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

AT THE

GLOBAL GAW STATION

LA RÉUNION

ILE DE LA RÉUNION, FRANCE

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C. Zellweger, M. Steinbacher and B. Buchmann

WMO World Calibration Centre WCC-Empa

Empa, Dübendorf, Switzerland

WCC-Empa Report 22/4

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WCC-Empa Report 22/4

Contact Information:

GAW World Calibration Centre WCC-Empa
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution - Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The first WCC-Empa[1] system and performance audit by at the La Réunion (RUN) global GAW station was conducted from 24 to 27 October 2022 in accordance with the WMO/GAW quality assurance system (WMO, 2017). A list of all WCC-Empa audits and the corresponding audit reports is available on the WCC-Empa website (www.empa.ch/gaw).

It was planned to conduct the audit at RUN together with the Mobile Laboratory (ML) of the Integrated Carbon Observation System (ICOS) programme. However, the ICOS ML equipment arrived late and only the parallel measurement overlapped with the WCC-Empa audit.

The following persons contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Mrs Claudia Zellweger	Empa, Dübendorf, Laboratory for Air Pollution / Environmental Technology
Mr Valentin Duflot	RUN, Station Manager, Head of the Observatory
Mr Jean-Marc Metzger	RUN, Station Operator
Dr Aurélie Colomb	Université Clermont Auvergne, PI for reactive gases

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

The report is distributed to the Réunion station manager and responsible scientists, the National Focal Point for GAW in France, and the World Meteorological Organization in Geneva. It will be published as a WMO/GAW report and made available on the internet (www.empa.ch/web/s503/wcc-empa).

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

Management and operation of the station

The RUN station is a French-Belgian collaboration between the Université de La Réunion, the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), the Université Clermont Auvergne, and the Royal Belgian Institute for Space Aeronomy (BIRA). The operation of the observatory is managed and coordinated by the Université de La Réunion, and the station is visited daily by technical and administrative staff. More information can be found on of the RUN station website (https://opar.univ-reunion.fr/).

Station location and access

RUN (21.0796°S, 55.3841°E, 2160 m a.s.l.) is located on the island of La Réunion in the middle of the southwest Indian Ocean. It is influenced by south-easterly trade winds near the ground and by westerly winds in the free troposphere. La Réunion is far away from anthropogenic sources of pollution and local pollution is very low. The station is located on the slope of the Maïdo volcanic peak, well above the island's settlements. It is therefore expected that the impact of emissions on the island will be very low. The station is accessible by road all year round.

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

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

Station facilities

The facilities at the site consist of a large building with laboratories, a workshop, kitchen, meeting rooms, and offices for scientists and technicians, and a residential area with six double rooms for overnight stays. A complete overview of the facilities can be found in Baray et al. (2013). The RUN observatory is an ideal platform for continuous atmospheric research and measurement campaigns.

Measurement programme

RUN hosts a comprehensive measurement programme, and an overview of measured species is available on the station website and GAWSIS. The activities at RUN are embedded in several international programmes and research infrastructures, such as ICOS (Integrated Carbon Observation System), the Aerosol Robotic Network (AERONET), the Southern Hemisphere Additional Ozonesondes (SHADOZ) Network, and the Network for the Detection of Atmospheric Composition Change (NDACC).

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

> **Recommendation 1 (***, important, ongoing)**
> *It is recommended that GAWSIS is updated yearly 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 outdated station contacts).*

Data submission

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

Submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2020-20321).

Submission to the World Data Centre for Greenhouse Gases (WDCGG):
No GHG data has been submitted to WDCGG.
CH_4 (2018-2022), CO_2 (2018-2022), and CO (2018-2022) can be obtained from the ICOS data portal (https://data.icos-cp.eu/).

> **Recommendation 2 (***, important, ongoing)**
> *Data submission to the official World Data Centres of the GAW programme is an obligation of all GAW stations. It is recommended to submit data to the respective data centres at least once a year. Hourly data are required for all parameters. Available data for CO_2, CH_4, and CO must be submitted to the WDCGG.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCRG and the ICOS carbon portal was reviewed and all time series accessed appeared to be sound. The data presented in this report were accessed on 20 February 2023. Summary graphs and a brief description of the findings are provided in the Appendix.

Documentation

Electronic station and instrument logbooks are available at RUN. In addition, handwritten notes are kept in laboratory notebooks and checklists are available for the ozone instrument. Instrument manuals are available at the site, and the information reviewed was comprehensive and up to date.

Air inlet system

Surface ozone:

Location of air intake: Top of the laboratory building, ~1.5 m above the flat roof.

Inlet protection: Protection against rainwater / snow / insects with a stainless steel cap.

Inlet system: Approx. 11 m ½ inch PFA tubing to small glass manifold with flow rate of 21 l/min, from there connection to instrument with ¼ inch PFA tubing with flow of approx. 1.2 l/min controlled by the analyser. Some of the connections are made of stainless steel, which is not optimal for ozone measurements. However, the loss is expected to be minimal due to the short residence time.

Inlet filter: PTFE inlet filter

Residence time: < 5 s

Manifold of the reactive gases inlet.

Recommendation 3 (*, minor, 2023)
It is recommended to replace the stainless steel parts in the ozone inlet system with PFA or PTFE parts.

Carbon monoxide, methane and carbon dioxide:

Location of air intake: Top of the laboratory building, ~1.5 m above the flat roof.

Inlet protection: Rainwater/snow/insects protection with a stainless steel cap.

Inlet system: Approx. 11 m ½ inch Dekabon tubing with high flow rate, from there connection to the instrument with 1/8 stainless steel tubing. The air is dried using a Nafion dryer (MD-070-144S-4).

The inlet system for the GHG and CO measurements is fully suitable in terms of inlet design, sampling location, materials, and residence time.

Surface ozone measurements

Surface ozone measurements at RUN were established in 2012, and continuous time series are available since then.

Instrumentation. RUN is equipped with an ozone analyser (Thermo Scientific 49i).

Standards. No standard is available at the site. Calibration is carried out every three months by Atmo Réunion (https://atmo-reunion.net/). This is done with an ANSYCO 4TO3, which is basically an ozone generator that has been calibrated against a reference instrument. This method is not suitable for ozone calibrations because the stability of the ozone generators is usually inferior to the stability of the ozone analyser. In addition, the efficiency of ozone generation is also likely to depend on ambient pressure (i.e. altitude), which makes calibration of the ANSYCO 4TO3 at an altitude lower than RUN questionable.

Data acquisition. A custom built data acquisition system programmed in LabView is available at RUN. The system including backup policy, data transfer and data evaluation is adequate.

Intercomparison (performance audit). The RUN ozone analyser (OA) 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 first comparison showed that the Ozone Analyser (OA) that was running was not working in good condition. The span coefficient was set to 1.582, and the instrument was reading approximately 40% higher than the WCC-Empa reference. However, with these span settings, a higher deviation would be expected, and several instrument checks were made to identify the problem. The instrument passed the A/B ozone check (applying 500 nmol mol^{-1} of ozone and reading the analyser output for both measurement cells separately), although it was relatively unstable and poorly reproducible. Leaking solenoid valves were ruled out by checking both valves individually for internal leaks. Finally, a faulty ozone scrubber was found to be the cause of the problem. The scrubber was replaced with the one previously used in the instrument. A second comparison was made with the repaired analyser. Due to the unrealistically large span coefficient, new calibration settings were applied before comparing the repaired instrument.

The results of the initial (pre-repair) and final (post-repair) comparisons are summarised below in relation to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data were acquired using the WCC-Empa data acquisition system. The 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). The uncertainties shown below do not include the uncertainty of the ozone absorption cross section, 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).

Thermo Scientific 49i #0706721025 (BKG 0.4 nmol mol^{-1}, SPAN 1.582), prior to scrubber replacement:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] – 1.15 nmol mol^{-1}) / 1.397 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.15e-05 * X_{O3}^2) (1b)

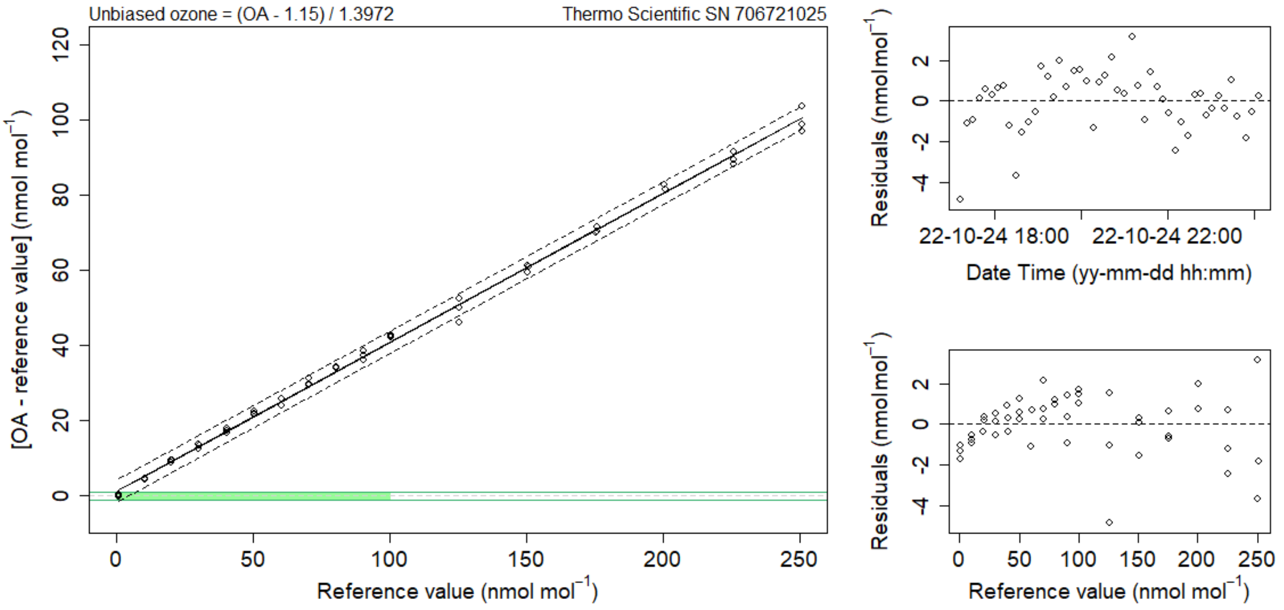

Figure 1. *Left: Bias of the RUN ozone analyser (Thermo Scientific 49i #0706721025, BKG 0.4 nmol mol^{-1}, COEF 1.582, initial condition, unrepaired) with respect to the SRP as a function of mole fraction. Each point represents the average of ten 40 second averages at a given level. The green area corresponds to the relevant mole 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 mole fraction (bottom).*

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

A large bias was observed due to the high span factor, which was overcompensating for expected lower readings due to the broken ozone scrubber.

A second comparison was made after replacement of the scrubber and determination of new calibration settings by a two point calibration at 0 and 500 nmol mol^{-1}. The result after repair and calibration was as follows:

Thermo Scientific 49i #0706721025 (BKG -0.1 nmol mol^{-1}, SPAN 1.011), after scrubber replacement:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] - 0.02 nmol mol^{-1}) / 0.9991 (1c)

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

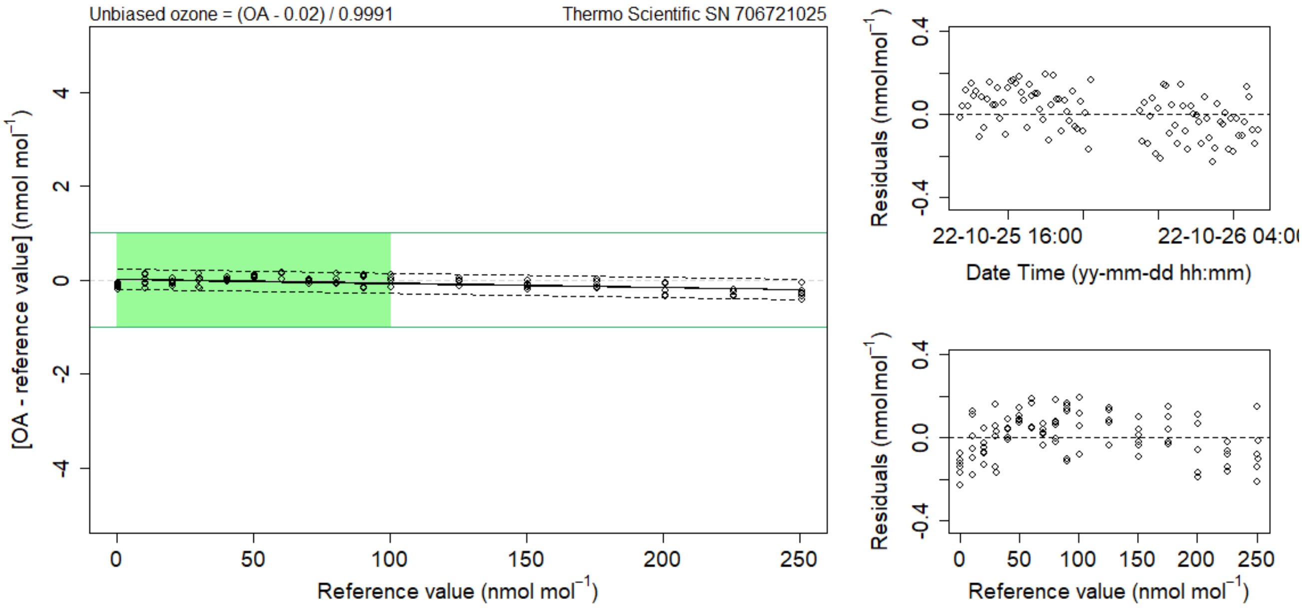

Figure 2. *Left: Bias of the RUN ozone analyser (Thermo Scientific 49i #0706721025, BKG -0.4 nmol mol^{-1}, COEF 1.011, final condition, scrubber replaced) with respect to the SRP as a function of mole fraction. Each point represents the average of ten 40 second averages at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines 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 mole fraction (bottom).*

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

Agreement within the WMO/GAW DQOs was found after replacement of the scrubber and the determination of new calibration settings. The instrument was in a good working order after the repair, and also passed the A/B ozone check.

