11-17 22:55	80.05	0.05	8.70	0.19	-71.35	-89.13
2021-11-17 23:15	19.92	0.04	4.03	0.10	-15.89	-79.77
2021-11-17 23:35	150.06	0.06	15.00	0.18	-135.06	-90.00
2021-11-17 23:45	59.98	0.07	6.51	2.03	-53.47	-89.15
2021-11-17 23:55	175.01	0.05	17.73	0.20	-157.28	-89.87
2021-11-18 00:05	49.98	0.13	6.74	0.25	-43.24	-86.51
2021-11-18 00:15	190.00	0.08	19.20	0.10	-170.80	-89.89
2021-11-18 00:25	30.03	0.05	5.17	0.14	-24.86	-82.78
2021-11-18 00:35	-0.05	0.08	2.26	0.10	2.31	NA
2021-11-18 00:45	29.98	0.06	4.90	0.11	-25.08	-83.66
2021-11-18 00:55	59.98	0.04	7.88	0.15	-52.10	-86.86
2021-11-18 01:15	69.98	0.08	8.97	0.13	-61.01	-87.18
2021-11-18 01:25	150.04	0.05	16.30	0.04	-133.74	-89.14
2021-11-18 01:35	10.01	0.12	3.16	0.06	-6.85	-68.43
2021-11-18 01:45	39.99	0.07	6.03	0.14	-33.96	-84.92
2021-11-18 02:05	125.02	0.05	14.38	0.10	-110.64	-88.50
2021-11-18 02:15	190.00	0.06	20.45	0.09	-169.55	-89.24
2021-11-18 02:25	50.00	0.09	7.23	0.17	-42.77	-85.54
2021-11-18 02:35	79.95	0.06	10.19	0.18	-69.76	-87.25
2021-11-18 02:55	20.03	0.05	4.25	0.14	-15.78	-78.78
2021-11-18 03:05	0.07	0.14	2.02	0.11	1.95	NA
2021-11-18 03:15	10.06	0.10	2.97	0.15	-7.09	-70.48
2021-11-18 03:25	50.02	0.05	7.21	0.14	-42.81	-85.59
2021-11-18 03:35	124.96	0.03	15.10	0.25	-109.86	-87.92
2021-11-18 03:45	99.95	0.06	12.81	0.20	-87.14	-87.18
2021-11-18 03:55	189.95	0.09	23.03	0.21	-166.92	-87.88
2021-11-18 04:05	174.95	0.03	21.29	0.12	-153.66	-87.83
2021-11-18 04:15	40.00	0.05	6.26	0.11	-33.74	-84.35
2021-11-18 04:35	79.95	0.05	10.92	0.31	-69.03	-86.34
2021-11-18 04:45	60.03	0.04	9.00	0.24	-51.03	-85.01
2021-11-18 04:55	90.03	0.10	12.65	0.22	-77.38	-85.95
2021-11-18 05:05	150.03	0.08	19.11	0.14	-130.92	-87.26
2021-11-18 05:15	69.95	0.08	10.07	0.20	-59.88	-85.60
2021-11-18 05:25	30.04	0.06	5.63	0.17	-24.41	-81.26
2021-11-18 05:35	0.08	0.16	2.04	0.18	1.96	NA
2021-11-18 05:45	99.98	0.08	14.64	0.22	-85.34	-85.36

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 (%)
2021-11-18 05:55	40.00	0.12	7.27	0.07	-32.73	-81.83
2021-11-18 06:05	90.00	0.07	13.78	0.10	-76.22	-84.69
2021-11-18 06:15	125.02	0.04	18.00	0.07	-107.02	-85.60
2021-11-18 06:25	79.97	0.02	12.88	0.14	-67.09	-83.89
2021-11-18 06:45	20.04	0.10	4.67	0.18	-15.37	-76.70
2021-11-18 07:05	150.02	0.09	24.76	0.24	-125.26	-83.50
2021-11-18 07:15	60.00	0.08	10.54	0.08	-49.46	-82.43
2021-11-18 07:25	175.02	0.03	28.66	0.21	-146.36	-83.62
2021-11-18 07:35	50.05	0.05	9.32	0.20	-40.73	-81.38
2021-11-18 07:45	190.00	0.03	30.92	0.21	-159.08	-83.73
2021-11-18 07:55	30.04	0.09	6.10	0.10	-23.94	-79.69
2021-11-18 08:05	-0.03	0.09	1.35	0.09	1.38	NA
2021-11-18 08:15	29.98	0.08	6.14	0.12	-23.84	-79.52
2021-11-18 08:25	60.02	0.07	11.09	0.22	-48.93	-81.52
2021-11-18 08:45	70.00	0.10	13.19	0.11	-56.81	-81.16
2021-11-18 08:55	150.01	0.10	26.63	0.20	-123.38	-82.25
2021-11-18 09:05	10.33	0.40	3.24	0.18	-7.09	-68.64
2021-11-18 09:15	40.00	0.07	8.26	0.15	-31.74	-79.35

Table 7. *Comparison of the CPT ozone calibrator (OC) Thermo Scientific 49i-PS #708821231 (BKG -0.1 nmol mol^{-1}, COEF 1.019) against SRP#15 at Empa.*

Date – Time	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-SRP (nmol mol^{-1})	OC-SRP (%)
2022-03-01 13:39	176.81	0.28	178.05	0.26	1.24	0.70
2022-03-01 13:40	177.62	NA	178.20	NA	0.58	0.33
2022-03-01 13:51	200.79	0.32	202.35	0.29	1.56	0.78
2022-03-01 14:04	127.38	0.15	128.77	0.25	1.39	1.09
2022-03-01 14:05	127.87	0.24	128.79	0.24	0.92	0.72
2022-03-01 14:14	228.29	0.28	229.85	0.26	1.56	0.68
2022-03-01 14:24	60.91	0.41	61.52	0.21	0.61	1.00
2022-03-01 14:35	0.13	0.39	-0.02	0.31	-0.15	NA
2022-03-01 14:49	251.43	0.34	252.92	0.21	1.49	0.59
2022-03-01 15:01	152.97	0.23	154.12	0.17	1.15	0.75
2022-03-01 15:11	89.08	0.34	89.77	0.20	0.69	0.77
2022-03-01 15:24	101.00	0.31	101.85	0.11	0.85	0.84
2022-03-01 15:33	32.90	0.14	32.76	0.13	-0.14	-0.43
2022-03-01 15:35	32.28	0.14	32.86	0.27	0.58	1.80
2022-03-01 15:44	61.55	0.39	61.84	0.19	0.29	0.47
2022-03-01 15:56	0.05	0.42	0.05	0.20	0.00	0.00
2022-03-01 16:08	99.58	0.34	100.53	0.20	0.95	0.95
2022-03-01 16:21	127.54	0.02	128.12	0.34	0.58	0.45
2022-03-01 16:22	127.17	0.13	128.17	0.25	1.00	0.79
2022-03-01 16:32	250.97	0.24	252.52	0.28	1.55	0.62
2022-03-01 16:42	32.19	0.10	32.53	0.13	0.34	1.06
2022-03-01 16:44	32.68	0.09	32.63	0.18	-0.05	-0.15
2022-03-01 16:51	89.70	0.41	90.06	0.29	0.36	0.40
2022-03-01 17:02	228.03	0.20	229.59	0.39	1.56	0.68

Date – Time	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-SRP (nmol mol^{-1})	OC-SRP (%)
2022-03-01 17:05	227.41	0.04	229.15	0.07	1.74	0.77
2022-03-01 17:16	152.96	0.17	153.63	0.20	0.67	0.44
2022-03-01 17:17	152.49	NA	153.70	NA	1.21	0.79
2022-03-01 17:28	176.69	0.29	177.81	0.26	1.12	0.63
2022-03-01 17:41	201.13	0.34	202.70	0.29	1.57	0.78
2022-03-01 17:53	0.13	0.34	0.10	0.15	-0.03	NA
2022-03-01 18:03	32.88	0.15	33.05	0.13	0.17	0.52
2022-03-01 18:16	250.88	0.38	252.56	0.40	1.68	0.67
2022-03-01 18:26	88.78	0.41	89.44	0.36	0.66	0.74
2022-03-01 18:35	61.31	0.18	61.66	0.18	0.35	0.57
2022-03-01 18:47	227.99	0.23	229.28	0.26	1.29	0.57
2022-03-01 19:00	101.90	0.37	102.75	0.16	0.85	0.83
2022-03-01 19:06	102.67	NA	102.90	NA	0.23	0.22
2022-03-01 19:13	176.76	0.22	177.76	0.27	1.00	0.57
2022-03-01 19:25	152.89	0.15	153.88	0.21	0.99	0.65
2022-03-01 19:26	152.37	0.18	153.67	0.25	1.30	0.85
2022-03-01 19:38	200.65	0.27	202.05	0.23	1.40	0.70
2022-03-01 19:53	125.40	0.41	126.08	0.26	0.68	0.54
2022-03-01 20:04	61.37	0.37	61.72	0.32	0.35	0.57
2022-03-01 20:18	152.70	0.15	153.32	0.04	0.62	0.41
2022-03-01 20:19	152.32	0.10	153.57	0.16	1.25	0.82
2022-03-01 20:28	252.82	0.30	254.05	0.33	1.23	0.49
2022-03-01 20:29	251.97	0.28	253.79	0.37	1.82	0.72
2022-03-01 20:40	-0.02	0.28	0.08	0.19	0.10	NA
2022-03-01 20:53	100.21	0.32	100.66	0.24	0.45	0.45
2022-03-01 21:02	32.22	0.24	32.78	0.26	0.56	1.74
2022-03-01 21:03	33.09	0.37	32.74	0.11	-0.35	-1.06
2022-03-01 21:18	225.17	0.21	226.34	0.33	1.17	0.52
2022-03-01 21:28	89.25	0.45	90.04	0.26	0.79	0.89
2022-03-01 21:40	127.25	0.22	128.08	0.16	0.83	0.65
2022-03-01 21:41	127.58	0.03	128.20	0.10	0.62	0.49
2022-03-01 21:53	200.79	0.30	202.15	0.18	1.36	0.68
2022-03-01 22:06	176.46	0.35	177.64	0.23	1.18	0.67
2022-03-01 22:20	201.33	0.29	202.72	0.26	1.39	0.69
2022-03-01 22:33	152.47	0.03	153.75	0.19	1.28	0.84
2022-03-01 22:34	152.95	0.17	153.74	0.19	0.79	0.52
2022-03-01 22:44	-0.01	0.27	0.09	0.20	0.10	NA
2022-03-01 22:57	99.84	0.33	100.31	0.18	0.47	0.47
2022-03-01 23:07	32.76	0.17	32.95	0.17	0.19	0.58
2022-03-01 23:16	61.80	0.22	61.97	0.21	0.17	0.28
2022-03-01 23:29	229.02	0.27	230.57	0.21	1.55	0.68
2022-03-01 23:45	125.82	0.31	126.53	0.29	0.71	0.56
2022-03-01 23:57	176.54	0.20	177.59	0.26	1.05	0.59
2022-03-02 00:07	89.51	0.30	90.24	0.19	0.73	0.82
2022-03-02 00:19	252.85	0.26	254.45	0.19	1.60	0.63
2022-03-02 00:20	252.38	0.12	254.30	0.14	1.92	0.76
2022-03-02 00:30	61.28	0.27	61.65	0.31	0.37	0.60
2022-03-02 00:42	127.03	0.32	127.94	0.24	0.91	0.72

