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

AT THE

REGIONAL GAW STATION
CHOLPON-ATA
KYRGYZSTAN
JUNE 2023

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The first WCC-Empa[1] system and performance audit at the Cholpon-Ata (CPA) regional GAW station, operated by Kyrgyz Hydromet, the hydrometeorology service under the ministry of emergency situation of the Kyrgyz Republic, was conducted from 26 to 29 June 2023 in accordance with the WMO/GAW quality assurance system (WMO, 2017). A list of all WCC-Empa audits and related audit reports is available from the GAW Empa website. The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Dr Martin Steinbacher	Empa, Dübendorf, QA/SAC Switzerland
Ms Begaim Alipova	Kyrgyz Hydromet, Head of the Air Pollution Observation Department
Ms Kanykei Suiunbekova	Kyrgyz Hydromet, Specialist of the Air Pollution Observation Department
Mr Argen Syiabekov	Kyrgyz Hydromet, Engineer 1st class
Ms Gulzat Ibrayeva	Kyrgyz Hydromet, Station Operator Cholpon-Ata

This report summarises the assessment of the Cholpon-Ata GAW station in general and of surface ozone, methane, carbon dioxide, and carbon monoxide in particular.

The report will be distributed to Kyrgyz Hydromet, the Cholpon-Ata station manager, the national focal point for GAW in the Kyrgyz Republic, and the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and made available on the WCC-Empa webpage.

The recommendations found in this report are categorised as minor, important and critical, and are accompanied by a priority (*** indicates high, ** medium and * low priority) and a proposed completion date.

Station management and operation

The station is operated and managed by Kyrgyz Hydromet. The station is manned by a station operator and administrative staff during the working hours of the observatory.

Surface ozone, carbon monoxide and greenhouse gas measurements were established in 2016 as part of the Capacity Building and Twinning for Climate Observing Systems (CATCOS) project, funded by the Swiss Agency for Development and Cooperation (SDC), with MeteoSwiss as the coordinating partner. Implementation was carried out by the CATCOS project team and QA/SAC Switzerland.

Station location and access

The Cholpon-Ata Lake Observatory (42.6369°N, 77.0675°E, 1613 m a.s.l.) is located about 2 km west of the village of Cholpon Ata (~12'000 inhabitants) on the northern shore of Lake Issyk-Kul, surrounded by the mountain ranges of eastern Kyrgyzstan. Basic meteorological measurements at the site began in 1928. Despite the proximity of human settlements, the regular air flow from Lake Issyk-Kul ensures that greenhouse gas measurements are representative of a geographically large area in the region. The site is suitable for a regional GAW station. Access by road is possible throughout the year. Further information is available from GAWSIS.

[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.

Station facilities and infrastructure

The Cholpon-Ata station has basic laboratory and office facilities: Kitchen and sanitation facilities are available. Internet access is available with sufficient bandwidth, and the instruments are connected to an Uninterruptable Power Supply (UPS). However, the remaining capacity of the UPS batteries is low. The laboratory is not air-conditioned, and the room temperature shows diurnal and seasonal variations. The installed equipment is not very sensitive to changes in laboratory temperature, and the facilities are sufficient to support the current measurement programme. However, more space and air conditioning will be required if the measurement programme is expanded.

> **Recommendation 1 (**, important, 2024)**
> *It is recommended to install an air conditioning system to minimise environmental influences on the measurements.*
>
> **Recommendation 2 (**, important, 2024)**
> *The UPS batteries need to be replaced. Alternatively, the purchase of a new UPS system should be considered.*

Measurement programme

The CPA GAW station hosts a small measurement programme of trace gases observations. An overview of the species measured is available from GAWSIS.

The information available on GAWSIS was reviewed as part of the audit. It was last updated in 2021, and the information was still largely up-to-date. However, more details (e.g. instrument characteristics) should be added, and the list of station contacts needs to be revised.

> **Recommendation 3 (**, important, ongoing)**
> *It is recommended to update GAWSIS annually or when major changes occur. Some of the reviewed information needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface (e.g. deletion of station contacts).*

Data submission

As of September 2023, the following CPA data within the scope of the audit have been submitted to the World Data Centres:

Kyrgyz Hydromet, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2016-2021).

Kyrgyz Hydromet, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2016-2022), CO_2 (2016-2022), CO (2016-2022)

Data shown in this report were accessed on 6 September 2023. Most data within the scope of the audit (CH_4, CO_2, CO) were submitted with a submission delay of less than one year. Most recent O_3 data (for 2022) were not yet submitted due to indications of a decline in instrument sensitivity. The continuation of this timely submission practice for CO_2, CH_4, and CO is recommended. A reprocessing of the O3 data and a resubmission is required.

Data evaluation continues to rely on the support of external partners, and is carried out partly through the twinning partnership between Kyrgyz Hydromet and QA/SAC Switzerland. Responsibility for data analysis and data ownership needs to be transferred to Kyrgyz Hydromet.

Recommendation 4 (*, critical, ongoing)**
Kyrgyz Hydromet staff need to be more involved in the data validation process. Kyrgyz Hydromet is also encouraged to actively use the available data for scientific purposes.

Data review

As part of the system audit, WDCRG and WDCGG were reviewed. Summary plots and a brief description of the findings are presented in the Appendix. The most critical issue found was the trend in the ozone time series, which is likely to be due to degradation of the ozone scrubber.

Recommendation 5 (*, critical, 2024)**
The ozone time series submitted to the WDCRG need to be withdrawn, re-analysed and resubmitted if corrections are possible.

Documentation

Information is recorded in electronic logbooks (ELOG). The electronic logbooks are stored locally on the data acquisition PC. While ELOG entries are transferred to Switzerland along with the data files, it was noted that no back-up was available at Kyrgyz Hydromet. Instrument manuals are available on site. The information reviewed was comprehensive and up to date.

Recommendation 6 (, important, 2024)**
An automatic transfer of the ELOG files to Kyrgyz Hydromet should be established as an off-site backup of the logbook entries.

Air inlet system

Ozone: The air inlet is located 10 m above ground on top of an inlet mast mounted on the roof of the station building. It is protected from rain by a downward facing Teflon filter holder to prevent from coarse dust and insects entering the tubing. The inlet line consists of a ~10 m long ¼" PFA tube that runs directly to the ozone instrument. The flow rate in the line of approximately 1 l/min is controlled by the ozone analyser. A PFTE filter (5 µm pore size) mounted on the backside of the analyser protects the instrument from fine dust. The residence time is approximately 10 seconds.

GHG and CO measurements: Same air inlet location as for ozone. The inlet line is protected from rain by a downward facing filter holder. The inlet line consists of a ~10 m long ¼" Synflex-1300 tubing connected directly to the instrument valve box. The flow rate in the line of approximately 5 l/min is controlled by an external pump. The instrument is protected against dust by a stainless steel (7 µm) inlet filter mounted just upstream of the valve box. The residence time is approximately 8 seconds.

A schematic overview of the installation is shown below.

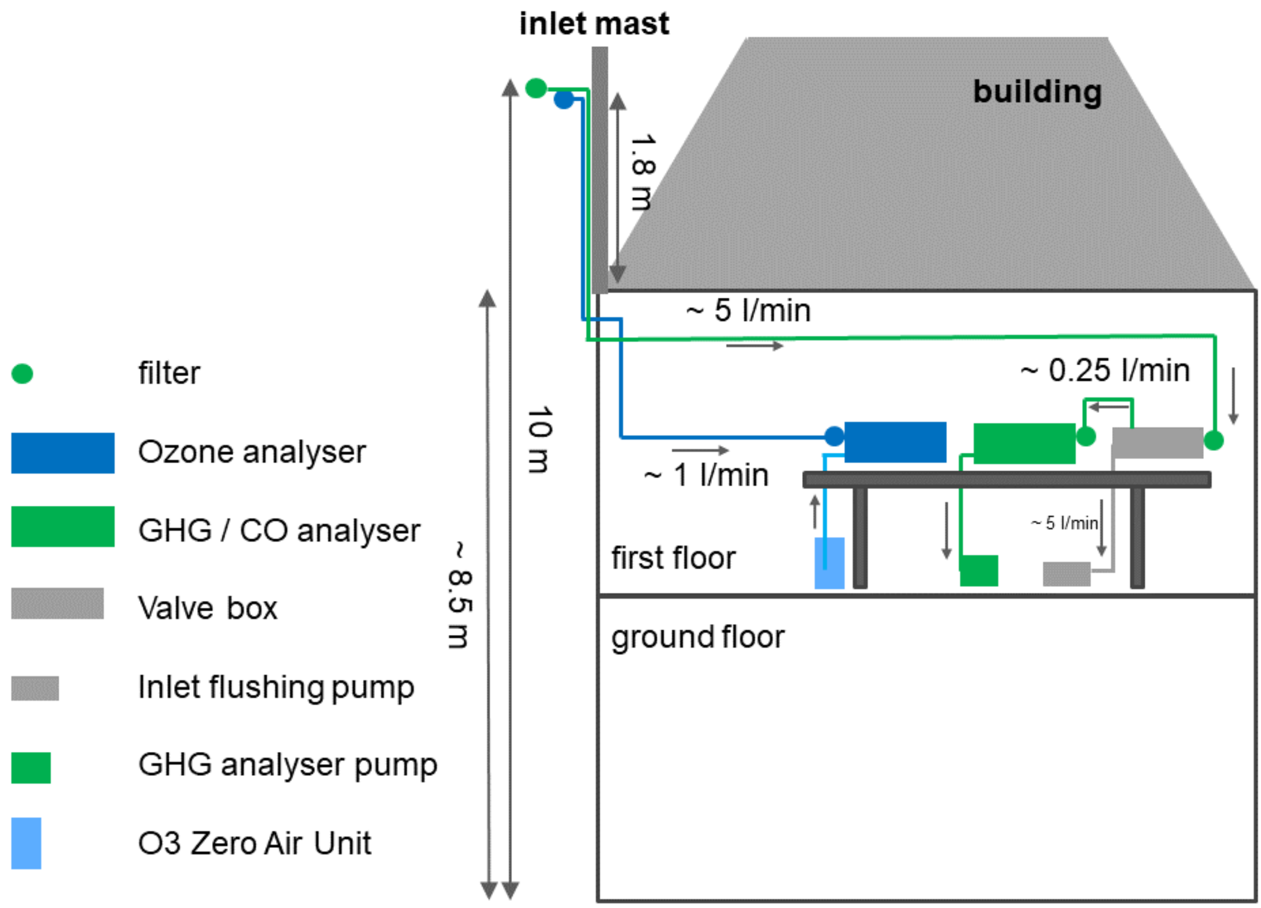

Figure 1. *Schematic of the of the CPA inlet design.*

The inlet systems are adequate in terms of material and residence time and no changes are required.

Data acquisition

Currently, data of the gaseous species are acquired as hourly text files with a time resolution of one minute using a commercial data acquisition system (Breitfuss GmbH; EasyComp and MKT/Anavis). These files contain all necessary ancillary information from the instruments, with the exception of the pressure sensor reading of the ozone instrument. Data transfer to Empa is operational. Automatic data transfer to Kyrgyz Hydromet has yet to be established.

> **Recommendation 7 (***, important, 2024)**
> *An automatic data transfer to Kyrgyz Hydromet should be established as an off-site backup of the data, which is a prerequisite for taking over the full data ownership and data processing by Kyrgyz Hydromet (see also recommendation 4).*

Surface ozone measurements

Surface ozone measurements at CPA were established in August 2016 as part of the CATCOS project (Phase 2), and continuous time series have been available since then.

Instrumentation. CPA is equipped with an ozone analyser (Thermo Scientific 49i) with an internal ozone source for instrument performance checks.

Standards. No ozone standard is available. The instrument was calibrated at WCC-Empa in 2016 prior to the installation at CPA, and no further calibrations have been performed since then until the current audit.

> **Recommendation 8 (***, important, 2024)**
> *It is recommended to purchase an ozone calibrator with traceability to the WMO/GAW ozone reference for regular checks of the instrument. The recommended interval for checking with an ozone calibrator is three months.*

Intercomparison (performance audit). The CPA analyser was compared to 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 to generate a random sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}.

