WCC-Empa Report 24/2

System and performance audit of Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide at the Global GAW Station Chacaltaya, Bolivia, August 2024

Submitted to the World Meteorological Organization by

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Acknowledgements

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1 Executive summary

The 1st WCC-Empa[1] system and performance audit at the Chacaltaya global GAW station (CHC) was conducted from 9 to 15 August 2024 in accordance with the WMO/GAW quality assurance system (Wmo, 2017). A list of all WCC-Empa audits and the corresponding audit reports are available on the Empa GAW website. The following persons contributed to this audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr Marcos Andrade	University Mayor de San Andrés, station manager
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Ms Laura Ticona	University Mayor de San Andrés, associated researcher (greenhouse gases)
Ing Fabricio Avila	University Mayor de San Andrés, research technician
Ms Zarela Tuco	University Mayor de San Andrés, associated researcher (greenhouse gases)
Mr Fernando Velarde	University Mayor de San Andrés, research assistant (reactive gases)

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

The report will be distributed to the station manager of the Chacaltaya GAW station and to the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and made available on the WCC-Empa website.

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.

[1]WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of Empa, the Swiss Federal Laboratories for Materials Science and Technology. Its mandate is to conduct system and performance audits at Global GAW stations based on mutual agreement.

2 Site description and operation

2.1 Station management

The Laboratory for Atmospheric Physics of the University Mayor de San Andrés (UMSA) in La Paz manages the CHC station and liaises with the World Meteorological Organization. The station was officially inaugurated as a GAW station in 2012 but has a long history of cosmic ray research. The establishment of GAW activities at CHC has been done in close collaboration with international partners such as the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), the Italian National Research Council (CNR) and the Leibnitz Institute for Tropospheric Research (TROPOS). A twinning partnership with LSCE and TROPOS supports the operation of the station. Data management and processing are also integrated into the Integrated Carbon Observation System (ICOS) Atmosphere Thematic Centre (ATC).

More information is available on the CHC website.

Recommendation 1 (, important, ongoing)**
The partnership between CHC and European institutions has proven to be successful and beneficial for all parties involved. These relationships are important for sustainability and scientific exchange and should be continued in the longer term.

Recommendation 2 (, important, ongoing)**
UMSA should explore all opportunities for training of station operators and scientists. Attendance at GAWTEC and other training courses is highly recommended, and knowledge needs to be shared within UMSA.

2.2 Location and access

The Chacaltaya Global GAW station (CHC) is located in the Bolivian Andes (16°21.014'S, 68º07.886'W, 5240 m above sea level). The station is about 25 km in a straight line from the centre of La Paz. Chacaltaya is a mountain with an open horizon to the south and west. Behind it (i.e. to the north and east) the high peaks of the mountain range separate it from the Amazon basin. The climate in Chacaltaya is generally dry and semi-desert, with annual rainfall of around 680 mm. Access to the site by road is possible throughout the year by 4WD vehicles and takes approximately two hours from La Paz. Further information is available from GAWSIS.

2.3 Station facilities

CHC provides laboratory and office facilities with high-speed internet access and mobile phone coverage. These facilities include a small dining room with kitchen and workshops. Basic accommodation is also available for visiting researchers. The laboratories are not temperature controlled and only heaters are available. The room temperature varies considerably, but this is acceptable for the current instrumentation. CHC provides an ideal platform for ongoing atmospheric research with limited space available for campaign-based experiments.

Recommendation 3 (*, minor, if the measurement programme is extended)
The temperature stability in the laboratory needs to be improved if more temperature sensitive instruments are installed. This is not necessary for the current equipment.

2.4 Measurement programme

CHC hosts a measurement programme covering reactive and greenhouse gases, aerosol physical, chemical and optical properties, and ancillary meteorological variables. An overview of the measured species is available on the CHC website and on GAWSIS.

The information available on GAWSIS was reviewed as part of the audit. The last update was made by CHC staff in February 2024 and the information found on GAWSIS was up to date.

2.5 Data management and data processing

The data management and processing of the GHG and CO measurements takes place at the Integrated Carbon Observation System (ICOS) carbon portal. Data are automatically transferred to the ICOS data portal once a day. Ozone data are managed and processed locally by the station PI.

2.6 Data submission

As of September 2024, the following CHC data within the scope of the audit were available at the World Data Centres:

CHC, submitted to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2012-2023).

No data were submitted to the World Data Centre for Greenhouse Gases (WDCGG). The data presented in this report were accessed on 25 July 2024.

> **Recommendation 4 (***, critical, 2025)**
> *Data submission to the World Data Centres is an obligation for stations participating in the GAW programme. The delay in submission should not exceed one year. GHG and CO data have to be submitted to WDCGG.*

2.7 Data review

As part of the system audit, data within the scope of WCC-Empa available at WDCRG was reviewed, and the ozone time series accessed appeared plausible. However, a problem with the ozone instrument was found during this audit and the data needs to be checked (see recommendations in the ozone section). Summary graphs and a brief description of the findings are provided in the Appendix.

2.8 Documentation

Electronic logbooks are available for all instruments and the station itself. Instrument manuals are available at the site. The information was comprehensive and up to date.

2.9 Air inlet system

GHGs and CO are sampled from an inlet on the roof of the station, approximately 10 m above the ground. The air inlet is an inverted stainless-steel bucket connected to a ¼" Synflex-1300 tubing. The length of Synflex tubing is approximately 7 m. A filter (Universal Filter FS-2K, MC Tech Group) protects the instrument and the valve unit and the air is dried by a Nafion dryer (Perma Pure model MD-070-144S-4).

The surface ozone air inlet is located close to the building wall, 6 m above the floor. It consists of approximately 2 m of PTFE tubing and is protected by a PFA filter holder with a PTFE filter. The flow rate is ~1 litre per minute and the inlet is protected from rain and snow by an inverted plastic cup. The residence time is less than 10 seconds. A leak test carried out by WCC-Empa during the audit showed an ozone loss of about 1%, due to the use of 6 mm PTFE tubing and a ¼ inch filter holder. The metadata records show that this happened sometime after August 2018. The tubing was replaced with ¼" PFA tubing during the audit.

The location of the ozone air inlet was discussed during the audit, as the location of the air inlet was not optimal. The CHC station staff then installed an alternative inlet on the roof, and parallel measurements were carried out over a period of one month. The average difference between the two inlet systems was found to be about 1 nmol mol^{-1}, while the hourly differences ranged from -3.9 to 3.8 nmol mol^{-1}. WCC-Empa recommends that the rooftop location be used as the inlet for the CHC surface ozone measurements.

Recommendation 5 (*, minor, 2025)
It is recommended that the newly installed roof inlet be used as the inlet for surface ozone measurements.

3 Performance audit

3.1 Surface ozone measurements

Surface ozone measurements at CHC started in 2011 and continuous time series data are available since April 2012.

Instrumentation. At the time of the audit, a Thermo Scientific ozone analyser (model 49i) was available. In addition, the ozone analyser of the El Alto measurement site was also available. This analyser is normally used for ozone measurements near the El Alto airport, but serves as a backup instrument in case of failure of the CHC analyser.

Standards. There is no ozone standard available at CHC. The station is equipped with an ozone generator (SYCOS KT-O3) and the Thermo 49i analyser has an internal ozone generator. Both are useful for checking instruments but are not suitable for calibrating ozone instruments. The SYCOS KT-O3 is unable to detect an atmospheric pressure lower than 600 hPa (CHC pressure is approx. 534 hPa). Therefore, it should not be used at CHC. The CHC instrument was calibrated at the Regional Calibration Centre (RCC) for surface ozone in Buenos Aires in 2017, and no calibrations have been performed since then.

> **Recommendation 6 (**, important, 2025)**
> *It is recommended to purchase an ozone calibrator to calibrate the ozone instruments operated at CHC, El Alto and La Paz. Traceability to a NIST Standard Reference Photometer (SRP) needs to be established.*

Data acquisition. A custom-built system programmed in LabVIEW is used for ozone data acquisition. 1 minute time resolution is available for ozone and ancillary data.

Intercomparison (performance audit). The Thermo Scientific ozone analysers of CHC and El Alto were compared to the WCC-Empa Travelling Standard (TS) with traceability to SRP#15. The internal ozone generator of the TS was used to generate a random sequence of ozone levels from 0 to 250 nmol mol^{-1}. The result of the comparisons is summarised below in relation to the WMO GAW Data Quality Objectives (DQOs) (Wmo, 2013). The data were collected using the WCC-Empa data acquisition system.

The following equations characterise the instrument bias 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 $1.1476\text{x}10^{-17}$ cm^2 (Hearn, 1961), the uncertainties reported below do not include the uncertainty of the ozone absorption cross section.

The initial comparison of the CHC ozone analyser showed significantly low readings of the CHC instrument. A broken ozone scrubber was identified as the cause of the low readings. The results were as follows:

CHC analyser Thermo Scientific 49i #A3NAC-001029 (BKG -0.3 nmol mol^{-1}, COEF 1.006), poor scrubber:

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] – 1.39 nmol mol^{-1}) / 0.7082 (1)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt ((0.54 nmol mol^{-1})^2 + 2.08e-05 * $X_{O3}{}^2$) (2)

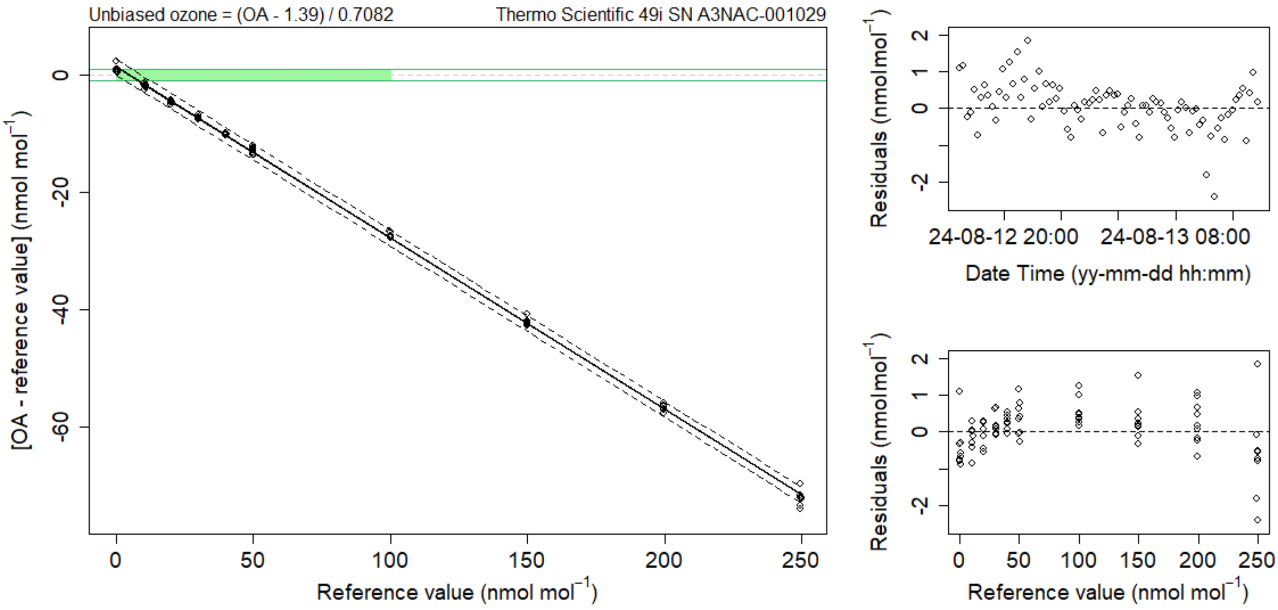

Figure 1. *Left: Bias of the CHC ozone analyser (Thermo Scientific 49i #A3NAC-001029, BKG -0.3 nmol mol^{-1}, COEF 1.006, bad scrubber) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated by green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

The failed ozone scrubber was then replaced and the comparison repeated. The results after scrubber replacement were as follows:

CHC analyser Thermo Scientific 49i #A3NAC-001029 (BKG -0.3 nmol mol^{-1}, COEF 1.006), good scrubber:

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] – 0.22 nmol mol^{-1}) / 1.0084 (3)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt ((0.54 nmol mol^{-1})^2 + 2.09e-05 * X_{O3}^2) (4)

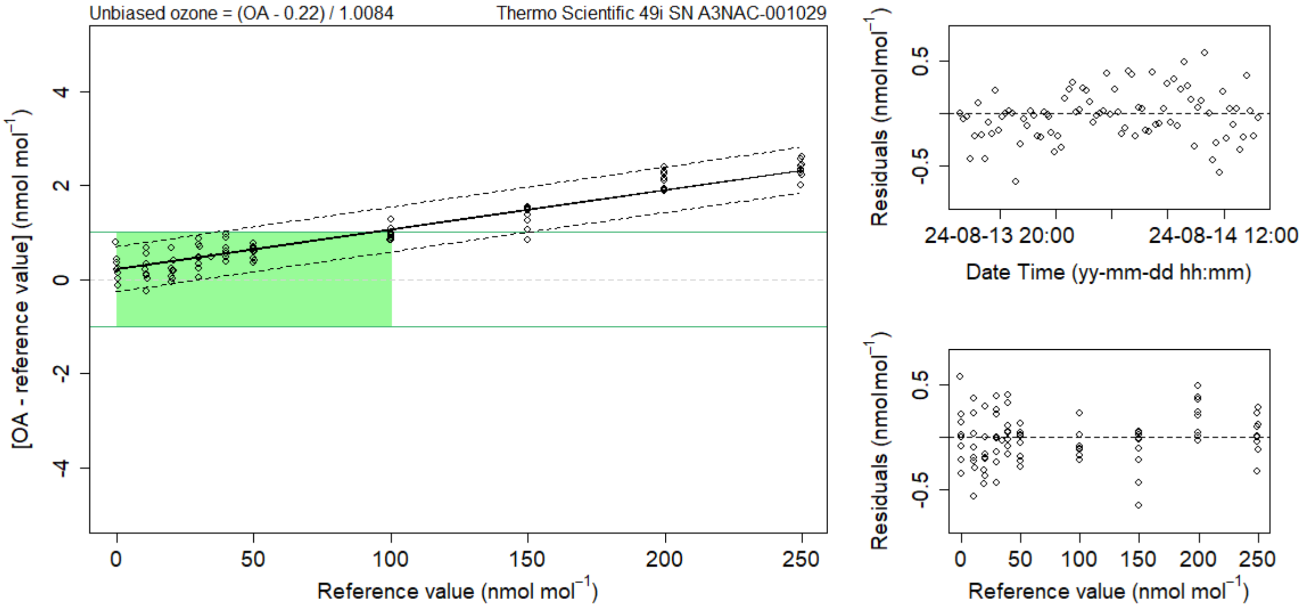

Figure 2. *Left: Bias of the CHC ozone analyser (Thermo Scientific 49i #A3NAC-001029, BKG -0.3 nmol mol^{-1}, COEF 1.006, new scrubber) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated by green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

The results of the CHC ozone analyser comparisons can be summarised as follows:

The first comparison of the CHC ozone analyser with the WCC-Empa reference instrument showed low readings of the CHC instrument due to a faulty ozone scrubber. Replacement of the scrubber solved the problem and confirmed that the instrument is well calibrated. However, the existing data series will need to be reviewed to identify the period of the faulty scrubber.