The following recommendations are made for the ozone measurements at RUN:

> **Recommendation 4 (***, critical, 2023)**
> *Due to the analyser malfunctioning prior to the current audit, all ozone data need to be re-analysed. The period of time when the scrubber efficiency was reduced needs to be identified and the data from this period needs to be flagged as invalid.*

A change in the current calibration practice is also required. The ozone generator used by Atmo Réunion is not suitable for calibrating the instrument at RUN. This is also reflected in the large changes in the span coefficient that were made during these past "calibrations", which are summarised in the table below.

Table 1. *History of the O_3 span coefficient settings of the Thermo Scientific 49i #0706721025 ozone analyser.*

Date of the calibration	O_3 span coefficient	Remarks
2018-02-22	1.466	
2018-07-10	1.473	
2018-12-11	1.440	
2019-03-21	1.451	
2019-08-28	1.527	
2019-10-15	1.440	
2020-06-19	1.478	
2020-09-15	1.372	
2020-12-16	1.619	
2021-05-07	1.482	
2021-06-26	1.556	
2021-09-23	1.424	
2021-12-03	1.471	
2022-10-04	1.582	
2022-10-26	1.011	Value determined by WCC-Empa during this audit

The ozone span coefficient usually remains stable for many years in case of a well-functioning and well-maintained instrument. It is often an indication of an instrument malfunction when the value has to be adjusted significantly. In this case, the variability of the span coefficient is extremely large, with no clear trend. This is most likely due to the instability of the ozone generator used as a reference during calibration. It is strongly recommended to keep the calibration settings as determined during this audit, and to use the comparison with the ATMO ozone generator only as for instrument checks (e.g. A/B ozone test).

Recommendation 5 (*, critical, 2023)**
The current calibration settings (BKG -0.1 nmol mol^{-1}, SPAN 1.011) as after the second comparison by WCC-Empa should NOT be changed.

In addition, the following minor recommendations are made:

Recommendation 6 (*, minor, 2023)
Currently, the old ozone scrubber is used in the RUN analyser. This scrubber is still functioning but should be replaced by a new scrubber.

Recommendation 7 (*, minor, 2024)
Due to the age of the ozone instrument, replacement of the analyser should be considered.

Carbon monoxide measurements

Continuous measurements of CO at RUN started in 2012 using Cavity Ring Down Spectroscopy (CRDS).

Instrumentation. The following instrument was available during the audit:
Picarro G2401 (near-IR CRDS) with a Nafion dryer (MD-070-144S-2) for drying the sample air.

Standards. Four reference standards from the ICOS Flask and Calibration Laboratory (FCL) are available at RUN. ICOS FCL ensures traceability to the GAW reference scales through the assignment of the nominal amount fractions in their fillings by comparison with laboratory cylinders obtained from the GAW Central Calibration Laboratory (CCL) in Boulder, USA. Target cylinders are also available for quality control purposes. The ICOS FCL standards were also analysed on the WCC-Empa CRDS instrument during the audit. Table 2 shows the results of the comparison.

Table 2 *ICOS FCL CO calibration standards at RUN as of October 2022 and the results of the WCC-Empa analysis.*

Cylinder ID	ICOS FCL CO (X2014A) (nmol mol^{-1})	WCC-Empa CO (X2014A) (nmol mol^{-1})	FCL.- WCC CO (X2014A) (nmol mol^{-1})
CAL1_615388	42.61	41.86	0.75
CAL2_615363	71.68	66.09	5.59
CAL3_615368	155.39	152.80	2.59
CAL4_D856128	257.11	254.16	2.95

Calibration. Calibrations using the four ICOS FCL standards are performed every 29 days. The tanks are run in sequence and this is repeated 3 times. Data from the first cycle is discarded to allow for stabilisation due to moisture in the Nafion dryer. At the time of the audit, a short term target was run every 49.5 hours.

Data acquisition. The Picarro G2401 has an internal data acquisition, and high resolution (1 to 2 seconds resolution) raw data files are sent daily to the ICOS Atmospheric Thematic Centre (ATC) where processing is performed. See Hazan et al. (2016) for details of the ATC processing.

Intercomparison (performance audit). The comparison involved repeated challenges of the RUN instrument with randomised carbon monoxide levels using WCC-Empa travelling standards.

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

Picarro G2401 #1163-CFKADS2045:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 2.94 nmol mol^{-1}) / 0.9952 (2a)

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

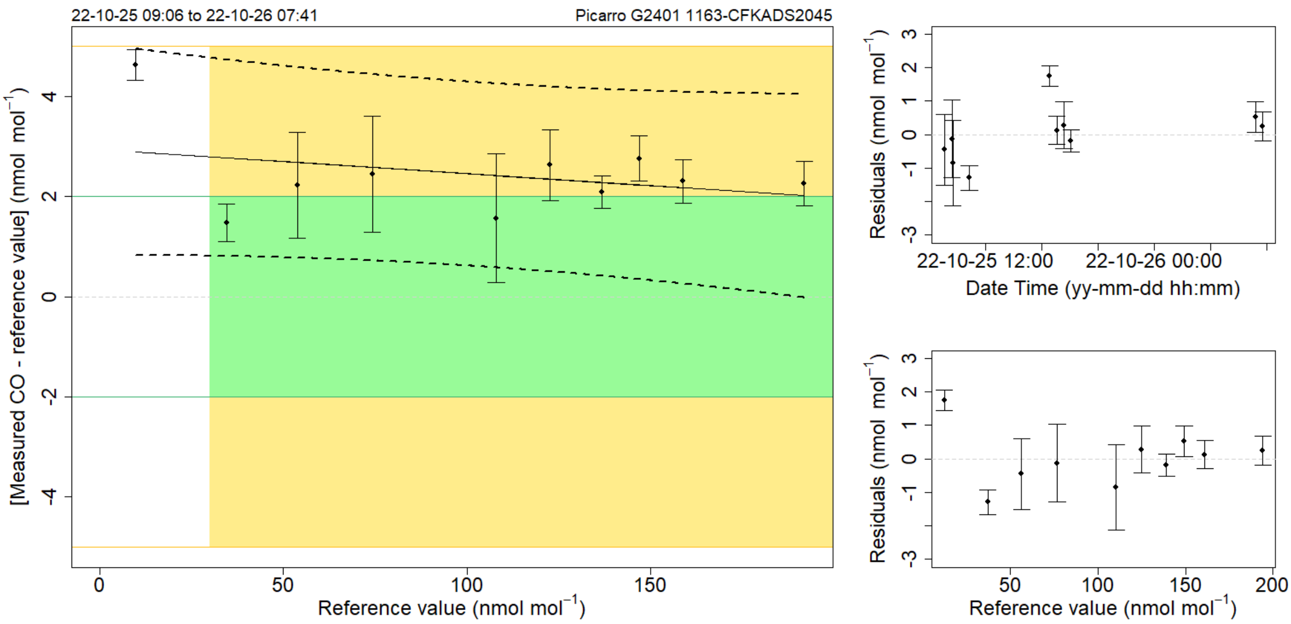

Figure 3. *Left: Bias of the RUN Picarro G2401 #1163-CFKADS2045 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each 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 mole fraction range relevant for RUN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The comparison results were within the extended network compatibility goal of 5 nmol mol^{-1} in the relevant range of amount fractions. The bias was about 2 nmol mol^{-1}, but slightly higher at low amount fractions.

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

Recommendation 8 (, important, 2023)**
The CRDS measurement technique shows a linear response for CO in the amount fraction range at least from 0 to 4000 nmol mol^{-1}. In order to minimise the influence of standard drift, WCC-Empa recommends that the calibration strategy focuses on higher CO amount fractions, and also includes CO free air (or N_2 6.0) to compensate for a zero offset. If standards with an amount fraction higher than 500 nmol mol^{-1} are used, the linearity of the analyser and the traceability to the CCL must be checked.

Methane measurements

Continuous measurements of CH_4 at RUN started in 2012 using Cavity Ring Down Spectroscopy (CRDS).

Instrumentation. Same instrument as for CO,

Standards. Same standards as for CO. The standards were also analysed on the WCC-Empa CRDS instrument during the audit. The result of the comparison is shown in Table 3.

Table 3 *ICOS FCL CH_4 calibration standards available at RUN as of October 2022 and the results of the WCC-Empa analysis.*

Cylinder ID	ICOS FCL CH_4 (X2004A) (nmol mol^{-1})	WCC-Empa CH_4 (X2004A) (nmol mol^{-1})	FCL.- WCC CH_4 (X2004A) (nmol mol^{-1})
CAL1_615388	1749.65	1749.39	0.26
CAL2_615363	1889.77	1889.98	-0.21
CAL3_615368	1994.07	1994.37	-0.30
CAL4_D856128	2196.89	2197.56	-0.67

Data acquisition. See CO.

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

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

Picarro G2401 #1163-CFKADS2045:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.98 nmol mol^{-1}) / 0.9986 (3a)

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

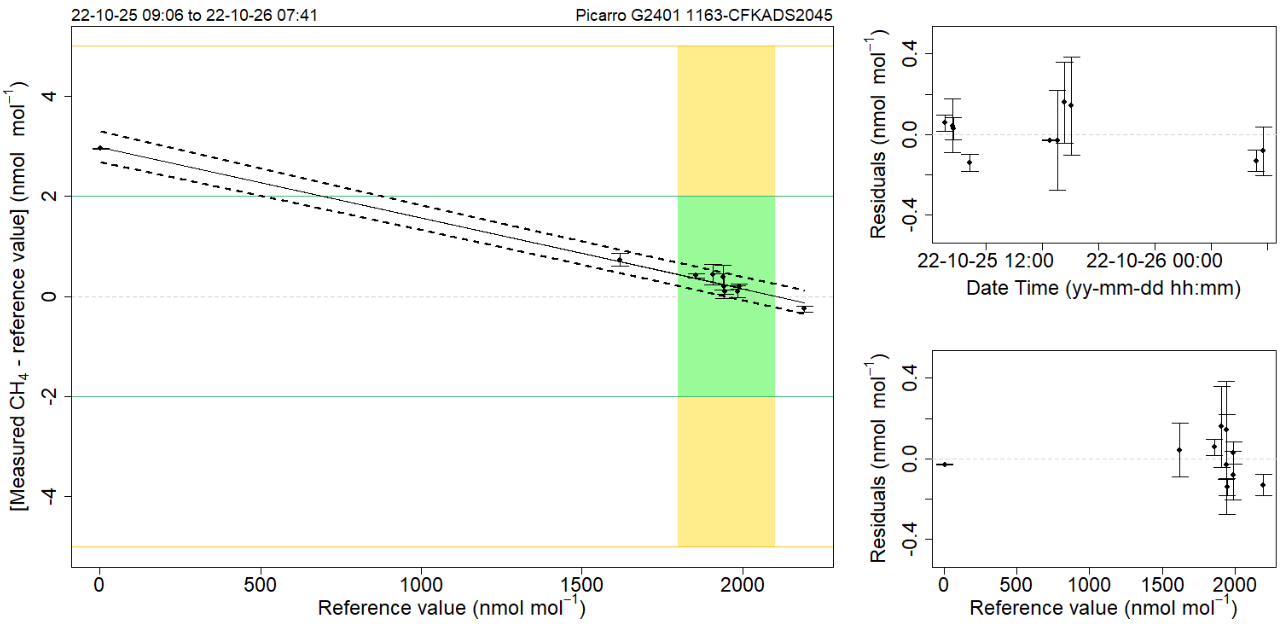

Figure 4. *Left: Bias of the Picarro G2401 #1163-CFKADS2045 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of the individual 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 mole fraction range relevant for RUN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

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

Carbon dioxide measurements

Continuous measurements of CO_2 at RUN started in 2012 using Cavity Ring Down Spectroscopy (CRDS).

Instrumentation. Same instrument as for CO.

Standards. Same standards as for CO. The standards were also analysed on the WCC-Empa CRDS instrument during the audit. The result of the comparison is shown in Table 4.

Table 4 *ICOS FCL CO_2 calibration standards at RUN as of October 2022 and the results of the WCC-Empa analysis.*

Cylinder ID	ICOS FCL CO_2 (X2007*) ($\mu mol\ mol^{-1}$)	WCC-Empa CO_2 (X2007*) ($\mu mol\ mol^{-1}$)	FCL.- WCC CO_2 (X2007*) ($\mu mol\ mol^{-1}$)
CAL1_615388	379.51	379.38	0.13
CAL2_615363	399.99	399.87	0.12
CAL3_615368	421.54	421.56	-0.02
CAL4_D856128	460.47	460.47	0.00

Data acquisition. See CO.