The initial comparison showed that the CPA analyser read significantly lower than the WCC-Empa reference. Several instrument checks were carried out to determine the cause of the low readings and a faulty ozone scrubber was identified as the cause of the malfunction. The initial instrument checks also revealed that the pressure sensor of the CPA instrument was reading approximately 46 hPa above ambient pressure. WCC-Empa replaced the ozone scrubber and adjusted the pressure sensor, and a second comparison was made with the repaired instrument.

> **Recommendation 9 (***, critical, ongoing)**
> *The pressure sensor of the Thermo Scientific 49i should be compared to ambient pressure at least once a month. The pressure sensor must be disconnected or the instrument pump switched off during the comparison. The span must be adjusted if the difference exceeds 2 hPa. It is recommended that this is done when the ozone span is checked and that the readings and adjustments are recorded in the checklist that was provided by QA/SAC Switzerland.*

The results of the first and second comparison are summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data were collected using the WCC-Empa data acquisition system. The following equations characterise the instrument bias of and the remaining uncertainty after bias compensation. Uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). As the measurements refer to a conventionally agreed value of the ozone absorption cross section of 11.476x10^{-18} cm^2 molecule^{-1} (Hearn, 1961), the uncertainties reported below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #1304556621 (BKG 0.0 nmol mol^{-1}, SPAN 1.011), before ozone scrubber replacement and pressure sensor adjustment:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] - 0.86 nmol mol^{-1}) / 0.2306 (1)

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

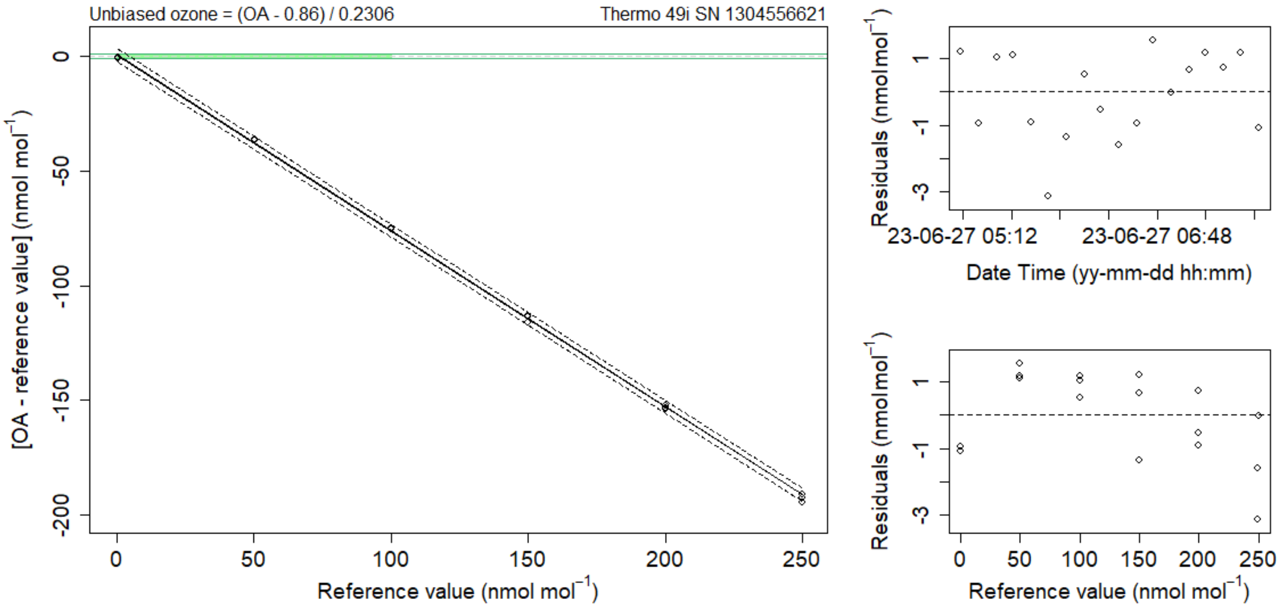

Figure 2. *Left: Bias of the CPA ozone analyser (Thermo Scientific 49i #1304556621, BKG -0.0 nmol mol^{-1}, COEF 1.011, initial condition, unrepaired) with respect to the SRP as a function of amount fraction. Each point represents the average of ten 40 second averages at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines 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 amount fraction (bottom).*

The result of the initial comparisons can be summarised as follows:

A large bias was observed due to the faulty ozone scrubber CPA ozone analyser. In addition, the pressure sensor of the CPA instrument read 46 hPa (5.5%) above ambient pressure. The CPA instrument read approximately 77% lower than the WCC-Empa reference. Most of the bias was due to the faulty ozone scrubber and only a small proportion could be explained by the bias of the pressure sensor.

The ozone scrubber was then replaced by WCC-Empa and the pressure sensor was adjusted to ambient pressure. To confirm the correct operation of the CPA instrument after the repair, a second comparison was made between the CPA analyser and the WCC-Empa TS. The result was as follows:

Thermo Scientific 49i #1304556621 (BKG 0.0 nmol mol^{-1}, SPAN 1.011), after ozone scrubber replacement and pressure sensor adjustment:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.00 nmol mol^{-1}) / 0.9998 (3)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.08e-05 * X_{O3}^2) (4)

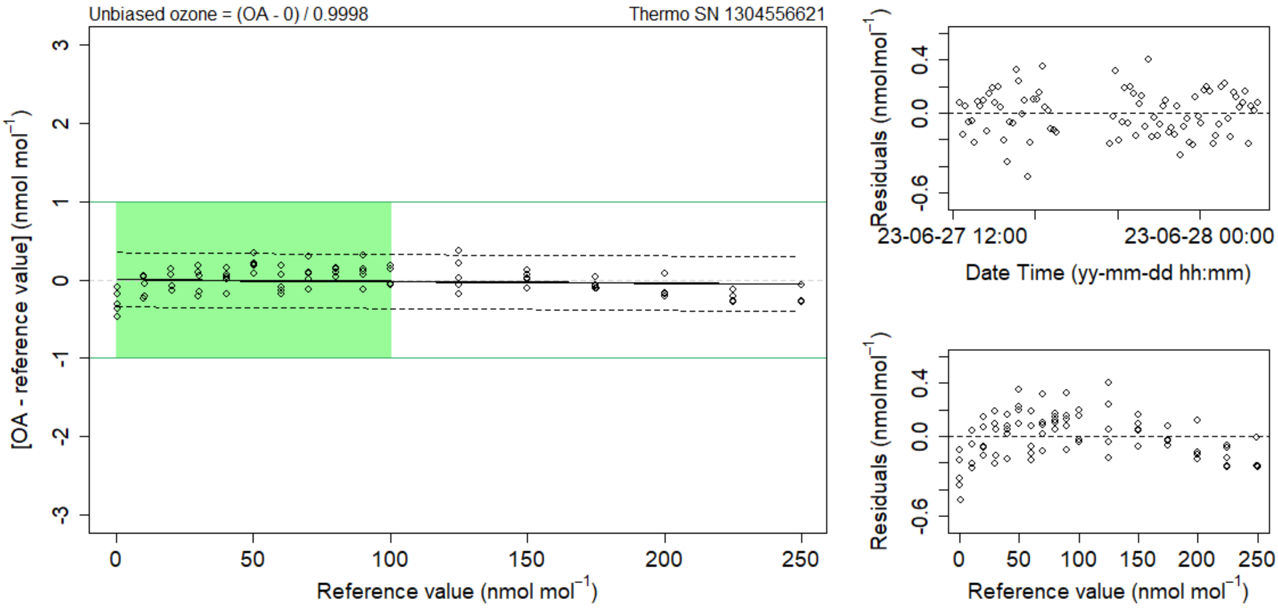

Figure 3. *Left: Bias of the CPA ozone analyser (Thermo Scientific 49i #1304556621, BKG -0.0 nmol mol^{-1}, COEF 1.011, final condition, replaced ozone scrubber board) with respect to the SRP as a function of amount fraction. Each point represents the average of ten 40 second averages at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines 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 amount fraction (bottom).*

The result of the second comparisons can be summarised as follows:

Agreement within the WMO/GAW DQOs was found after the replacement of the ozone scrubber of the CPA ozone analyser. The result confirms that the initial calibration of the instrument performed at WCC-Empa at the beginning of the CATCOS project is still valid. However, a thorough re-analysis of the CPA time series is required to determine the point in time when the ozone scrubber degradation started. This should be done by comparing historical data with the most likely unbiased data from after the current audit. In addition, the data from the span checks performed by the CPA staff should be considered.

Recommendation 10 (*, critical, 2024)**
All ozone data need to be re-analysed. The time of the ozone scrubber failure must be determined and data for that period must be flagged as invalid if correction is not possible.

In addition, the CPA ozone instrument was purchased in 2015 and is reaching the end of its expected lifetime, which is 10 to 15 years. Replacement of the analyser should be considered.

Recommendation 11 (, important, 2024)**
Replacement of the CPA ozone instrument should be considered. This needs to be included in the CPA station budget planning.

Carbon monoxide measurements

Carbon monoxide measurements at CPA were established in 2016 as part of the CATCOS project (Phase 2), and continuous time series are available since then.

Instrumentation. Picarro G2401 (CRDS). Until the current audit, the air was not dried, and a humidity correction was applied. A drying system (Permapure Nafion dryer PD-50T-12MPS operating in reflux mode with the Picarro pump for the vacuum) was installed during the audit. The humidity correction is still applied to compensate for the residual water content.

Standards. At the time of the audit, four NOAA laboratory standards and five working standards were available at CPA. An overview of the available standards is given in Table 7 in the Appendix.

Calibration schemes with the following sequence were/are being implemented:

Before the current audit:

Air-TG-LS1-Air-TG-Air-TG-Air-TG-LS1-LS2-LS3-LS4-LS5-Air-TG-LS2.
Standards (TG: target tank, LS: laboratory standards) were measured for 20 minutes, and air for 3000 minutes (i.e. 50 hours). The first five minutes after valve switching were discarded.

After the current audit:

Air-TG-Air-TG-LS2-LS4-Air-TG-Air-TG-LS1-LS2-N2-LS3-LS4-Air-TG-LS2-LS4.
Standards are measured for 20 minutes, and air for 1800 minutes. The first five minutes after valve switching are discarded. Compared to the previous sequence, CO is calibrated by additional measurements of a pure nitrogen cylinder (quality 6.0, CO 0.07 nmol mol^{-1}) and a standard containing high CO (3135.54 nmol mol^{-1}).

Intercomparison (performance audit). The comparison involved repeated challenges of the CPA instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The TS were analysed twice. The first comparison was made using the calibration standards that were available before the current audit (Table 1), and the second comparison was made after the implementation of the new calibration scheme (Table 2). The second comparison was only done for three TS as one TS became part of the new calibration standard suite.