Date – Time	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-SRP (nmol mol^{-1})	OC-SRP (%)
2022-03-02 00:48	127.70	NA	127.80	NA	0.10	0.08
2022-03-02 00:55	176.91	0.18	178.05	0.18	1.14	0.64
2022-03-02 01:05	89.60	0.24	90.07	0.27	0.47	0.52
2022-03-02 01:17	152.27	0.11	153.52	0.23	1.25	0.82
2022-03-02 01:18	152.63	0.09	153.48	0.15	0.85	0.56
2022-03-02 01:30	200.50	0.26	201.85	0.16	1.35	0.67
2022-03-02 01:40	252.10	0.21	253.97	0.32	1.87	0.74
2022-03-02 01:49	32.11	0.28	32.64	0.21	0.53	1.65
2022-03-02 01:52	32.62	0.13	32.81	0.19	0.19	0.58
2022-03-02 02:02	100.24	0.34	101.09	0.30	0.85	0.85
2022-03-02 02:14	0.21	0.39	0.06	0.19	-0.15	NA
2022-03-02 02:29	228.55	0.27	230.19	0.15	1.64	0.72
2022-03-02 02:43	201.05	0.39	202.19	0.27	1.14	0.57
2022-03-02 02:56	101.83	0.21	102.44	0.20	0.61	0.60
2022-03-02 03:05	89.96	0.36	90.17	0.16	0.21	0.23
2022-03-02 03:15	32.42	0.05	32.97	0.27	0.55	1.70
2022-03-02 03:16	32.69	0.14	32.92	0.14	0.23	0.70
2022-03-02 03:28	126.28	0.21	127.50	0.21	1.22	0.97
2022-03-02 03:40	176.79	0.28	177.87	0.17	1.08	0.61
2022-03-02 03:50	61.09	0.32	61.65	0.25	0.56	0.92
2022-03-02 04:02	251.70	0.30	253.55	0.19	1.85	0.74
2022-03-02 04:11	228.25	0.40	229.87	0.35	1.62	0.71
2022-03-02 04:16	227.08	NA	229.50	NA	2.42	1.07
2022-03-02 04:24	152.85	0.17	153.92	0.16	1.07	0.70
2022-03-02 04:27	152.31	0.11	153.95	0.16	1.64	1.08
2022-03-02 04:36	-0.10	0.25	0.04	0.19	0.14	NA
2022-03-02 04:51	199.67	0.32	200.91	0.16	1.24	0.62
2022-03-02 05:04	152.86	0.22	153.77	0.26	0.91	0.60
2022-03-02 05:05	152.32	NA	154.00	NA	1.68	1.10
2022-03-02 05:17	176.68	0.31	177.83	0.22	1.15	0.65
2022-03-02 05:30	101.34	0.25	102.06	0.20	0.72	0.71
2022-03-02 05:39	89.34	0.36	90.09	0.24	0.75	0.84
2022-03-02 05:51	251.52	0.37	253.36	0.23	1.84	0.73
2022-03-02 06:02	0.07	0.36	0.11	0.15	0.04	NA
2022-03-02 06:12	33.02	0.26	33.06	0.26	0.04	0.12
2022-03-02 06:22	61.57	0.23	61.94	0.25	0.37	0.60
2022-03-02 06:35	126.99	0.39	127.83	0.25	0.84	0.66
2022-03-02 06:39	127.65	NA	127.60	NA	-0.05	-0.04
2022-03-02 06:47	227.29	0.15	229.27	0.08	1.98	0.87
2022-03-02 06:48	227.67	0.14	229.08	0.23	1.41	0.62

Calibration Standards for CO, CH_4, and CO_2

Table 8 shows and overview of available standard gases for the calibration of the CO, CH_4, and CO_2 instruments.

Table 8 *Calibration standards at CPT as of November 2021.*

Cylinder ID	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2(X2019) (µmol mol^{-1})	Usage
CA06790	55.25	1870.53	416.81	NOAA reference standard
CA06842	62.10	1865.13	415.22	NOAA reference standard
CB08934	84.14	1952.56	435.36	NOAA reference standard
CB12306	111.96	2040.11	449.12	NOAA reference standard
CB12410	51.39	1864.38	408.25	NOAA reference standard

Carbon Monoxide Comparisons

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

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

Table 9. Experimental details of CPT 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 Tables 21 and 22.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #3498-CFKADS2350
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
Station Analyser (CO, CO_2)	
Model, S/N	Picarro 2302 #835-CKADS2026
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
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 10. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3498-CFKADS2350 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-02-26 16:31:15)	171122_FA02788	71.9	0.6	71.5	0.7	4	-0.4	-0.5
(21-02-26 16:31:15)	171204_FF31496	155.6	0.7	152.1	0.6	4	-3.5	-2.2
(21-02-26 16:31:15)	171128_FA01477	113.4	0.3	111.3	0.6	4	-2.1	-1.9
(21-02-26 16:31:15)	180318_FF30491	188.9	0.6	184.1	0.6	4	-4.8	-2.6
(21-02-26 16:31:15)	181128_FF61471	104.2	0.7	102.5	0.6	4	-1.7	-1.7
(21-03-03 04:35:30)	171122_FA02785	50.3	0.8	50.9	0.1	4	0.6	1.1
(21-03-03 04:35:30)	171123_FA02789	93.7	0.7	91.8	0.2	4	-1.9	-2.1
(21-03-03 04:35:30)	201207_FB03887	30.2	1.1	31.0	0.2	4	0.8	2.6
(21-02-25 18:27:00)	171201_FA02773	0.2	0.3	1.6	0.4	3	1.4	NA
(21-03-03 04:35:30)	160622_FB03911	310.5	1.4	300.8	0.5	4	-9.7	-3.1
(21-11-17 11:53:00)	180318_FF61491	282.1	1.3	274.4	0.8	3	-7.7	-2.7
(21-11-17 12:18:40)	160622_FA02479	210.2	0.7	205.5	0.6	3	-4.8	-2.3
(21-11-17 12:44:00)	210927_FF61508	46.8	2.4	48.1	0.7	3	1.3	2.8
(21-11-17 13:09:00)	171124_FA01467	142.5	1.0	140.5	0.4	3	-2.0	-1.4
(21-11-17 13:34:00)	171123_FA02770	118.0	1.2	117.9	0.4	3	-0.2	-0.2
(22-01-31 00:00:00)	180318_FF61491	282.1	1.3	273.8	0.4	2	-8.4	-3.0
(22-01-31 00:00:00)	160622_FA02479	210.2	0.7	205.6	0.2	2	-4.7	-2.2
(22-01-31 00:00:00)	210927_FF61508	46.8	2.4	48.8	0.2	2	2.0	4.3
(22-01-31 00:00:00)	171124_FA01467	142.5	1.0	140.6	0.1	2	-1.9	-1.3
(22-01-31 00:00:00)	171123_FA02770	118.0	1.2	116.3	0.1	2	-1.7	-1.5

Table 11. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro 2302 #835-CKADS2026 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-02-26 16:31:15)	171122_FA02788	71.9	0.6	72.8	1.2	4	1.0	1.3
(21-02-26 16:31:15)	171204_FF31496	155.6	0.7	149.9	0.6	4	-5.7	-3.7
(21-02-26 16:31:15)	171128_FA01477	113.4	0.3	110.9	0.7	4	-2.4	-2.2
(21-02-26 16:31:15)	180318_FF30491	188.9	0.6	180.6	1.0	4	-8.3	-4.4
(21-02-26 16:31:15)	181128_FF61471	104.2	0.7	103.2	1.0	4	-1.1	-1.0
(21-03-03 04:35:30)	171122_FA02785	50.3	0.8	54.6	1.4	4	4.3	8.5
(21-03-03 04:35:30)	171123_FA02789	93.7	0.7	94.0	1.3	4	0.4	0.4
(21-03-03 04:35:30)	201207_FB03887	30.2	1.1	37.2	0.8	4	7.0	23.0

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-02-25 18:27:00)	171201_FA02773	0.2	0.3	10.2	0.3	3	10.0	NA
(21-03-03 04:35:30)	160622_FB03911	310.5	1.4	290.8	0.3	4	-19.7	-6.4

Methane Comparisons

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

Table 12 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 CPT data acquisition system. The standards used for the calibration of the CPT instruments are shown in Table 8.