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

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

Picarro G2401 #1163-CFKADS2045:

Unbiased CO_2 mixing ratio: X_{CO2} ($\mu mol\ mol^{-1}$) = (CO_2 – 0.50 $\mu mol\ mol^{-1}$) / 0.99888 (4a)

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

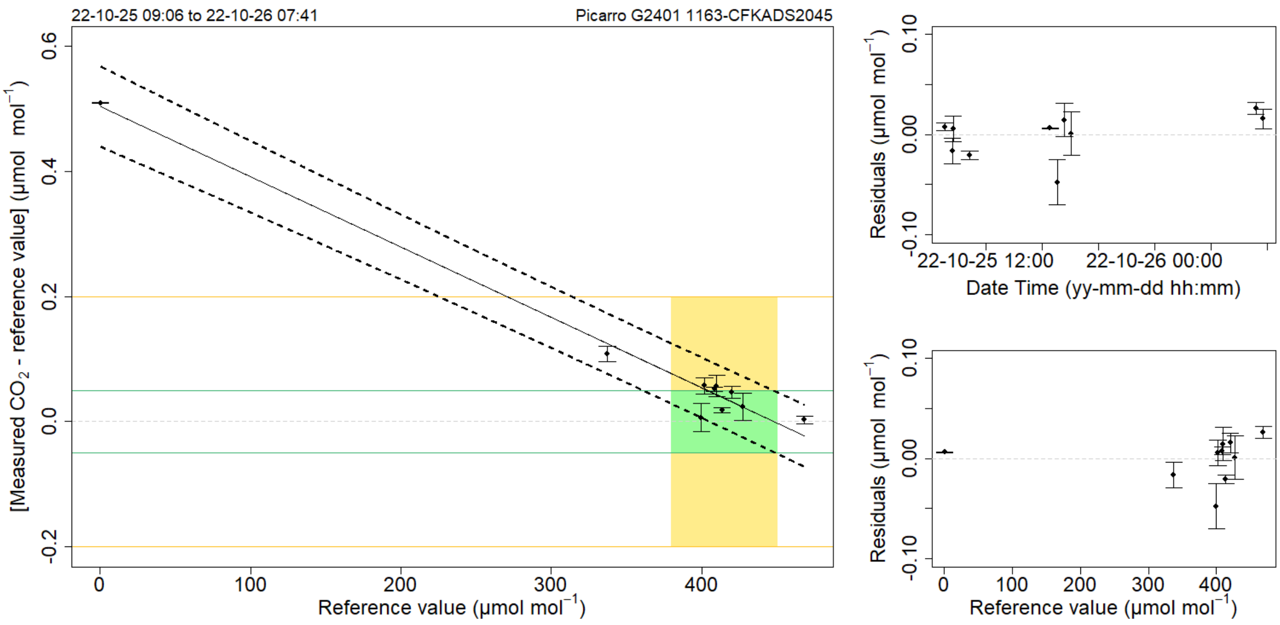

Figure 5. *Left: Bias of the Picarro G2401 #1163-CFKADS2045 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of the individual 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 mole fraction range relevant for RUN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:
The results were mostly within the WMO/GAW network compatibility goal in the relevant amount fraction range. The bias shows a slight dependence on the amount fraction with an offset of about 0.5 µmol mol^{-1} at the zero point. Due to the good results in the relevant range of amount fractions, no further action is required.

RUN PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the RUN 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 mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone the mole 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 mole fraction range. Figure 6 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 comparisons 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 RUN audit are shown as coloured dots in Figure 6, and are also summarised in Table 5. The percentages of all WCC-Empa audits that met the DQOs or extended DQOs (eDQOs) are also shown in Table 5.

The results were within the DQOs for O_3 after scrubber replacement, and for CH_4 and CO_2 measurements. The CO results were within the extended network compatibility goal, mainly due to a large offset at low CO amount fractions.

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

Compound / instrument	**Range**	**Unit**	**RUN within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**
O_3 (Thermo Scientific 49i #0706721025) old scrubber	0 -100	nmol mol^{-1}	✗	66	NA
O_3 (Thermo Scientific 49i #0706721025) new scrubber	0 -100	nmol mol^{-1}	✓	66	NA
CO (Picarro G2401 CFKADS2414, ICOS ATC analysis)	30 - 300	nmol mol^{-1}	✓	18	50
CH_4 (Picarro G2401 CFKADS2414, ICOS ATC analysis)	1750 - 2100	nmol mol^{-1}	✓	76	94
CO_2 (Picarro G2401 CFKADS2414, ICOS ATC analysis)	380 - 450	µmol mol^{-1}	✓	48	73

[1] Percentage of stations within the eDQO and DQO

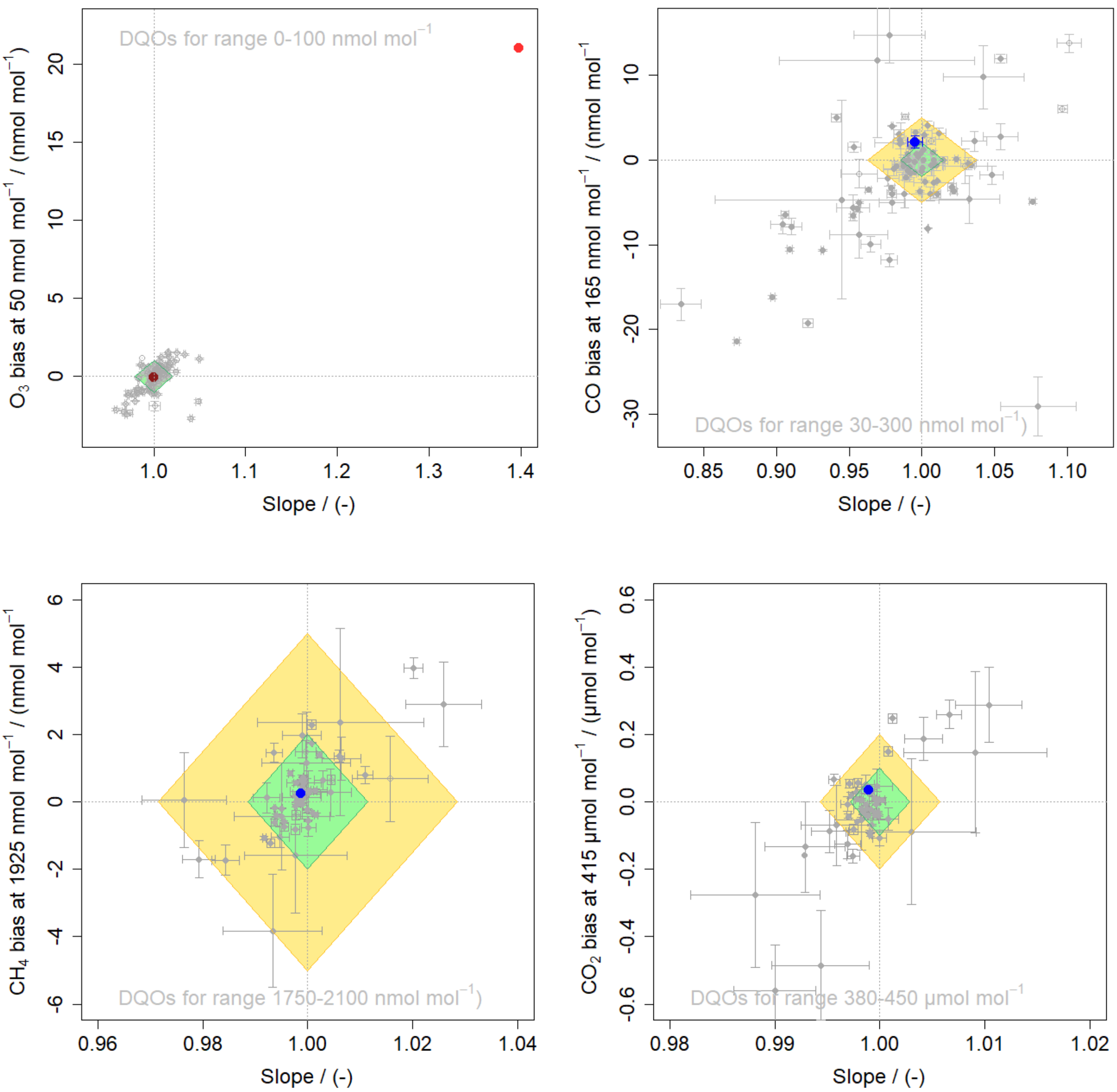

Figure 6. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the middle of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show the RUN results (red: Thermo Scientific 49i with faulty scrubber, dark red: same analyser with replaced scrubber, blue: Picarro G2401). Filled symbols refer to a comparison with the same calibration scale at the station and at the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. Coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow) where available.*

PARALLEL MEASUREMENTS OF AMBIENT AIR

The audit included parallel measurements of CO_2, CH_4 and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401). The TI was running from 26 October through 7 December 2022 at RUN. The TI was connected to a spare inlet line of the RUN station. The TI sampled air using the following sequence: 2210 min ambient air followed by 60 min measurement of three standard gases, each for 20 min. The sample air was dried by a Nafion dryer (Perma Pure Model PD-50T-12MPS) in reflux mode using the Picarro pump for the vacuum in the purge air stream. To account for the residual effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix.

The ICOS-ML also carried out an audit at the RUN station. Their measurements, using the same inlet system as the WCC-Empa TI, started on 4 November 2022. ICOS-ML also used a Picarro G2401 instrument for the parallel measurements. Details of the measurement setup can be found in the ICOS-ML audit report, which is available on request from the ICOS-ML or the RUN station.

The results of the ambient air comparison are presented below. The RUN data were processed by the ICOS ATC.

Figures 7 to 9 show the comparison of hourly CO, CH_4, and CO_2 measurements between the WCC-Empa TI, the ICOS-ML TI and the RUN Picarro G2401 analyser. Hourly averages were calculated based on 1 minute data. The results of the ambient air comparison can be summarised as follows:

Carbon Monoxide

On average, the RUN, the WCC-Empa and the ICOS-ML CO measurements agreed within the WMO/GAW network compatibility goal. The offset observed in the comparison of the WCC-Empa travelling standards and the RUN CO standard gases was not found during the ambient air comparison. The temporal variation was well captured by all instruments.

Methane

Excellent agreement within the WMO/GAW network compatibility goals was found between the WCC-Empa TI, the ICOS-ML TI and the RUN instrument. This confirms the results of the WCC-Empa performance audit using travelling standards. The temporal variation was well captured by all instruments; and the deviation between the instruments was small.

Carbon dioxide

Temporal variability was well captured by all instruments. On average, the agreement was within the WMO/GAW network compatibility goal for all instruments, confirming the results of the WCC-Empa travelling standard comparison. However, a small number of values with higher deviations were observed for both the WCC-Empa and the ICOS-ML TI. These are probably due to insufficient stabilisation time after the standard measurements by the WCC-Empa TI and slightly different data coverage due to calibration and are therefore not relevant for the audit.

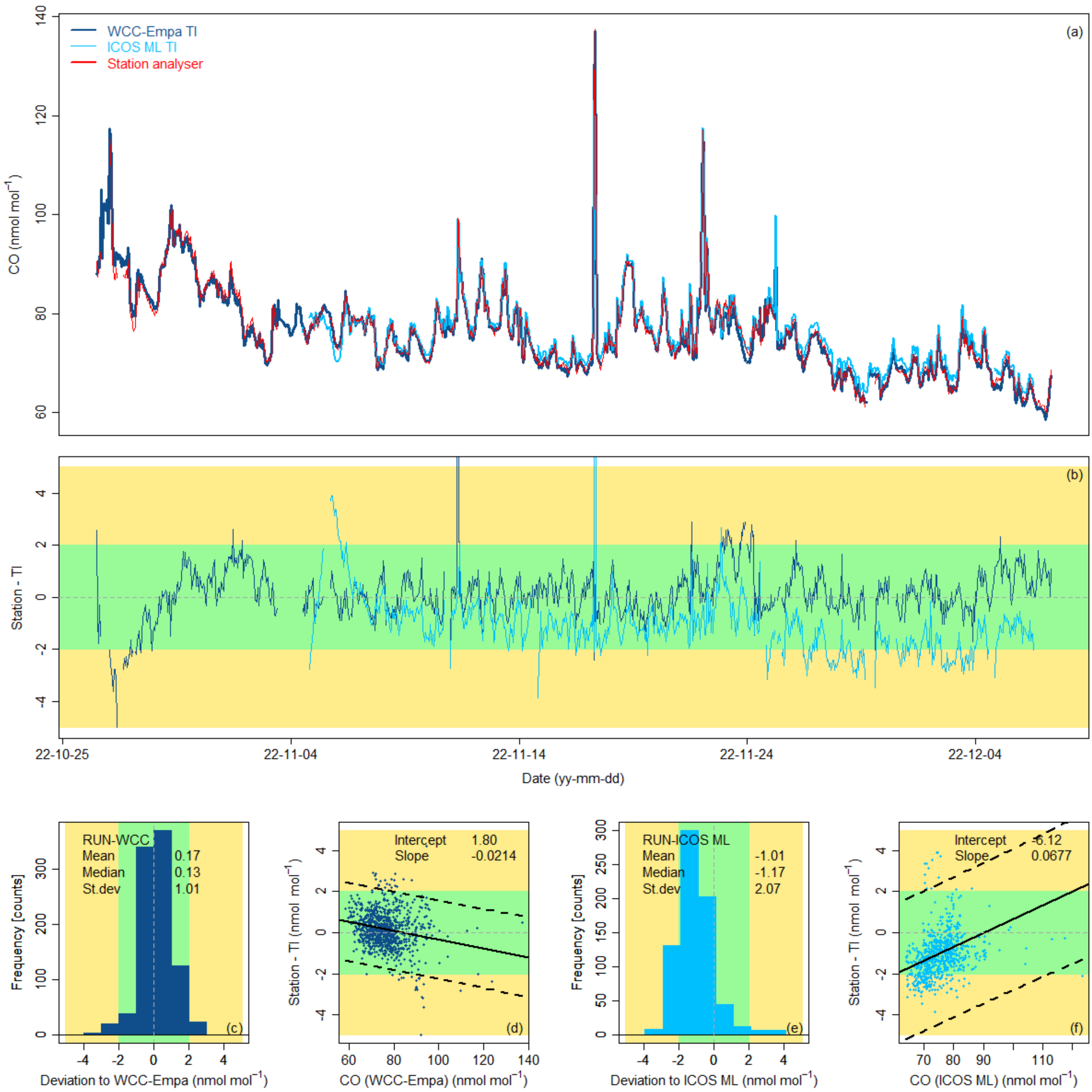

Figure 7. *(a) Comparison of the Picarro G2401#1163-CFKADS2045 with the WCC-Empa and ICOS-ML travelling instruments for CO. Time series based on hourly data are shown. (b) Difference between the station instrument and the WCC-Empa and ICOS-ML travelling instruments. (c) and (e) CO deviation histograms for the Picarro G2401#1163-CFKADS2045 analyser compared to the WCC-Empa TI and the ICOS-ML TI. (d) and (f) Bias of the RUN instrument as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