Table 1 *Calibration standards used for the first comparison of the WCC-Empa TS.*

Cylinder ID	CH_4 (X2004A) (nmol mol^{-1})	CO_2(X2019) (µmol mol^{-1})	CO (X2014A) (nmol mol^{-1})	Calibration gas for
CB10918	2009.21	485.79	273.66	CH_4, CO_2, CO
CB11252	1786.08	380.41	94.79	CH_4, CO_2, CO
CC498775	2654.61	412.22	235.84	CH_4, CO_2, CO
CB11257	1925.28	421.21	191.46	CH_4, CO_2, CO
150219_CB11167	2161.32	441.14	381.58	CH_4, CO_2, CO
150311_CB11202	1688.20	353.91	157.03	CH_4, CO_2, CO

Table 2 *Calibration standards used for the second comparison of the WCC-Empa TS.*

Cylinder ID	CH_4 (X2004A) (nmol mol^{-1})	CO_2(X2019) (µmol mol^{-1})	CO (X2014A) (nmol mol^{-1})	Calibration gas for
CB10918	2009.21	485.79	273.66	CH_4, CO_2
CB11252	1786.08	380.41	94.79	CH_4, CO_2
CC498775	2654.61	412.22	235.84	CH_4, CO_2
CB11257	1925.28	421.21	191.46	CH_4, CO_2
230418_CC2519	0.13	0.07	2.29	CO
220811_CC750937	2184.6	415.79	3135.54	CH_4, CO_2, CO

The following equations characterise the instrument bias. The result is further illustrated in Figures 4 and 5 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1944-CFKADS2158, first comparison:

Unbiased CO amount fraction: X_{CO} (nmol mol^{-1}) = (CO + 6.91 nmol mol^{-1}) / 0.9943 (5)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.2 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (6)

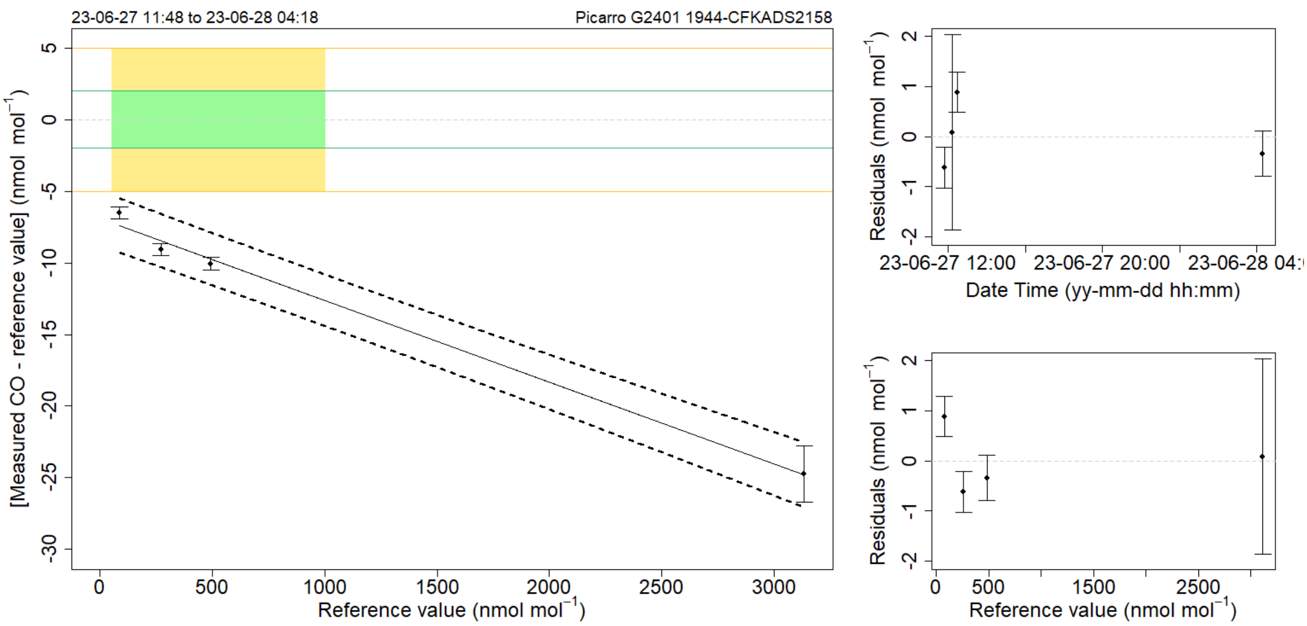

Figure 4. *Left: Bias of the CPA Picarro G2401 #1944-CFKADS2158 carbon monoxide instrument (initial comparison) with respect to the WMO-X2014A reference scale as a function of amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of 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 amount fraction range relevant for CPA. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

Picarro G2401 #1944-CFKADS2158, second comparison, i.e. with new suite of standards:

Unbiased CO amount fraction: X_{CO} (nmol mol^{-1}) = (CO + 4.31 nmol mol^{-1}) / 1.0001 (7)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (3.8 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (8)

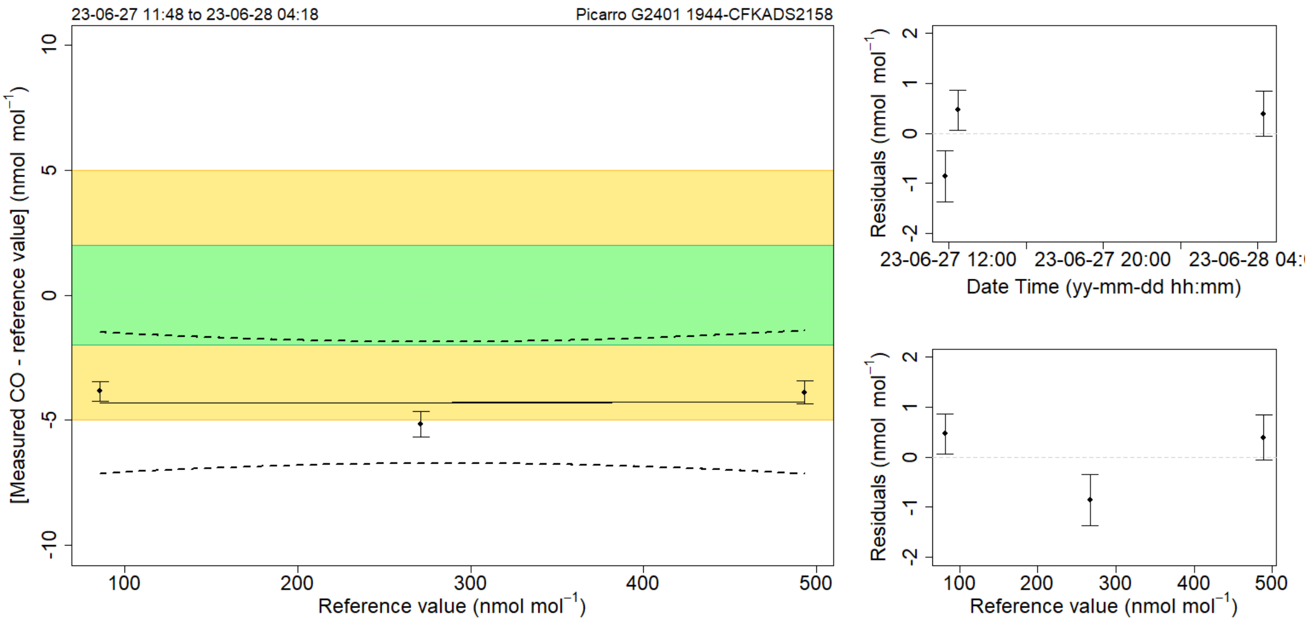

Figure 5. *Same as above, for the second comparison.*

The results of the comparisons can be summarised as follows:

The agreement between the CPA CO analyser and the WCC-Empa reference value improved significantly after the implementation of the new calibration scheme using CO standards with low and high amount fractions. Part of the bias in the first comparison with the previous calibration scheme is most likely due to instability (drift) of the CO standards.

The CPA instrument has performed well, but replacement of the analyser should be considered to sustain the measurements.

Recommendation 12 (, important, 2025)**
Replacement of the CPA CRDS instrument will be required in the near future due to the age of the instrument. This needs to be included in the budget planning of the CPA station.

Methane measurements

See the section on carbon monoxide measurements above for the instrumentation, standards and comparison procedure. As for CO, a different set of standards was used for the second comparison, corresponding to the set of standards used operationally after the audit. However, the pure nitrogen standard is not used for CH_4 calibration, nor is a particularly high CH_4 standard used, as the high CO standard contains CH_4 amount fractions close to ambient air.

The following equations characterise the instrument bias. The result is further illustrated in Figures 6 and 7 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G2401 #1944-CFKADS2158, first comparison:

Unbiased CH_4 amount fraction: X_{CH4} (nmol mol^{-1}) = (CH_4 – 0.07 nmol mol^{-1}) / 1.0005 (9)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.4 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (10)

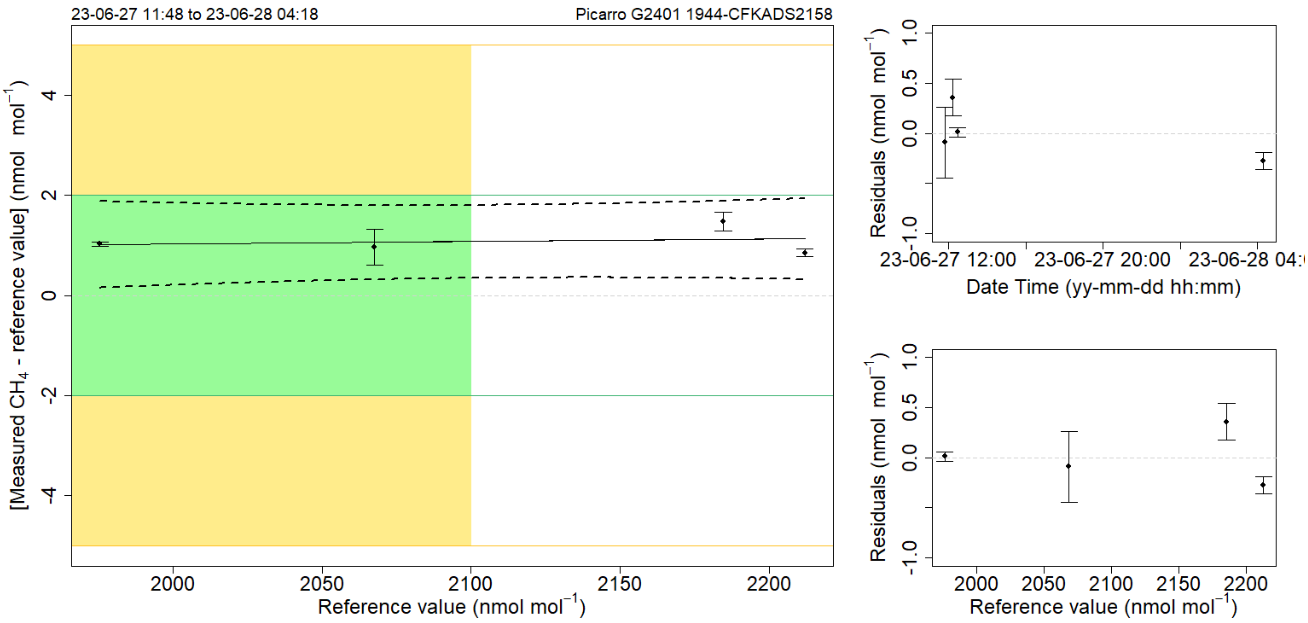

Figure 6. *Left: Bias of the Picarro G2401 #1944-CFKADS2158 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the amount fraction range relevant for CPA. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

Picarro G2401 #1944-CFKADS2158, second comparison, i.e. with new suite of standards:

Unbiased CH_4 amount fraction: X_{CH4} (nmol mol^{-1}) = (CH_4 – 3.22 nmol mol^{-1}) / 0.9987 (11)

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

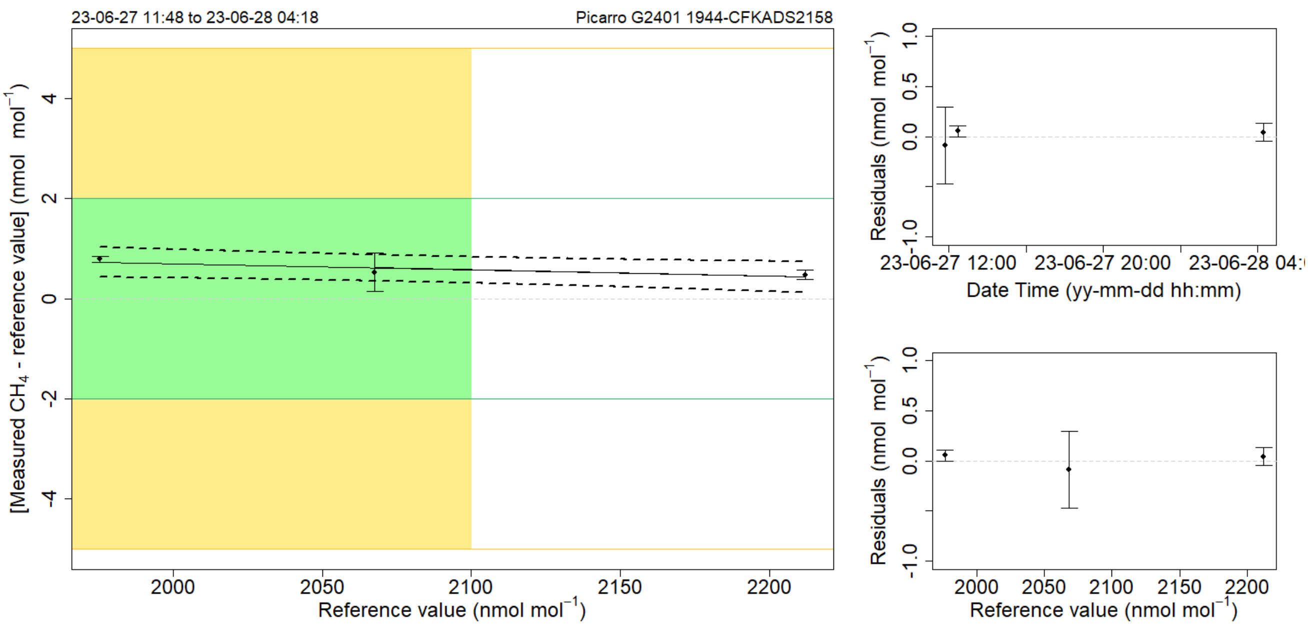

Figure 7. *Same as above, second comparison.*

The result of the comparison can be summarised as follows:

Excellent agreement well within the WMO/GAW compatibility goal was found for both comparisons. Therefore, no immediate action is required. However, the instrument is reaching the end of its expected lifetime, which is approximately 10 years, and replacement should be planned (see recommendation in the CO section).