Table 12. Experimental details of CPT 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 Tables 21 and 22.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #3498-CFKADS2350
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
Station Analyser (CH_4, CO_2)	
Model, S/N	Picarro 2301 #923-CFADS2201
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
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 13. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3498-CFKADS2350 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-02-26 16:31:15)	171122_FA02788	1619.01	0.06	1619.82	0.05	4	0.81	0.05
(21-02-26 16:31:15)	171204_FF31496	1947.42	0.02	1947.72	0.04	4	0.30	0.02
(21-02-26 16:31:15)	171128_FA01477	1862.05	0.04	1862.57	0.04	4	0.52	0.03
(21-02-26 16:31:15)	180318_FF30491	1984.94	0.03	1985.28	0.05	4	0.34	0.02
(21-02-26 16:31:15)	181128_FF61471	1989.76	0.03	1989.97	0.04	4	0.21	0.01
(21-03-03 04:35:30)	171122_FA02785	1856.36	0.04	1856.88	0.06	4	0.53	0.03
(21-03-03 04:35:30)	171123_FA02789	1718.71	0.05	1719.45	0.04	4	0.74	0.04
(21-03-03 04:35:30)	201207_FB03887	1945.74	0.07	1946.10	0.06	4	0.36	0.02
(21-02-25 18:27:00)	171201_FA02773	1.36	0.27	4.60	0.07	3	3.24	NA
(21-03-03 04:35:30)	160622_FB03911	2352.46	0.02	2352.19	0.12	4	-0.27	-0.01
(21-11-17 11:53:00)	180318_FF61491	1973.01	0.06	1973.67	0.01	3	0.66	0.03
(21-11-17 12:18:40)	160622_FA02479	2191.26	0.08	2191.99	0.03	3	0.73	0.03
(21-11-17 12:44:00)	210927_FF61508	1789.88	0.04	1790.45	0.02	3	0.57	0.03
(21-11-17 13:09:00)	171124_FA01467	1805.75	0.06	1806.46	0.01	3	0.71	0.04
(21-11-17 13:34:00)	171123_FA02770	1905.99	0.08	1906.65	0.02	3	0.66	0.03
(22-01-31 00:00:00)	180318_FF61491	1973.01	0.00	1974.07	0.20	2	1.06	0.05
(22-01-31 00:00:00)	160622_FA02479	2191.26	0.03	2192.35	0.09	2	1.09	0.05
(22-01-31 00:00:00)	210927_FF61508	1789.88	0.01	1790.77	0.02	2	0.89	0.05
(22-01-31 00:00:00)	171124_FA01467	1805.75	0.03	1806.81	0.01	2	1.06	0.06
(22-01-31 00:00:00)	171123_FA02770	1905.99	0.03	1907.00	0.02	2	1.01	0.05

Table 14. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #923-CFADS2201 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-02-26 16:31:15)	171122_FA02788	1619.01	0.06	1618.35	0.30	4	-0.66	-0.04
(21-02-26 16:31:15)	171204_FF31496	1947.42	0.02	1947.23	0.50	4	-0.19	-0.01
(21-02-26 16:31:15)	171128_FA01477	1862.05	0.04	1862.34	0.35	4	0.29	0.02
(21-02-26 16:31:15)	180318_FF30491	1984.94	0.03	1985.45	0.32	4	0.51	0.03
(21-02-26 16:31:15)	181128_FF61471	1989.76	0.03	1990.29	0.23	4	0.53	0.03
(21-03-03 04:35:30)	171122_FA02785	1856.36	0.04	1856.40	0.17	4	0.04	0.00
(21-03-03 04:35:30)	171123_FA02789	1718.71	0.05	1718.76	0.26	4	0.05	0.00
(21-03-03 04:35:30)	201207_FB03887	1945.74	0.07	1946.39	0.24	4	0.65	0.03
(21-02-25 18:27:00)	171201_FA02773	1.36	0.27	-1.03	0.55	3	-2.39	NA
(21-03-03 04:35:30)	160622_FB03911	2352.46	0.02	2353.85	0.18	4	1.39	0.06
(21-11-27 18:57:15)	180318_FF61491	1973.01	0.06	1972.22	0.81	4	-0.79	-0.04
(21-11-27 19:07:45)	160622_FA02479	2191.26	0.08	2191.54	0.91	4	0.28	0.01

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-11-27 19:17:45)	210927_FF61508	1789.88	0.04	1790.48	0.39	4	0.60	0.03
(21-11-27 19:27:45)	171124_FA01467	1805.75	0.06	1807.01	0.49	4	1.26	0.07
(21-11-27 19:37:45)	171123_FA02770	1905.99	0.08	1906.67	0.21	4	0.68	0.04

Carbon Dioxide Comparisons

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

Table 15 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 CPT data acquisition system. The standards used for the calibration of the CPT instruments are shown in Table 8.

Table 15. Experimental details of CPT 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 Tables 21 and 22.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #3498-CFKADS2350
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
Station Analyser (CO, CO_2)	
Model, S/N	Picarro G2302 #835-CKADS2026
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
Station Analyser (CH_4, CO_2)	
Model, S/N	Picarro G2301 #923-CFADS2201
Principle	CRDS
Drying system	Cryogenic trap (-40°C)
Comparison procedures	WCC-Empa TS were connected to spare calibration gas ports.
Connection	

Results

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

Table 16. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3498-CFKADS2350 instrument (AL) with the WCC-Empa TS (February and March 2021: WMO-X2007; November 2021 and January 2022: WMO-X2019 CO_2 scale).*

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(21-02-26 16:31:15)	171122_FA02788	337.12	0.01	337.12	0.01	4	0.00	0.00
(21-02-26 16:31:15)	171204_FF31496	428.35	0.01	428.33	0.01	4	-0.02	0.00
(21-02-26 16:31:15)	171128_FA01477	408.40	0.01	408.37	0.03	4	-0.03	-0.01
(21-02-26 16:31:15)	180318_FF30491	419.97	0.02	419.94	0.00	4	-0.04	-0.01
(21-02-26 16:31:15)	181128_FF61471	401.70	0.01	401.69	0.01	4	-0.01	0.00
(21-03-03 04:35:30)	171122_FA02785	408.40	0.01	408.26	0.01	4	-0.14	-0.03
(21-03-03 04:35:30)	171123_FA02789	391.54	0.03	391.55	0.01	4	0.01	0.00
(21-03-03 04:35:30)	201207_FB03887	413.30	0.06	413.31	0.07	4	0.02	0.00
(21-02-25 18:27:00)	171201_FA02773	0.33	0.04	0.49	0.01	3	0.16	NA
(21-03-03 04:35:30)	160622_FB03911	427.13	0.01	427.11	0.00	4	-0.02	0.00
(21-11-17 11:53:00)	180318_FF61491	418.55	0.03	418.37	0.02	3	-0.18	-0.04
(21-11-17 12:18:40)	160622_FA02479	427.85	0.05	427.73	0.01	3	-0.12	-0.03
(21-11-17 12:44:00)	210927_FF61508	411.54	0.04	411.42	0.01	3	-0.12	-0.03
(21-11-17 13:09:00)	171124_FA01467	397.21	0.02	397.11	0.01	3	-0.10	-0.03
(21-11-17 13:34:00)	171123_FA02770	404.27	0.02	404.18	0.01	3	-0.09	-0.02
(22-01-31 00:00:00)	180318_FF61491_2	418.55	0.03	418.59	0.00	2	0.04	0.01
(22-01-31 00:00:00)	160622_FA02479_2	427.85	0.05	427.90	0.02	2	0.05	0.01
(22-01-31 00:00:00)	210927_FF61508_2	411.54	0.04	411.53	0.02	2	-0.01	0.00
(22-01-31 00:00:00)	171124_FA01467_2	397.21	0.02	397.21	0.00	2	0.00	0.00
(22-01-31 00:00:00)	171123_FA02770_2	404.27	0.02	404.30	0.01	2	0.04	0.01

Table 17. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2301 #923-CFADS2201 instrument (AL) with the WCC-Empa TS (February and March 2021: WMO-X2007; November 2021: WMO-X2019 CO_2 scale).*

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(21-02-26 16:31:15)	171122_FA02788	337.12	0.01	337.11	0.07	4	-0.02	-0.01
(21-02-26 16:31:15)	171204_FF31496	428.35	0.01	428.48	0.05	4	0.13	0.03
(21-02-26 16:31:15)	171128_FA01477	408.40	0.01	408.58	0.12	4	0.18	0.04
(21-02-26 16:31:15)	180318_FF30491	419.97	0.02	420.28	0.14	4	0.31	0.07
(21-02-26 16:31:15)	181128_FF61471	401.70	0.01	401.97	0.14	4	0.26	0.06
(21-03-03 04:35:30)	171122_FA02785	408.40	0.01	408.29	0.06	4	-0.10	-0.02
(21-03-03 04:35:30)	171123_FA02789	391.54	0.03	391.58	0.14	4	0.04	0.01

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(21-03-03 04:35:30)	201207_FB03887	413.30	0.06	413.55	0.15	4	0.25	0.06
(21-02-25 18:27:00)	171201_FA02773	0.33	0.04	2.31	0.10	3	1.98	NA
(21-03-03 04:35:30)	160622_FB03911	427.13	0.01	427.45	0.19	4	0.32	0.07
(21-11-27 18:57:15)	180318_FF61491	418.55	0.03	418.49	0.10	4	-0.06	-0.01
(21-11-27 19:07:45)	160622_FA02479	427.85	0.05	427.85	0.13	4	0.00	0.00
(21-11-27 19:17:45)	210927_FF61508	411.54	0.04	411.54	0.03	4	0.00	0.00
(21-11-27 19:27:45)	171124_FA01467	397.21	0.02	397.16	0.09	4	-0.05	-0.01
(21-11-27 19:37:45)	171123_FA02770	404.27	0.02	404.31	0.17	4	0.04	0.01

Table 18. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2302 #835-CKADS2026 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 (%)
(21-02-26 16:31:15)	171122_FA02788	337.12	0.01	337.08	0.03	4	-0.04	-0.01
(21-02-26 16:31:15)	171204_FF31496	428.35	0.01	428.32	0.04	4	-0.03	-0.01
(21-02-26 16:31:15)	171128_FA01477	408.41	0.01	408.36	0.05	4	-0.05	-0.01
(21-02-26 16:31:15)	180318_FF30491	420.00	0.00	419.94	0.03	4	-0.06	-0.01
(21-02-26 16:31:15)	181128_FF61471	401.71	0.00	401.68	0.04	4	-0.02	0.00
(21-03-03 04:35:30)	171122_FA02785	408.30	0.00	408.25	0.04	4	-0.05	-0.01
(21-03-03 04:35:30)	171123_FA02789	391.55	0.00	391.54	0.02	4	-0.01	0.00
(21-03-03 04:35:30)	201207_FB03887	413.25	0.01	413.28	0.06	4	0.03	0.01
(21-02-25 18:27:00)	171201_FA02773	0.29	0.03	0.35	0.02	3	0.06	NA
(21-03-03 04:35:30)	160622_FB03911	427.12	0.01	427.10	0.03	4	-0.01	0.00
(21-03-03 04:35:30)	160622_FB03911	427.12	0.01	427.10	0.03	4	-0.01	0.00

Determination of the water vapour interference (Picarro G2401 #3498-CFKADS2350)

The water vapour correction function of the Picarro G2401 #3498-CFKADS2350 instrument was determined during the audit on 18 November 2021 at CPT according to the method described by Rella et al. (2013) (see Figure 32). It is recommended that this function is confirmed in at least yearly intervals.