> **Recommendation 7 (***, critical, 2025)**
> *All ozone data need to be re-analysed. The time of the ozone scrubber failure must be determined and data for this period must be flagged as invalid if correction is not possible. It is also recommended that the ozone data be withdrawn from the WDCRG in the interim and resubmitted once the invalid data have been identified.*

In addition, the CHC ozone instrument is more than 10 years old and is reaching the end of its expected lifetime, which is 10 to 15 years. Replacement of the analyser should be considered.

> **Recommendation 8 (**, important, 2025)**
> *Replacement of the CHC ozone instrument should be considered. This needs to be included in the budget planning of the CHC station.*

Comparisons were also made with the El Alto ozone analyser and the results are summarised below.

Thermo Scientific 49i #1201207413 (BKG +0.0 nmol mol^{-1}, COEF 1.017):

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] + 0.95 nmol mol^{-1}) / 1.0089 (5)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt ((0.55 nmol mol^{-1})^2 + 2.10e-05 * X_{O3}^2)(6)

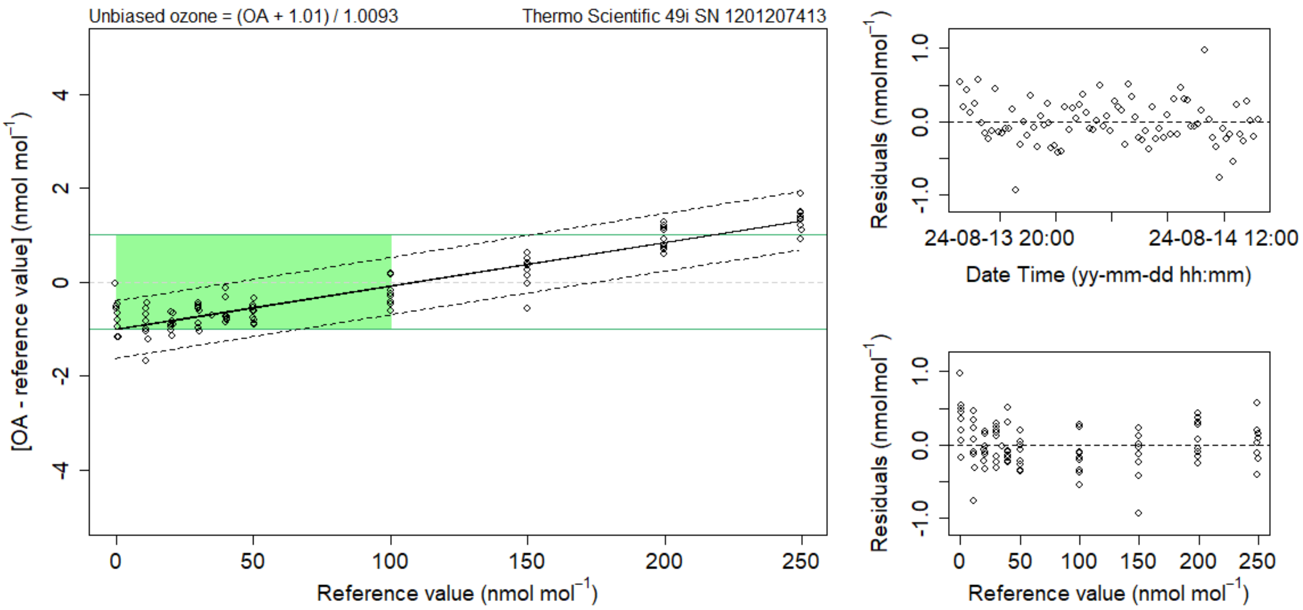

Figure 3. *Left: Bias of the CHC ozone analyser (Thermo Scientific 49i #1201207413, BKG +0.0 nmol mol^{-1}, COEF 1.017) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated by green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

The results of the comparisons of the El Alto ozone analyser can be summarised as follows:

The instrument is well calibrated but has also reached the end of its expected lifetime. It is recommended to replace the analyser with a new instrument.

3.2 Carbon monoxide measurements

Continuous measurements of CO at CHC started in 2016, and continuous data are available since then.

Instrumentation. CHC is equipped with a Picarro G2401 CRDS analyser and a custom-built calibration system. The sample air is dried using a Nafion dryer (Perma Pure MD-070-144S-04).

Standards. Four reference standards from LSCE are available at CHC. LSCE provides traceability to the GAW reference scales by assigning nominal amount fractions in their standards by comparison with laboratory cylinders obtained from the GAW Central Calibration Laboratory (CCL). Target cylinders are also available for quality control purposes. The LSCE CO standards were also analysed on the WCC-Empa CRDS instrument during the audit. The results of the comparison are shown in Table 1.

Table 1. *LSCE CO calibration standards at CHC as of August 2024 and the results of the WCC-Empa analysis.*

Cylinder ID	**LSCE** CO (X2014A) (nmol mol^{-1})	**WCC-Empa** CO (X2014A) (nmol mol^{-1})	**LSCE - WCC** CO (X2014A) (nmol mol^{-1})
D262999	61.18	65.85	-4.67
D262988	101.90	107.21	-5.31
D215872	157.50	160.98	-3.48
D262996	203.97	210.61	-6.64

Calibration. Ambient air (600 min) and a short-term target tank (20 min) are run alternately for 361.6 h (15 cycles), followed by a sequence of the 4 calibration standards (each tank for 30 min, 3 cycles), a long-term target (30 min) and another target tank run (20 min).

Data acquisition. The internal data acquisition of the CRDS analyser is used and the highest resolution (1-2 s resolution) raw data files are stored. Raw data files are sent daily to the ICOS Atmospheric Thematic Centre (ATC) for processing, see Hazan et al. (2016).

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

The following equations characterise the instrument bias and the results are further illustrated in Figure 4 with respect to the WMO/GAW compatibility goals and the extended compatibility goals (Wmo, 2024):

Picarro G2401 #2519-CFKADS2226:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 5.15 nmol mol^{-1}) / 0.9981 (7)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt ((2.2 nmol mol^{-1})^2 + 1.01e-04 * X_{CO}^2) (8)

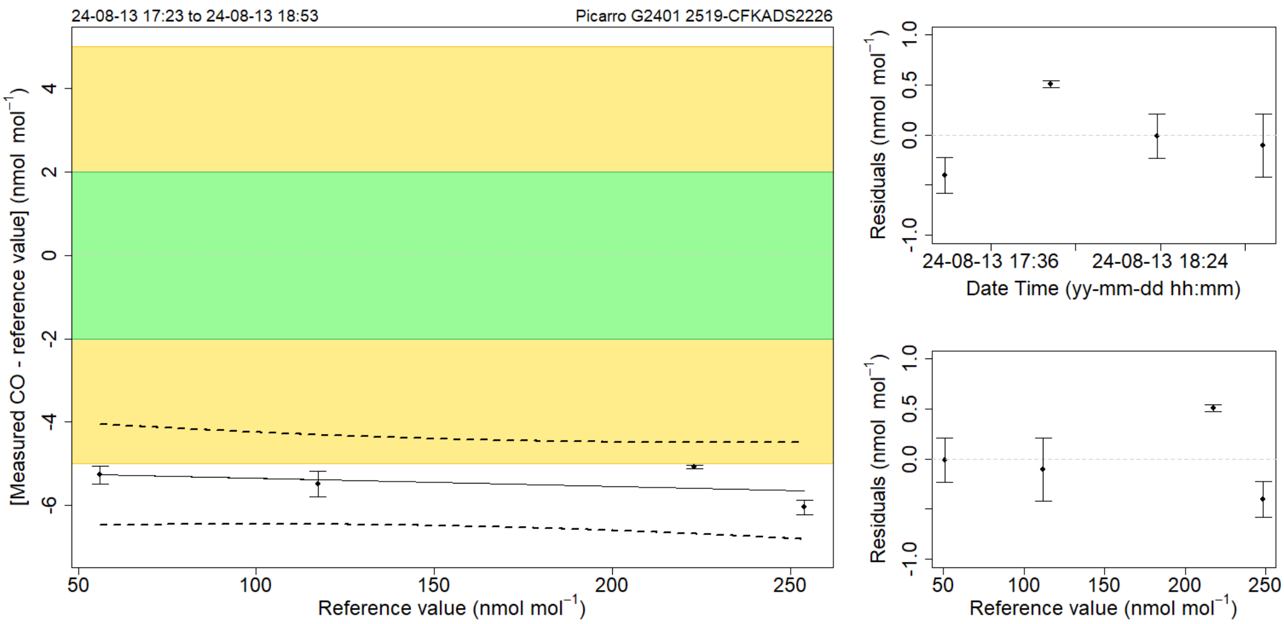

Figure 4. *Left: Bias of the PICARRO G2401 #2519-CFKADS2226 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CHC. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

CHC measurements were about 5.2 nmol mol^{-1} lower compared to WCC-Empa. ATC is currently not considering any drift for the CO standards used at CHC, in contrast to other stations in the ICOS network. An internal audit organised by the LSCE based on round robin cylinder measurements in August 2023 showed an average bias of 4.9 nmol mol^{-1}, which was attributed to CO drift in the CHC cylinders over the last 8 years since their initial calibration at the LSCE. These results are in good agreement with the results of the current WCC-Empa audit. Therefore, the CHC performance could be further improved by applying a drift correction to the CHC standards. However, the exact determination of the drift rates will be difficult as the recalibration of the CHC standards at the LSCE is not feasible for logistical reasons.

Recommendation 9 (, important, 2025)**
It is recommended to apply a drift correction to the CO standards. It is also recommended to recalibrate the CHC standards at the LSCE at the end of their lifetime.

3.3 Methane measurements

Continuous measurements of CH_4 at CHC started in 2014 with a Picarro ESP-1000, which was replaced by a Picarro G2401 in 2016, and continuous data are available since then.

Instrumentation, standards, calibration and data acquisition. See CO.

The LSCE CH_4 standards were also analysed on the WCC-Empa CRDS instrument during the audit. The results of the comparison are shown in Table 2.

Table 2. *LSCE CH_4 calibration standards at CHC as of August 2024 and the results of the WCC-Empa analysis.*

Cylinder ID	**LSCE** CH_4 (X2004A) (nmol mol^{-1})	**WCC-Empa** CH_4 (X2004A) (nmol mol^{-1})	**LSCE - WCC** CH_4 (X2004A) (nmol mol^{-1})
D262999	1834.13	1833.48	0.65
D262988	1987.48	1987.09	0.39
D215872	2032.38	2031.86	0.52
D262996	2326.08	2325.91	0.17

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

The following equation characterises the instrument bias. The results are further illustrated in Figure 5 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (Wmo, 2024).

Picarro G2401 #2519-CFKADS2226:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.66 nmol mol^{-1}) / 0.9990 (9)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt ((0.3 nmol mol^{-1})^2 + 1.30e-07 * X_{CH4}^2) (10)

The result of the comparison can be summarised as follows:

Excellent agreement, well within the WMO/GAW network compatibility goal, was found in the relevant range of amount fractions. The good results indicate that the whole system, including calibration procedures and standard gases, is fully adequate and no further action is required.

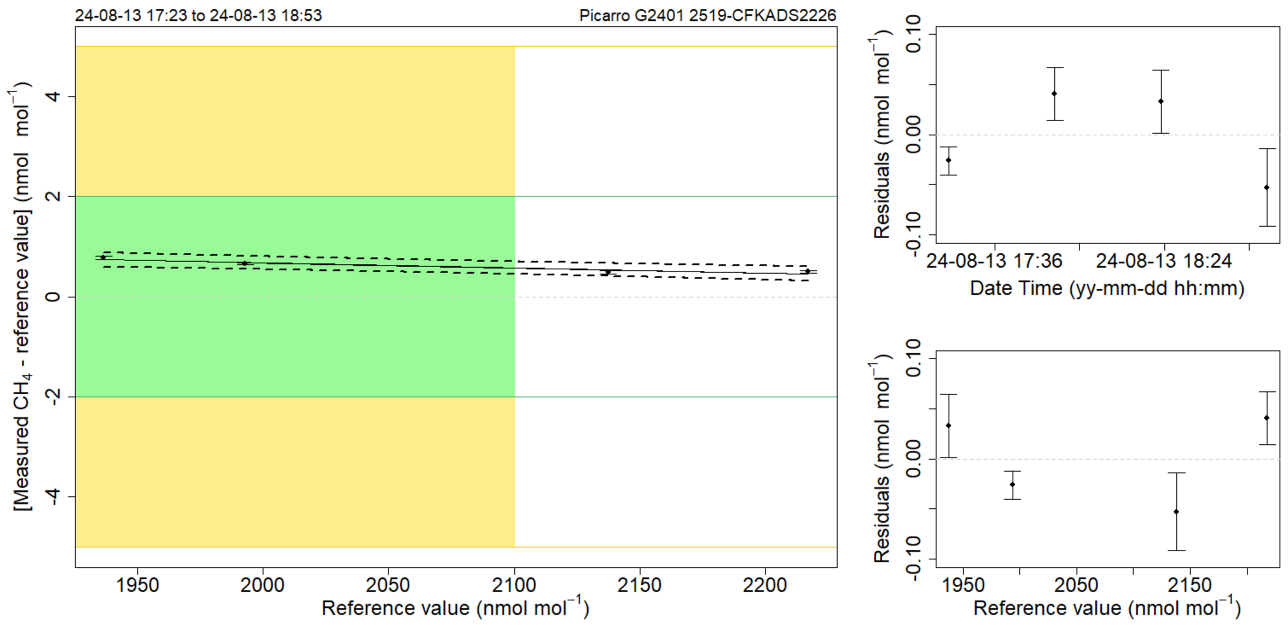

Figure 5. *Left: Bias of the Picarro G2401 #2519-CFKADS2226 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CHC. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

3.4 Carbon dioxide measurements

Continuous measurements of CO_2 at CHC started in 2014 with a Picarro ESP-1000, which was replaced by a Picarro G2401 in 2016, and continuous data are available since then.