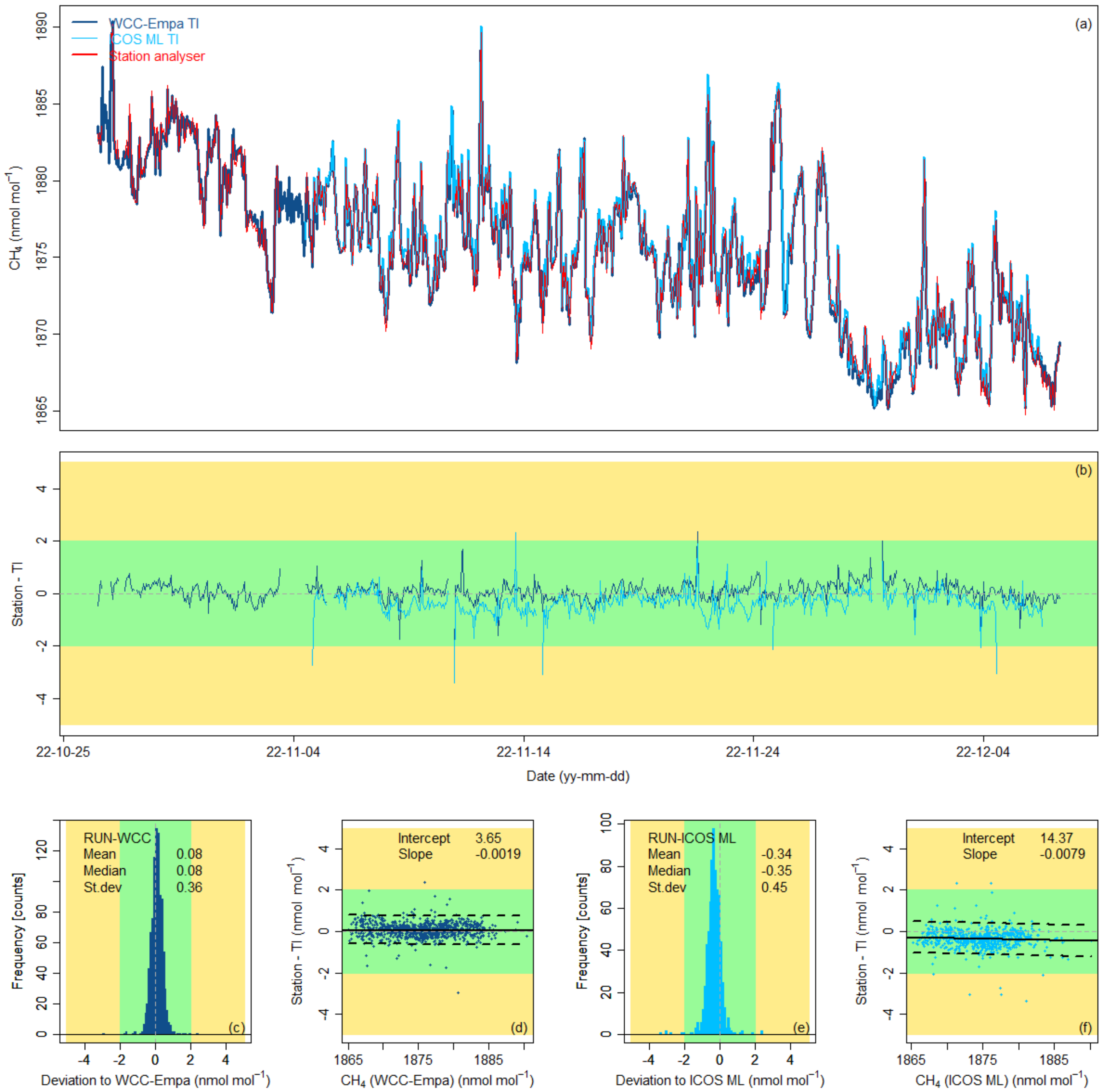

Figure 8. *Top: (a) Comparison of the Picarro G2401#1163-CFKADS2045 with the WCC-Empa and ICOS-ML travelling instruments for CH_4. Time series based on hourly data are shown. (b) Difference between the station instrument and the WCC-Empa and ICOS-ML travelling instruments. (c) and (e) CH_4 deviation histograms for the Picarro G2401#1163-CFKADS2045 analyser compared to the WCC-Empa TI and the ICOS-ML TI. (d) and (f) Bias of the RUN instrument as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

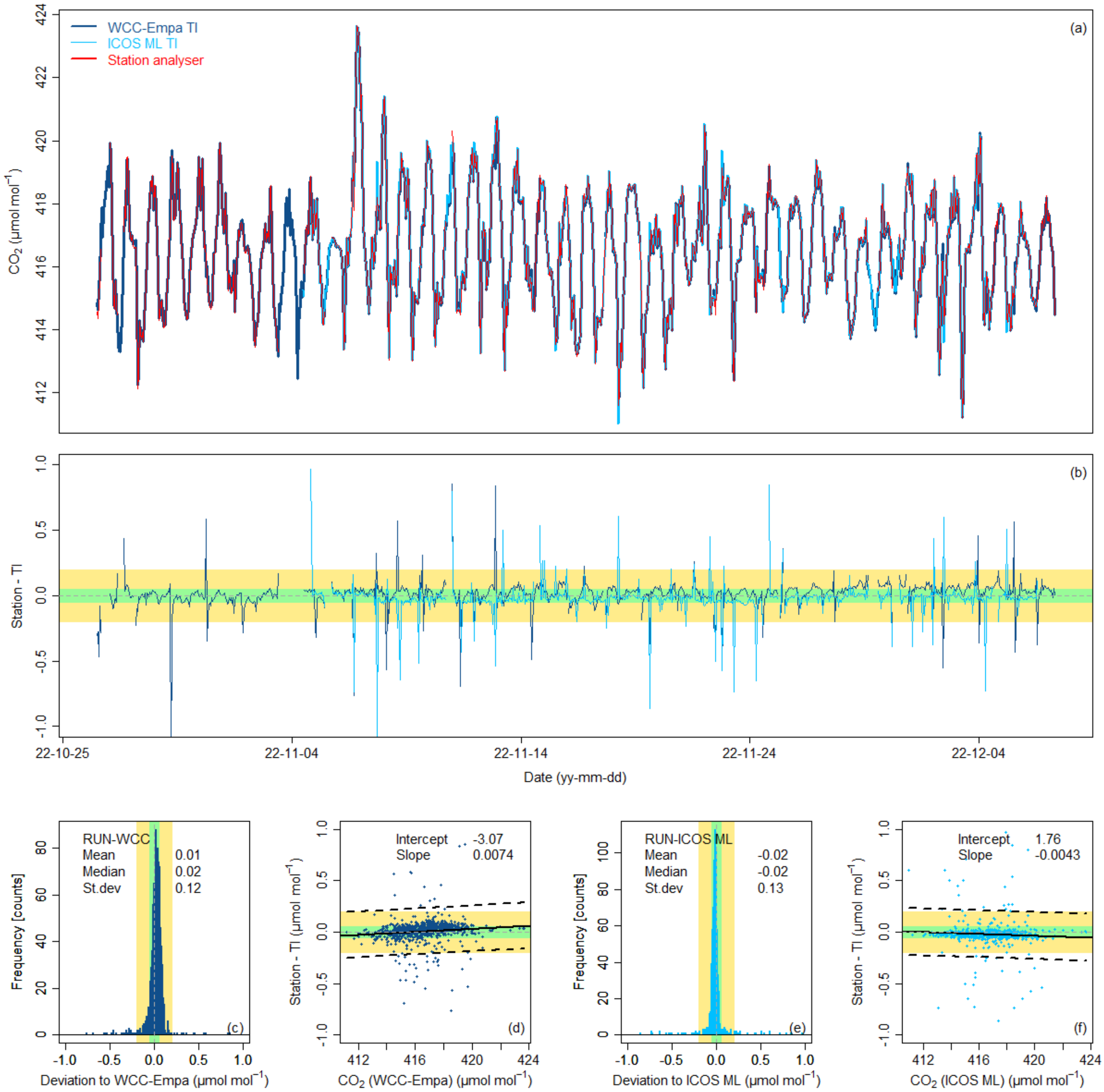

Figure 9. *Top: (a) Comparison of the Picarro G2401#1163-CFKADS2045 with the WCC-Empa and ICOS-ML travelling instruments for CO_2. Time series based on hourly data are shown. (b) Difference between the station instrument and the WCC-Empa and ICOS-ML travelling instruments. (c) and (e) CO_2 deviation histograms for the Picarro G2401#1163-CFKADS2045 analyser compared to the WCC-Empa TI and the ICOS-ML TI. (d) and (f) Bias of the RUN instrument as a function of the CO_2 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

CONCLUSIONS

The global GAW station La Réunion provides extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects. The RUN GAW activities are well coordinated and represent a very important contribution to the WMO/GAW programme. Thus, the continuation of the La Réunion measurement series is very important for the GAW programme.

Most of the measurements evaluated were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant amount fraction range. A problem with the ozone instrument was resolved during the audit. However, the existing pre-audit ozone time series need to be carefully re-evaluated. Submission of greenhouse gas and carbon monoxide data to the WMO/GAW Data Centre is also strongly recommended.

Table 6 summarises the results of the performance audit and ambient air comparison compared to the WMO/GAW compatibility goals. Note that Table 6 only covers the amount fractions relevant to RUN, while Table 5 further above covers a wider range of amount fractions.

Table 6. *Synthesis of the performance audit results for the TS and ambient air comparisons. A tick mark indicates that the compatibility goal (green) or the extended compatibility goal (orange) has been met on average. Tick marks in brackets indicate that the goal was only partially met in the relevant mole fraction range (performance audit only), and ✗ indicates results outside the compatibility goals.*

Comparison type	O_3 (initial, unrepaired) Thermo Scientific 49i	O_3 (final, repaired) Thermo Scientific 49i	CO Picarro G2401 ICOS ATC analysis	CH_4 Picarro G2401 ICOS ATC analysis	CO_2 Picarro G2401 ICOS ATC analysis
TS	✗	✓	✓	✓	✓
Air WCC-Empa	NA	NA	✓	✓	✓
Air ICOS-ML	NA	NA	✓	✓	✓

NA: no comparison was made

SUMMARY RANKING OF THE LA RÉUNION GAW STATION

System Audit Aspect	Adequacy[#]	Comment
Measurement programme	(5)	Comprehensive programme
Access	(5)	Year round access
Facilities		
Laboratory and office space	(5)	Adequate, with space for additional research campaigns
Internet access	(5)	Sufficient band-width, glass fibre
Air Conditioning	(5)	Air conditioned
Power supply	(5)	Reliable and stable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(4)	Skilled staff, more training of local operators needed
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(4)	Adequate instrumentation but issues with maintenance
CH_4/CO_2 Picarro G2401	(5)	State of the art instrumentation
CO Picarro G2401	(4)	Adequate instrument
Standards		
O_3	(0)	Calibration with ozone generator not adequate, no standard available
CO, CO_2, CH_4	(5)	Full traceability to the GAW reference through ICOS FCL
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(4)	Skilled staff, appropriate procedures
Data submission WDCRG	(3)	Ozone data partly submitted, large data gaps
Data submission WDCGG	(0)	GHG and CO data can only be accessed from ICOS carbon portal, no submission to WDCGG yet

[#]0: inadequate thru 5: adequate.

Dübendorf, July 2023

Dr C. Zellweger
WCC-Empa

Dr M. Steinbacher
QA/SAC Switzerland

Dr B. Buchmann
Head of Department

APPENDIX

Data review

The following figures show summary plots of RUN data accessed from WDCRG and the ICOS carbon portal on 20 February 2023. No data were submitted to WDCRG. The plots show time series of hourly data, frequency distribution and diurnal and seasonal variations.