Carbon dioxide measurements

See the section on carbon monoxide measurements above for instrumentation, standards and comparison procedure. As for CO, a different set of standards was used for the second comparison, corresponding to the set of standards used operationally after the audit. However, the pure nitrogen standard is not used for CO_2 calibration, nor is a particularly high CO_2 standard used, as the high CO standard contains amount fractions of CO_2 close to ambient air.

The following equations characterise the instrument bias. The result is further illustrated in Figures 8 and 9 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1944-CFKADS2158, first comparison:

Unbiased CO_2 amount fraction: X_{CO2} (μmol mol^{-1}) = (CO_2 + 0.32 μmol mol^{-1}) / 1.00067 (13)

Remaining standard uncertainty: u_{CO2} (μmol mol^{-1}) = sqrt (0.001 μmol mol^{-1} + 3.28e-8 * $X_{CO2}{}^2$) (14)

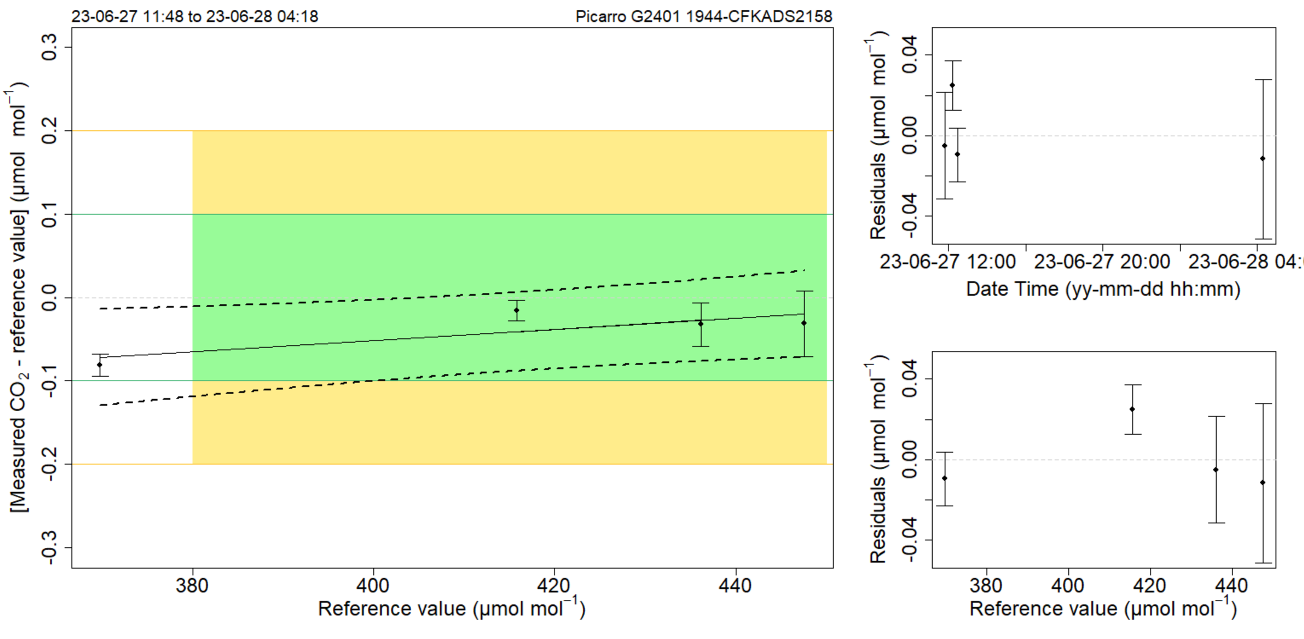

Figure 8. *Left: Bias of the Picarro G2401 #1944-CFKADS2158 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the amount fraction range relevant for CPA. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

Picarro G2401 #1944-CFKADS2158, second comparison, i.e. with new suite of standards:

Unbiased CO_2 amount fraction:	X_{CO2} (µmol mol^{-1}) = (CO_2 + 0.22 µmol mol^{-1}) / 1.00055	(15)
Remaining standard uncertainty:	u_{CO2} (µmol mol^{-1}) = sqrt (0.001 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2)	(16)

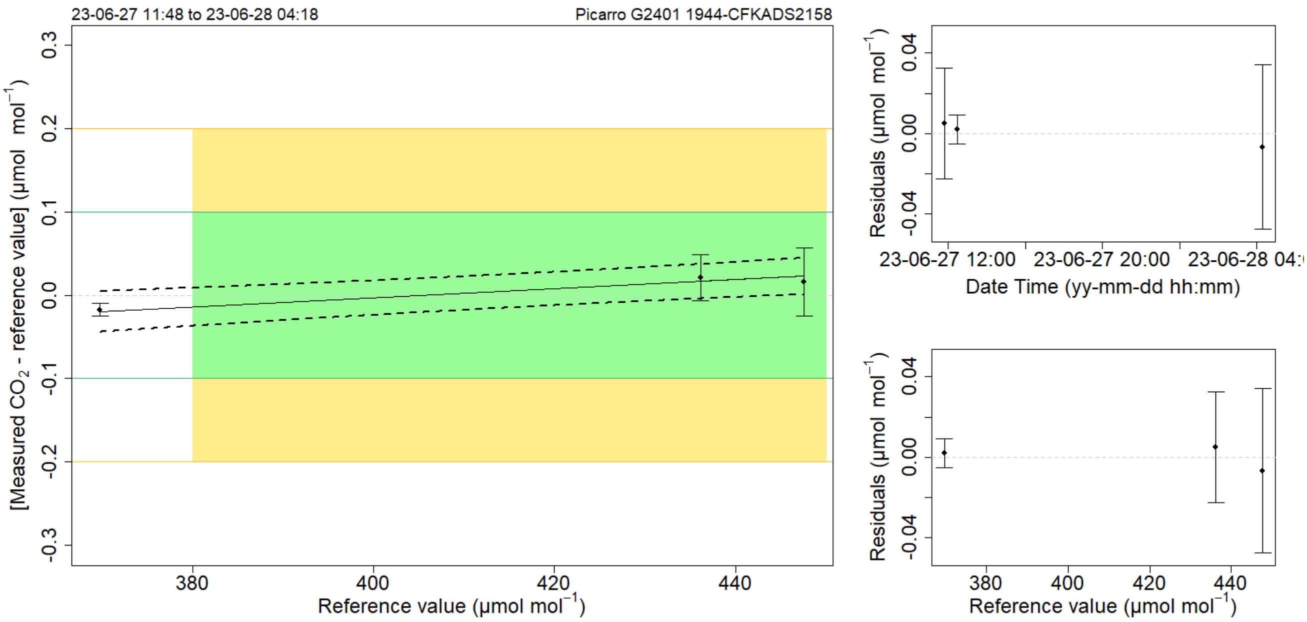

Figure 9. *Same as above, for the second comparison.*

The result of the comparison can be summarised as follows:

Excellent agreement well within the WMO/GAW compatibility goal was found for both comparisons in the relevant amount fraction range. Therefore, no immediate action is required. However, the instrument is reaching the end of its expected lifetime, which is approximately 10 years, and replacement should be planned (see recommendation in the CO section).

COMPARISON OF CPA PERFORMANCE AUDIT RESULTS WITH OTHER STATIONS

This section compares the results of the CPA performance audit with other station audits conducted by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO and N_2O, but is also applicable to other compounds. Basically, the bias in the centre of the relevant amount fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant amount fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone, the amount fraction range of 0-100 ppb was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 10 shows the bias vs. the slope of the WCC-Empa performance audits 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 exclude cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current CPA audit are shown as coloured dots in Figure 10. Note that the result of the initial ozone comparison is not shown as the deviations from the reference were too large.

The results were within the DQOs for O_3 (after the repair of the instrument), CH_4, and CO_2. The extended WMO/GAW network compatibility goals were met for CO with the new calibration scheme.

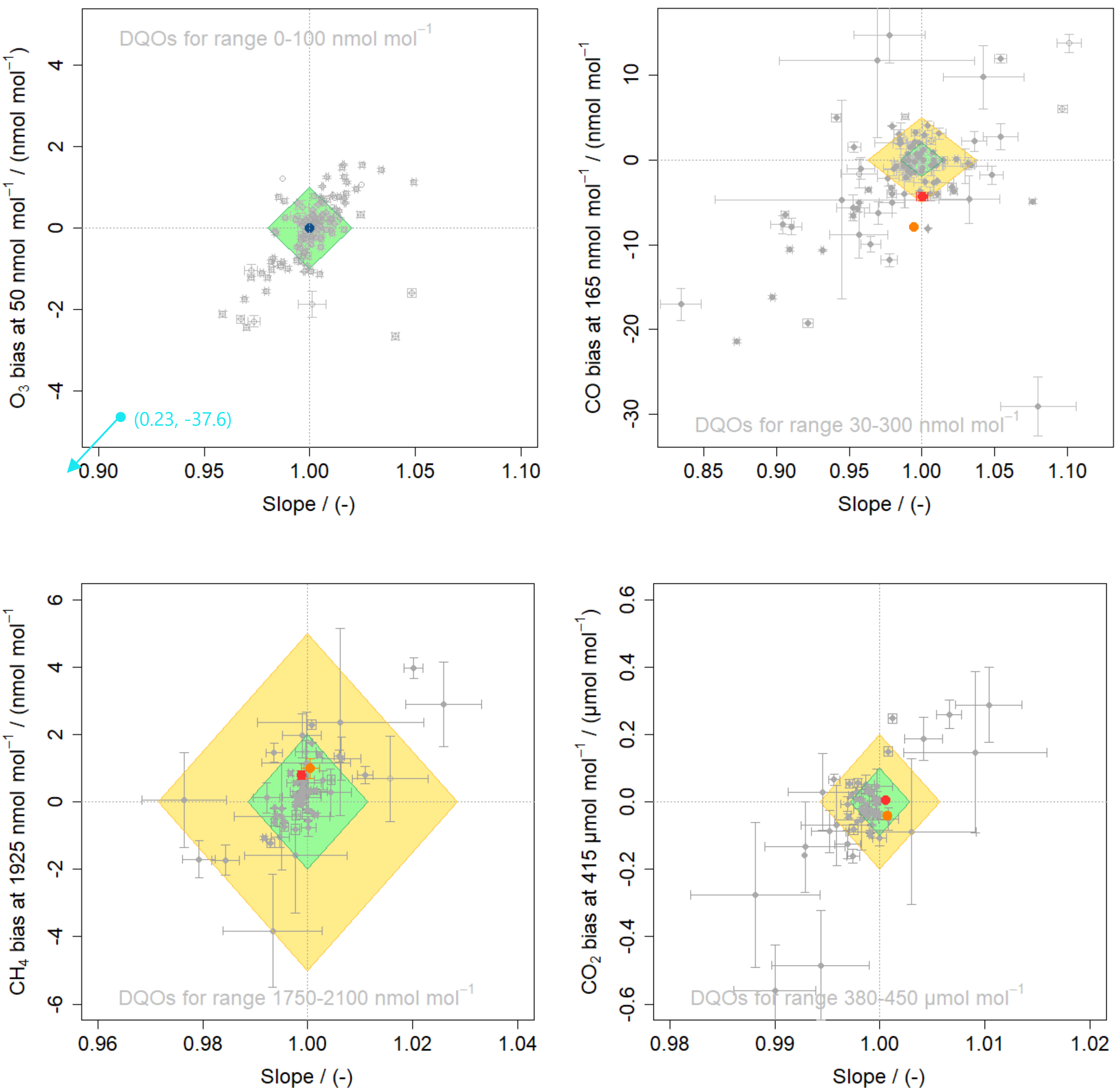

Figure 10. *Bias of O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) in the centre of the relevant amount fraction range versus the slope of the performance audits performed by WCC-Empa. The grey dots correspond to previous performance audits by WCC-Empa at various stations, while the coloured dots show CPA results (light blue: Thermo Scientific 49i with bad scrubber, dark blue: repaired Thermo Scientific 49i, orange: Picarro G2401, first comparison, red: Picarro G2401, second comparison). 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 comparison refers to the repaired instrument. The initial comparison of the unrepaired instrument did not meet the WMO/GAW DQOs.*

CONCLUSIONS

Measurements of greenhouse and reactive gases were established at the regional GAW station Cholpon-Ata in 2016 as part of the CATCOS project. Since then, continuous time series are available. These time series are highly valuable as they cover a region where data availability is extremely sparse. The CPA station has sufficient laboratory space, and hosts a small number of observations.