Instrumentation, standards, calibration and data acquisition. See CO.

The LSCE CO_2 standards were also analysed on the WCC-Empa CRDS instrument during the audit. The results of the comparison are shown in Table 3.

Table 3 *LSCE CO_2 calibration standards at CHC as of August 2024 and the results of the WCC-Empa analysis.*

Cylinder ID	**LSCE** CO_2 (X2019A) (nmol mol^{-1})	**WCC-Empa** CO_2 (X2019A) (nmol mol^{-1})	**LSCE - WCC** CO_2 (X2019A) (nmol mol^{-1})
D262999	372.10	372.09	0.01
D262988	392.04	392.03	0.01
D215872	412.16	412.16	0.00
D262996	451.93	451.91	0.02

Intercomparison (performance audit). The comparison consisted of repeated challenges of the CHC instrument with randomly selected CO_2 levels from travelling standards.

The following equations characterise the instrument bias. The result is further illustrated in Figure 6 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (Wmo, 2024).

Picarro G2401 #2519-CFKADS2226:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 - 0.19 µmol mol^{-1}) / 0.9996 (11)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt ((0.08 µmol mol^{-1})^2 + 3.28e-8 * $X_{CO2}{}^2$) (12)

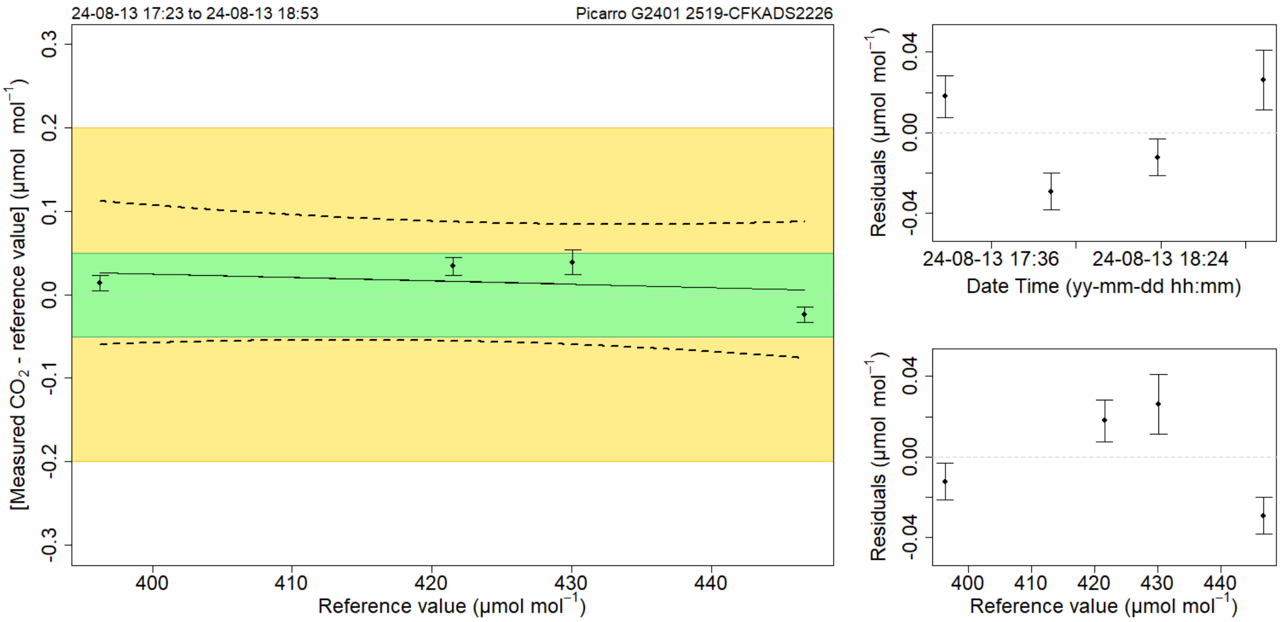

Figure 6. *Left: Bias of the Picarro G2401 #2519-CFKADS2226 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for CHC. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

The result was within the WMO/GAW network compatibility goal for the southern hemisphere in the relevant CO_2 range. The bias showed no significant dependence on the amount fraction. Based on the excellent results, no further action is required. The measurement setup is fully adequate.

4 Comparison of CHC performance audit results with other stations

This section compares the results of the CHC performance audit with other station audits conducted by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO, but is also applicable to other compounds. Essentially, the bias in the middle of the relevant amount fraction range is plotted against the slope of the linear regression analysis of the performance audits. The relevant amount fraction ranges are taken from the recommendation of the GGMT-2019 meeting (Wmo, 2024) for CO_2, CH_4, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone, the amount fraction range of 0--100 nmol mol^{-1} was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 7 shows the bias vs. slope of the WCC-Empa performance audits by for O_3, CO, CH_4 and CO_2, The grey dots show all comparisons made during the WCC-Empa audits for the main station analysers but exclude cases with known instrumental problems. Where an adjustment was made during an audit, only the final comparison is shown. The results of the current CHC audit are shown as coloured dots in Figure 7.

For the surface ozone analysers, the results were within the DQOs for the CHC and El Alto instruments after the scrubber replacement on the CHC instrument. Prior to the scrubber replacement, this instrument was well outside the DQOs. The Southern Hemisphere (SH) WMO/GAW network compatibility goals were met for CH_4 and CO_2. CO comparisons slightly exceeded the extended WMO/GAW network compatibility goals due to drift of the standard gases.

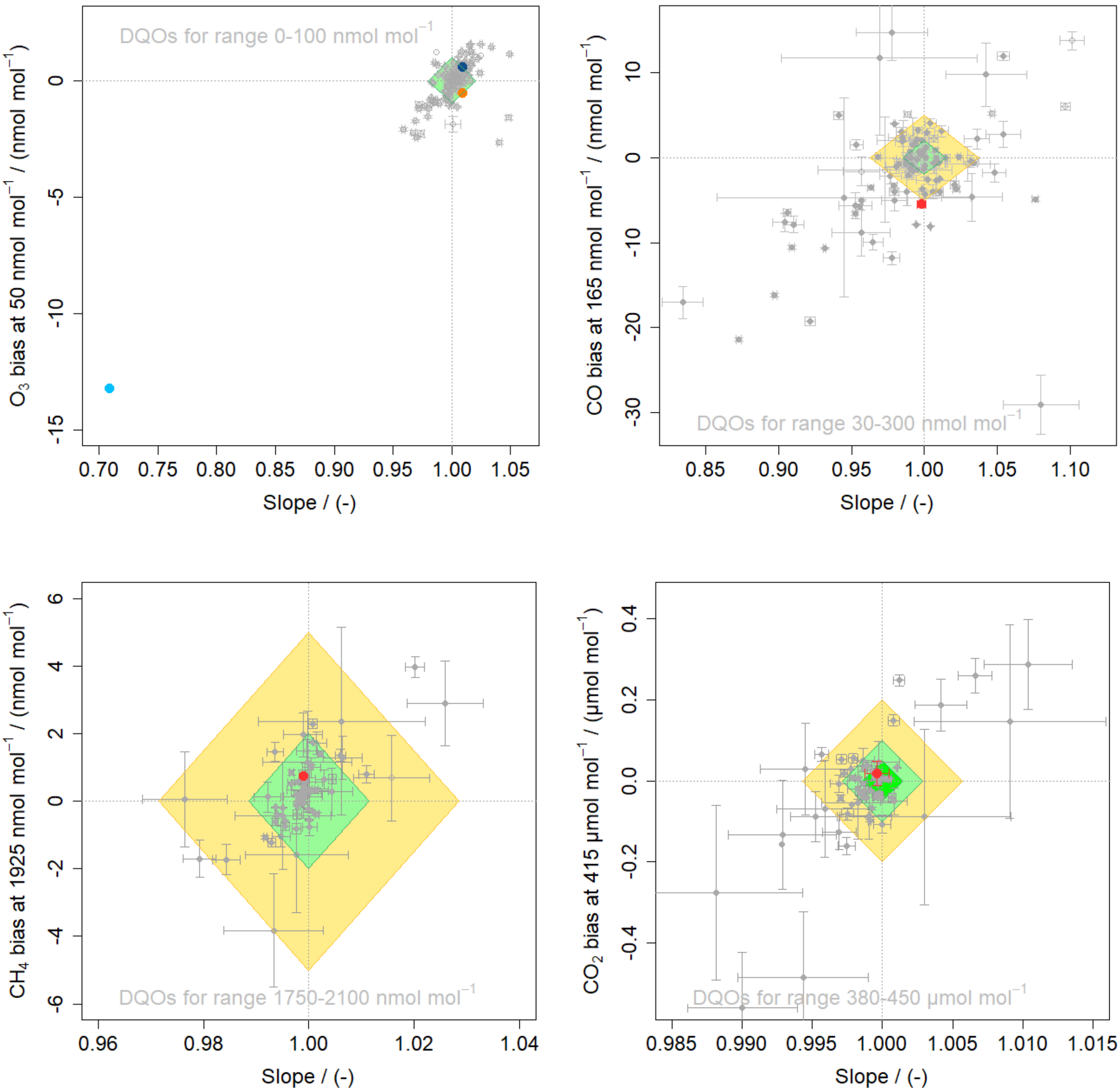

Figure 7. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show CHC results (light blue: CHC Thermo 49i, broken scrubber, dark blue: CHC Thermo 49i, repaired, orange: El Alto Thermo 49i, red: Picarro G2401). Filled symbols refer to a comparison with the same calibration scale at the station and at the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green, southern and northern hemisphere shades for CO_2) and the extended compatibility goals (yellow).*

5 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 #617-CFKADS2001). The CHC CRDS instrument was compared with the TI between 14 August 2024 and 30 September 2024. The TI was connected to an independent inlet line leading to the same inlet location as the CHC analyser. The TI sampled air in the following sequence: 2765 min ambient air from the independent inlet followed by 60 min measurement of three standard gases, each for 20 min. The sample air was dried using a Nafion dryer (Perma Pure model PD-50T-12MPS) in reflux mode with the Picarro pump for the vacuum in the purge air stream. To account for the residual effect of water vapour, a correction function (Rella et al., 2013; Zellweger et al., 2012) was applied to the CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The CHC data have been processed by the ICOS ATC.

The comparison period can be divided into two periods. During the first period from 14 August to 16 September 2024, no changes were made to the CHC inlet system. During this period, a small leak was detected in the CHC inlet system. Figures 8 to 10 show the comparison of hourly CO, CH_4 and CO_2 measurements between the WCC-Empa TI and the CHC instruments for this period. For the CRDS instruments, hourly averages were calculated based on 1 minute data with simultaneous data availability from the station analysers and the WCC-Empa TI.

The results for this period confirmed the findings of the travelling standard comparisons for CO and CH_4. However, a significant diurnal cycle was found in the CO_2 bias, indicating a leak in the inlet system. It was then decided to swap the inlet lines on 16 September 2024 to confirm this hypothesis. The high-resolution data (1-min averages) of CO_2 for this period are shown in Figure 11. The agreement between the CHC and the WCC instrument was relatively good before the arrival of the station staff at 14:00. Thereafter, the CHC instrument read higher CO_2 levels due to the presence of a leak and increased indoor concentrations. After the inlet lines were swapped, the WCC instrument read higher because it was connected to the bad inlet line.

It was then decided to replace the CHC inlet line with new tubing and fittings on 19 September 2024. The CO_2 comparison for the remaining period from 19 to 30 September is shown in Figure 12. The diurnal cycle of the bias was no longer present and the agreement between the CHC and the WCC-Empa instruments was excellent. CO and CH_4 are not shown for this period as the influence of the leak in the inlet line was negligible and the results were similar to the first period.

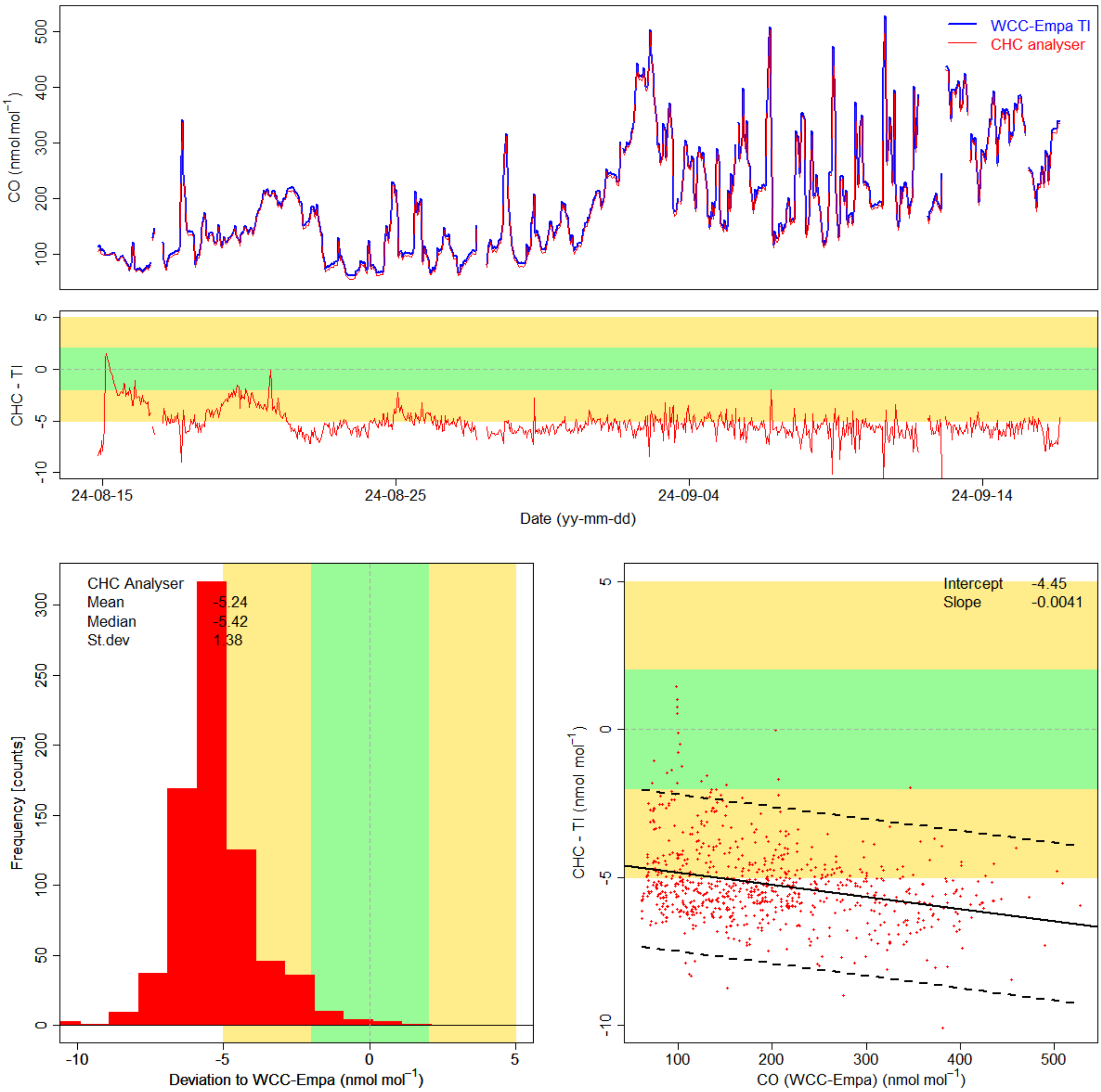

Figure 8. *Top: Comparison of Picarro G2401 #2519-CFKADS2226 with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G2401 #2519-CFKADS2226 analyser compared to the WCC-Empa TI. Bottom right: CHC instrument bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