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

Surface ozone:

Ozone data were only available for the years 2020 and 2021, with a large data gap of more than 6 months. The graph below shows the data for the period from 2020 to 2021.

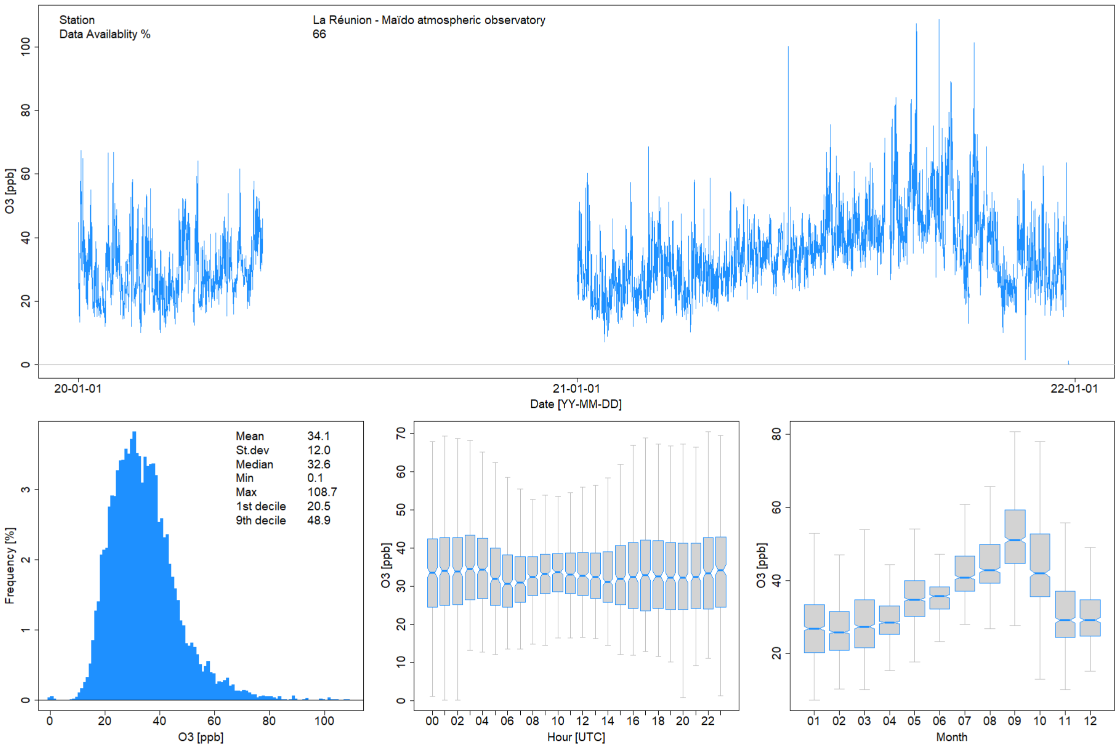

Figure 10. *O_3 data for the period from 2020 to 2021 obtained from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range. This dataset shows the final revised data.*

- At a first glance, the data sets look mostly sound in terms of mole fraction, trend, seasonal and diurnal variation. However, values tend to be high.
- Considering the results of the performance audit (broken ozone scrubber) and the fact that the calibration settings have been changed frequently, the data are expected to have a significant bias that will be difficult or impossible to correct.
- Revision or withdrawal of the data is required as recommended in the performance audit section of this report.

Carbon monoxide:

Data from the ICOS carbon portal:

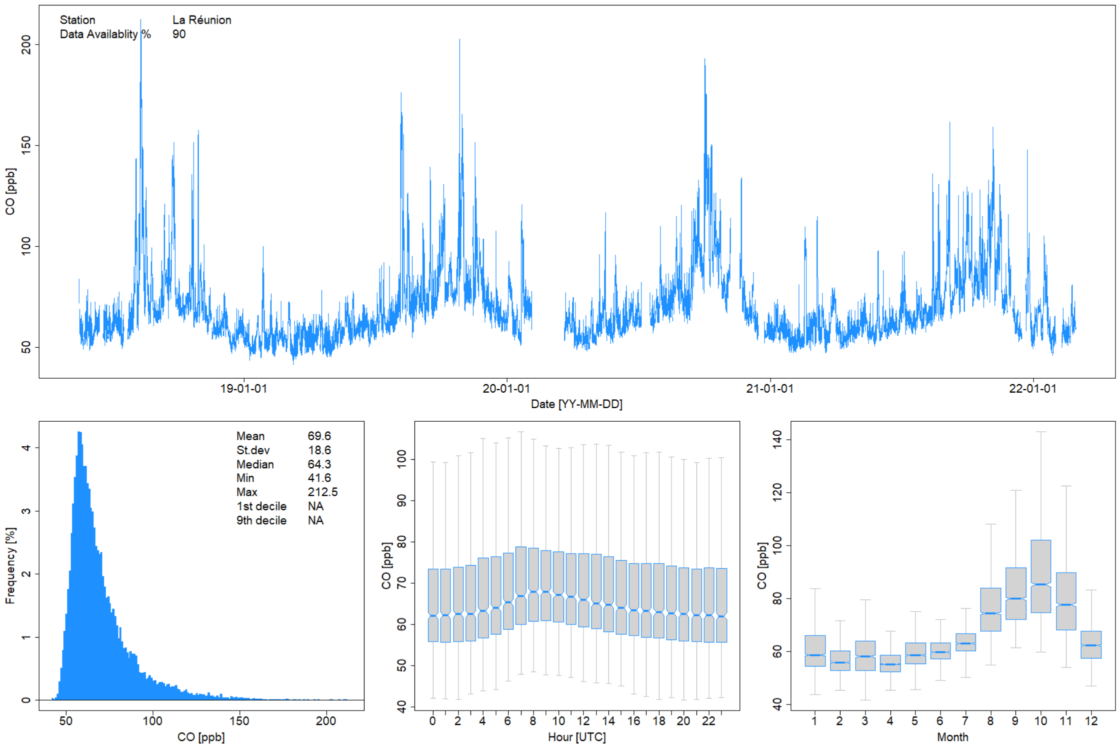

Figure 11. *RUN in-situ CO data (2018-2022) from the ICOS carbon portal. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation. The horizontal blue line indicates to the median and the blue boxes show the interquartile range.*

- The RUN CO data set looks good in terms of the mole fraction, the trend, the seasonal variation and the diurnal variation.

Methane:

Data from the ICOS carbon portal:

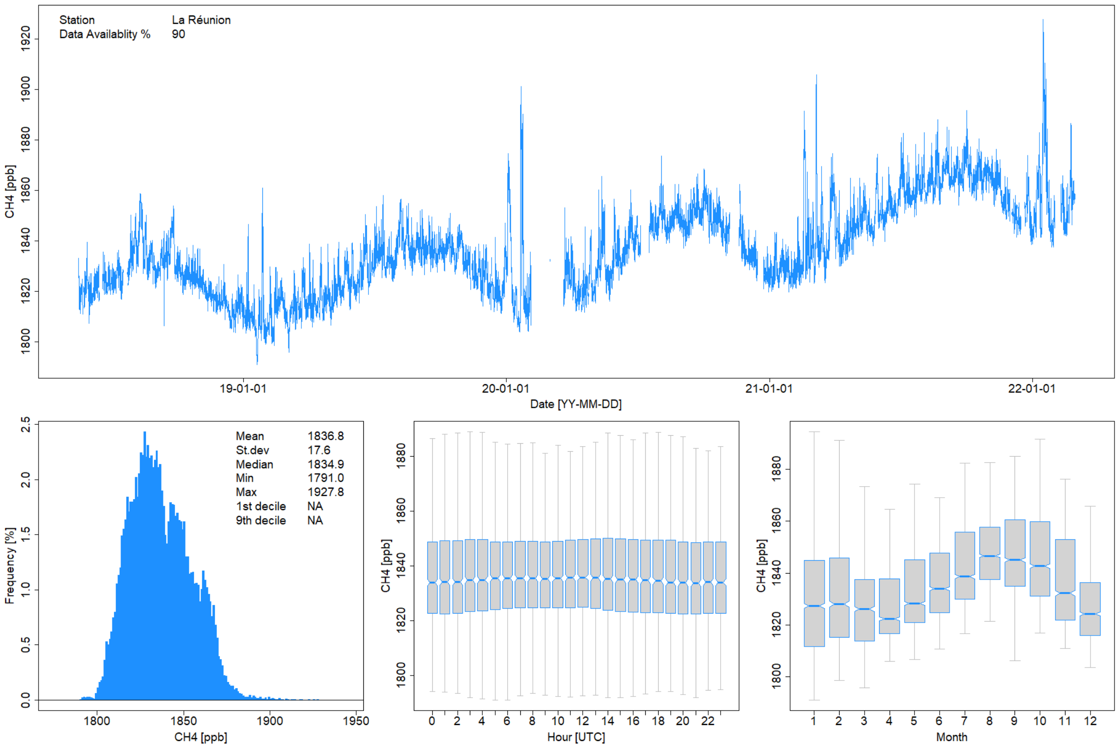

Figure 12. *RUN in-situ* CH_4 *data (2018-2022) from the ICOS carbon portal. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation. The horizontal blue line indicates the median and the blue boxes show the interquartile range.*

- The RUN CH_4 set looks good in terms of mole fraction, trend, seasonal and diurnal variation.

Carbon dioxide:

Data from the ICOS carbon portal:

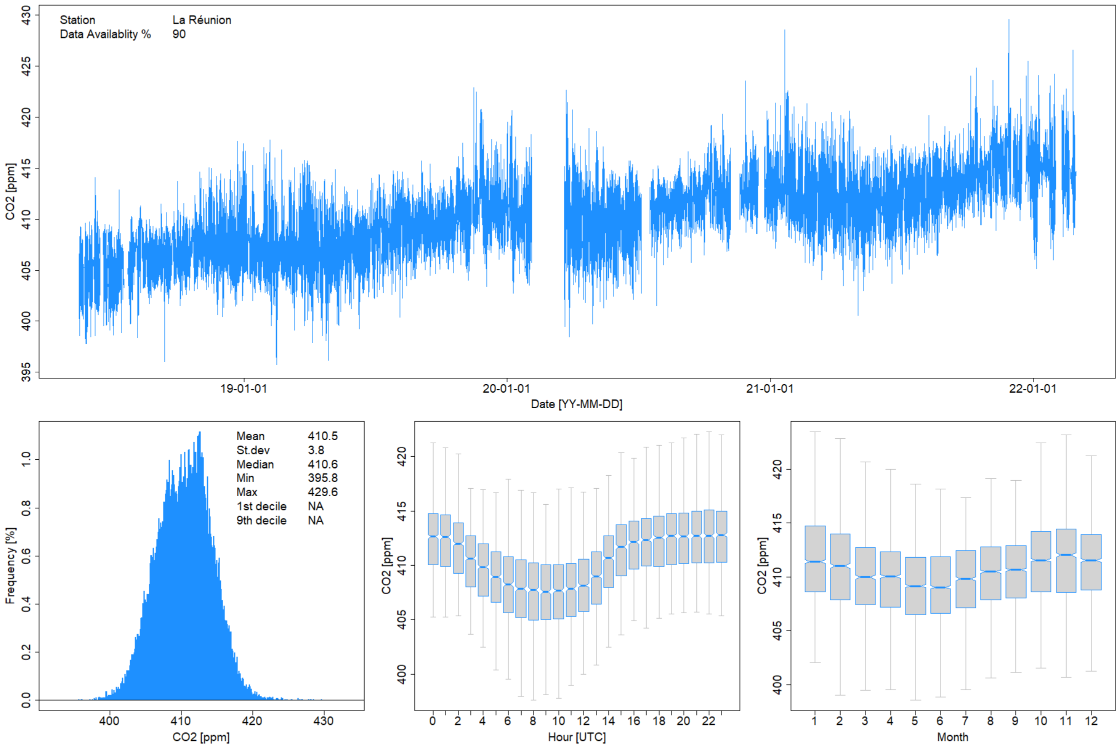

Figure 13. *RUN in-situ CO_2 data (2018-2022) from the ICOS carbon portal. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation. The horizontal blue line indicates the median and the blue boxes show the interquartile range.*

- The RUN CO_2 data set looks good in terms of mole fraction, trend, seasonal and diurnal variation.

Surface Ozone Comparisons

All procedures were carried out in accordance with the standard operating procedure (WCC-Empa SOP) and included comparisons of the transfer 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 to generate a randomised sequence of ozone levels from 0 to 250 nmol mol-1. Zero air was generated using a custom-built zero air generator (Nafion dryer, Purafil, activated charcoal). The TS was connected to the station analyser using approximately 1.5 m of PFA tubing. Table 7 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation were recorded by the WCC-Empa and RUN data acquisition systems.

Table 7. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #CM22117100 (WCC-Empa)
Settings	BKG +0.0 COEF 1.009
Pressure readings (hPa)	Ambient 790.7; TS 791.8, (no adjustment was made)
RUN analyser (OA)	
Model, S/N	Thermo Scientific 49i #0706721025
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG +0.4 nmol mol^{-1}, COEF 1.582 (initial comparison) BKG -0.4 nmol mol^{-1}, COEF 1.011 (final comparison)
Pressure readings (hPa)	Ambient 791.6; TS 792.9, (no adjustment was made)

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 given in Table 5 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) prior to 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 tables (individual monitoring sites) and also in the Executive Summary.