The assessed greenhouse gas measurements were of high data quality and met the WMO/GAW network compatibility goal in the relevant amount fraction range. The observed bias of the CO measurements was slightly larger, but within the extended WMO/GAW network compatibility goal after the implementation of a new calibration scheme. A problem with the surface ozone instrument was resolved during the audit, and traceability to the WMO reference was restored. However, historical ozone data from 2016 onwards needs to be carefully re-evaluated. Historical data should be compared with recent data after the audit to identify potential systematic biases and to identify the period of ozone breakthrough over the scrubber.

The continuation of the Cholpon-Ata measurement series is very important for GAW, and continued investment and training of the station staff are needed to ensure high data quality and availability.

Table 3 summarises the results of the performance audit in relation to the WMO/GAW compatibility goals.

Table 3. *Summary of the performance audit results. A tick mark indicates that the compatibility goal (green) or the extended compatibility goal (orange) has been met on average, and ✗ indicates results exceeding the compatibility goals.*

Compound / Instrument	**Range**	**Unit**	**CPA within DQO/eDQO**
O_3 (Thermo 49i (BKG 0.0, SPAN 1.011), broken scrubber	0 -100	nmol mol^{-1}	✗
O_3 (Thermo 49i (BKG 0.0, SPAN 1.011), repaired	0 -100	nmol mol^{-1}	✓
CO (Picarro G2401) 1st comparison	30 - 300	nmol mol^{-1}	✗
CO (Picarro G2401) 2nd comparison	30 - 300	nmol mol^{-1}	✓
CH_4 (Picarro G2401) 1st comparison	1750 - 2100	nmol mol^{-1}	✓
CH_4 (Picarro G2401) 2nd comparison	1750 - 2100	nmol mol^{-1}	✓
CO_2 (Picarro G2401) 1st comparison	380 - 450	µmol mol^{-1}	✓
CO_2 (Picarro G2401) 2nd comparison	380 - 450	µmol mol^{-1}	✓

SUMMARY RANKING OF THE CHOLPON-ATA GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(4)	Small measurement programme, adequate for a regional station.
Access	(5)	Year-round access.
Facilities		
Laboratory and office space	(4)	Adequate, with little space for additional research campaigns.
Internet access	(4)	Low but sufficient bandwidth.
Air-conditioning	(1)	None, temperature fluctuates.
Power supply	(3)	Mostly reliable with few power cuts. UPS batteries need to be replaced.
General management and operation		
Organisation	(3)	Well-coordinated and managed, but a budget is needed to support measurements.
Competence of staff	(3)	More training needed.
Air Inlet System	(4)	Basic but adequate systems.
Instrumentation		
Ozone	(4)	Replacement recommended due to age.
$CO/CH_4/CO_2$ (Picarro G2401)	(5)	State of the art instrumentation, reaching end of expected lifetime.
Standards		
O_3	(0)	Not available.
CO, CO_2, CH_4	(5)	Full traceability to the GAW reference, standards from the CCL.
Data management		
Data acquisition	(4)	Fully adequate system, data stored locally, no transfer to server.
Data processing	(3)	Dependent on external partners
Data submission	(4)	All data submitted, usually within one year. Dependent on external partners.

#0: inadequate thru 5: adequate.

Dübendorf, January 2024

Dr C. Zellweger
WCC-Empa

Martin Steinbacher

Dr M. Steinbacher
QA/SAC Switzerland

APPENDIX

List of recommendations

The recommendations made in this report are summarised below, with an indication of priority, significance and proposed completion date.

#	Recommendation	Priority	Significance	Date
1	It is recommended to install an air conditioning system to minimise environmental influences on the measurements.	Medium	Important	2024
2	The UPS batteries need to be replaced. Alternatively, the purchase of a new UPS system should be considered.	Medium	Important	2024
3	It is recommended to update GAWSIS annually or when major changes occur. Some of the reviewed information needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface (e.g. deletion of station contacts).	Medium	Important	2024
4	Kyrgyz Hydromet staff need to be more involved in the data validation process. Kyrgyz Hydromet is also encouraged to actively use the available data for scientific purposes.	High	Critical	Ongoing
5	The ozone time series submitted to the WDCRG need to be withdrawn, re-analysed and resubmitted if corrections are possible.	High	Critical	2024
6	An automatic transfer of the ELOG files to Kyrgyz Hydromet should be established as an off-site backup of the logbook entries.	Medium	Important	2024
7	An automatic data transfer to Kyrgyz Hydromet should be established as an off-site backup of the data, which is a prerequisite for taking over the full data ownership and data processing by Kyrgyz Hydromet.	High	Important	2024
8	It is recommended to purchase an ozone calibrator with traceability to the WMO/GAW ozone reference for regular checks of the instrument. The recommended interval for checking with an ozone calibrator is three months.	High	Important	2024
9	The pressure sensor of the Thermo Scientific 49i should be compared to ambient pressure at least once a month. The pressure sensor must be disconnected or the instrument pump switched off during the comparison. The span must be adjusted if the difference exceeds 2 hPa. It is recommended that this is done when the ozone span is checked and that the readings and adjustments are recorded in the checklist that was provided by QA/SAC Switzerland.	High	Critical	Ongoing
10	All ozone data need to be re-analysed. The time of the ozone scrubber failure must be determined and data for that period must be flagged as invalid if correction is not possible.	High	Critical	2024
11	Replacement of the CPA ozone instrument should be considered. This needs to be included in the CPA station budget planning.	Medium	Important	2024
12	Replacement of the CPA CRDS instrument will be required in the near future due to the age of the instrument. This needs to be included in the budget planning of the CPA station.	Medium	Important	2025

Data review

The following figures show summary plots of CPA data downloaded on 6 September 2023 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distributions, and diurnal and seasonal variations.

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

Surface ozone:

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

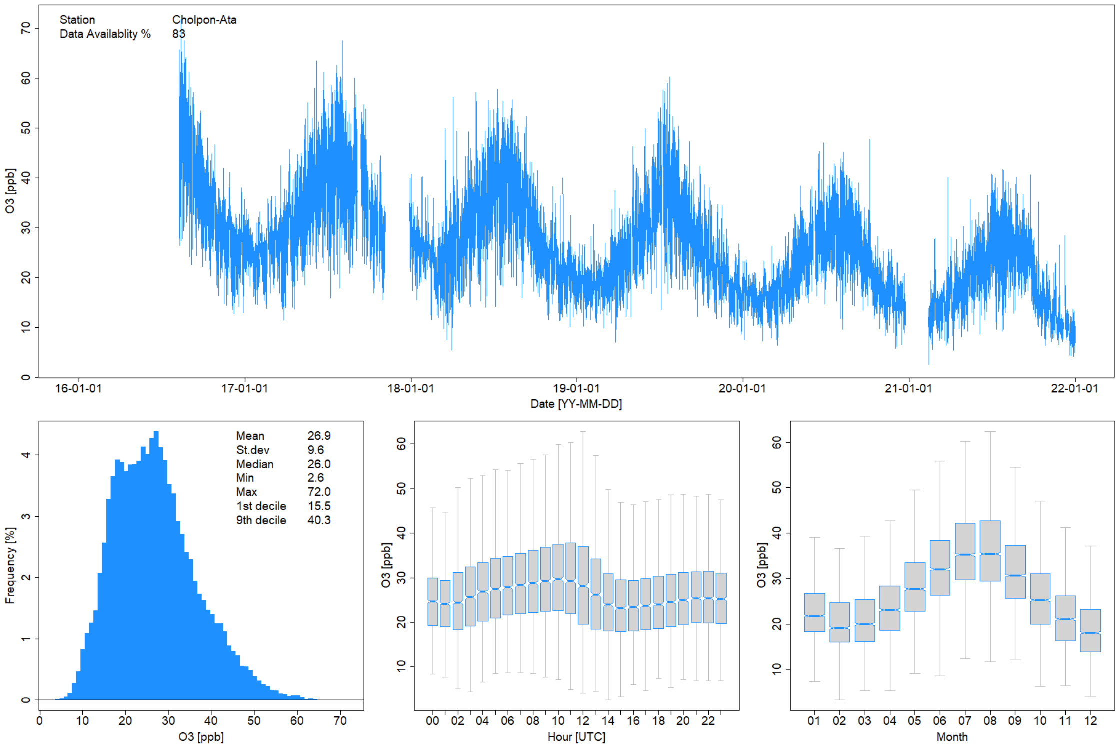

Figure 11. *O_3 data for the period from 2016 to 2021 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation. The horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- A significant negative trend was observed between 2016 and 2021.
- The trend is most likely not real and is caused by the degradation of the ozone scrubber.
- The data need to be withdrawn and re-analysed. This has already been initiated.

Carbon monoxide:

The CO data submitted by Kyrgyz Hydromet is shown below.

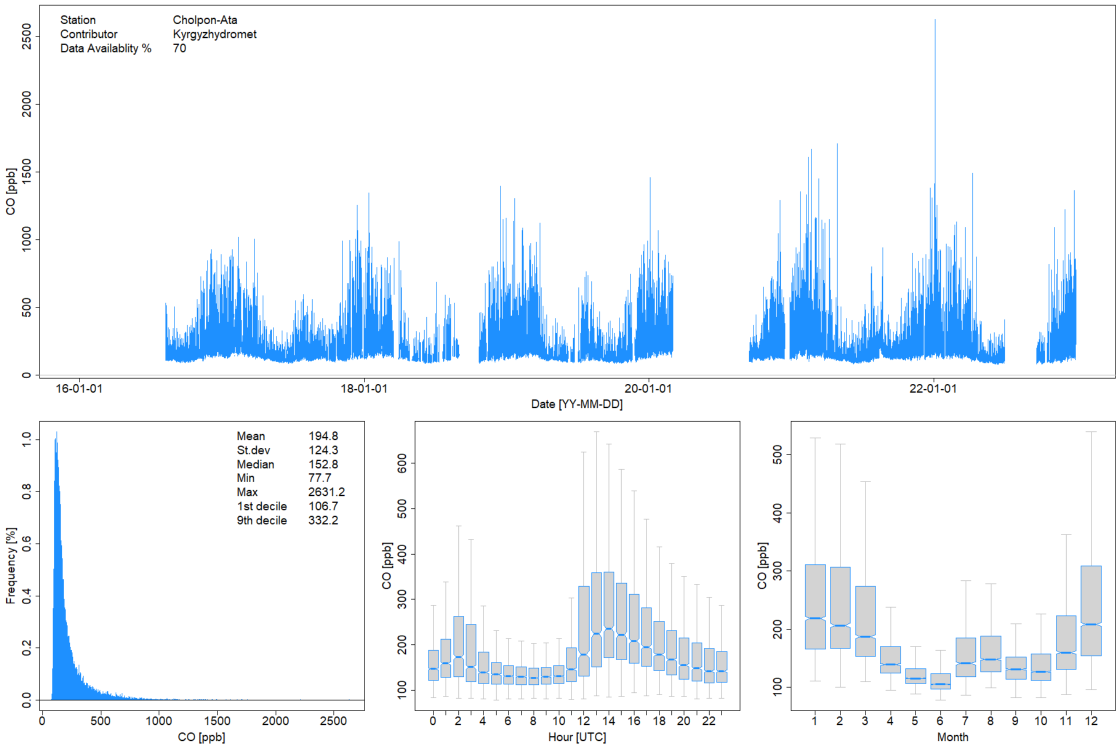

Figure 12. *Cholpon-Ata in-situ CO data (2016-2022) submitted by Kyrgyz Hydromet. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation. The horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- The Kyrgyz Hydromet dataset looks good in terms of amount fraction, trend, seasonal and diurnal variation.