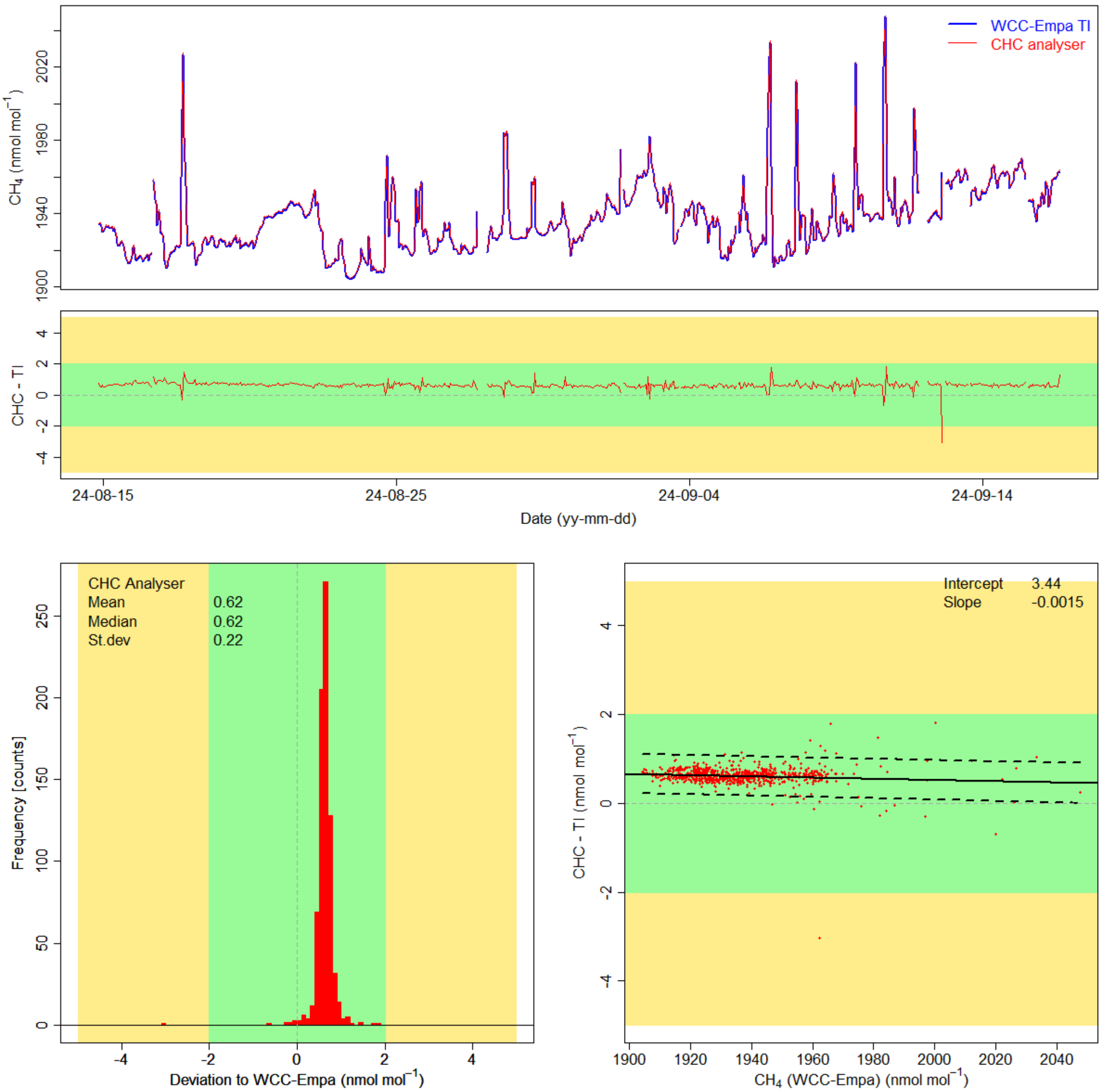

Figure 9. *Top: Comparison of Picarro G2401 #2519-CFKADS2226 with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CH_4 deviation histograms for the G2401 #2519-CFKADS2226 analyser compared to the WCC-Empa TI. Bottom right: CHC instrument bias as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

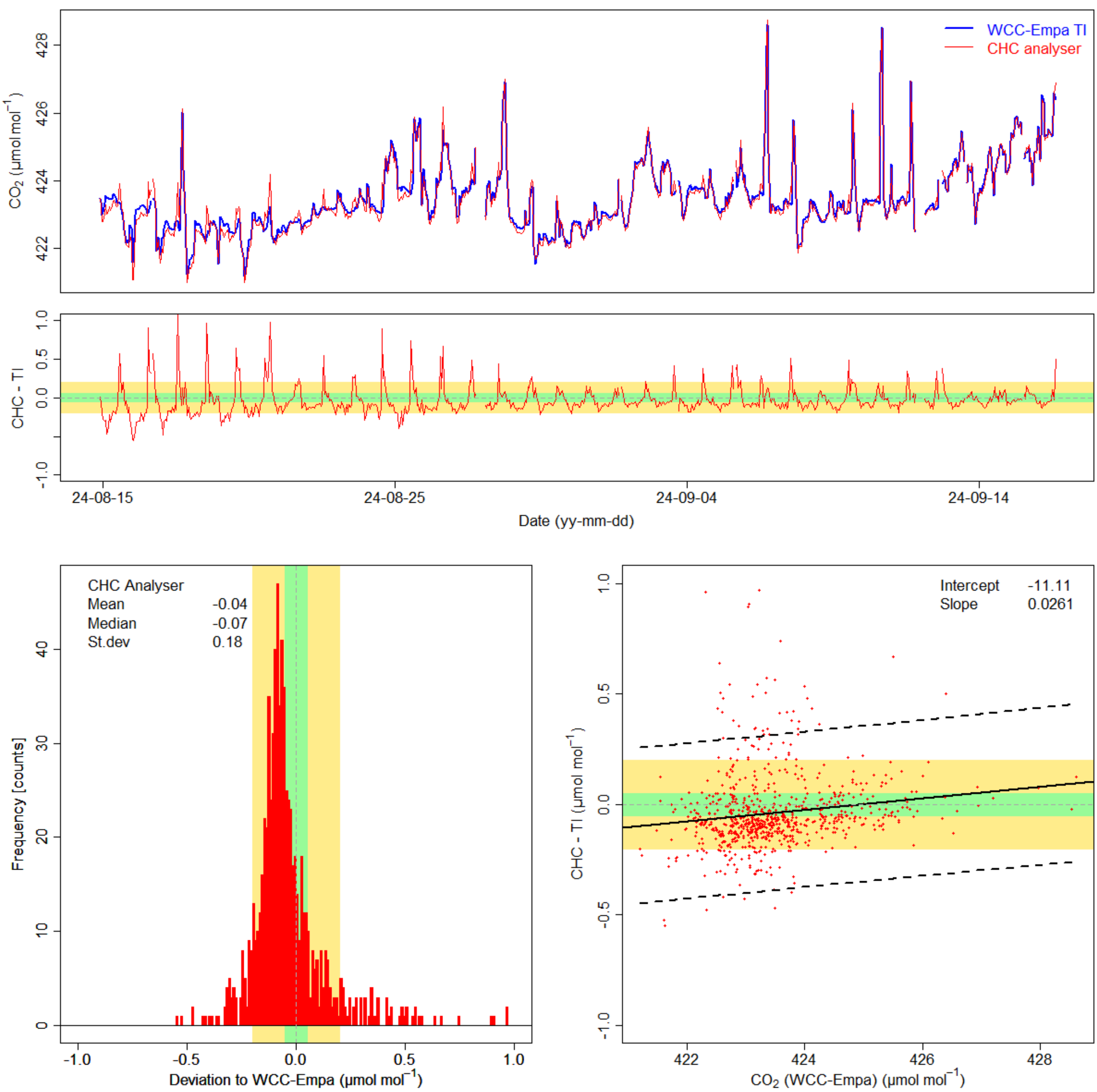

Figure 10. *Top: Comparison of Picarro G2401 #2519-CFKADS2226 with the WCC-Empa travelling instrument for CO_2 for the period from 14 August to 16 September 2024. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO_2 deviation histograms for the Picarro G2401 #2519-CFKADS2226 analyser compared to the WCC-Empa TI. Bottom right: CHC instrument bias as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

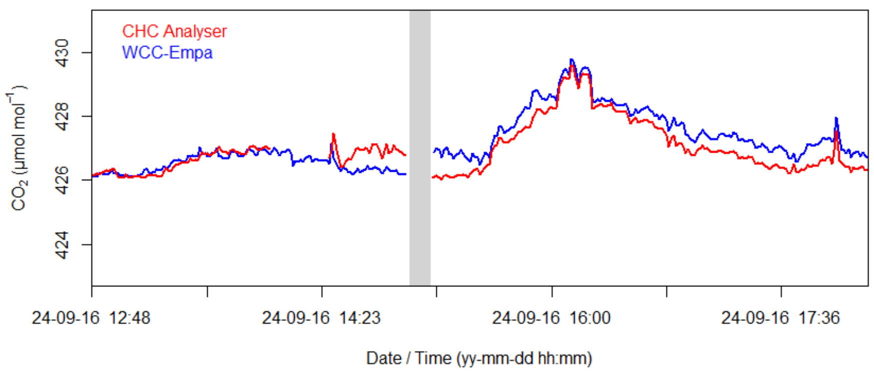

Figure 11. *High-resolution CO_2 comparison data for the CHC and WCC-Empa instruments. The grey area indicates the time of the inlet switch.*

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

5.1 Carbon monoxide

CHC ambient air measurements were about 5 nmol mol^{-1} lower compared to WCC-Empa. This is in good agreement with the TS comparison and confirms the results of the performance audit. For further improvement, a drift correction as recommended above or an alternative calibration approach using zero air and a standard with a high CO amount fraction (> 1 µmol mol^{-1}) should be implemented.

5.2 Methane

Good agreement within the WMO/GAW network compatibility goals was found between the TI and the CHC instrument, confirming the results of the travelling standard comparisons. Temporal variability was well captured by both instruments.

5.3 Carbon dioxide

On average, the agreement between the WCC-Empa TI and the CHC instrument was within the WMO/GAW compatibility goal for the SH (-0.04 µmol mol^{-1}) during both comparison periods. However, a leak in the inlet line resulted in a significant diurnal cycle of the bias and higher variability. The problem was solved during the audit by replacing the inlet line, and perfect agreement between CHC and WCC-Empa was found. A thorough analysis performed by the CHC staff after the audit showed that the leak in the inlet line was most likely caused by the work in preparation for the current audit on 10 August 2024. Therefore, data prior to that date was most likely not affected.

Recommendation 10 (, important, 2025)**
It is recommended that the inlet line is regularly checked for leaks. The second line installed for the audit can be used for this purpose.

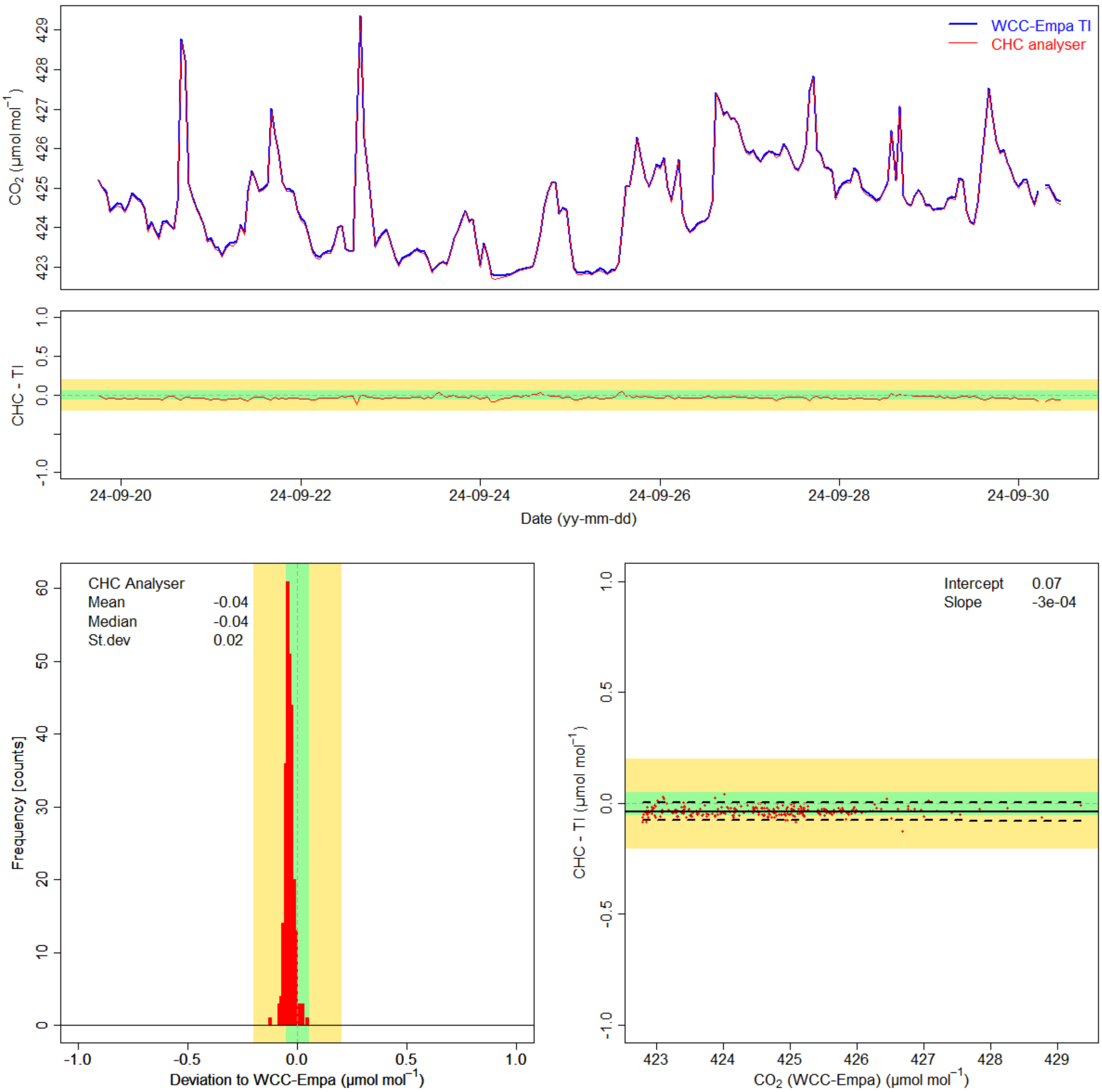

Figure 12. *Top: Comparison of Picarro G2401 #2519-CFKADS2226 with the WCC-Empa travelling instrument for CO_2 for the period from 19 - 30 September 2024. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO_2 deviation histograms for the Picarro G2401 #2519-CFKADS2226 analyser compared to the WCC-Empa TI. Bottom right: CHC instrument bias as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

6 Conclusions

The Chacaltaya Global GAW Station has been contributing to the GAW programme since 2012. The location of the station is unique and allows for a variety of research opportunities. In addition to being able to measure unpolluted air masses in the free troposphere over continental South America, the station is also exposed to seasonal emissions from forest fires in the Amazon and occasionally sees emissions from the nearby cities of El Alto and La Paz. This allows the study of different air masses and makes CHC a very important contributor to the GAW programme.