Carbon monoxide is only reported as a water vapour corrected mole fraction by the Picarro G2401 instrument. If the correction for water vapour spectroscopic cross-talk and dilution was implemented in the instrument correctly, the ratio of COcorr/COdry is equal to 1 over the entire water vapour range. This was not the case, which indicates that the implemented water vapour correction for CO is not appropriate. This is frequently observed (Zellweger et al., 2019), and therefore, drying of the air as implement at CPT, is recommended.

The following functions were obtained to compensate for the humidity interference for CO_2 and CH_4:

$CO_2(dry) = CO_2(wet) / (1 – 0.015300* H_{rep} + 0.000059* H_{rep}^2)$

$CH_4(dry) = CH_4 (wet) / (1 – 0.011966* H_{rep} – 0.000047 * H_{rep}^2)$

Where H_{rep} corresponds to the Picarro reported water mixing ratio in %.

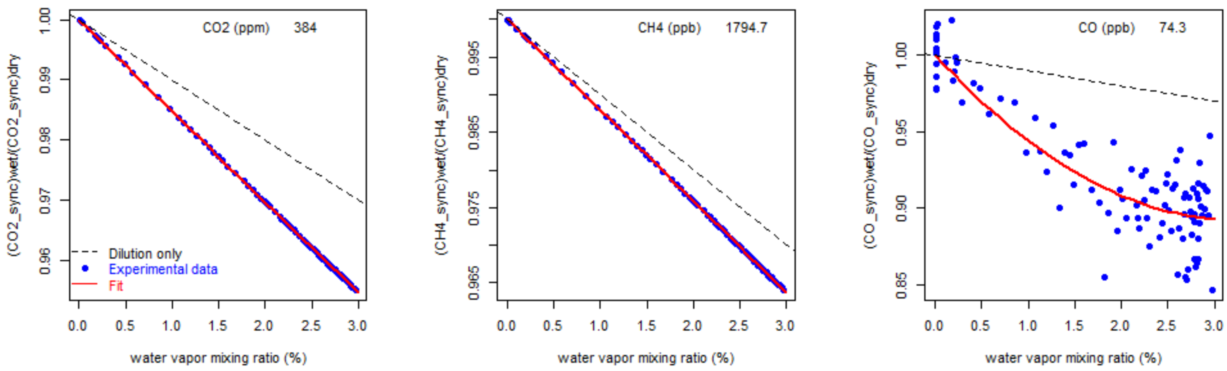

Figure 32. *Quadratic fits for the CPT Picarro G2401 #3498-CFKADS2350 instrument of CO_2wet/CO_2dry, CH_4wet/CH_4dry and COcorr/COdry vs. H_2O mixing ratios.*

The Picarro built-in internal water vapour correction does not sufficiently account for the influence of H_2O on the spectroscopy, as shown in Figure 33. Significant deviations were observed for all parameters. Water vapour levels after the cryogenic trap are low, and therefore, a bias for CO is not expected when the systems is operated using a dryer. Nevertheless, the correction has to be still applied for CO_2 and CH_4 to reach the WMO/GAW network compatibility goals.

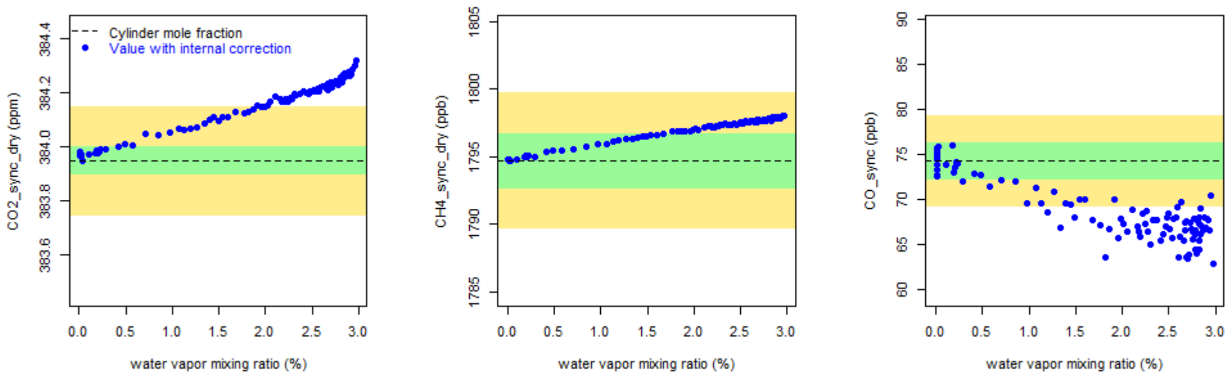

Figure 33. *H_2O dependency for CO_2, CH_4 and CO of a working tank measured by the CPT Picarro G2401 #3498-CFKADS2350. The blue dots are internally corrected values measured by the Picarro G2401. The green and yellow areas correspond to the WMO network compatibility and extended network compatibility goals.*

WCC-Empa Traveling Standards

Ozone

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

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

WCC-Empa TS: Thermo Scientific 49i-PS #1171430027, BKG 0.0, 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 34). 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)).

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

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

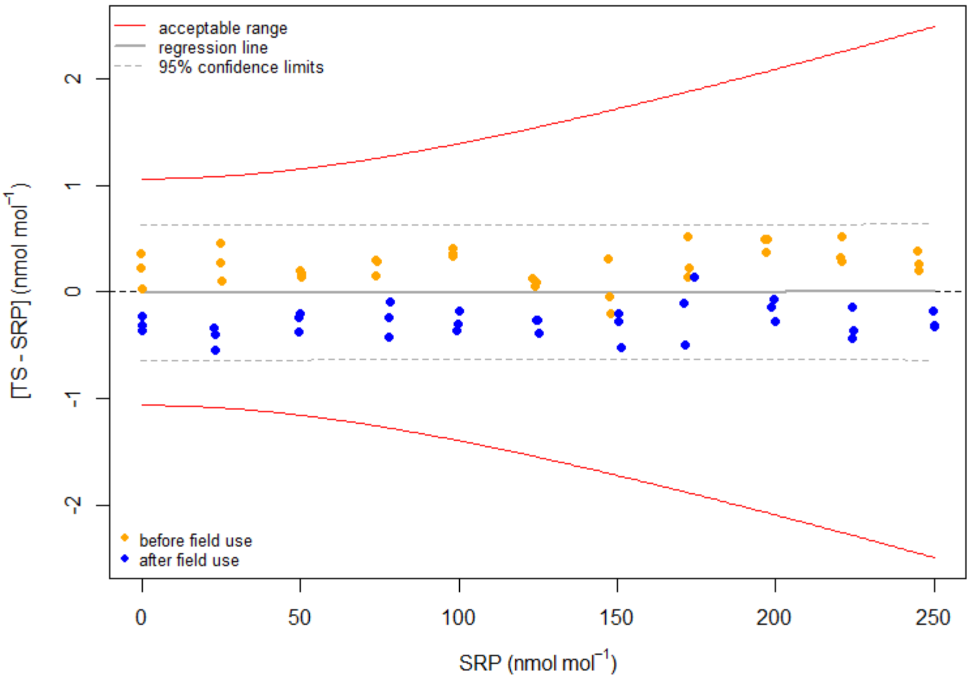

Figure 34. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

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})
2021-10-05	1	0	0.12	0.27	0.15	0.14
2021-10-05	1	75	74.19	0.14	74.48	0.16
2021-10-05	1	125	123.97	0.37	124.03	0.15
2021-10-05	1	50	50.36	0.22	50.54	0.14
2021-10-05	1	195	197.15	0.42	197.65	0.09
2021-10-05	1	220	220.54	0.42	220.86	0.17
2021-10-05	1	25	24.88	0.20	25.33	0.10
2021-10-05	1	150	147.81	0.33	147.61	0.14
2021-10-05	1	100	98.31	0.55	98.72	0.10
2021-10-05	1	175	172.55	0.29	172.78	0.13
2021-10-05	1	245	245.10	0.52	245.36	0.17
2021-10-05	2	75	73.88	0.60	74.18	0.10
2021-10-05	2	145	147.26	0.27	147.57	0.18
2021-10-05	2	25	24.91	0.23	25.19	0.15
2021-10-05	2	195	197.01	0.38	197.39	0.15
2021-10-05	2	170	172.07	0.27	172.58	0.13
2021-10-05	2	100	98.23	0.20	98.60	0.09
2021-10-05	2	50	50.35	0.37	50.49	0.10
2021-10-05	2	0	-0.12	0.23	0.11	0.11
2021-10-05	2	125	124.44	0.31	124.54	0.12
2021-10-05	2	220	220.72	0.23	221.01	0.24
2021-10-05	2	245	244.93	0.27	245.13	0.14
2021-10-05	3	75	73.89	0.31	74.04	0.05
2021-10-05	3	25	25.15	0.56	25.26	0.06
2021-10-05	3	50	50.03	0.25	50.23	0.10
2021-10-05	3	100	98.05	0.30	98.38	0.06
2021-10-05	3	195	196.49	0.30	196.98	0.12
2021-10-05	3	125	123.05	0.20	123.18	0.13
2021-10-05	3	170	172.42	0.37	172.56	0.11
2021-10-05	3	145	147.40	0.19	147.36	0.24
2021-10-05	3	0	-0.07	0.27	0.28	0.11
2021-10-05	3	220	220.79	0.57	221.31	0.61
2021-10-05	3	245	244.82	0.24	245.21	0.16
2022-07-13	4	250	250.08	0.31	249.77	0.14
2022-07-13	4	80	77.84	0.35	77.43	0.22
2022-07-13	4	100	100.12	0.34	99.95	0.15
2022-07-13	4	125	124.99	0.35	124.73	0.13
2022-07-13	4	225	224.30	0.31	224.16	0.16
2022-07-13	4	150	150.31	0.28	150.11	0.26
2022-07-13	4	0	0.20	0.34	-0.16	0.09
2022-07-13	4	200	198.65	0.28	198.51	0.14
2022-07-13	4	25	22.91	0.19	22.58	0.16
2022-07-13	4	170	171.41	0.40	170.92	0.29
2022-07-13	4	50	49.74	0.46	49.51	0.16
2022-07-13	5	175	174.18	0.29	174.33	0.13