Methane:

The CH_4 data submitted by Kyrgyz Hydromet is shown below.

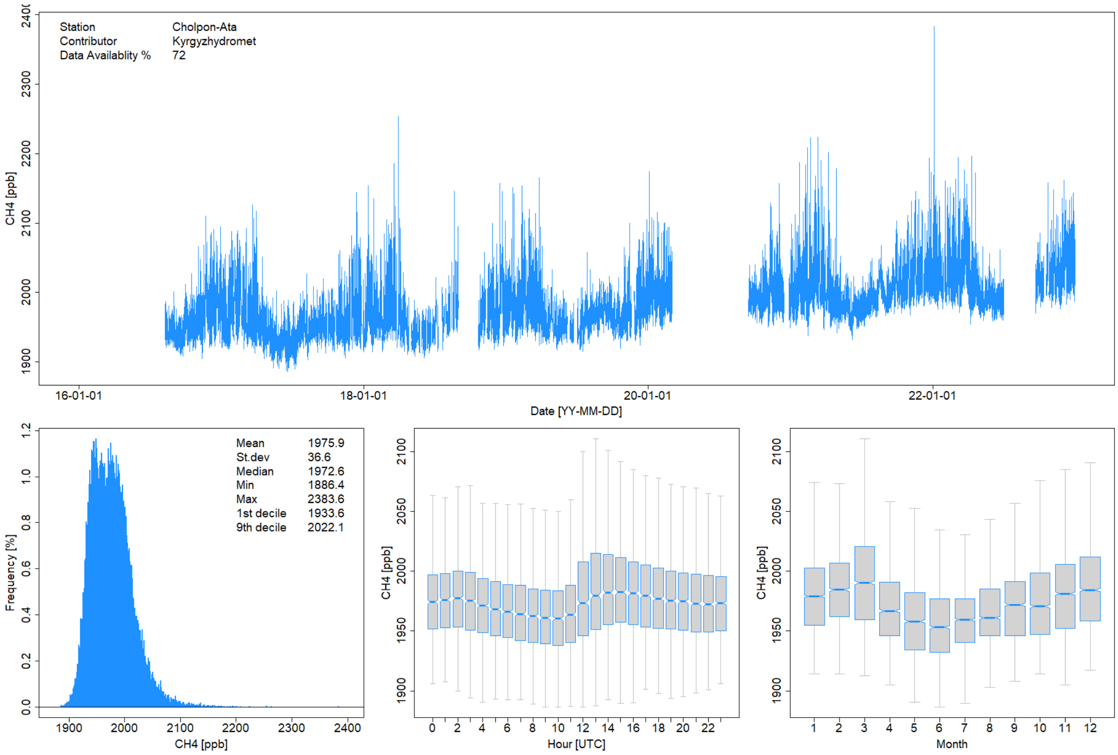

Figure 13. *Cholpon-Ata in-situ CH_4 data (2016-2022) submitted by Kyrgyz Hydromet. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation. The horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- The Kyrgyz Hydromet dataset looks sound in terms of amount fraction, trend, seasonal and diurnal variation.

Carbon dioxide:

The CO_2 data submitted by Kyrgyz Hydromet is shown below.

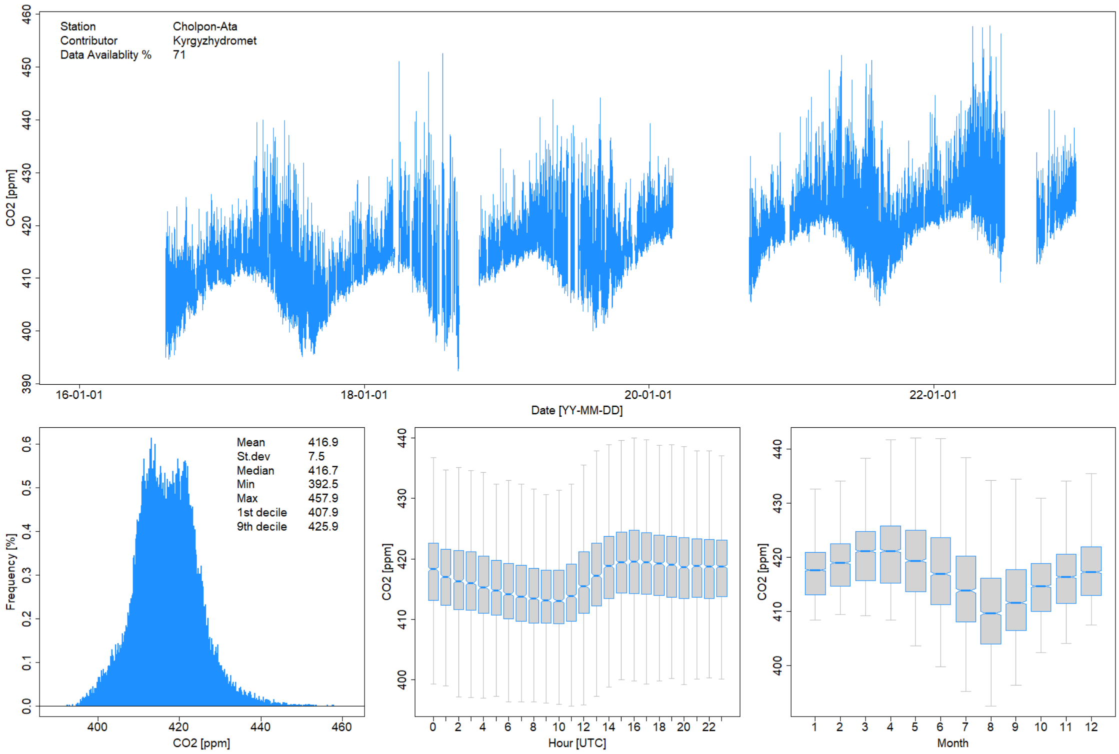

Figure 14. *Cholpon-Ata in-situ CO_2 data (2016-2022) submitted by Kyrgyz Hydromet. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation. The horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- The Kyrgyz Hydromet data set looks sound in terms of amount fraction, trend, seasonal and diurnal variation.

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 250 nmol mol^{-1}. Zero air was generated using a custom-built zero air generator (Nafion dryer, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 4 details the experimental setup for the comparisons of the station analyser with the travelling standard. The data used for the evaluation was recorded by the WCC-Empa and CPA data acquisition systems.

Table 4. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #CM22117101 (WCC-Empa)
Settings	BKG 0.0, COEF 1.009
Pressure readings (hPa)	Ambient 838.1;TS 837.0 (no adjustment was made)
CPA analyser (OA)	
Model, S/N	Thermo Scientific 49i #1304556621
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG 0.0 nmol mol^{-1}, COEF 1.011
Pressure readings (hPa)	Initial: Ambient 838.1; OA 883.8 Final: Ambient 833.0; OA 881.7; the pressure sensor of the OA was adjusted to ambient pressure (833.0 hPa) before the final comparison.

Results

Each ozone level was measured for approximately ten minutes, and the last ten 40 s averages were aggregated. These aggregates were used to evaluate the comparison. All results are valid for the calibration factors as given in Table 4 above. The travelling standard (TS) readings were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment was applied as for the ambient air analysis.
The results of the assessment are presented in the following table (individual measurement points) and are further discussed in the Executive Summary.

Table 5. *Comparison of the CPA ozone analyser (OA) Thermo Scientific 49i #1304556621 (BKG 0.0 nmol mol^{-1}, COEF 1.011, initial comparison) 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 (%)
2023-06-27 05:11	149.95	0.12	36.63	0.09	-113.32	-75.57
2023-06-27 05:20	0.52	0.19	0.04	0.09	-0.48	NA
2023-06-27 05:29	100.08	0.17	24.99	0.28	-75.09	-75.03
2023-06-27 05:37	50.17	0.18	13.53	0.20	-36.64	-73.03
2023-06-27 05:46	199.89	0.15	46.04	0.37	-153.85	-76.97
2023-06-27 05:54	249.76	0.21	55.32	0.28	-194.44	-77.85

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 (%)
2023-06-27 06:03	149.98	0.09	34.09	0.24	-115.89	-77.27
2023-06-27 06:12	100.02	0.19	24.46	0.23	-75.56	-75.54
2023-06-27 06:20	199.90	0.21	46.44	0.22	-153.46	-76.77
2023-06-27 06:29	249.75	0.12	56.86	0.13	-192.89	-77.23
2023-06-27 06:38	0.40	0.21	0.03	0.13	-0.37	NA
2023-06-27 06:46	50.25	0.11	14.00	0.15	-36.25	-72.14
2023-06-27 06:55	249.81	0.18	58.45	0.36	-191.36	-76.60
2023-06-27 07:04	149.92	0.18	36.10	0.11	-113.82	-75.92
2023-06-27 07:12	50.16	0.13	13.62	0.21	-36.54	-72.85
2023-06-27 07:21	199.87	0.13	47.69	0.19	-152.18	-76.14
2023-06-27 07:29	100.04	0.20	25.12	0.27	-74.92	-74.89
2023-06-27 07:38	0.50	0.19	-0.11	0.16	-0.61	NA

Table 6. *Comparison of the CPA ozone analyser (OA) Thermo Scientific 49i #1304556621 (BKG 0.0 nmol mol^{-1}, COEF 1.011, final comparison after replacement of the ozone scrubber) 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 (%)
2023-06-27 12:22	90.10	0.25	90.16	0.25	0.06	0.07
2023-06-27 12:31	224.86	0.17	224.65	0.29	-0.21	-0.09
2023-06-27 12:39	80.02	0.16	80.05	0.28	0.03	0.04
2023-06-27 12:48	174.90	0.16	174.80	0.27	-0.10	-0.06
2023-06-27 12:56	10.33	0.18	10.28	0.20	-0.05	-0.48
2023-06-27 13:05	249.78	0.13	249.51	0.35	-0.27	-0.11
2023-06-27 13:13	70.07	0.20	70.15	0.34	0.08	0.11
2023-06-27 13:22	124.95	0.20	124.97	0.45	0.02	0.02
2023-06-27 13:30	50.12	0.16	50.20	0.24	0.08	0.16
2023-06-27 13:39	199.94	0.16	199.76	0.22	-0.18	-0.09
2023-06-27 13:47	20.15	0.11	20.29	0.48	0.14	0.69
2023-06-27 13:56	60.12	0.12	60.30	0.18	0.18	0.30
2023-06-27 14:04	40.16	0.16	40.23	0.16	0.07	0.17
2023-06-27 14:13	100.09	0.09	100.27	0.26	0.18	0.18
2023-06-27 14:21	149.96	0.14	149.97	0.31	0.01	0.01
2023-06-27 14:30	30.15	0.11	29.94	0.18	-0.21	-0.70
2023-06-27 14:39	0.47	0.14	0.11	0.14	-0.36	NA
2023-06-27 14:48	175.00	0.20	174.90	0.17	-0.10	-0.06
2023-06-27 14:56	20.24	0.13	20.16	0.18	-0.08	-0.40
2023-06-27 15:05	90.14	0.15	90.45	0.21	0.31	0.34
2023-06-27 15:13	125.04	0.26	125.25	0.41	0.21	0.17
2023-06-27 15:22	249.73	0.17	249.67	0.37	-0.06	-0.02
2023-06-27 15:30	149.94	0.23	150.00	0.22	0.06	0.04
2023-06-27 15:39	0.59	0.14	0.11	0.16	-0.48	NA
2023-06-27 15:48	224.79	0.23	224.52	0.28	-0.27	-0.12
2023-06-27 15:56	80.03	0.18	80.12	0.26	0.09	0.11
2023-06-27 16:05	70.15	0.19	70.24	0.36	0.09	0.13
2023-06-27 16:13	100.07	0.16	100.21	0.21	0.14	0.14