The GHG measurements evaluated 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 than the extended WMO/GAW network compatibility goal due to drift in the CO standards. 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 2017 onwards need to be carefully re-evaluated. Historical data should be compared with recent data after the audit to identify potential systematic biases and to determine the period of ozone breakthrough over the scrubber.

The continuation of the CHC measurement series is very important to GAW, and continued investment and training of station staff is required to ensure high data quality and availability. The continuation of the partnership between CHC and LSCE is highly valuable in terms of both sustainability and science.

Table 4 summarises the results of the performance audit with travelling standards and the ambient air comparison in relation to the WMO/GAW compatibility goals.

Table 4. *Summary of the results of the performance audit and parallel measurement in Chacaltaya. A tick mark in the table indicates that the compatibility goal (green) or the extended compatibility goal (orange) has been met on average, and ✗ indicates results that exceed the compatibility goals.*

Compound / Instrument	**Range**	**Unit**	**CHC within DQO/eDQO**
O_3 (Thermo Scientific 49i #A3NAC-001029), CHC, broken scrubber	0 -100	nmol mol^{-1}	✗
O_3 (Thermo Scientific 49i #A3NAC-001029), CHC, repaired	0 -100	nmol mol^{-1}	✓
O_3 (Thermo Scientific 49i #1201207413), backup instrument, El Alto	0 -100	nmol mol^{-1}	✓
CO (Picarro G2401 #2519-CFKADS2226)	30 - 300	nmol mol^{-1}	✗
CO (Picarro G2401 #2519-CFKADS2226), parallel measurements	NA	nmol mol^{-1}	✗
CH_4 (Picarro G2401 #2519-CFKADS2226)	1750 - 2100	nmol mol^{-1}	✓
CH_4 (Picarro G2401 #2519-CFKADS2226), parallel measurements	NA	nmol mol^{-1}	✓
CO_2 (Picarro G2401 #2519-CFKADS2226)	380 - 450	µmol mol^{-1}	✓
CO_2 (Picarro G2401 #2519-CFKADS2226), parallel measurements	NA	µmol mol^{-1}	✓

7 Summary ranking of the Chacaltaya GAW station

System Audit Aspect	Adequacy#	Comment
Measurement programme	(4)	A small but important programme
Access	(5)	Year-round access
Facilities		
Laboratory and office space	(5)	Adequate, with some space for additional research campaigns
Internet access	(5)	High-speed connection
Air Conditioning	(2)	No air conditioning, temperature fluctuations > 10°C, but suitable for current instrumentation
Power supply	(4)	Mostly reliable and stable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(4)	Skilled and motivated staff
Air Inlet System	(4)	Mostly adequate inlet systems, leak in GHG inlet has been repaired
Instrumentation		
Ozone (Themo Scientific 49i)	(4)	Adequate but reaching the end of lifetime
CH_4/CO_2/CO Picarro G2401	(5)	State of the art instrumentation
Standards		
O_3	(0)	Not available
CO, CO_2, CH_4	(5)	Traceability to the WMO/GAW reference trough LSCE.
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(5)	Qualified staff, appropriate procedures
Data submission WDCRG	(4)	Timely submission, some data gaps
Data submission WDCGG	(0)	GHG and CO data not submitted

#0: inadequate thru 5: adequate.

Appendix

A1. List of recommendations

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

#	Recommendation	Priority	Significance	Date
1	The partnership between CHC and European institutions has proven to be successful and beneficial for all parties involved. These relationships are important for sustainability and scientific exchange and should be continued in the longer term.	Medium	Important	Ongoing
2	UMSA should explore all opportunities for training of station operators and scientists. Attendance at GAWTEC and other training courses is highly recommended, and knowledge needs to be shared within UMSA.	Medium	Important	Ongoing
3	T The temperature stability in the laboratory needs to be improved if more temperature sensitive instruments are installed. This is not necessary for the current equipment.	Low	Minor	Extension of the programme
4	Data submission to the World Data Centres is an obligation for stations participating in the GAW programme. The delay in submission should not exceed one year. GHG and CO data have to be submitted to WDCGG.	High	Critical	2025
5	It is recommended that the newly installed roof inlet be used as the inlet for surface ozone measurements.	Low	Minor	2025
6	It is recommended to purchase an ozone calibrator to calibrate the ozone instruments operated at CHC, El Alto and La Paz. Traceability to a NIST Standard Reference Photometer (SRP) needs to be established.	Medium	Important	2025
7	All ozone data need be re-analysed. The time of the ozone scrubber failure must be determined and data for this period must be flagged as invalid if correction is not possible. It is also recommended that the ozone data be withdrawn from the WDCRG in the interim and resubmitted once the invalid data have been identified.	High	Critical	2025
8	Replacement of the CHC ozone instrument should be considered. This needs to be included in the budget planning of the CHC station.	Medium	Important	2025
9	It is recommended to apply a drift correction to the CO standards. It is also recommended to recalibrate the CHC standards at the LSCE at the end of their lifetime.	Medium	Important	2025
10	It is recommended that the inlet line is regularly checked for leaks. The second line installed for the audit can be used for this purpose.	Medium	Important	2025

A2. Data review

The following figures show summary plots of CHC data obtained from the WDCRG on 27 July 2024. The plots show time series of hourly data, frequency distribution and diurnal and seasonal variations. No data were available from WDCGG.

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

Surface ozone:

The in-situ O_3 data submitted by UMSA are shown in the figure below.

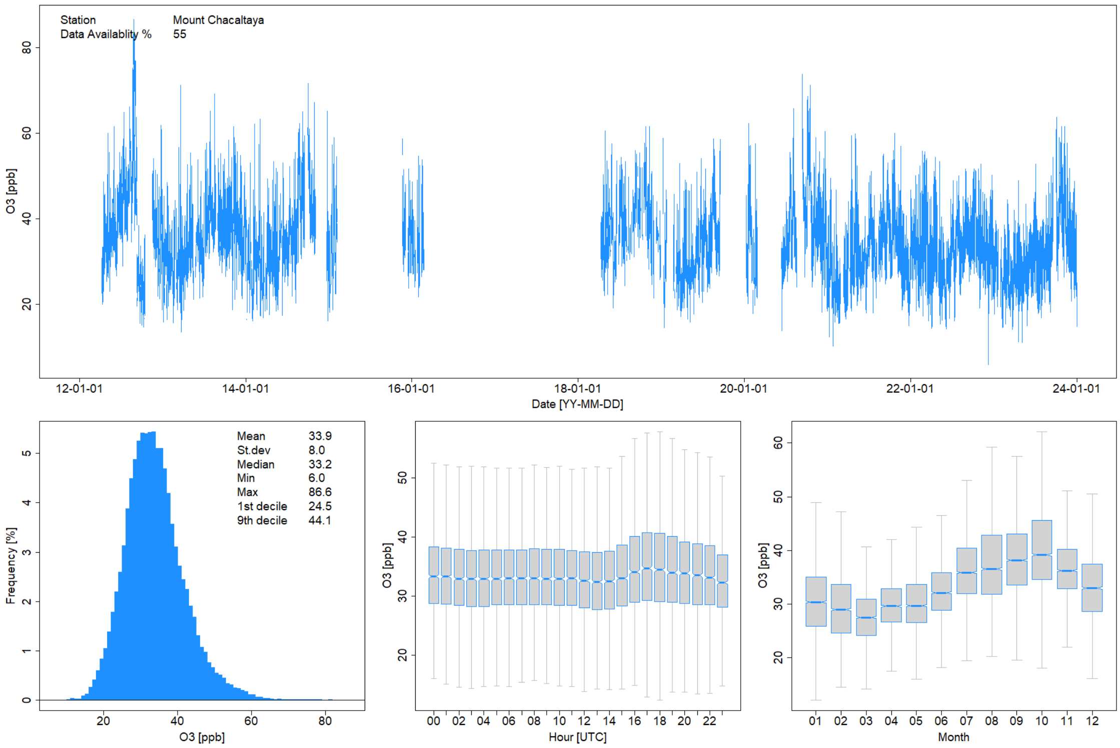

Figure 13. *WDCRG O_3 data for the period 2012 to 2023. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line shows the median and the blue boxes show the interquartile range.*

- The dataset looks good at first glance in terms of amount fraction, trend, seasonal and diurnal variation.
- However, the values may be too low as an instrumental problem was found during the audit.
- The data need further quality control.

A3. Surface ozone comparisons

All procedures were carried out according to the standard operating procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the standard reference photometer at Empa before and after the analyser comparison. The internal ozone generator of the WCC-Empa transfer standard was used to generate a randomised sequence of ozone levels ranging from 0 to 500 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 analysers and calibrators using approximately 1.5 m of PFA tubing. Table 5 details the experimental setup for the comparisons between the travelling standard and the station instruments. The data used for the evaluation were recorded by the WCC-Empa and CHC data acquisition systems.

Table 5. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #0810-153 (WCC-Empa)
Settings	BKG +0.0 COEF 1.009
Pressure readings (hPa)	Initial: Ambient 544.8; TS 546.8 The pressure sensor was calibrated before the comparisons. Final: Ambient 544.8; TS 544.7
CHC ozone analyser (OA)	
Model, S/N	Thermo Scientific 49i #A3NAC-001029
Principle	UV absorption
Settings	BKG -0.3 nmol mol^{-1}, COEF 1.006
Pressure readings (hPa)	Initial: Ambient 544.8; OA 543.7 The pressure sensor was calibrated before the comparisons. Final: Ambient 544.8; OA 544.8
El Alto ozone analyser (OA)	
Model, S/N	Thermo Scientific 49i #1201207413
Principle	UV absorption
Settings	BKG +0.0 nmol mol^{-1}, COEF 1.017
Pressure readings (hPa)	Initial: Ambient 545.0; OA 549.7 The pressure sensor was calibrated before the comparisons. Final: Ambient 545.0; OA 544.9

Results

Each ozone level was measured for fifteen minutes, and the last five 1-minute averages were aggregated. These aggregates were used to evaluate the comparison. All results are valid for the calibration factors given in Table 5 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) before to the ozone analyser values were evaluated. The same treatment was applied as for the ambient air analysis.
The results of the assessment are shown in the following table (individual measurement points) and are also presented in the Executive Summary.

Table 6. *Comparison of the main CHC ozone analyser (OA) Thermo Scientific 49i #A3NAC-001029 (BKG -0.3 nmol mol^{-1}, COEF 1.006, broken 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 (%)
2024-08-12 16:57	0.15	0.36	2.59	0.72	2.44	NA
2024-08-12 17:12	50.02	0.20	37.98	0.35	-12.04	-24.07
2024-08-12 17:27	199.67	0.20	142.57	0.43	-57.10	-28.60
2024-08-12 17:42	149.91	0.19	107.45	0.31	-42.46	-28.32
2024-08-12 17:57	99.92	0.18	72.66	0.54	-27.26	-27.28
2024-08-12 18:12	249.62	0.10	177.44	0.35	-72.18	-28.92
2024-08-12 18:27	20.14	0.17	15.94	0.22	-4.20	-20.85
2024-08-12 18:42	29.94	0.15	23.23	0.28	-6.71	-22.41
2024-08-12 18:57	40.15	0.20	30.19	0.31	-9.96	-24.81
2024-08-12 19:12	10.14	0.33	8.61	0.03	-1.53	-15.09
2024-08-12 19:27	0.28	0.18	1.25	0.13	0.97	NA
2024-08-12 19:42	40.01	0.15	30.18	0.55	-9.83	-24.57
2024-08-12 19:57	199.71	0.17	143.88	0.23	-55.83	-27.96
2024-08-12 20:12	20.10	0.48	15.92	0.34	-4.18	-20.80
2024-08-12 20:27	99.85	0.19	73.36	0.25	-26.49	-26.53
2024-08-12 20:42	30.05	0.47	23.32	0.34	-6.73	-22.40
2024-08-12 20:57	149.85	0.13	109.06	0.31	-40.79	-27.22
2024-08-12 21:12	10.39	0.43	9.04	0.23	-1.35	-12.99
2024-08-12 21:27	50.04	0.34	37.63	0.31	-12.41	-24.80
2024-08-12 21:42	249.59	0.25	179.98	0.42	-69.61	-27.89
2024-08-12 21:57	0.46	0.25	1.43	0.13	0.97	NA
2024-08-12 22:12	40.07	0.26	30.31	0.24	-9.76	-24.36
2024-08-12 22:27	99.96	0.18	73.19	0.29	-26.77	-26.78
2024-08-12 22:42	10.67	0.87	8.99	0.71	-1.68	-15.75
2024-08-12 22:57	199.70	0.13	143.47	0.39	-56.23	-28.16
2024-08-12 23:12	30.05	0.26	22.85	0.20	-7.20	-23.96
2024-08-12 23:27	49.99	0.24	37.44	0.28	-12.55	-25.11
2024-08-12 23:42	20.11	0.27	15.89	0.31	-4.22	-20.98
2024-08-12 23:57	149.82	0.25	108.03	0.44	-41.79	-27.89
2024-08-13 00:12	249.53	0.10	178.02	0.24	-71.51	-28.66
2024-08-13 00:27	0.51	0.34	1.17	0.15	0.66	NA
2024-08-13 00:42	249.62	0.20	177.39	0.26	-72.23	-28.94
2024-08-13 00:57	20.07	0.38	15.67	0.20	-4.40	-21.92
2024-08-13 01:12	49.96	0.20	36.73	0.21	-13.23	-26.48
2024-08-13 01:27	10.59	0.44	8.61	0.48	-1.98	-18.70
2024-08-13 01:42	199.76	0.09	143.02	0.08	-56.74	-28.40
2024-08-13 01:57	30.13	0.27	22.87	0.16	-7.26	-24.10
2024-08-13 02:12	40.06	0.05	30.00	0.20	-10.06	-25.11
2024-08-13 02:27	99.96	0.28	72.65	0.71	-27.31	-27.32
2024-08-13 02:42	149.84	0.15	107.74	0.24	-42.10	-28.10
2024-08-13 02:57	0.59	0.16	1.13	0.16	0.54	NA
2024-08-13 03:12	50.00	0.23	37.16	0.34	-12.84	-25.68
2024-08-13 03:27	199.63	0.05	143.25	0.23	-56.38	-28.24
2024-08-13 03:42	149.81	0.13	107.85	0.38	-41.96	-28.01
2024-08-13 03:57	99.90	0.05	72.51	0.20	-27.39	-27.42