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-07-13	5	150	150.50	0.23	150.22	0.13
2022-07-13	5	25	23.15	0.14	22.74	0.19
2022-07-13	5	100	99.19	0.34	98.84	0.10
2022-07-13	5	225	224.05	0.30	223.62	0.08
2022-07-13	5	200	199.91	0.19	199.63	0.08
2022-07-13	5	80	77.83	0.42	77.59	0.20
2022-07-13	5	125	125.23	0.30	124.85	0.16
2022-07-13	5	250	249.86	0.29	249.54	0.26
2022-07-13	5	50	49.62	0.28	49.25	0.30
2022-07-13	5	0	-0.05	0.15	-0.28	0.12
2022-07-13	6	80	78.23	0.27	78.14	0.17
2022-07-13	6	100	99.68	0.17	99.38	0.18
2022-07-13	6	50	49.89	0.27	49.69	0.21
2022-07-13	6	170	171.12	0.42	171.02	0.37
2022-07-13	6	250	249.46	0.26	249.29	0.12
2022-07-13	6	200	199.27	0.28	199.20	0.13
2022-07-13	6	0	0.02	0.29	-0.29	0.20
2022-07-13	6	150	151.37	0.40	150.85	0.51
2022-07-13	6	225	224.57	0.26	224.21	0.17
2022-07-13	6	25	23.17	0.31	22.63	0.24
2022-07-13	6	125	124.49	0.26	124.23	0.14

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) of the WMO/GAW programme for Carbon Monoxide, Carbon Dioxide and Methane. NOAA was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL through travelling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

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

The CO_2 values of the first TS batch were converted to the WMO-X2007 scale by dividing with a factor of 1.00049 (WCC-Empa internal relationship between the WMO-X2007 and WMO-X2019 scales) for the comparison with CPT.

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

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy).
CO and N_2O: LGR 913-0015 (Mid-IR Spectroscopy).
CO, CO_2 and CH_4: Picarro G2401 (Cavity Ring-Down Spectroscopy).

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

For N_2O, data of the LGR 913-0015 was used, because this instrument shows less cross-sensitivity to CO compared to the Aerodyne mini-cw.

Table 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 22, and Figures 35 to 39 show the analysis of the TS over time.

Table 20. *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 21. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, and N_2O. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, and (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
160622_FB03911	600	2352.46	0.02	427.34	0.01	330.34	0.05	330.29	0.01
171122_FA02785	1410	1856.36	0.04	408.49	0.02	341.63	0.02	341.8	0.02
171122_FA02788	1800	1619.01	0.06	337.29	0.01	283.54	0.01	283.92	0.15
171123_FA02789	1080	1718.71	0.05	391.73	0.03	316.48	0.04	316.6	0.03
171128_FA01477	1780	1862.05	0.04	408.6	0.01	337.33	0.01	337.39	0.01
171201_FA02773	120	1.36	0.27	0.33	0.04	0.51	0.04	6.38	1.06
171204_FF31496	1760	1947.42	0.02	428.56	0.01	335.87	0.02	335.88	0.03
180318_FF30491	1630	1984.94	0.03	420.18	0.02	330.63	0.03	330.64	0.02
181128_FF61471	1700	1989.76	0.03	401.9	0.01	333.07	0.02	333.16	0.01
201207_FB03887	1410	1945.74	0.07	413.5	0.06	329.74	0.01	330.03	0.07
160622_FA02479	1310	2191.26	0.08	427.85	0.05	333.08	0.05	333.08	0.02
171123_FA02770	1990	1905.99	0.08	404.27	0.02	325.84	0.06	325.93	0.01
171124_FA01467	1210	1805.75	0.06	397.21	0.02	325.72	0.04	325.73	0.04
180318_FF61491	1000	1973.01	0.06	418.55	0.03	330.65	0.03	330.64	0.03
210927_FF61508	2140	1789.88	0.04	411.54	0.04	337.4	0.06	337.55	0.08

Table 22. *Calibration summary of the WCC-Empa travelling standards for CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, and (L) LGR.*

TS	Press. (psi)	CO (P) (nmol mol^{-1})	sd	CO (A) (nmol mol^{-1})	sd	CO (L) (nmol mol^{-1})	sd
160622_FB03911	600	310.5	1.36	309.76	0.8	308.78	0.62
171122_FA02785	1410	50.32	0.8	49.12	0.13	51.28	0.04
171122_FA02788	1800	71.87	0.63	70.81	0.1	71.47	0.03
171123_FA02789	1080	93.68	0.67	92.3	0.9	92.69	0.16
171128_FA01477	1780	113.38	0.27	111.65	0.14	112.08	0.07
171201_FA02773	120	0.16	0.26	0.58	0.68	0.04	0.2
171204_FF31496	1760	155.59	0.67	154.29	0.1	153.93	0.05
180318_FF30491	1630	188.88	0.64	187.44	0.29	186.77	0.06
181128_FF61471	1700	104.23	0.69	102.59	0.17	103.47	0.35
201207_FB03887	1410	30.2	1.11	28.36	0.23	31.71	0.44
160622_FA02479	16062	210.23	0.7	207.81	0.26	206.72	0.11
171123_FA02770	17112	118.04	1.23	115.75	0.85	115.45	0.69
171124_FA01467	17112	142.46	0.98	140.12	0.26	139.47	0.07
180318_FF61491	18031	282.12	1.26	279.35	0.87	278.04	0.73
210927_FF61508	21092	46.77	2.36	45.03	1.88	46.22	1.27

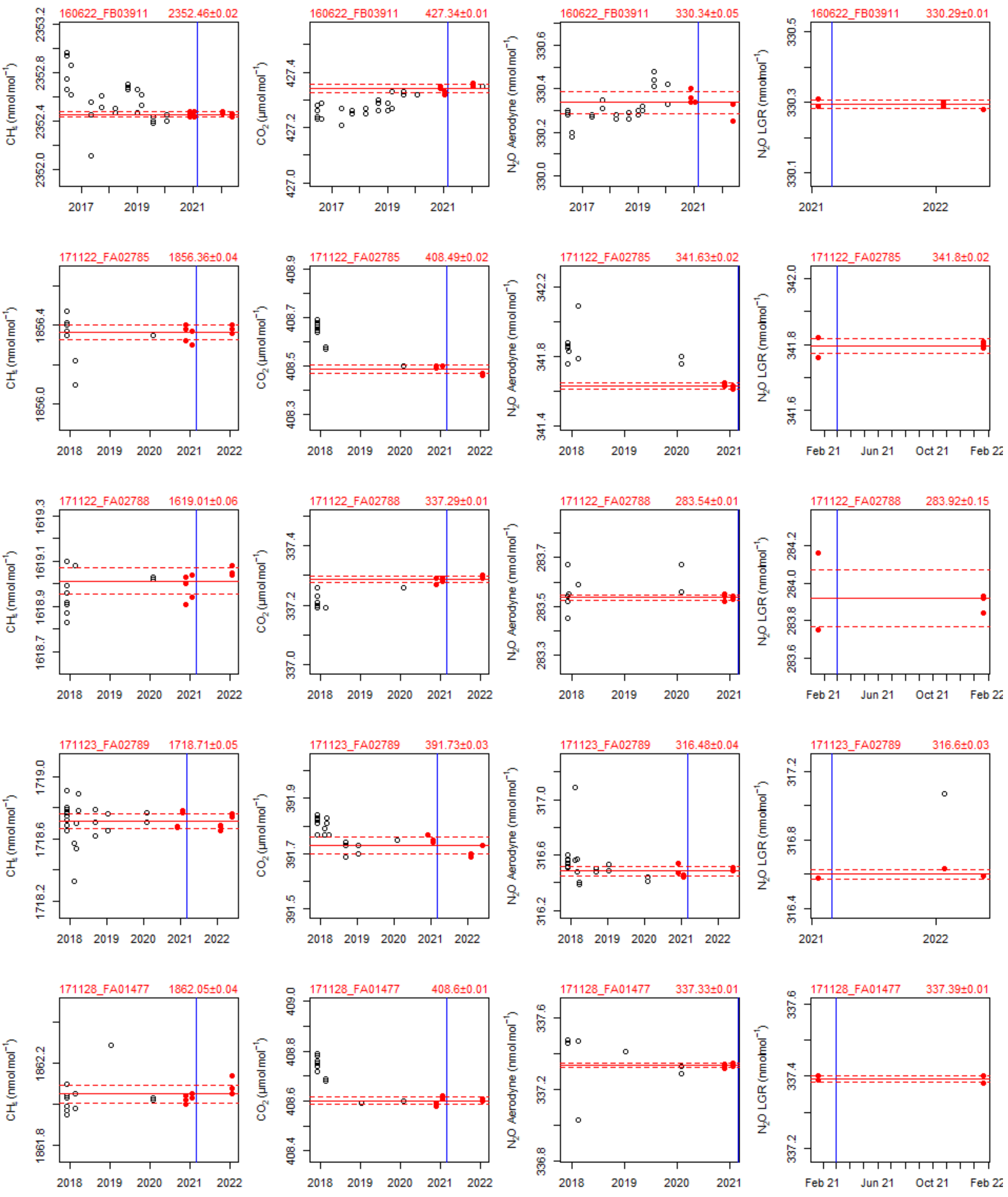

Figure 35. *Results of the WCC-Empa TS (1st batch) calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