Table 8. *Comparison of the RUN ozone analyser (OA) Thermo Scientific 49i #0706721025 (BKG 0.4 nmol mol^{-1}, COEF 1.582, faulty 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 (%)
2022-10-24 17:14	125.49	0.14	171.67	0.31	46.18	36.80
2022-10-24 17:23	60.39	0.19	84.42	0.49	24.03	39.79
2022-10-24 17:31	90.51	0.05	126.69	0.36	36.18	39.97
2022-10-24 17:40	30.30	0.21	43.61	0.46	13.31	43.93
2022-10-24 17:48	50.35	0.13	72.11	0.34	21.76	43.22
2022-10-24 17:57	40.34	0.10	57.83	0.37	17.49	43.36
2022-10-24 18:05	175.65	0.17	247.21	0.43	71.56	40.74

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-10-24 18:14	70.42	0.07	100.26	0.29	29.84	42.37
2022-10-24 18:22	225.71	0.17	315.32	0.70	89.61	39.70
2022-10-24 18:31	250.78	0.16	347.89	0.58	97.11	38.72
2022-10-24 18:39	150.57	0.20	209.98	0.36	59.41	39.46
2022-10-24 18:48	0.86	0.15	1.29	0.21	0.43	NA
2022-10-24 18:57	10.37	0.15	15.13	0.30	4.76	45.90
2022-10-24 19:05	100.44	0.14	143.20	0.49	42.76	42.57
2022-10-24 19:14	80.39	0.13	114.69	0.31	34.30	42.67
2022-10-24 19:22	20.40	0.18	29.83	0.20	9.43	46.23
2022-10-24 19:31	200.61	0.26	283.42	0.63	82.81	41.28
2022-10-24 19:40	60.44	0.11	86.28	0.21	25.84	42.75
2022-10-24 19:51	100.53	0.19	143.09	0.32	42.56	42.34
2022-10-24 19:59	125.52	0.10	178.09	0.27	52.57	41.88
2022-10-24 20:08	80.42	0.15	114.50	0.37	34.08	42.38
2022-10-24 20:17	0.91	0.15	1.12	0.18	0.21	NA
2022-10-24 20:26	40.29	0.14	58.38	0.32	18.09	44.90
2022-10-24 20:34	50.38	0.14	72.80	0.37	22.42	44.50
2022-10-24 20:43	70.42	0.14	101.71	0.25	31.29	44.43
2022-10-24 20:51	30.28	0.11	44.00	0.17	13.72	45.31
2022-10-24 21:00	20.28	0.07	29.84	0.35	9.56	47.14
2022-10-24 21:11	250.77	0.19	354.65	0.69	103.88	41.42
2022-10-24 21:19	200.70	0.21	282.31	0.58	81.61	40.66
2022-10-24 21:28	10.42	0.12	14.80	0.17	4.38	42.03
2022-10-24 21:36	90.53	0.10	129.06	0.35	38.53	42.56
2022-10-24 21:45	225.64	0.29	317.14	1.16	91.50	40.55
2022-10-24 21:53	150.76	0.16	211.89	0.33	61.13	40.55
2022-10-24 22:02	175.68	0.16	246.01	0.58	70.33	40.03
2022-10-24 22:11	225.75	0.21	314.16	0.44	88.41	39.16
2022-10-24 22:19	125.47	0.11	175.43	0.37	49.96	39.82
2022-10-24 22:28	0.93	0.24	0.73	0.31	-0.20	NA
2022-10-24 22:37	150.64	0.05	211.93	0.43	61.29	40.69
2022-10-24 22:45	90.48	0.11	127.94	0.47	37.46	41.40
2022-10-24 22:54	175.58	0.18	245.77	0.33	70.19	39.98
2022-10-24 23:02	40.41	0.15	57.25	0.39	16.84	41.67
2022-10-24 23:11	70.46	0.13	99.86	0.26	29.40	41.73
2022-10-24 23:19	20.21	0.14	29.05	0.24	8.84	43.74
2022-10-24 23:28	100.48	0.12	142.58	0.48	42.10	41.90
2022-10-24 23:36	10.38	0.20	14.89	0.16	4.51	43.45
2022-10-24 23:48	250.84	0.30	349.80	0.80	98.96	39.45
2022-10-24 23:56	30.27	0.16	42.92	0.56	12.65	41.79
2022-10-25 00:05	50.43	0.13	71.89	0.37	21.46	42.55

Table 9. *Comparison of the RUN ozone analyser (OA) Thermo Scientific 49i #0706721025 (BKG -0.4 nmol mol^{-1}, COEF 1.011, repaired) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-10-25 13:27	250.85	0.22	250.63	0.30	-0.22	-0.09
2022-10-25 13:35	70.35	0.11	70.34	0.28	-0.01	-0.01
2022-10-25 13:44	100.49	0.08	100.54	0.26	0.05	0.05
2022-10-25 13:52	40.35	0.18	40.37	0.30	0.02	0.05
2022-10-25 14:01	175.67	0.15	175.68	0.30	0.01	0.01
2022-10-25 14:09	50.49	0.14	50.56	0.21	0.07	0.14
2022-10-25 14:18	200.66	0.22	200.61	0.25	-0.05	-0.02
2022-10-25 14:27	0.63	0.15	0.53	0.13	-0.10	NA
2022-10-25 14:36	125.46	0.18	125.45	0.26	-0.01	-0.01
2022-10-25 14:44	225.63	0.07	225.39	0.20	-0.24	-0.11
2022-10-25 14:53	80.36	0.08	80.38	0.21	0.02	0.02
2022-10-25 15:01	90.50	0.12	90.59	0.25	0.09	0.10
2022-10-25 15:10	20.33	0.17	20.37	0.15	0.04	0.20
2022-10-25 15:18	60.38	0.14	60.39	0.32	0.01	0.02
2022-10-25 15:27	10.31	0.14	10.44	0.21	0.13	1.26
2022-10-25 15:35	150.67	0.20	150.53	0.32	-0.14	-0.09
2022-10-25 15:44	30.32	0.19	30.36	0.19	0.04	0.13
2022-10-25 15:52	10.39	0.10	10.30	0.14	-0.09	-0.87
2022-10-25 16:01	90.40	0.15	90.46	0.21	0.06	0.07
2022-10-25 16:09	30.27	0.06	30.42	0.20	0.15	0.50
2022-10-25 16:18	60.46	0.14	60.58	0.38	0.12	0.20
2022-10-25 16:26	250.80	0.17	250.74	0.35	-0.06	-0.02
2022-10-25 16:35	80.43	0.14	80.56	0.30	0.13	0.16
2022-10-25 16:43	50.36	0.09	50.44	0.09	0.08	0.16
2022-10-25 16:52	200.71	0.14	200.62	0.21	-0.09	-0.04
2022-10-25 17:00	225.78	0.12	225.54	0.21	-0.24	-0.11
2022-10-25 17:09	125.50	0.13	125.55	0.22	0.05	0.04
2022-10-25 17:17	40.50	0.16	40.56	0.14	0.06	0.15
2022-10-25 17:26	150.56	0.15	150.54	0.21	-0.02	-0.01
2022-10-25 17:35	175.66	0.17	175.62	0.20	-0.04	-0.02
2022-10-25 17:43	70.45	0.09	70.43	0.31	-0.02	-0.03
2022-10-25 17:52	20.35	0.14	20.32	0.19	-0.03	-0.15
2022-10-25 18:00	100.57	0.15	100.69	0.32	0.12	0.12
2022-10-25 18:09	0.65	0.18	0.54	0.07	-0.11	- NA
2022-10-25 18:18	40.37	0.14	40.39	0.15	0.02	0.05
2022-10-25 18:26	60.42	0.14	60.57	0.24	0.15	0.25
2022-10-25 18:35	50.44	0.15	50.48	0.24	0.04	0.08
2022-10-25 18:43	125.49	0.14	125.47	0.22	-0.02	-0.02
2022-10-25 18:52	225.77	0.16	225.51	0.37	-0.26	-0.12
2022-10-25 19:00	70.50	0.14	70.52	0.21	0.02	0.03
2022-10-25 19:09	150.65	0.14	150.54	0.18	-0.11	-0.07
2022-10-25 19:17	175.68	0.17	175.51	0.19	-0.17	-0.10
2022-10-25 19:26	10.32	0.26	10.44	0.15	0.12	1.16
2022-10-25 19:34	200.68	0.16	200.46	0.26	-0.22	-0.11
2022-10-25 19:43	20.33	0.15	20.25	0.28	-0.08	-0.39
2022-10-25 19:51	80.51	0.12	80.52	0.20	0.01	0.01

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-10-25 20:00	250.64	0.25	250.35	0.39	-0.29	-0.12
2022-10-25 20:08	30.26	0.17	30.25	0.17	-0.01	-0.03
2022-10-25 20:18	0.62	0.14	0.47	0.06	-0.15	NA
2022-10-25 20:26	90.49	0.14	90.59	0.29	0.10	0.11
2022-10-25 23:01	70.35	0.21	70.33	0.22	-0.02	-0.03
2022-10-25 23:09	20.35	0.12	20.22	0.25	-0.13	-0.64
2022-10-25 23:18	100.41	0.14	100.39	0.20	-0.02	-0.02
2022-10-25 23:27	0.46	0.16	0.34	0.09	-0.12	NA
2022-10-25 23:35	40.34	0.15	40.31	0.20	-0.03	-0.07
2022-10-25 23:44	80.46	0.15	80.48	0.27	0.02	0.02
2022-10-25 23:52	200.70	0.18	200.35	0.41	-0.35	-0.17
2022-10-26 00:01	30.44	0.14	30.46	0.32	0.02	0.07
2022-10-26 00:09	250.71	0.08	250.29	0.21	-0.42	-0.17
2022-10-26 00:18	125.49	0.23	125.54	0.20	0.05	0.04
2022-10-26 00:26	90.47	0.10	90.54	0.12	0.07	0.08
2022-10-26 00:38	150.55	0.10	150.34	0.14	-0.21	-0.14
2022-10-26 00:46	60.36	0.13	60.37	0.27	0.01	0.02
2022-10-26 00:55	10.41	0.16	10.36	0.18	-0.05	-0.48
2022-10-26 01:03	225.77	0.14	225.45	0.25	-0.32	-0.14
2022-10-26 01:12	50.38	0.13	50.49	0.27	0.11	0.22
2022-10-26 01:20	175.70	0.18	175.60	0.31	-0.10	-0.06
2022-10-26 01:29	100.49	0.17	100.34	0.20	-0.15	-0.15
2022-10-26 01:37	200.68	0.16	200.35	0.24	-0.33	-0.16
2022-10-26 01:46	150.59	0.15	150.51	0.13	-0.08	-0.05
2022-10-26 01:54	40.32	0.19	40.30	0.24	-0.02	-0.05
2022-10-26 02:03	80.50	0.16	80.44	0.11	-0.06	-0.07
2022-10-26 02:11	70.56	0.14	70.48	0.25	-0.08	-0.11
2022-10-26 02:20	250.71	0.10	250.36	0.31	-0.35	-0.14
2022-10-26 02:29	50.40	0.09	50.45	0.10	0.05	0.10
2022-10-26 02:37	175.69	0.15	175.53	0.28	-0.16	-0.09
2022-10-26 02:46	90.57	0.12	90.39	0.17	-0.18	-0.20
2022-10-26 02:55	0.67	0.21	0.46	0.10	-0.21	NA
2022-10-26 03:03	225.80	0.16	225.46	0.19	-0.34	-0.15
2022-10-26 03:12	60.39	0.12	60.40	0.23	0.01	0.02
2022-10-26 03:20	125.52	0.14	125.39	0.23	-0.13	-0.10
2022-10-26 03:29	20.32	0.17	20.27	0.21	-0.05	-0.25
2022-10-26 03:37	10.43	0.19	10.44	0.20	0.01	0.10
2022-10-26 03:46	30.45	0.10	30.27	0.13	-0.18	-0.59
2022-10-26 03:54	80.40	0.16	80.32	0.28	-0.08	-0.10
2022-10-26 04:03	10.39	0.25	10.22	0.21	-0.17	-1.64
2022-10-26 04:11	225.68	0.16	225.48	0.27	-0.20	-0.09
2022-10-26 04:20	250.82	0.16	250.51	0.34	-0.31	-0.12
2022-10-26 04:29	90.50	0.14	90.33	0.16	-0.17	-0.19
2022-10-26 04:37	150.56	0.19	150.40	0.34	-0.16	-0.11
2022-10-26 04:45	125.51	0.11	125.55	0.27	0.04	0.03
2022-10-26 04:54	50.50	0.16	50.55	0.21	0.05	0.10
2022-10-26 05:03	0.57	0.19	0.51	0.11	-0.06	NA
2022-10-26 05:12	30.27	0.23	30.12	0.41	-0.15	-0.50

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-10-26 05:20	20.37	0.10	20.30	0.22	-0.07	-0.34
2022-10-26 05:20	20.37	0.10	20.30	0.22	-0.07	-0.34

Carbon Monoxide Comparisons

All procedures were performed 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 below.

Table 10 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation were recorded by the RUN data acquisition system.