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 (%)
2023-06-27 16:22	50.11	0.14	50.46	0.25	0.35	0.70
2023-06-27 16:30	10.22	0.14	10.27	0.19	0.05	0.49
2023-06-27 16:39	40.20	0.10	40.21	0.22	0.01	0.02
2023-06-27 16:47	199.95	0.21	199.78	0.21	-0.17	-0.09
2023-06-27 16:56	60.08	0.15	59.94	0.22	-0.14	-0.23
2023-06-27 17:04	30.23	0.20	30.08	0.14	-0.15	-0.50
2023-06-27 19:39	249.81	0.17	249.53	0.30	-0.28	-0.11
2023-06-27 19:47	99.97	0.17	99.92	0.17	-0.05	-0.05
2023-06-27 19:56	70.05	0.14	70.35	0.23	0.30	0.43
2023-06-27 20:04	10.34	0.19	10.13	0.20	-0.21	-2.03
2023-06-27 20:13	224.85	0.19	224.73	0.22	-0.12	-0.05
2023-06-27 20:21	30.15	0.16	30.33	0.18	0.18	0.60
2023-06-27 20:30	150.04	0.20	149.93	0.31	-0.11	-0.07
2023-06-27 20:38	50.13	0.13	50.32	0.30	0.19	0.38
2023-06-27 20:47	80.15	0.12	80.28	0.39	0.13	0.16
2023-06-27 20:55	199.86	0.24	199.64	0.27	-0.22	-0.11
2023-06-27 21:04	20.21	0.21	20.27	0.39	0.06	0.30
2023-06-27 21:12	90.08	0.26	90.19	0.42	0.11	0.12
2023-06-27 21:22	0.33	0.20	0.23	0.11	-0.10	NA
2023-06-27 21:30	125.09	0.10	125.46	0.41	0.37	0.30
2023-06-27 21:39	60.12	0.17	59.93	0.30	-0.19	-0.32
2023-06-27 21:47	174.89	0.18	174.82	0.24	-0.07	-0.04
2023-06-27 21:56	40.17	0.13	40.00	0.22	-0.17	-0.42
2023-06-27 22:04	224.86	0.23	224.73	0.34	-0.13	-0.06
2023-06-27 22:13	40.17	0.24	40.21	0.42	0.04	0.10
2023-06-27 22:21	30.12	0.22	30.22	0.32	0.10	0.33
2023-06-27 22:30	20.23	0.14	20.09	0.20	-0.14	-0.69
2023-06-27 22:38	70.15	0.23	70.03	0.38	-0.12	-0.17
2023-06-27 22:47	125.05	0.13	124.86	0.41	-0.19	-0.15
2023-06-27 22:55	149.97	0.19	149.99	0.28	0.02	0.01
2023-06-27 23:05	0.36	0.12	0.04	0.21	-0.32	NA
2023-06-27 23:13	90.10	0.10	89.98	0.22	-0.12	-0.13
2023-06-27 23:22	100.06	0.14	100.00	0.34	-0.06	-0.06
2023-06-27 23:30	249.85	0.18	249.58	0.28	-0.27	-0.11
2023-06-27 23:39	10.24	0.25	10.00	0.29	-0.24	-2.34
2023-06-27 23:47	199.94	0.11	200.01	0.27	0.07	0.04
2023-06-27 23:56	174.89	0.17	174.83	0.26	-0.06	-0.03
2023-06-28 00:04	60.12	0.16	60.03	0.24	-0.09	-0.15
2023-06-28 00:13	80.08	0.09	80.24	0.12	0.16	0.20
2023-06-28 00:21	50.13	0.20	50.31	0.17	0.18	0.36
2023-06-28 00:30	40.18	0.13	40.34	0.19	0.16	0.40
2023-06-28 00:38	224.88	0.11	224.60	0.31	-0.28	-0.12
2023-06-28 00:47	199.85	0.14	199.63	0.23	-0.22	-0.11
2023-06-28 00:55	20.21	0.21	20.13	0.29	-0.08	-0.40
2023-06-28 01:04	100.06	0.12	100.24	0.20	0.18	0.18
2023-06-28 01:12	50.15	0.12	50.36	0.25	0.21	0.42
2023-06-28 01:21	125.00	0.22	124.93	0.49	-0.07	-0.06
2023-06-28 01:30	0.37	0.35	0.19	0.19	-0.18	NA

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 (%)
2023-06-28 01:39	90.11	0.14	90.24	0.23	0.13	0.14
2023-06-28 01:47	80.06	0.12	80.16	0.17	0.10	0.12
2023-06-28 01:56	10.21	0.18	10.25	0.13	0.04	0.39
2023-06-28 02:04	174.91	0.17	174.95	0.25	0.04	0.02
2023-06-28 02:13	149.94	0.10	150.07	0.09	0.13	0.09
2023-06-28 02:21	249.85	0.16	249.57	0.20	-0.28	-0.11
2023-06-28 02:30	30.21	0.13	30.26	0.24	0.05	0.17
2023-06-28 02:38	70.15	0.18	70.15	0.20	0.00	0.00
2023-06-28 02:47	60.16	0.16	60.22	0.29	0.06	0.10

Calibration standards for CO, CH_4, and CO_2

Table 7 provides an overview of the standard gases available for the calibration of the CO, CH_4, and CO_2 instruments.

Table 7 *Calibration standards available at CPA as of June 2023.*

Cylinder ID	Pressure (psi)	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2 (X2019) (µmol mol^{-1})	Usage
CB10918	1180	273.66	2009.21	485.79	NOAA reference standard
CB11252	1280	94.79	1786.08	380.41	NOAA reference standard
CC498775	1310	235.84	2654.61	412.22	NOAA reference standard
CB11257	1200	191.46	1925.28	421.21	NOAA reference standard
150219_CB11167	410	381.58	2161.32	441.14	Laboratory standard
150311_CB11202	580	157.03	1688.20	353.91	Laboratory standard
210406_CB08810	1890	369.8	1975.48	85.68	Laboratory standard
201209_CC726933	1890	436.16	2067.62	271.14	Laboratory standard
220811_CC750913	1980	447.62	2211.91	493.32	Laboratory standard
230418_CC2519	2000	0.07	0.13	2.29	Nitrogen 6.0, zero calibration for CO
220811_CC750937	2000	415.79	2184.6	3135.54	Laboratory standard, high CO

Carbon monoxide comparisons

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

Table 8 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the CPA data acquisition system. The standards used for the calibration of the CPA instruments are shown in Table 8.

Table 8. Experimental details of CPA CO comparison.

Travelling standard (TS)	
WCC-Empa travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 17.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #1944-CFKADS2158
Principle	CRDS
Drying system	None the comparisons with the WCC-Empa TS. A Permapure Nafion dryer PD-50T-12MPS operating in reflux mode with the Picarro pump for the vacuum was installed after the comparisons.
Comparison procedure	
Connection	WCC-Empa TS were connected to spare calibration gas ports of the calibration unit.

Results

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

Table 9. *CO aggregates of the first comparison (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #1944-CFKADS2158 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 (%)
(23-06-27 11:48:45)	201209_CC726933	271.1	0.6	262.1	0.4	4	-9.1	-3.4
(23-06-27 12:13:30)	220811_CC750937	3135.5	0.4	3110.8	2.0	4	-24.7	-0.8
(23-06-28 04:18:00)	220811_CC750913	493.3	0.2	483.3	0.5	4	-10.1	-2.0
(23-06-27 12:28:15)	210406_CB08810	85.7	0.1	79.2	0.4	4	-6.5	-7.6

Table 10. *CO aggregates of the second comparison (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #1944-CFKADS2158 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 (%)
(23-06-27 11:48:45)	201209_CC726933	271.1	0.6	266.0	0.5	4	-5.2	-1.9
(23-06-28 04:18:00)	220811_CC750913	493.3	0.2	489.4	0.5	4	-3.9	-0.8
(23-06-27 12:28:15)	210406_CB08810	85.7	0.1	81.8	0.4	4	-3.8	-4.5

Methane comparisons

Procedure: same as for CO, see above.

Results

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

Table 11. *CH_4 aggregates of the first comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1944-CFKADS2158 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 (%)
(23-06-27 11:48:45)	201209_CC726933	2067.62	0.01	2068.59	0.35	4	0.97	0.05
(23-06-27 12:13:30)	220811_CC750937	2184.60	0.03	2186.07	0.19	4	1.47	0.07
(23-06-28 04:18:00)	220811_CC750913	2211.91	0.04	2212.76	0.08	4	0.85	0.04
(23-06-27 12:28:15)	210406_CB08810	1975.48	0.01	1976.51	0.05	4	1.03	0.05

Table 12. *CH_4 aggregates of the second comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1944-CFKADS2158 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 (%)
(23-06-27 11:48:45)	201209_CC726933	2067.62	0.01	2068.14	0.38	4	0.52	0.03
(23-06-28 04:18:00)	220811_CC750913	2211.91	0.04	2212.38	0.09	4	0.47	0.02
(23-06-27 12:28:15)	210406_CB08810	1975.48	0.01	1976.27	0.05	4	0.79	0.04

Carbon dioxide comparisons

Procedure: same as for CO, see above.

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. *CO_2 aggregates of the first comparison (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #1944-CFKADS2158 instrument (AL) with the WCC-Empa TS (WMO-X2019 CO_2 scale).*

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(23-06-27 11:48:45)	201209_CC726933	436.16	0.01	436.13	0.03	4	-0.03	-0.01
(23-06-27 12:13:30)	220811_CC750937	415.79	0.01	415.77	0.01	4	-0.02	0.00
(23-06-28 04:18:00)	220811_CC750913	447.62	0.01	447.59	0.04	4	-0.03	-0.01
(23-06-27 12:28:15)	210406_CB08810	369.80	0.01	369.72	0.01	4	-0.08	-0.02

Table 14. *CO_2 aggregates of the second comparison (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #1944-CFKADS2158 instrument (AL) with the WCC-Empa TS (WMO-X2019 CO_2 scale).*

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(23-06-27 11:48:45)	201209_CC726933	436.16	0.01	436.18	0.03	4	0.02	0.00
(23-06-28 04:18:00)	220811_CC750913	447.62	0.01	447.64	0.04	4	0.02	0.00
(23-06-27 12:28:15)	210406_CB08810	369.80	0.01	369.78	0.01	4	-0.02	-0.01

WCC-Empa traveling standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the SRP 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 #CM22117101, BKG 0.0, COEF 1.009

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

The results of the TS calibration before and after the audit are given in Table 15. The TS passed the assessment criteria defined for maximum acceptable bias before the audit (Klausen et al., 2003) (cf. Figure 15). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone amount fraction produced (and measured) by the TS can be calculated (Equation 6a). The uncertainty of the TS (Equation 6b) was previously estimated (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([\text{TS}] + 0.29\ \text{nmol mol}^{-1}) / 1.0023 \quad (17)$$

$$u_{TS}\ (\text{nmol mol}^{-1}) = \text{sqrt}\ ((0.43\ \text{nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (18)$$