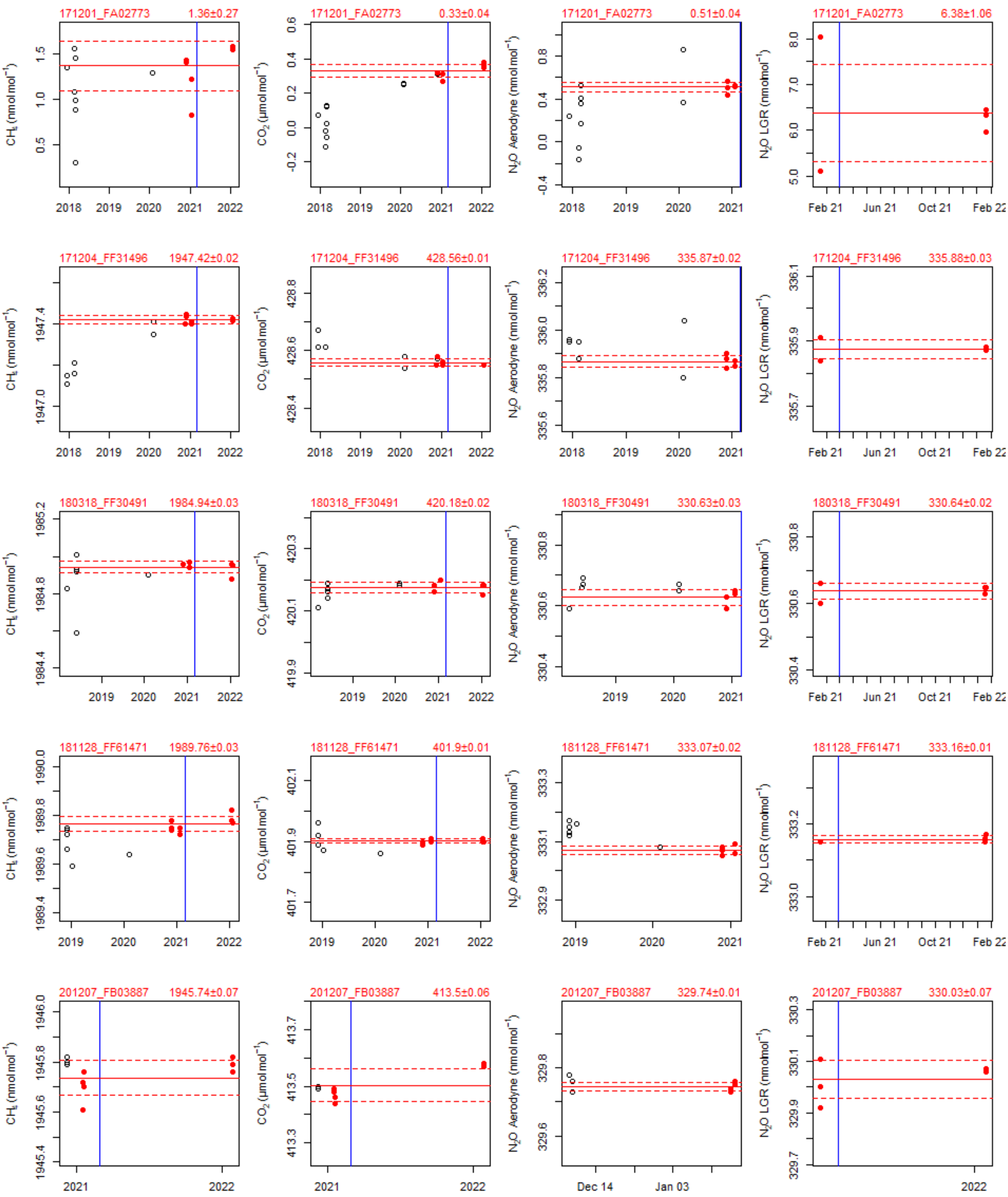

Figure 36. *Results of the WCC-Empa TS (1st batch) calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

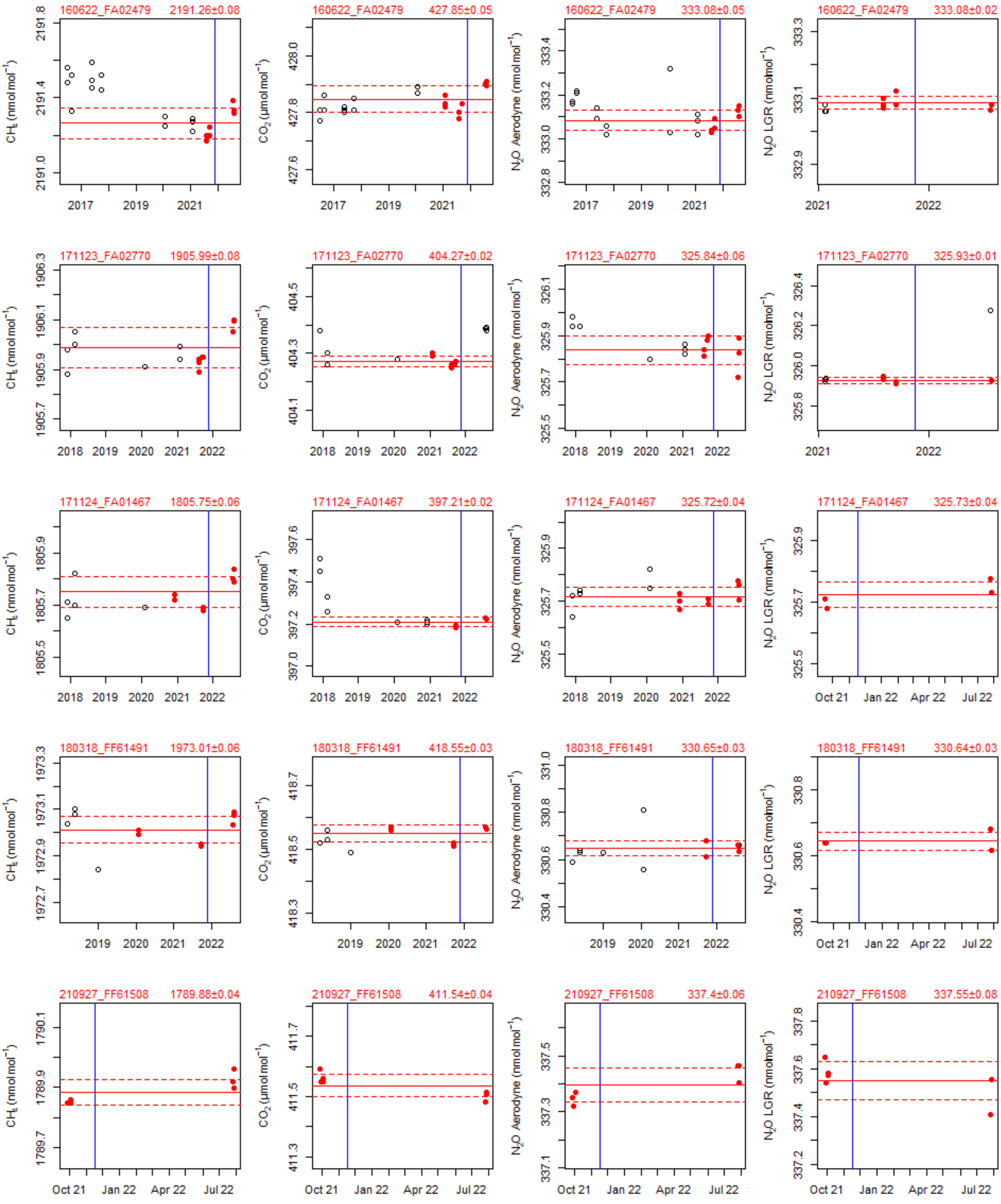

Figure 37. *Results of the WCC-Empa TS (2nd batch) calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

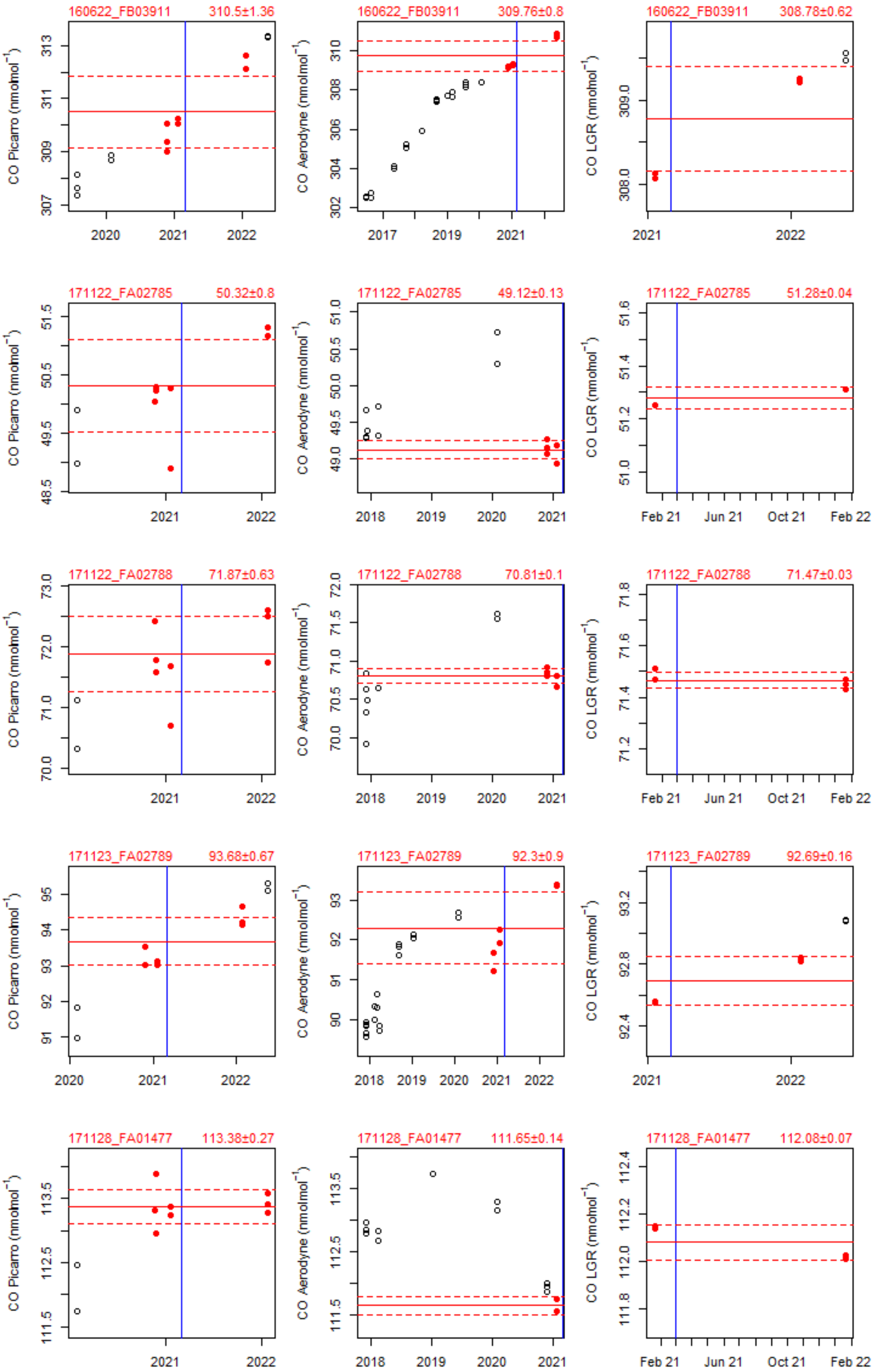

Figure 38. *Results of the WCC-Empa TS (1st batch) calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