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 (%)
2024-08-13 04:12	249.58	0.02	177.64	0.18	-71.94	-28.82
2024-08-13 04:27	20.09	0.19	15.50	0.15	-4.59	-22.85
2024-08-13 04:42	30.09	0.20	22.77	0.14	-7.32	-24.33
2024-08-13 04:57	40.16	0.27	30.08	0.37	-10.08	-25.10
2024-08-13 05:12	10.71	0.50	8.55	0.36	-2.16	-20.17
2024-08-13 05:27	0.34	0.18	0.83	0.07	0.49	NA
2024-08-13 05:42	40.04	0.12	29.83	0.23	-10.21	-25.50
2024-08-13 05:57	199.72	0.20	142.92	0.24	-56.80	-28.44
2024-08-13 06:12	20.23	0.41	15.62	0.21	-4.61	-22.79
2024-08-13 06:27	99.94	0.24	72.43	0.38	-27.51	-27.53
2024-08-13 06:42	30.05	0.06	22.85	0.21	-7.20	-23.96
2024-08-13 06:57	149.85	0.12	107.65	0.26	-42.20	-28.16
2024-08-13 07:12	11.08	0.46	9.11	0.36	-1.97	-17.78
2024-08-13 07:27	50.10	0.29	36.62	0.35	-13.48	-26.91
2024-08-13 07:42	249.62	0.06	177.63	0.19	-71.99	-28.84
2024-08-13 07:57	0.30	0.45	0.82	0.17	0.52	NA
2024-08-13 08:12	39.92	0.11	29.61	0.42	-10.31	-25.83
2024-08-13 08:27	99.94	0.11	72.32	0.27	-27.62	-27.64
2024-08-13 08:42	10.55	0.56	8.88	0.18	-1.67	-15.83
2024-08-13 08:57	199.67	0.14	142.12	0.23	-57.55	-28.82
2024-08-13 09:12	30.06	0.20	22.59	0.27	-7.47	-24.85
2024-08-13 09:27	50.02	0.17	36.81	0.31	-13.21	-26.41
2024-08-13 09:42	20.14	0.15	15.21	0.20	-4.93	-24.48
2024-08-13 09:57	149.87	0.23	107.21	0.55	-42.66	-28.46
2024-08-13 10:12	249.54	0.17	176.30	0.30	-73.24	-29.35
2024-08-13 10:27	0.30	0.46	0.83	0.18	0.53	NA
2024-08-13 10:42	249.59	0.06	175.75	0.25	-73.84	-29.58
2024-08-13 10:57	20.12	0.39	15.09	0.32	-5.03	-25.00
2024-08-13 11:12	50.07	0.38	36.58	0.48	-13.49	-26.94
2024-08-13 11:27	10.35	0.36	7.87	0.50	-2.48	-23.96
2024-08-13 11:42	199.71	0.14	142.66	0.29	-57.05	-28.57
2024-08-13 11:57	30.09	0.19	22.65	0.10	-7.44	-24.73
2024-08-13 12:12	39.99	0.30	29.95	0.28	-10.04	-25.11
2024-08-13 12:27	99.89	0.16	72.49	0.20	-27.40	-27.43
2024-08-13 12:42	149.83	0.05	108.05	0.31	-41.78	-27.88
2024-08-13 12:57	0.38	0.45	0.79	0.13	0.41	NA
2024-08-13 13:12	50.05	0.08	37.25	0.25	-12.80	-25.57
2024-08-13 13:27	199.65	0.16	143.76	0.15	-55.89	-27.99
2024-08-13 13:42	149.76	0.05	107.62	0.21	-42.14	-28.14

Table 7. *Comparison of the main CHC ozone analyser (OA) Thermo Scientific 49i #A3NAC-001029 (BKG -0.3 nmol mol*$^{-1}$*, COEF 1.006, fixed 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 (%)
2024-08-13 17:11	0.51	0.23	0.73	0.09	0.22	NA
2024-08-13 17:26	50.08	0.25	50.67	0.55	0.59	1.18
2024-08-13 17:41	199.73	0.10	201.60	0.14	1.87	0.94
2024-08-13 17:56	149.77	0.17	150.82	0.60	1.05	0.70
2024-08-13 18:11	99.83	0.09	100.68	0.36	0.85	0.85
2024-08-13 18:26	249.56	0.18	251.98	0.53	2.42	0.97
2024-08-13 18:41	20.22	0.39	20.39	0.48	0.17	0.84
2024-08-13 18:56	30.02	0.25	30.05	0.18	0.03	0.10
2024-08-13 19:11	40.05	0.11	40.52	0.12	0.47	1.17
2024-08-13 19:26	10.67	0.69	10.79	0.59	0.12	1.12
2024-08-13 19:41	0.15	0.12	0.59	0.06	0.44	NA
2024-08-13 19:56	40.09	0.32	40.48	0.54	0.39	0.97
2024-08-13 20:11	199.69	0.09	201.56	0.16	1.87	0.94
2024-08-13 20:26	20.78	0.94	21.17	0.94	0.39	1.88
2024-08-13 20:41	99.90	0.12	100.98	0.63	1.08	1.08
2024-08-13 20:56	29.96	0.31	30.43	0.49	0.47	1.57
2024-08-13 21:11	149.84	0.17	150.67	0.78	0.83	0.55
2024-08-13 21:26	11.48	0.59	11.50	0.35	0.02	0.17
2024-08-13 21:41	50.03	0.26	50.61	0.46	0.58	1.16
2024-08-13 21:56	249.65	0.14	251.86	0.48	2.21	0.89
2024-08-13 22:11	0.34	0.22	0.58	0.11	0.24	NA
2024-08-13 22:26	40.06	0.37	40.60	0.43	0.54	1.35
2024-08-13 22:41	99.92	0.08	100.77	0.36	0.85	0.85
2024-08-13 22:56	10.71	0.42	10.79	0.70	0.08	0.75
2024-08-13 23:11	199.73	0.06	201.64	0.35	1.91	0.96
2024-08-13 23:26	30.08	0.21	30.54	0.36	0.46	1.53
2024-08-13 23:30	34.68	NA	35.15	NA	0.47	1.36
2024-08-13 23:41	50.05	0.34	50.51	0.33	0.46	0.92
2024-08-13 23:56	20.54	0.63	20.57	0.56	0.03	0.15
2024-08-14 00:11	149.83	0.08	151.09	0.44	1.26	0.84
2024-08-14 00:26	249.56	0.07	251.56	0.28	2.00	0.80
2024-08-14 00:41	0.24	0.82	0.60	0.18	0.36	NA
2024-08-14 00:56	249.53	0.20	252.08	0.36	2.55	1.02
2024-08-14 01:11	20.06	0.35	20.73	0.46	0.67	3.34
2024-08-14 01:26	50.01	0.21	50.66	0.34	0.65	1.30
2024-08-14 01:41	10.90	0.60	11.23	0.69	0.33	3.03
2024-08-14 01:56	199.68	0.21	201.83	0.31	2.15	1.08
2024-08-14 02:11	30.19	0.34	30.88	0.44	0.69	2.29
2024-08-14 02:26	40.11	0.21	40.77	0.40	0.66	1.65
2024-08-14 02:41	99.91	0.21	100.88	0.45	0.97	0.97
2024-08-14 02:56	149.82	0.12	151.28	0.60	1.46	0.97
2024-08-14 03:11	0.06	0.20	0.27	0.50	0.21	NA
2024-08-14 03:26	50.00	0.20	50.66	0.25	0.66	1.32
2024-08-14 03:41	199.67	0.26	201.96	0.37	2.29	1.15
2024-08-14 03:56	149.78	0.11	151.26	0.49	1.48	0.99
2024-08-14 04:11	99.90	0.11	101.19	0.20	1.29	1.29

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 (%)
2024-08-14 04:26	249.53	0.27	251.87	0.38	2.34	0.94
2024-08-14 04:41	20.71	1.06	20.91	1.22	0.20	0.97
2024-08-14 04:56	30.12	0.20	30.45	0.41	0.33	1.10
2024-08-14 05:11	40.06	0.26	41.02	0.56	0.96	2.40
2024-08-14 05:26	10.77	0.96	11.45	1.00	0.68	6.31
2024-08-14 05:41	0.47	0.46	0.47	0.11	0.00	NA
2024-08-14 05:56	40.00	0.26	40.61	0.40	0.61	1.52
2024-08-14 06:11	199.73	0.21	201.67	0.54	1.94	0.97
2024-08-14 06:26	20.14	0.40	20.36	0.48	0.22	1.09
2024-08-14 06:41	99.89	0.13	100.78	0.39	0.89	0.89
2024-08-14 06:56	30.08	0.23	30.95	0.16	0.87	2.89
2024-08-14 07:11	149.81	0.12	151.19	0.28	1.38	0.92
2024-08-14 07:26	10.65	0.36	10.86	0.26	0.21	1.97
2024-08-14 07:41	49.90	0.16	50.59	0.30	0.69	1.38
2024-08-14 07:56	249.63	0.14	252.23	0.35	2.60	1.04
2024-08-14 08:11	0.49	0.48	0.62	0.23	0.13	NA
2024-08-14 08:26	40.03	0.29	40.91	0.71	0.88	2.20
2024-08-14 08:41	99.95	0.14	100.89	0.34	0.94	0.94
2024-08-14 08:56	11.02	0.50	11.56	0.53	0.54	4.90
2024-08-14 09:11	199.65	0.19	202.04	0.30	2.39	1.20
2024-08-14 09:26	30.09	0.41	30.82	0.49	0.73	2.43
2024-08-14 09:41	50.04	0.22	50.80	0.44	0.76	1.52
2024-08-14 09:56	20.04	0.16	20.11	0.38	0.07	0.35
2024-08-14 10:11	149.80	0.09	151.33	0.53	1.53	1.02
2024-08-14 10:26	249.63	0.14	252.08	0.57	2.45	0.98
2024-08-14 10:41	-0.26	0.36	0.53	0.13	0.79	NA
2024-08-14 10:56	249.56	0.11	251.88	0.49	2.32	0.93
2024-08-14 11:11	19.96	0.38	19.90	0.28	-0.06	-0.30
2024-08-14 11:26	50.04	0.20	50.40	0.53	0.36	0.72
2024-08-14 11:41	10.83	0.35	10.57	0.30	-0.26	-2.40
2024-08-14 11:56	199.70	0.06	201.81	0.31	2.11	1.06
2024-08-14 12:11	29.90	0.56	30.13	0.72	0.23	0.77
2024-08-14 12:26	40.09	0.27	40.69	0.19	0.60	1.50
2024-08-14 12:41	99.99	0.15	100.95	0.27	0.96	0.96
2024-08-14 12:56	149.79	0.11	151.31	0.36	1.52	1.01
2024-08-14 13:11	0.70	0.44	0.57	0.15	-0.13	NA
2024-08-14 13:26	50.17	0.18	50.58	0.36	0.41	0.82
2024-08-14 13:41	199.70	0.19	201.95	0.58	2.25	1.13
2024-08-14 13:56	149.80	0.18	151.30	0.56	1.50	1.00
2024-08-14 14:11	99.92	0.21	100.76	0.62	0.84	0.84
2024-08-14 14:26	249.47	0.08	251.75	0.17	2.28	0.91