Table 10. Experimental details of the RUN comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Tables 16 and 17.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #1163-CFKADS2045
Principle	Near-IR CRDS
Drying system	Nafion dryer
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 11. *CO aggregates calculated from individual analyses (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1163-CFKADS2045 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-10-25 09:39:40)	171122_FA02788	74.3	0.5	76.7	1.2	3	2.5	3.3
(22-10-26 07:11:00)	171124_FA02786	147.0	1.0	149.7	0.5	3	2.8	1.9
(22-10-25 17:35:00)	210415_FB03358	122.7	1.1	125.4	0.7	3	2.6	2.1
(22-10-25 09:43:00)	181128_FF61471	108.0	0.9	109.6	1.3	4	1.6	1.5
(22-10-25 18:05:00)	210415_FB03383	136.9	0.8	139.0	0.3	3	2.1	1.5
(22-10-25 17:05:00)	130819_FB03860	159.0	1.4	161.3	0.4	3	2.3	1.5
(22-10-25 09:06:40)	171122_FA02785	53.7	0.5	56.0	1.1	3	2.2	4.1
(22-10-25 10:53:00)	201207_FB03887	34.4	1.0	35.9	0.4	3	1.5	4.3

Date / Time	TS Cylinder	TS (nmol mol-1)	sdTS (nmol mol-1)	AL (nmol mol-1)	sdAL (nmol mol-1)	N	AL-TS (nmol mol-1)	AL-TS (%)
(22-10-25 16:35:00)	210412_FB03377	9.6	1.2	14.2	0.3	3	4.6	48.3
(22-10-26 07:41:00)	180318_FF30491	192.0	0.9	194.3	0.4	3	2.3	1.2

Methane comparisons

All procedures were performed 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 10 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation were recorded by the RUN data acquisition system.

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 12. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1163-CFKADS2045 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol-1)	sdTS (nmol mol-1)	AL (nmol mol-1)	sdAL (nmol mol-1)	N	AL-TS (nmol mol-1)	AL-TS (%)
(22-10-25 09:39:40)	171122_FA02788	1619.01	0.04	1619.74	0.13	3	0.73	0.05
(22-10-26 07:11:00)	171124_FA02786	2193.71	0.05	2193.46	0.06	3	-0.25	-0.01
(22-10-25 17:35:00)	210415_FB03358	1908.28	0.02	1908.72	0.20	3	0.44	0.02
(22-10-25 09:43:00)	181128_FF61471	1989.76	0.03	1989.95	0.06	4	0.19	0.01
(22-10-25 18:05:00)	210415_FB03383	1938.91	0.06	1939.29	0.24	3	0.38	0.02
(22-10-25 17:05:00)	130819_FB03860	1942.37	0.05	1942.57	0.25	3	0.20	0.01
(22-10-25 09:06:40)	171122_FA02785	1856.35	0.04	1856.76	0.04	3	0.41	0.02
(22-10-25 10:53:00)	201207_FB03887	1945.80	0.03	1945.89	0.04	3	0.09	0.00
(22-10-25 16:35:00)	210412_FB03377	2.74	0.06	5.69	0.00	3	2.95	NA
(22-10-26 07:41:00)	180318_FF30491	1984.95	0.04	1985.04	0.12	3	0.09	0.00

Carbon dioxide comparisons

All procedures were performed 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 10 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation were recorded by the RUN data acquisition system.

Results

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

Table 13. *CO_2 aggregates calculated from individual analyses (mean and standard deviation of the mean) for* each level when comparing the Picarro G2401 #1163-CFKADS2045 instrument (AL) with the WCC-Empa TS (WMO-X2007 CO_2 scale).

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(22-10-25 09:39:40)	171122_FA02788	337.27	0.01	337.38	0.01	3	0.11	0.03
(22-10-26 07:11:00)	171124_FA02786	468.51	0.02	468.51	0.01	3	0.00	0.00
(22-10-25 17:35:00)	210415_FB03358	409.93	0.01	409.99	0.02	3	0.06	0.01
(22-10-25 09:43:00)	181128_FF61471	401.90	0.00	401.96	0.01	4	0.06	0.01
(22-10-25 18:05:00)	210415_FB03383	427.36	0.01	427.38	0.02	3	0.02	0.00
(22-10-25 17:05:00)	130819_FB03860	399.87	0.01	399.88	0.02	3	0.01	0.00
(22-10-25 09:06:40)	171122_FA02785	408.46	0.01	408.51	0.00	3	0.05	0.01
(22-10-25 10:53:00)	201207_FB03887	413.58	0.00	413.60	0.00	3	0.02	0.00
(22-10-25 16:35:00)	210412_FB03377	0.24	0.01	0.75	0.00	3	0.51	NA
(22-10-26 07:41:00)	180318_FF30491	420.17	0.01	420.22	0.01	3	0.05	0.01

WCC-Empa travelling standards

Ozone

The WCC-Empa Travelling Standard (TS) was compared with the Standard Reference Photometer (SRP) before and after the audit. The instruments used were

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

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

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

The results of the TS calibration before and after the audit are shown in Table 14. The TS passed the pre-audit evaluation criteria defined for maximum acceptable bias (Klausen et al., 2003) (see Figure 14). The data were pooled and evaluated by linear regression analysis, taking into account the uncertainties of both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be calculated (Equation 6a). The uncertainty of the TS (Equation 6b) was previously estimated (see Equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (nmol mol}^{-1}\text{)} = ([TS] + 0.34 \text{ nmol mol}^{-1}) / 0.9983 \quad (6a)$$

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

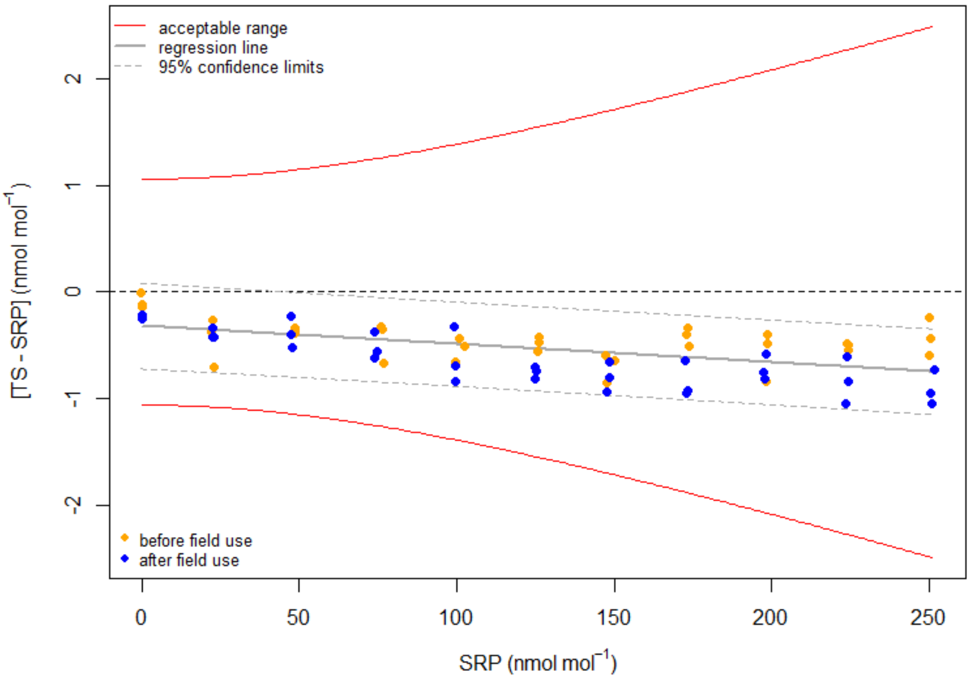

Figure 14. *Deviations between TS and SRP before and after use of the TS in the field.*

Table 14. Mean values calculated over a minimum five minutes for the comparison of the WCC-Empa Traveling Standard (TS) with the Standard Reference Photometer (SRP).

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-07-28	1	50	48.78	0.29	48.44	0.24
2022-07-28	1	20	22.33	0.27	22.07	0.15
2022-07-28	1	200	198.22	0.25	197.39	0.28
2022-07-28	1	125	125.59	0.41	125.04	0.18
2022-07-28	1	75	75.99	0.39	75.67	0.19
2022-07-28	1	175	173.70	0.26	173.19	0.18
2022-07-28	1	145	147.23	0.34	146.64	0.20
2022-07-28	1	0	0.04	0.20	-0.07	0.09
2022-07-28	1	250	250.03	0.44	249.43	0.20
2022-07-28	1	105	102.51	0.37	102.00	0.28
2022-07-28	1	225	224.38	0.48	223.83	0.12
2022-07-28	2	20	22.09	0.37	21.71	0.28
2022-07-28	2	75	76.33	0.26	75.98	0.19
2022-07-28	2	200	198.69	0.25	198.29	0.22
2022-07-28	2	100	100.60	0.24	100.17	0.12
2022-07-28	2	50	48.67	0.41	48.28	0.12
2022-07-28	2	175	173.06	0.35	172.67	0.21
2022-07-28	2	150	150.23	0.35	149.58	0.13
2022-07-28	2	250	250.27	0.14	249.84	0.16
2022-07-28	2	0	-0.17	0.34	-0.17	0.12
2022-07-28	2	225	223.80	0.39	223.31	0.25
2022-07-28	2	125	125.90	0.20	125.48	0.20
2022-07-28	3	50	48.77	0.28	48.40	0.27
2022-07-28	3	100	99.69	0.22	99.03	0.11
2022-07-28	3	225	224.32	0.13	223.82	0.16
2022-07-28	3	0	0.05	0.22	-0.10	0.07
2022-07-28	3	25	22.78	0.29	22.08	0.13
2022-07-28	3	75	76.94	0.43	76.27	0.17
2022-07-28	3	150	147.64	0.51	146.79	0.31
2022-07-28	3	125	125.98	0.20	125.50	0.14
2022-07-28	3	175	173.41	0.19	173.07	0.08
2022-07-28	3	200	198.75	0.35	198.27	0.14
2022-07-28	3	250	250.05	0.38	249.81	0.23
2023-01-20	4	175	173.38	0.30	172.46	0.14
2023-01-20	4	20	22.41	0.34	21.99	0.16
2023-01-20	4	150	147.70	0.31	146.76	0.19
2023-01-20	4	125	124.86	0.18	124.16	0.14
2023-01-20	4	250	250.81	0.26	249.76	0.22
2023-01-20	4	75	73.82	0.21	73.21	0.33
2023-01-20	4	100	99.12	0.42	98.80	0.13
2023-01-20	4	50	47.88	0.39	47.36	0.13
2023-01-20	4	225	224.14	0.40	223.30	0.18
2023-01-20	4	0	0.00	0.29	-0.21	0.10
2023-01-20	4	200	197.53	0.27	196.78	0.23

Date	Run	Level#	SRP (nmol mol-1)	sdSRP (nmol mol-1)	TS (nmol mol-1)	sdTS (nmol mol-1)
2023-01-20	5	100	99.37	0.24	98.67	0.25
2023-01-20	5	125	124.72	0.24	123.91	0.16
2023-01-20	5	200	197.76	0.20	196.94	0.16
2023-01-20	5	20	22.39	0.21	22.05	0.22
2023-01-20	5	175	172.99	0.25	172.04	0.20
2023-01-20	5	75	73.97	0.31	73.60	0.16
2023-01-20	5	225	223.98	0.19	223.37	0.15
2023-01-20	5	250	251.69	0.26	250.96	0.21
2023-01-20	5	45	47.41	0.31	47.01	0.17
2023-01-20	5	150	148.37	0.21	147.57	0.12
2023-01-20	5	0	0.15	0.24	-0.07	0.17
2023-01-20	6	75	74.55	0.25	74.00	0.17
2023-01-20	6	225	223.59	0.34	222.55	0.21
2023-01-20	6	200	198.33	0.20	197.75	0.20
2023-01-20	6	0	0.17	0.34	-0.09	0.12
2023-01-20	6	250	250.34	0.23	249.39	0.23
2023-01-20	6	45	47.35	0.25	47.12	0.21
2023-01-20	6	25	22.86	0.35	22.43	0.14
2023-01-20	6	150	148.33	0.40	147.67	0.13
2023-01-20	6	100	99.63	0.21	98.79	0.17
2023-01-20	6	125	125.16	0.22	124.42	0.14
2023-01-20	6	175	172.66	0.37	172.02	0.14

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) of the WMO/GAW programme for carbon monoxide, carbon dioxide and methane. NOAA has been designated by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL, which are regularly compared with the CCL by means of travelling standards and the addition of new laboratory standards from the CCL. The following calibration scales have been used to assign the mole fractions to the TS

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

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

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

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

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

Table 15 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including standard deviations of the WCC-Empa TS are given in Tables 16 and 17, and Figures 15 to 18 show the analysis of the TS over time.