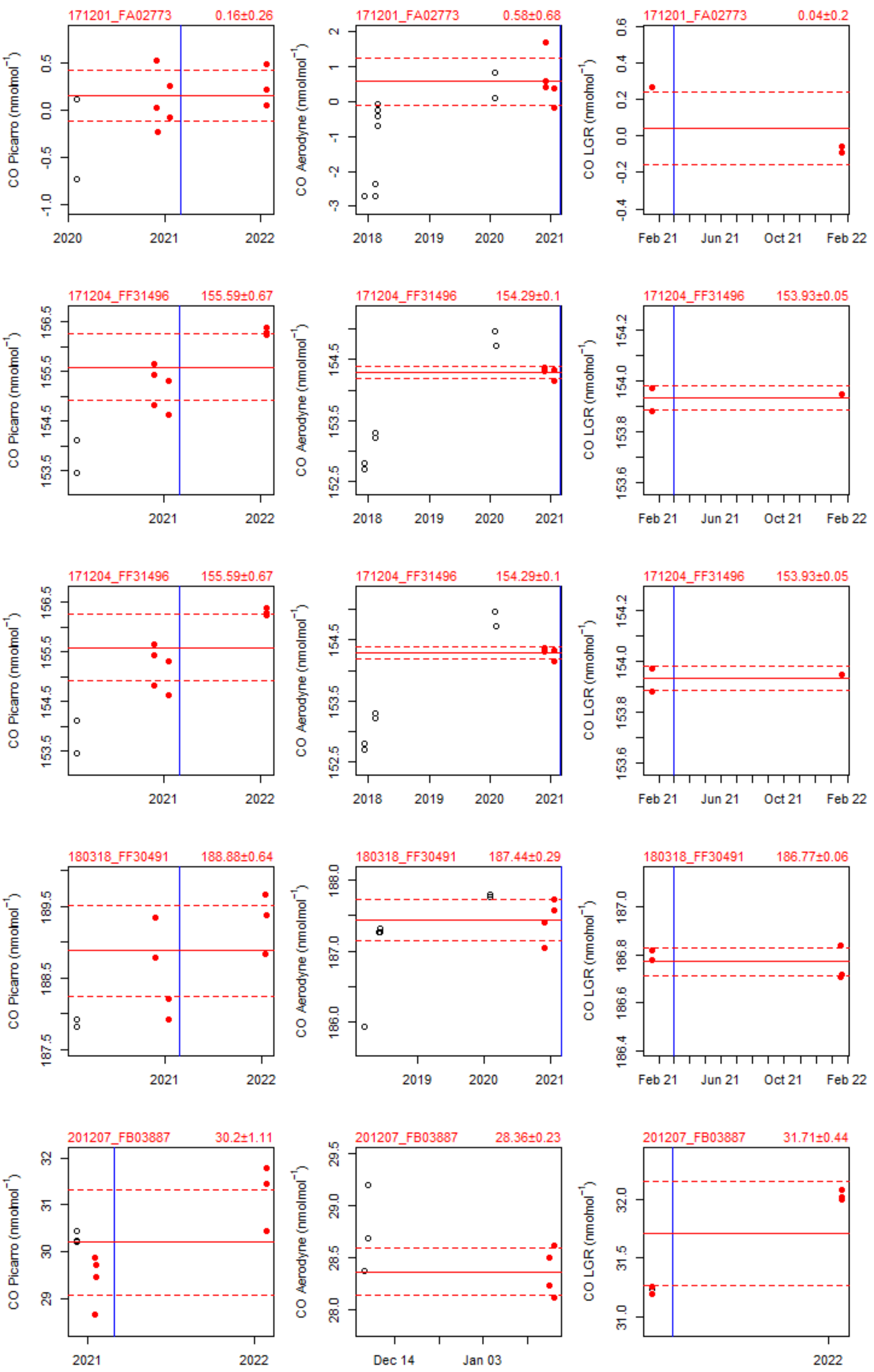

Figure 39. *Results of the WCC-Empa TS (1st batch) calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

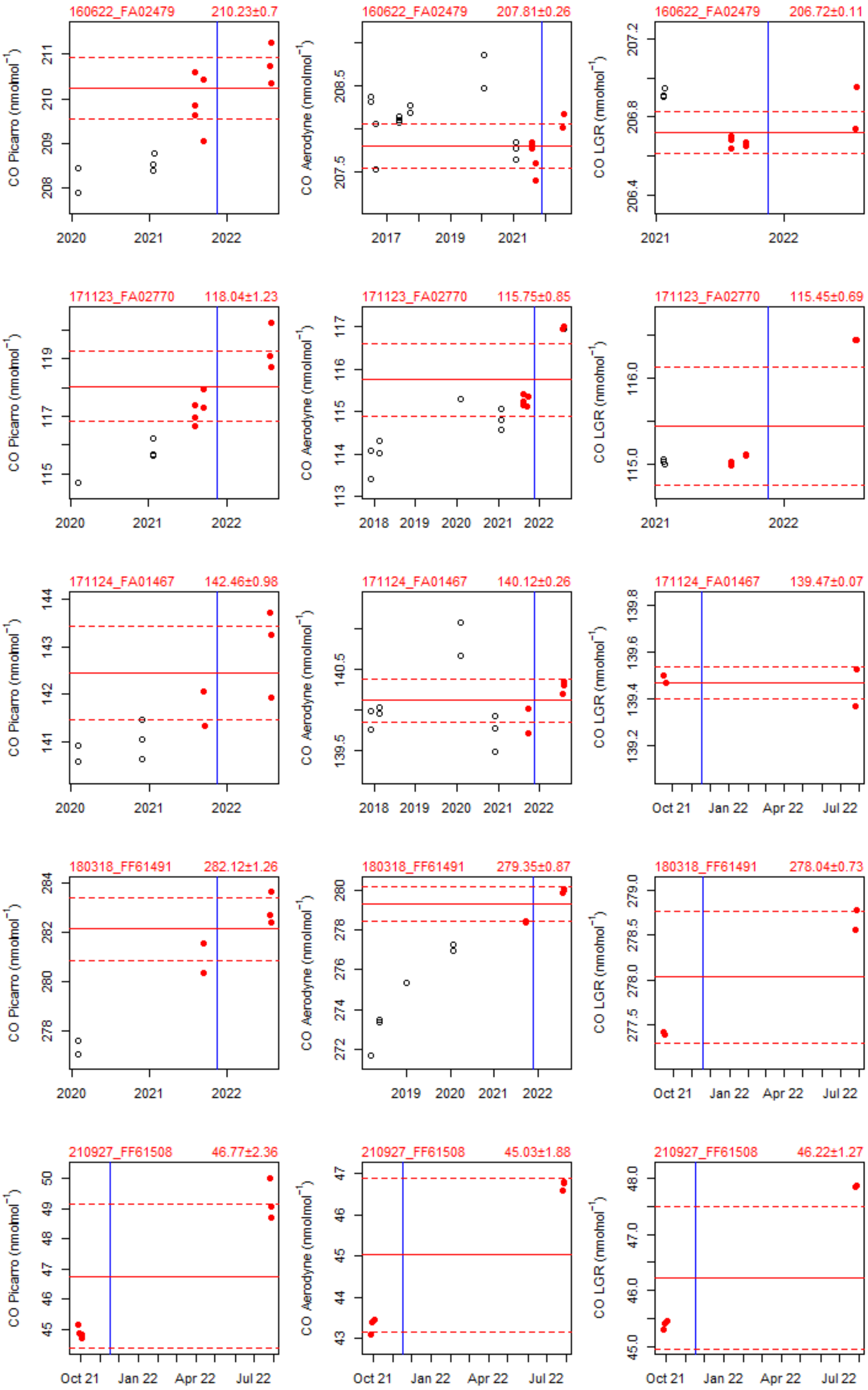

Figure 40. *Results of the WCC-Empa TS (2nd batch) calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH_4 and CO_2, the Picarro G2401 SN #617-CFKADS2001 was calibrated every 1445 min using one WCC-Empa TS as a working standard, and two TS as target tanks. The working standard was changed on 4 March 2022 due to low cylinder pressure. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 0.1 ppb for CH_4 and 0.04 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals.