Table 8. *Comparison of the El Alto ozone analyser (OA) Thermo Scientific 49i #1201207413 (BKG +0.0 nmol mol^{-1}, COEF 1.017) 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 (%)
2024-08-13 17:11	0.51	0.23	0.10	0.20	-0.41	NA
2024-08-13 17:26	50.08	0.25	49.77	0.74	-0.31	-0.62
2024-08-13 17:41	199.73	0.10	200.99	0.18	1.26	0.63
2024-08-13 17:56	149.77	0.17	150.28	0.38	0.51	0.34
2024-08-13 18:11	99.83	0.09	100.02	0.37	0.19	0.19
2024-08-13 18:26	249.56	0.18	251.41	0.73	1.85	0.74
2024-08-13 18:41	20.22	0.39	19.43	0.28	-0.79	-3.91
2024-08-13 18:56	30.02	0.25	29.18	0.28	-0.84	-2.80
2024-08-13 19:11	40.05	0.11	39.24	0.08	-0.81	-2.02
2024-08-13 19:26	10.67	0.69	9.69	0.52	-0.98	-9.18
2024-08-13 19:41	0.15	0.12	-0.34	0.20	-0.49	NA
2024-08-13 19:56	40.09	0.32	39.36	0.62	-0.73	-1.82
2024-08-13 20:11	199.69	0.09	200.36	0.19	0.67	0.34
2024-08-13 20:26	20.78	0.94	19.92	1.03	-0.86	-4.14
2024-08-13 20:41	99.90	0.12	99.74	0.47	-0.16	-0.16
2024-08-13 20:56	29.96	0.31	29.45	0.46	-0.51	-1.70
2024-08-13 21:11	149.84	0.17	149.29	0.63	-0.55	-0.37
2024-08-13 21:26	11.48	0.59	10.33	0.34	-1.15	NA
2024-08-13 21:41	50.03	0.26	49.53	0.32	-0.50	-1.00
2024-08-13 21:56	249.65	0.14	250.73	0.55	1.08	0.43
2024-08-13 22:11	0.34	0.22	-0.25	0.29	-0.59	NA
2024-08-13 22:26	40.06	0.37	39.38	0.64	-0.68	-1.70
2024-08-13 22:41	99.92	0.08	99.52	0.42	-0.40	-0.40
2024-08-13 22:56	10.71	0.42	9.94	0.54	-0.77	-7.19
2024-08-13 23:11	199.73	0.06	200.52	0.29	0.79	0.40
2024-08-13 23:26	30.08	0.21	29.65	0.61	-0.43	-1.43
2024-08-13 23:30	34.68	NA	34.02	NA	-0.66	-1.90
2024-08-13 23:41	50.05	0.34	49.19	0.32	-0.86	-1.72
2024-08-13 23:56	20.54	0.63	19.44	0.80	-1.10	-5.36
2024-08-14 00:11	149.83	0.08	149.80	0.63	-0.03	-0.02
2024-08-14 00:26	249.56	0.07	250.43	0.56	0.87	0.35
2024-08-14 00:41	0.24	0.82	-0.50	0.18	-0.74	NA
2024-08-14 00:56	249.53	0.20	250.68	0.37	1.15	0.46
2024-08-14 01:11	20.06	0.35	19.48	0.63	-0.58	-2.89
2024-08-14 01:26	50.01	0.21	49.55	0.47	-0.46	-0.92
2024-08-14 01:41	10.90	0.60	10.27	0.64	-0.63	-5.78
2024-08-14 01:56	199.68	0.21	200.88	0.51	1.20	0.60
2024-08-14 02:11	30.19	0.34	29.63	0.57	-0.56	-1.85
2024-08-14 02:26	40.11	0.21	39.43	0.49	-0.68	-1.70
2024-08-14 02:41	99.91	0.21	99.74	0.87	-0.17	-0.17
2024-08-14 02:56	149.82	0.12	150.21	0.54	0.39	0.26
2024-08-14 03:11	0.06	0.20	-0.39	0.25	-0.45	NA
2024-08-14 03:26	50.00	0.20	49.43	0.19	-0.57	-1.14
2024-08-14 03:41	199.67	0.26	200.57	0.34	0.90	0.45
2024-08-14 03:56	149.78	0.11	150.03	0.52	0.25	0.17
2024-08-14 04:11	99.90	0.11	100.12	0.43	0.22	0.22

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 (%)
2024-08-14 04:26	249.53	0.27	251.00	0.29	1.47	0.59
2024-08-14 04:41	20.71	1.06	20.10	1.06	-0.61	-2.95
2024-08-14 04:56	30.12	0.20	29.13	0.46	-0.99	-3.29
2024-08-14 05:11	40.06	0.26	39.99	0.58	-0.07	-0.17
2024-08-14 05:26	10.77	0.96	10.26	1.33	-0.51	-4.74
2024-08-14 05:41	0.47	0.46	-0.42	0.23	-0.89	NA
2024-08-14 05:56	40.00	0.26	39.18	0.31	-0.82	-2.05
2024-08-14 06:11	199.73	0.21	200.31	0.48	0.58	0.29
2024-08-14 06:26	20.14	0.40	19.25	0.61	-0.89	-4.42
2024-08-14 06:41	99.89	0.13	99.46	0.43	-0.43	-0.43
2024-08-14 06:56	30.08	0.23	29.60	0.22	-0.48	-1.60
2024-08-14 07:11	149.81	0.12	149.96	0.49	0.15	0.10
2024-08-14 07:26	10.65	0.36	9.71	0.36	-0.94	-8.83
2024-08-14 07:41	49.90	0.16	49.18	0.49	-0.72	-1.44
2024-08-14 07:56	249.63	0.14	250.99	0.39	1.36	0.54
2024-08-14 08:11	0.49	0.48	-0.62	0.19	-1.11	NA
2024-08-14 08:26	40.03	0.29	39.75	0.84	-0.28	-0.70
2024-08-14 08:41	99.95	0.14	99.73	0.39	-0.22	-0.22
2024-08-14 08:56	11.02	0.50	10.63	0.55	-0.39	-3.54
2024-08-14 09:11	199.65	0.19	200.79	0.20	1.14	0.57
2024-08-14 09:26	30.09	0.41	29.70	0.44	-0.39	-1.30
2024-08-14 09:41	50.04	0.22	49.47	0.36	-0.57	-1.14
2024-08-14 09:56	20.04	0.16	19.20	0.32	-0.84	-4.19
2024-08-14 10:11	149.80	0.09	150.15	0.43	0.35	0.23
2024-08-14 10:26	249.63	0.14	251.05	0.48	1.42	0.57
2024-08-14 10:41	-0.26	0.36	-0.23	0.17	0.03	NA
2024-08-14 10:56	249.56	0.11	250.86	0.29	1.30	0.52
2024-08-14 11:11	19.96	0.38	18.98	0.12	-0.98	-4.91
2024-08-14 11:26	50.04	0.20	49.19	0.72	-0.85	-1.70
2024-08-14 11:41	10.83	0.35	9.22	0.42	-1.61	-14.87
2024-08-14 11:56	199.70	0.06	200.43	0.39	0.73	0.37
2024-08-14 12:11	29.90	0.56	28.98	0.70	-0.92	-3.08
2024-08-14 12:26	40.09	0.27	39.32	0.31	-0.77	-1.92
2024-08-14 12:41	99.99	0.15	99.39	0.15	-0.60	-0.60
2024-08-14 12:56	149.79	0.11	150.41	0.43	0.62	0.41
2024-08-14 13:11	0.70	0.44	-0.42	0.13	-1.12	NA
2024-08-14 13:26	50.17	0.18	49.40	0.37	-0.77	-1.53
2024-08-14 13:41	199.70	0.19	200.80	0.48	1.10	0.55
2024-08-14 13:56	149.80	0.18	150.20	0.62	0.40	0.27
2024-08-14 14:11	99.92	0.21	99.66	0.53	-0.26	-0.26
2024-08-14 14:26	249.47	0.08	250.76	0.55	1.29	0.52

A4. Carbon monoxide comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (Wmo, 2007) and included comparisons of the travelling standards at Empa before and after the audit. The WCC-Empa travelling standards are 30 l aluminium cylinders containing a mixture of natural and synthetic air. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA and the assigned values and standard uncertainties are given below.

Results

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

Table 9. *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2519-CFKADS2226 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 (%)
(24-08-13 17:23:00)	201209_CC726934	254.1	2.2	248.0	0.2	3	-6.0	-2.4
(24-08-13 17:53:00)	210401_CC726936	223.1	1.5	218.1	0.0	3	-5.1	-2.3
(24-08-13 18:23:00)	190621_CB12164	56.2	2.1	50.9	0.2	3	-5.3	-9.4
(24-08-13 18:53:00)	230419_CC760594	117.3	2.2	111.9	0.3	3	-5.5	-4.7

A5. Methane comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (Wmo, 2007) and included comparisons of the travelling standards at Empa before and after the audit. The WCC-Empa travelling standards are 30 l aluminium cylinders containing a mixture of natural and synthetic air. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA and the assigned values and standard uncertainties are given below.

Results

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

Table 10. *CH_4 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2519-CFKADS2226 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 (%)
(24-08-13 17:23:00)	201209_CC726934	1992.89	0.08	1993.55	0.01	3	0.66	0.03
(24-08-13 17:53:00)	210401_CC726936	2217.20	0.09	2217.70	0.03	3	0.50	0.02
(24-08-13 18:23:00)	190621_CB12164	1936.53	0.12	1937.30	0.03	3	0.77	0.04
(24-08-13 18:53:00)	230419_CC760594	2137.36	0.13	2137.85	0.04	3	0.49	0.02

A6. Carbon dioxide comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (Wmo, 2007) and included comparisons of the travelling standards at Empa before and after the audit. The WCC-Empa travelling standards are 30 l aluminium cylinders containing a mixture of natural and synthetic air. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA and the assigned values and standard uncertainties are given below.

Results

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

Table 11. *CO_2 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2519-CFKADS2226 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 (%)
(24-08-13 17:23:00)	201209_CC726934	421.53	0.04	421.56	0.01	3	0.03	0.01
(24-08-13 17:53:00)	210401_CC726936	446.70	0.03	446.68	0.01	3	-0.02	0.00
(24-08-13 18:23:00)	190621_CB12164	396.26	0.04	396.27	0.01	3	0.01	0.00
(24-08-13 18:53:00)	230419_CC760594	430.08	0.07	430.12	0.01	3	0.04	0.01

A7. Calibration Standards for CO, CH_4 and CO_2

Table 12 provides an overview the standard gases available for calibration of the CO, CH_4 and CO_2 instruments.

Table 12 *CHC calibration standards as of June August 2024.*

Cylinder ID	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2 (X2019) (µmol mol^{-1})	Usage
D262999	61.18	1834.13	372.10	LSCE standard, Picarro G2401 (CAL1)
D262988	101.90	1987.48	392.04	LSCE standard, Picarro G2401 (CAL2)
D215872	157.50	2032.38	412.16	LSCE standard, Picarro G2401 (CAL3)
D262996	203.97	2326.08	451.93	LSCE standard, Picarro G2401 (CAL4)

A8. WCC-Empa ozone traveling standard

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

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

WCC-Empa TS: Thermo Scientific 49i-PS #0810-153, BKG 0.0, COEF 1.009

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

The results of the TS calibration before and after the audit are shown in Table . The TS passed the pre-audit evaluation criteria defined for maximum acceptable bias (Klausen et al., 2003) (see 13). The data were pooled and evaluated by linear regression analysis, taking into account the uncertainties of both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be calculated (equation 13). The uncertainty of the TS (equation 14) was previously estimated (see equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] + 0.15\ \text{nmol mol}^{-1}) / 1.0023 \quad (13)$$

$$u_{TS}\ (\text{nmol mol}^{-1}) = \text{sqrt}\ ((0.43\ \text{nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (14)$$

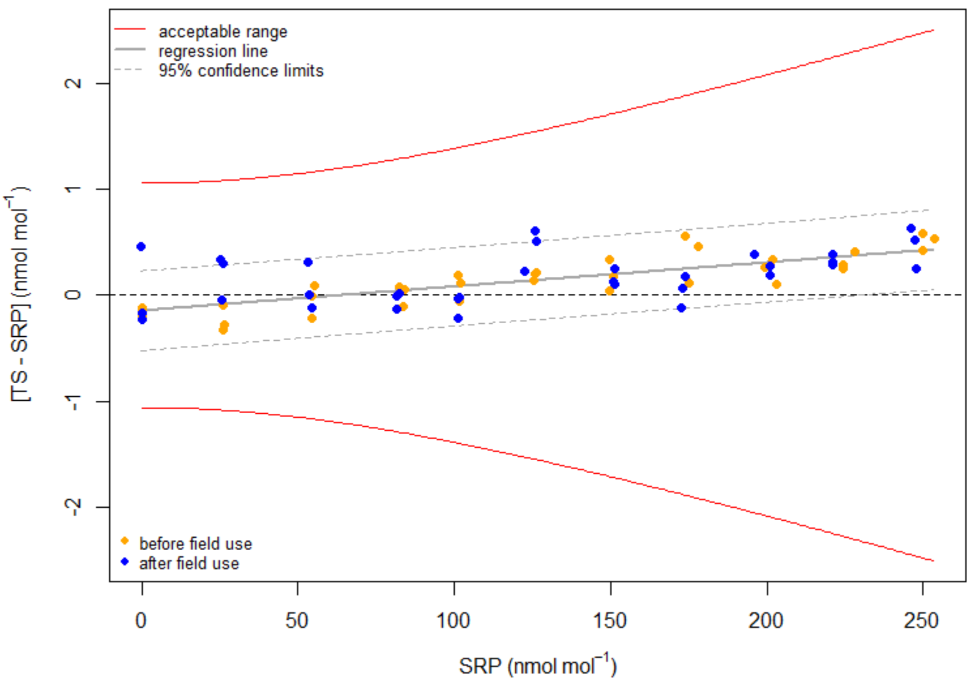

Figure 14. *Deviations between Traveling Standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS in the field.*

***Table 13**. Mean values calculated over at least five minutes for the comparison of the WCC-Empa Traveling Standard (TS) with the Standard Reference Photometer (SRP).*

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2024-04-26	1	100	101.98	0.34	102.10	0.27
2024-04-26	1	125	126.24	0.31	126.45	0.31
2024-04-26	1	25	26.41	0.23	26.13	0.97
2024-04-26	1	225	228.20	0.47	228.62	0.42
2024-04-26	1	150	150.91	0.15	151.09	0.39
2024-04-26	1	0	0.00	0.39	-0.13	0.30
2024-04-26	1	200	203.07	0.50	203.17	0.30
2024-04-26	1	50	55.24	0.15	55.33	0.27
2024-04-26	1	175	175.14	0.31	175.25	0.24
2024-04-26	1	75	83.94	0.22	83.99	0.26
2024-04-26	1	250	253.62	0.11	254.15	0.18
2024-04-26	2	100	101.44	0.22	101.39	0.38
2024-04-26	2	0	0.00	0.40	-0.21	0.42
2024-04-26	2	150	149.77	0.43	149.81	0.22
2024-04-26	2	175	178.08	0.27	178.54	0.30
2024-04-26	2	75	83.76	0.34	83.66	0.26
2024-04-26	2	200	202.00	0.36	202.34	0.18
2024-04-26	2	25	26.20	0.23	25.88	0.18
2024-04-26	2	250	250.01	0.41	250.60	0.48
2024-04-26	2	225	224.41	0.20	224.67	0.18
2024-04-26	2	50	54.57	0.15	54.36	0.18
2024-04-26	2	125	125.53	0.22	125.67	0.12
2024-04-26	3	200	199.33	0.37	199.60	0.20
2024-04-26	3	125	126.01	0.47	126.21	0.25
2024-04-26	3	250	250.02	0.29	250.44	0.20
2024-04-26	3	0	0.00	0.28	-0.12	0.25
2024-04-26	3	175	173.90	0.58	174.46	0.40
2024-04-26	3	50	54.45	0.23	54.44	0.19
2024-04-26	3	25	26.16	0.24	26.07	0.25
2024-04-26	3	150	149.50	0.25	149.84	0.22
2024-04-26	3	75	82.48	0.35	82.57	0.13
2024-04-26	3	225	224.56	0.22	224.85	0.33
2024-04-26	3	100	101.33	0.36	101.52	0.27
2024-12-19	4	100	101.36	0.17	101.14	0.28
2024-12-19	4	250	247.46	0.25	247.99	0.31
2024-12-19	4	200	201.17	0.18	201.36	0.30
2024-12-19	4	75	81.62	0.54	81.50	0.42
2024-12-19	4	50	54.34	0.31	54.23	0.43
2024-12-19	4	175	173.74	0.47	173.92	0.63
2024-12-19	4	150	151.22	0.20	151.47	0.16
2024-12-19	4	125	126.07	0.49	126.58	0.27
2024-12-19	4	225	221.05	0.34	221.34	0.49
2024-12-19	4	25	25.57	0.42	25.53	0.47
2024-12-19	4	0	-0.04	0.13	-0.21	0.36
2024-12-19	5	25	26.00	0.25	26.30	0.28