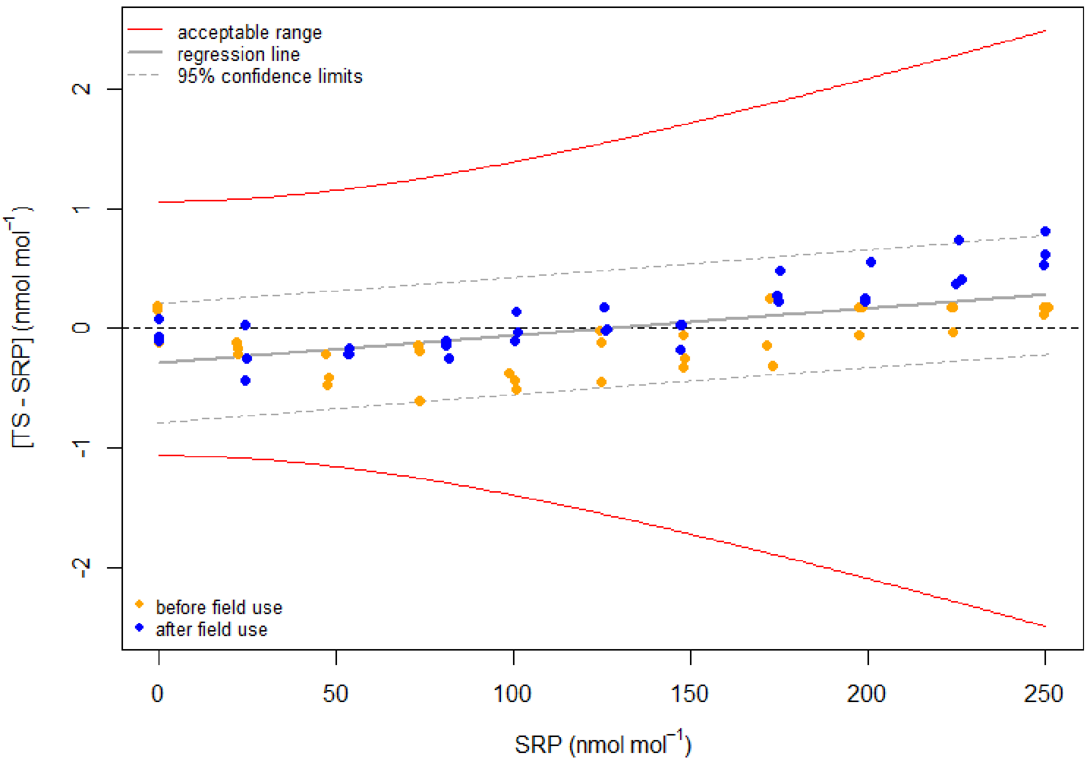

Figure 15. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before use of the TS at the field site.*

Table 15. 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})
2023-03-14	1	170	171.59	0.18	171.45	0.17
2023-03-14	1	225	223.81	0.36	223.78	0.24
2023-03-14	1	20	22.22	0.45	22.01	0.26
2023-03-14	1	100	98.95	0.39	98.57	0.27
2023-03-14	1	0	0.07	0.20	-0.05	0.15
2023-03-14	1	50	47.83	0.23	47.42	0.14
2023-03-14	1	150	147.79	0.18	147.47	0.27
2023-03-14	1	125	124.89	0.21	124.77	0.18
2023-03-14	1	250	249.42	0.26	249.54	0.20
2023-03-14	1	75	73.08	0.33	72.94	0.23
2023-03-14	1	195	197.40	0.24	197.57	0.19
2023-03-14	2	45	47.38	0.41	46.91	0.21
2023-03-14	2	150	148.30	0.26	148.05	0.12
2023-03-14	2	125	124.29	0.29	124.27	0.23
2023-03-14	2	195	197.40	0.11	197.34	0.25
2023-03-14	2	175	173.21	0.21	172.90	0.24
2023-03-14	2	75	73.44	0.45	72.84	0.16
2023-03-14	2	20	22.33	0.28	22.17	0.26
2023-03-14	2	0	-0.16	0.34	0.00	0.13
2023-03-14	2	250	249.44	0.23	249.62	0.24
2023-03-14	2	100	100.71	0.19	100.20	0.17
2023-03-14	2	225	223.35	0.28	223.53	0.18
2023-03-14	3	45	47.15	0.33	46.94	0.51
2023-03-14	3	170	172.10	0.18	172.34	0.20
2023-03-14	3	125	124.90	0.29	124.46	0.20
2023-03-14	3	225	223.66	0.29	223.84	0.15
2023-03-14	3	200	198.34	0.34	198.52	0.34
2023-03-14	3	20	21.95	0.20	21.83	0.16
2023-03-14	3	150	147.87	0.31	147.82	0.23
2023-03-14	3	100	100.45	0.21	100.01	0.22
2023-03-14	3	250	250.71	0.36	250.89	0.31
2023-03-14	3	0	-0.13	0.35	0.06	0.12
2023-03-14	3	75	73.44	0.38	73.26	0.13
2023-07-28	4	175	174.61	0.18	174.84	0.23
2023-07-28	4	125	125.73	0.26	125.91	0.15
2023-07-28	4	200	199.13	0.20	199.38	0.15
2023-07-28	4	225	226.15	0.21	226.56	0.22
2023-07-28	4	80	81.08	0.25	80.95	0.32
2023-07-28	4	100	100.32	0.25	100.21	0.20
2023-07-28	4	250	249.68	0.21	250.30	0.16
2023-07-28	4	55	53.41	0.20	53.20	0.27
2023-07-28	4	25	24.82	0.45	24.57	0.12
2023-07-28	4	145	147.17	0.25	146.99	0.17
2023-07-28	4	0	0.07	0.26	-0.04	0.18
2023-07-28	5	200	199.15	0.31	199.38	0.28

Date	Run	Level#	SRP (nmol mol⁻¹)	sdSRP (nmol mol⁻¹)	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)
2023-07-28	5	175	175.10	0.39	175.58	0.16
2023-07-28	5	55	53.57	0.29	53.35	0.34
2023-07-28	5	250	249.74	0.30	250.56	0.30
2023-07-28	5	80	81.04	0.47	80.93	0.41
2023-07-28	5	125	126.22	0.31	126.20	0.15
2023-07-28	5	145	147.23	0.19	147.26	0.15
2023-07-28	5	225	225.32	0.29	226.06	0.21
2023-07-28	5	100	101.30	0.27	101.27	0.18
2023-07-28	5	25	24.60	0.35	24.62	0.19
2023-07-28	5	0	0.06	0.31	-0.01	0.10
2023-07-28	6	80	81.80	0.23	81.55	0.25
2023-07-28	6	125	126.27	0.29	126.26	0.19
2023-07-28	6	145	147.36	0.26	147.38	0.19
2023-07-28	6	100	100.74	0.30	100.88	0.19
2023-07-28	6	175	174.48	0.29	174.75	0.19
2023-07-28	6	0	-0.10	0.32	-0.01	0.10
2023-07-28	6	225	224.77	0.23	225.14	0.21
2023-07-28	6	25	24.53	0.27	24.10	0.13
2023-07-28	6	250	249.35	0.23	249.88	0.25
2023-07-28	6	200	200.88	0.27	201.44	0.13
2023-07-28	6	55	53.58	0.71	53.42	0.36

#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 amount fractions to the TS, the following calibration scales were used:

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

More information about the NOAA calibration scales can be found on the NOAA website. The scales were transferred to the TS using the following instruments:

CO, CO_2 and CH_4: Picarro G2401 (Cavity Ring-Down Spectroscopy).
CO and N_2O: Los Gatos 23-r (Mid-IR 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.

Table 16 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 the standard deviations of the WCC-Empa TS are given in Table 17, and Figure 16 shows the analysis of the TS over time.

Table 16. *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 17. *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, (L) Los Gatos.*

TS	Press. (psi)	CH_4 (P) (nmol mol^{-1})	sd	CO_2(P) (µmol mol^{-1})	sd	N_2O (L) (nmol mol^{-1})	sd	CO (P) (nmol mol^{-1})	sd
210406_CB08810	1890	1975.48	0.01	369.8	0.01	354.28	0.01	85.68	0.06
201209_CC726933	1890	2067.62	0.01	436.16	0.01	338.89	0.03	271.14	0.62
220811_CC750937	2000	2184.6	0.03	415.79	0.01	388.59	0.15	3135.54	0.35
220811_CC750913	1980	2211.91	0.04	447.62	0.01	392.13	0.13	493.32	0.18
230418_CC2519	2000	0.13	0.03	0.07	0.01	6.17	NA	2.29	0.42

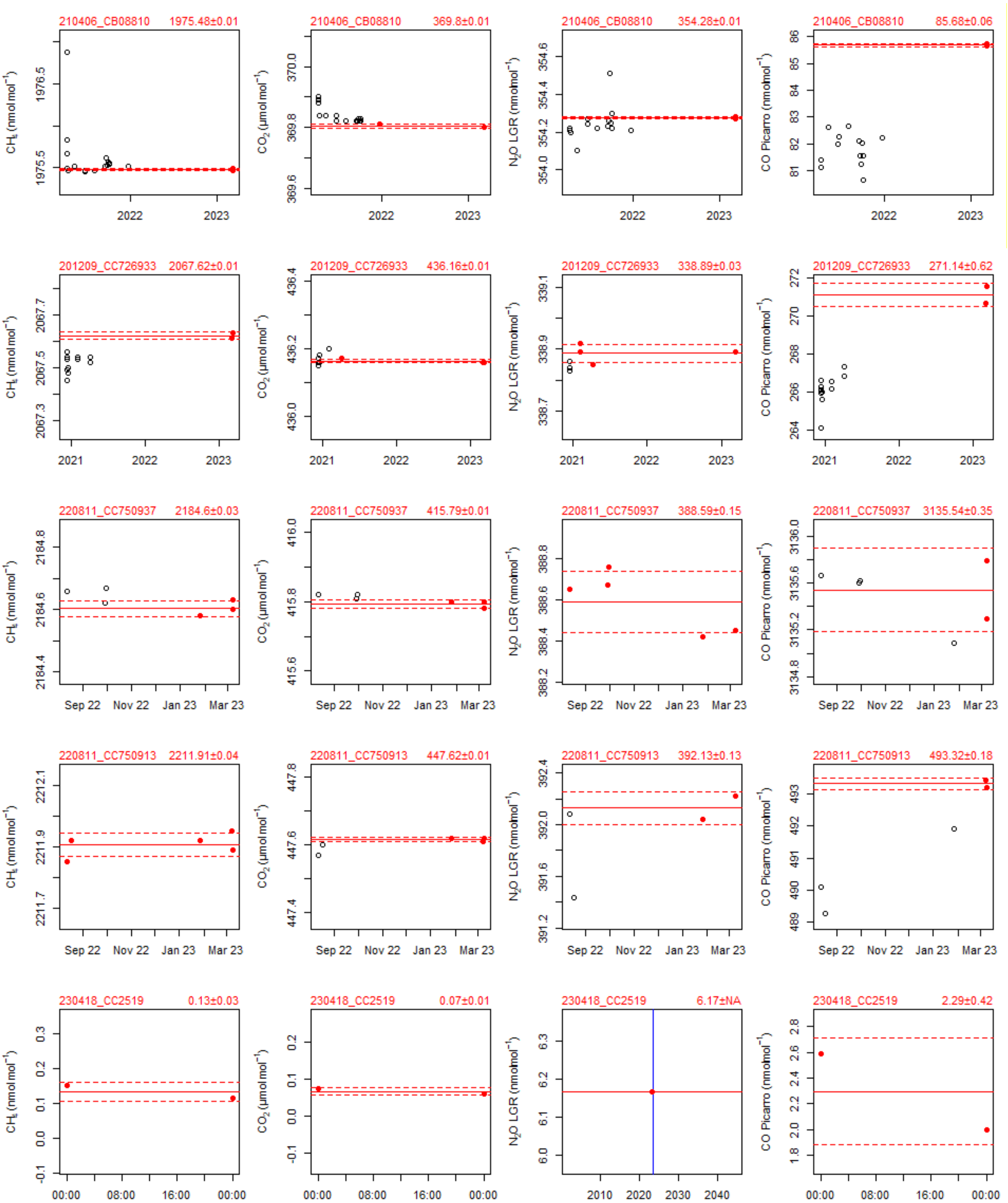

Figure 16. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, N_2O and DQCO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

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LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
CATCOS	Capacity Building and Twinning for Climate Observing Systems
CPA	Cholpon-Ata GAW Station
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
Kyrgyz Hydromet	Hydrometeorology service under the ministry of emergency situation of the Kyrgyz Republic
LS	Laboratory Standard (for calibration)
NA	Not Applicable
NOAA	National Oceanic and Atmospheric Administration
PC	Personal Computer
PI	Principle Investigator
QA/SAC	Quality Assurance / Science Activity Centre
SDC	Swiss Agency for Development and Cooperation
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