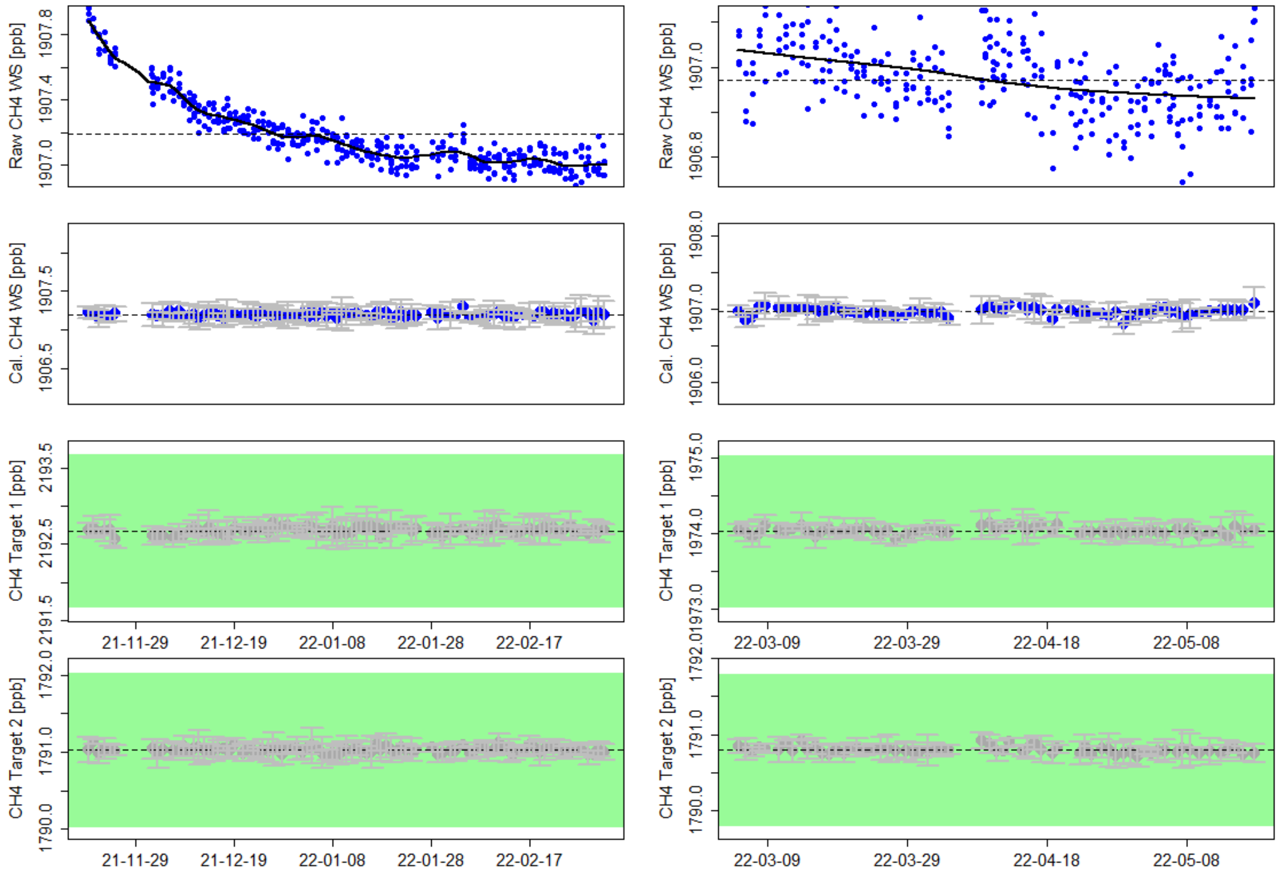

Figure 41. *CH_4 calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

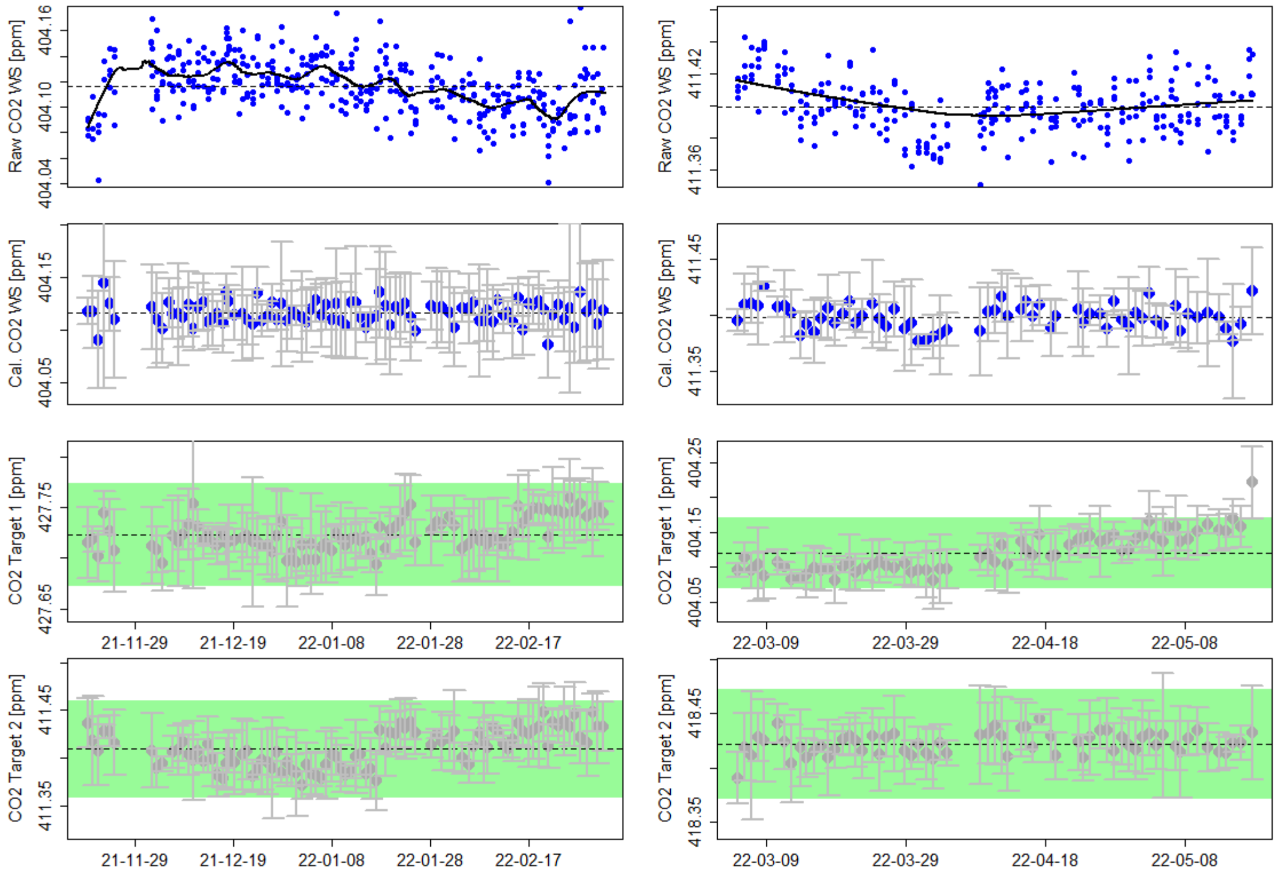

Figure 42. *CO_2 calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 1445 min with three WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

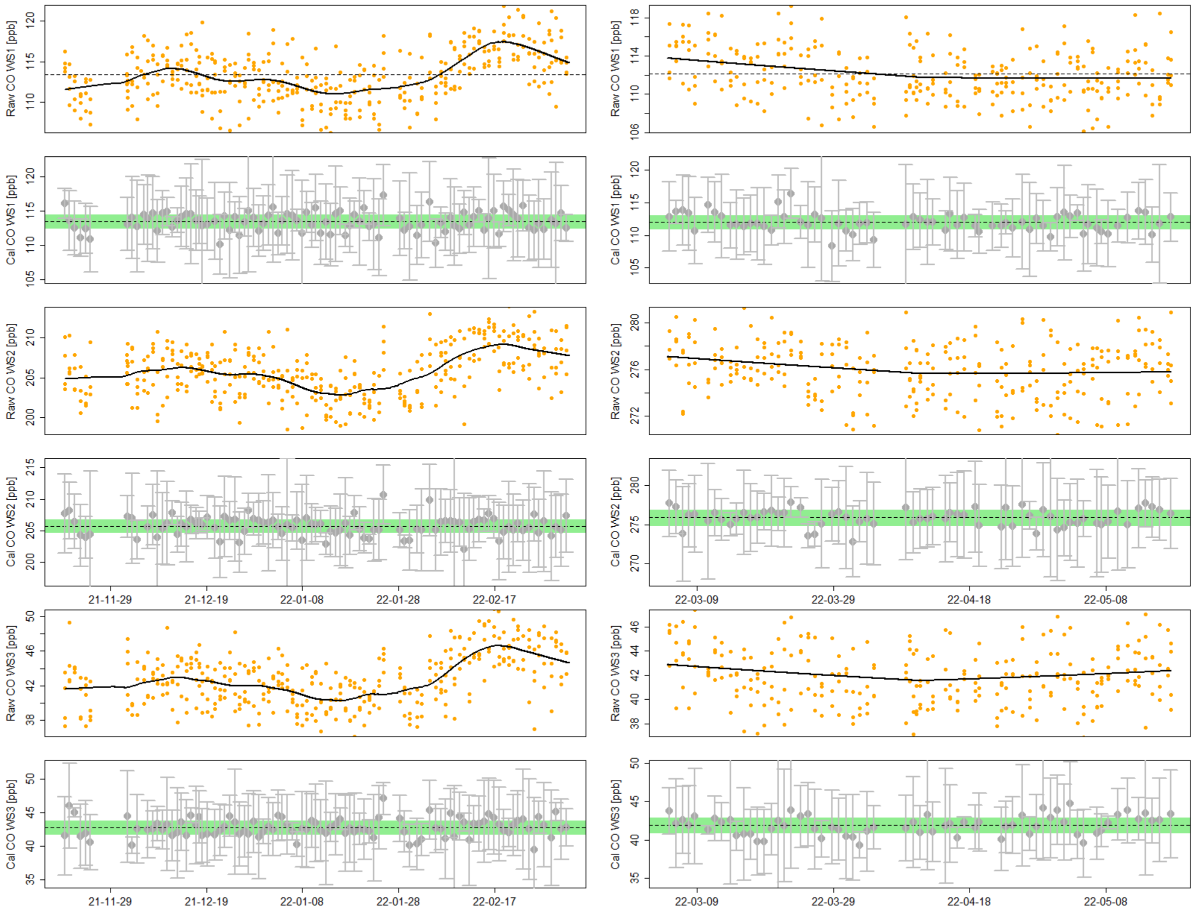

Figure 43. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

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LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
COEF	Coefficient
CPT	Cape Point GAW Station
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
FID	Flame Ionization Detection
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatography
GHG	Greenhouse Gases
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PI	Principle Investigator
SAWS	South African Weather Service
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