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2024-12-19	5	0	-0.15	0.35	0.30	0.62
2024-12-19	5	250	247.61	0.43	247.87	0.24
2024-12-19	5	50	53.31	0.46	53.63	0.45
2024-12-19	5	225	220.83	0.94	221.14	0.80
2024-12-19	5	175	172.39	0.24	172.27	0.42
2024-12-19	5	150	150.66	0.19	150.79	0.25
2024-12-19	5	125	125.99	0.27	126.61	0.21
2024-12-19	5	100	101.01	0.33	100.98	0.20
2024-12-19	5	200	195.83	0.37	196.22	0.50
2024-12-19	5	75	81.55	0.44	81.55	0.39
2024-12-19	6	250	246.24	0.60	246.87	0.34
2024-12-19	6	200	200.88	0.33	201.16	0.20
2024-12-19	6	25	25.32	0.26	25.65	0.39
2024-12-19	6	0	0.13	0.35	-0.09	0.41
2024-12-19	6	125	122.42	0.39	122.65	0.56
2024-12-19	6	175	172.79	0.19	172.86	0.35
2024-12-19	6	100	101.67	0.31	101.65	0.17
2024-12-19	6	150	151.23	0.57	151.34	0.36
2024-12-19	6	50	53.72	0.25	53.73	0.42
2024-12-19	6	75	82.40	0.40	82.41	0.28
2024-12-19	6	225	221.03	0.82	221.42	0.69

#The level is only indicative.

A9. WCC-Empa GHG and CO traveling standards

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

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

Table 14 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 15, and Figure 15 shows the analysis of the TS over time.

Table 14. *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 15. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, N_2O and CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (L) Los Gatos.*

TS	Pressure (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
190621_CB12164	1880	1936.53	0.12	396.26	0.04	322.10	0.39	56.15	2.06
201209_CC726934	1910	1992.89	0.08	421.53	0.04	338.19	0.16	254.05	2.20
210401_CC726936	1890	2217.20	0.09	446.70	0.03	376.82	0.44	223.12	1.48
230419_CC760594	2000	2137.36	0.13	430.08	0.07	369.77	0.40	117.34	2.15

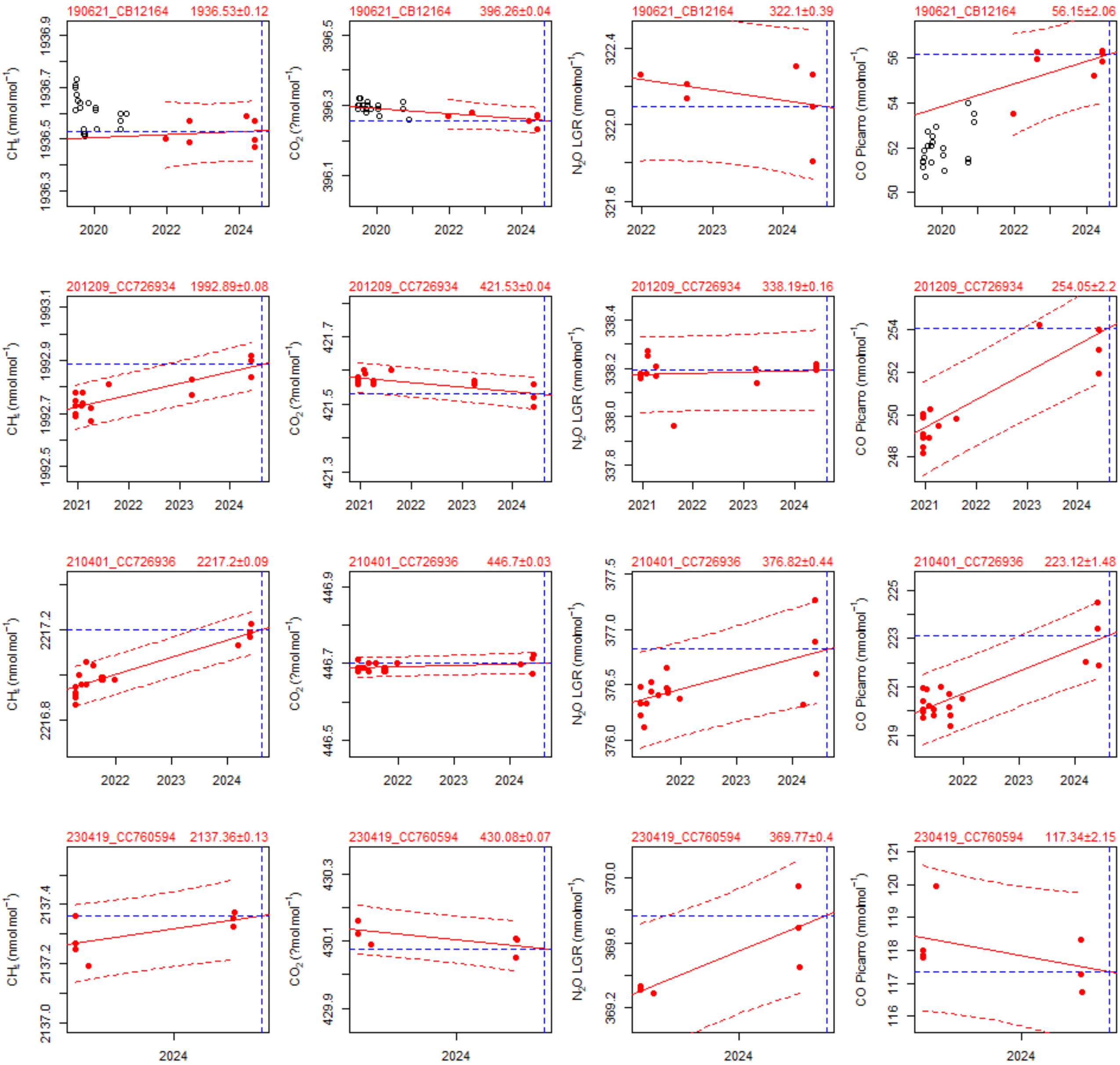

Figure 15. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, N_2O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the audit date.*

A10. 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 #617-CFKADS2001 was calibrated every 2765 minutes using one WCC-Empa TS as the working standard, and two TS as target tanks. Based on the working standard measurements, a Loess fit drift correction was applied to the data as shown in the figure below. The maximum drift between two WS measurements was approximately 0.5 nmol mol^{-1} for CH_4 and 0.1 µmol mol^{-1} for CO_2. All target cylinder measurements were within half of the WMO GAW compatibility goals.

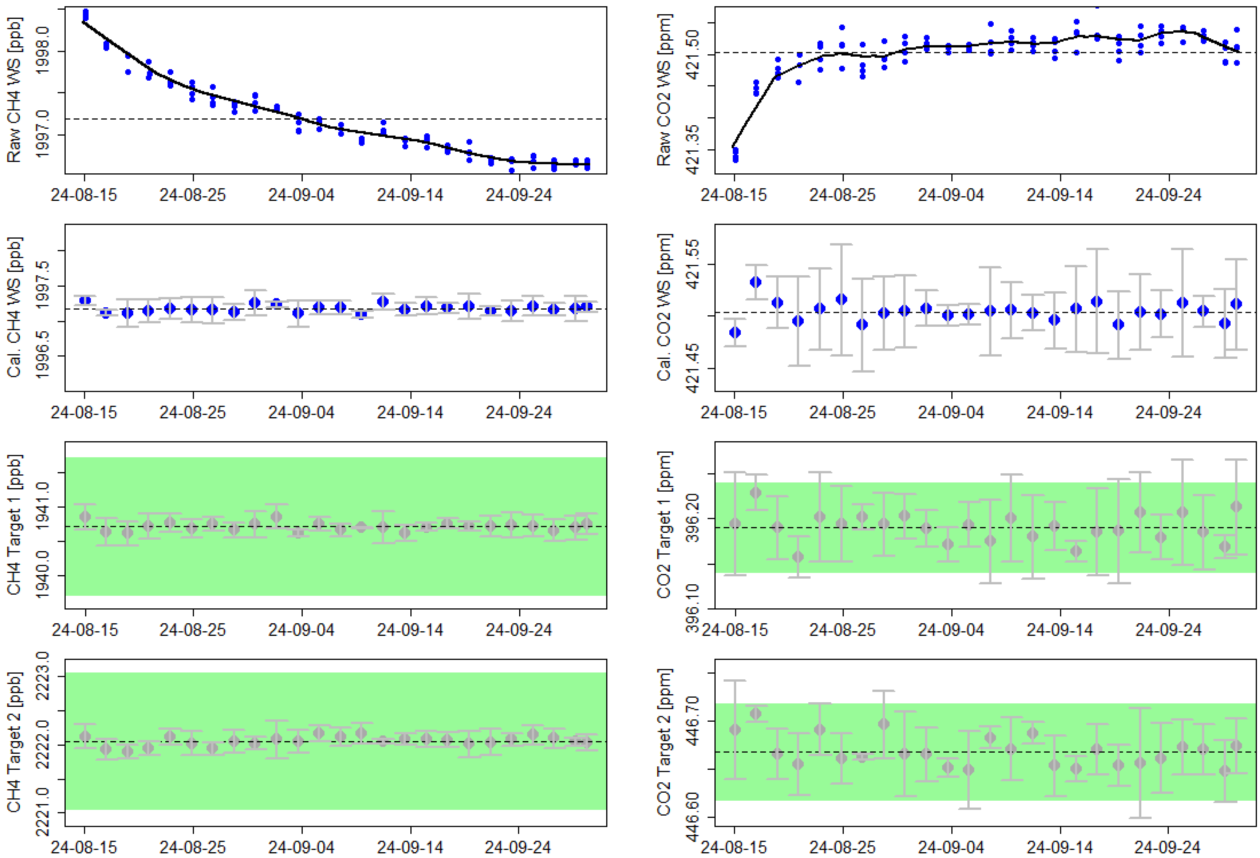

Figure 16. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The top panel shows the raw 1 min values of the working standard and the Loess fit (black line) used to account for the drift. The second panel shows the variation of the WS after applying the drift correction. The bottom panel shows the results from the two target cylinders. Individual points in the three lower panels are 5-minute averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 2765 minutes using three WCC-Empa TS as working standards. Based on the working standard measurements, a Loess fit drift correction using was first applied to the data, as shown in the figure below.

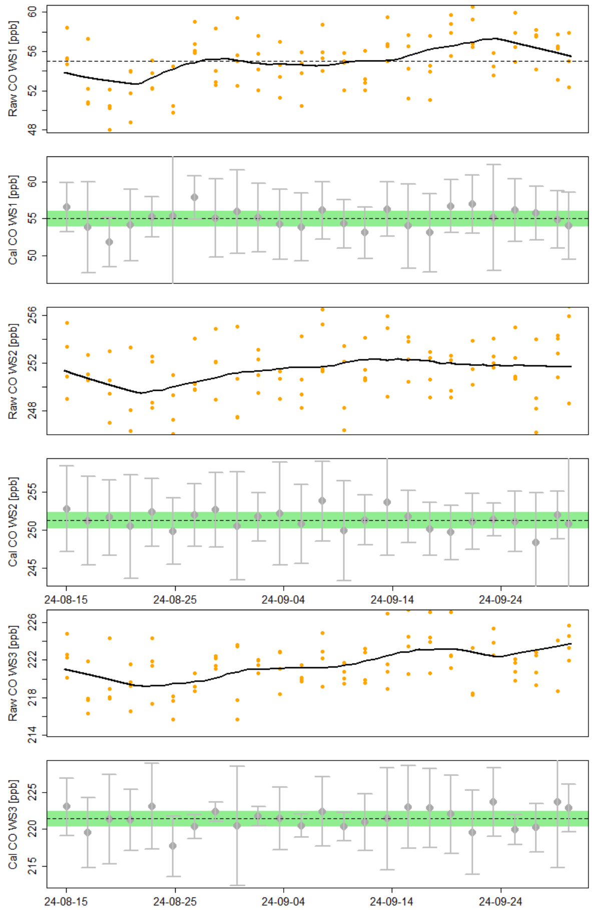

Figure 17. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show the raw 1 min values of the working standards and the Loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in these panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

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

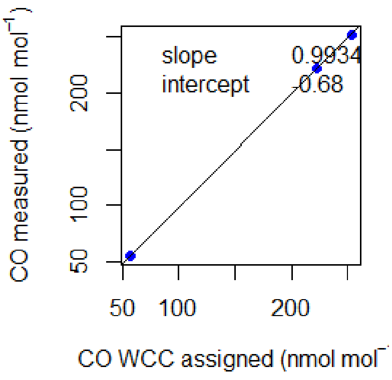

Figure 18. *CO calibration function based on the average values of the drift corrected working standard measurements.*

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List of abbreviations

ATC	Atmosphere Thematic Centre
BKG	Background
CCL	Central Calibration Laboratory
CHC	Chacaltaya GAW Station
COEF	Coefficient
CNR	Italian National Research Council
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
eDQO	Extended Data Quality Objective
FID	Flame Ionisation Detection
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
IR	Infrared
LGR	Los Gatos Research
LS	Laboratory Standard
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
QA/SAC	Quality Assurance/Science Activity Centre
RCC	Regional Calibration Centre
SH	Southern Hemisphere
SOP	Standard Operating Procedure
SN	Serial Number
SRP	Standard Reference Photometer
TI	Travelling Instrument
TROPOS	Leibnitz Institute for Tropospheric research
TS	Traveling Standard
UMSA	University Mayor de San Andrés
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