Table 15. *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 16. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, and N_2O. The letters in parentheses refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, (L) LGR.*

TS	**Press. (psi)**	**CH_4 (P) (nmol mol^{-1})**	**sd**	**CO_2(P) (µmol mol^{-1})**	**sd**	**N_2O (A) (nmol mol^{-1})**	**sd**	**N_2O (L) (nmol mol^{-1})**	**sd**
130819_FB03860	890	1942.37	0.05	399.87	0.01	327.37	0.04	327.48	0.08
171122_FA02785	1260	1856.35	0.04	408.46	0.01	341.66	0.12	341.85	0.03
171122_FA02788	1700	1619.01	0.04	337.27	0.01	283.60	0.13	283.97	0.19
171124_FA02786	1550	2193.71	0.05	468.51	0.02	377.85	0.69	377.79	0.04
180318_FF30491	1040	1984.95	0.04	420.17	0.01	330.63	0.34	330.65	0.01
181128_FF61471	1600	1989.76	0.03	401.90	0.00	333.08	0.48	333.15	0.02
201207_FB03887	320	1945.80	0.03	413.58	0.00	329.90	0.12	330.08	0.02
210412_FB03377	300	2.74	0.06	0.24	0.01	10.41	0.13	15.31	0.44
210415_FB03358	1980	1908.28	0.02	409.93	0.01	330.67	0.18	330.81	0.02
210415_FB03383	1930	1938.91	0.06	427.36	0.01	340.75	0.43	340.89	0.02

Table 17. *Calibration summary of the WCC-Empa travelling standards for CO. The letters in parentheses refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, (L) LGR.*

TS	**Press. (psi)**	**CO (P) (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**	**CO (L) (nmol mol^{-1})**	**sd**
130819_FB03860	890	158.95	1.40	155.50	0.34	154.60	0.36
171122_FA02785	1260	53.73	0.47	50.71	0.51	51.40	0.06
171122_FA02788	1700	74.25	0.47	71.81	0.39	71.46	0.07
171124_FA02786	1550	146.98	1.00	143.30	0.22	142.40	0.04
180318_FF30491	1040	192.04	0.91	187.92	0.32	186.75	0.14
181128_FF61471	1600	108.02	0.85	104.66	0.03	104.30	0.19
201207_FB03887	320	34.44	1.02	31.49	0.61	32.89	0.27
210412_FB03377	300	9.58	1.18	7.45	0.23	8.60	1.01
210415_FB03358	1980	122.73	1.09	119.34	0.13	118.59	0.12
210415_FB03383	1930	136.90	0.82	133.13	0.16	132.25	0.13

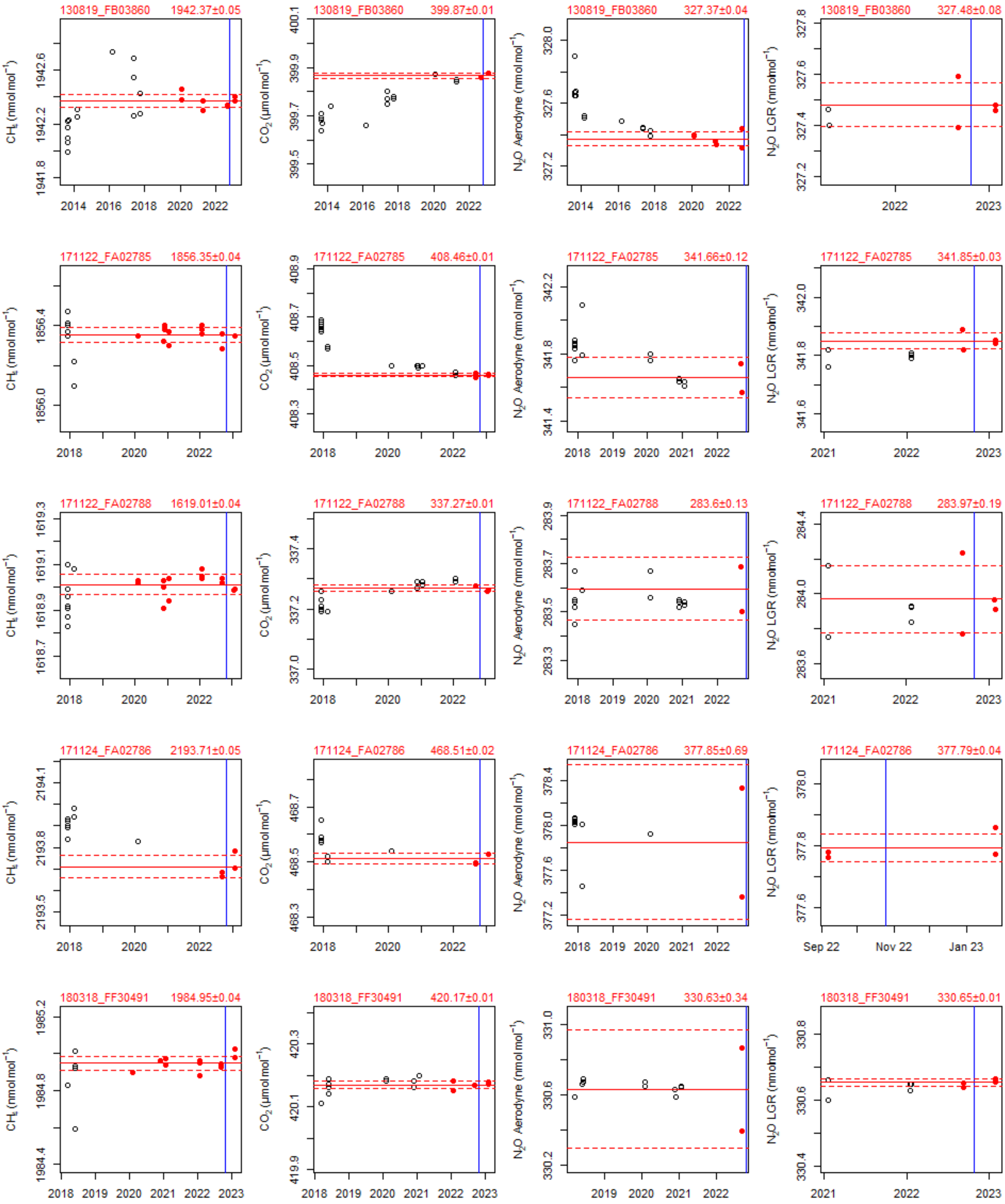

Figure 15. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points used to assign the values; the red dashed line corresponds to the standard deviation of the measurement.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

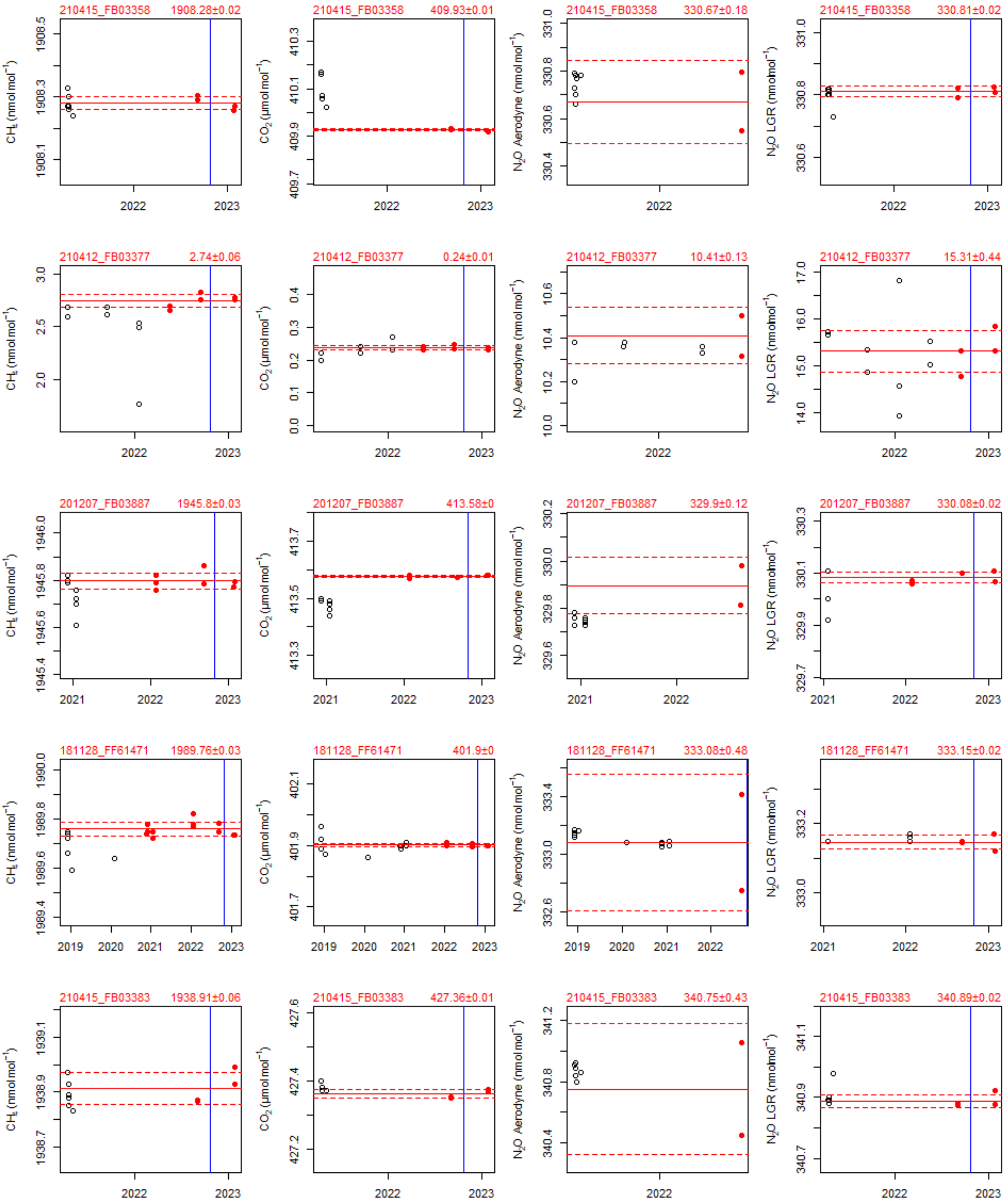

Figure 16. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points used to assign the values; the red dashed line corresponds to the standard deviation of the measurement.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

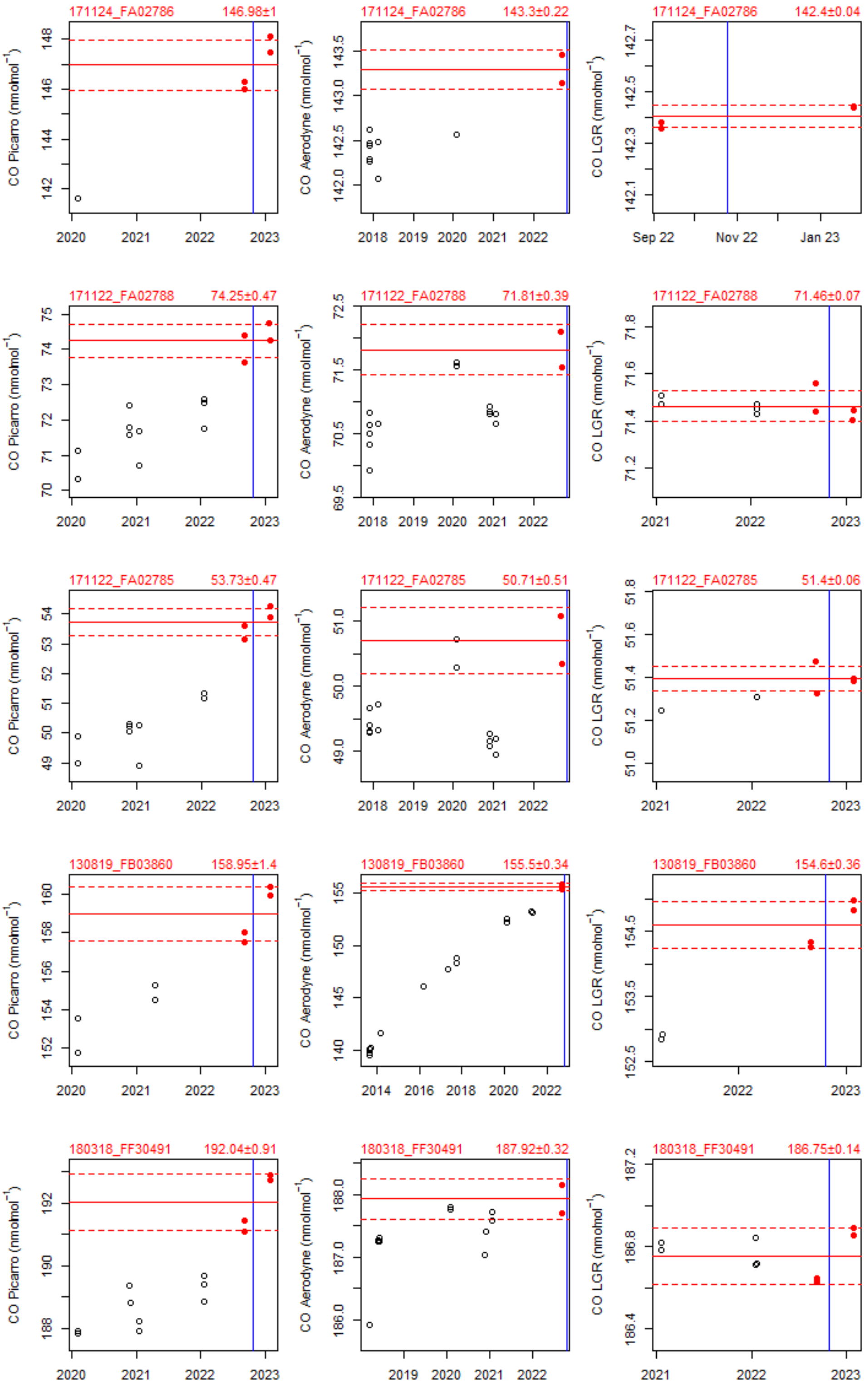

Figure 17. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points used to assign the values; the red dashed line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

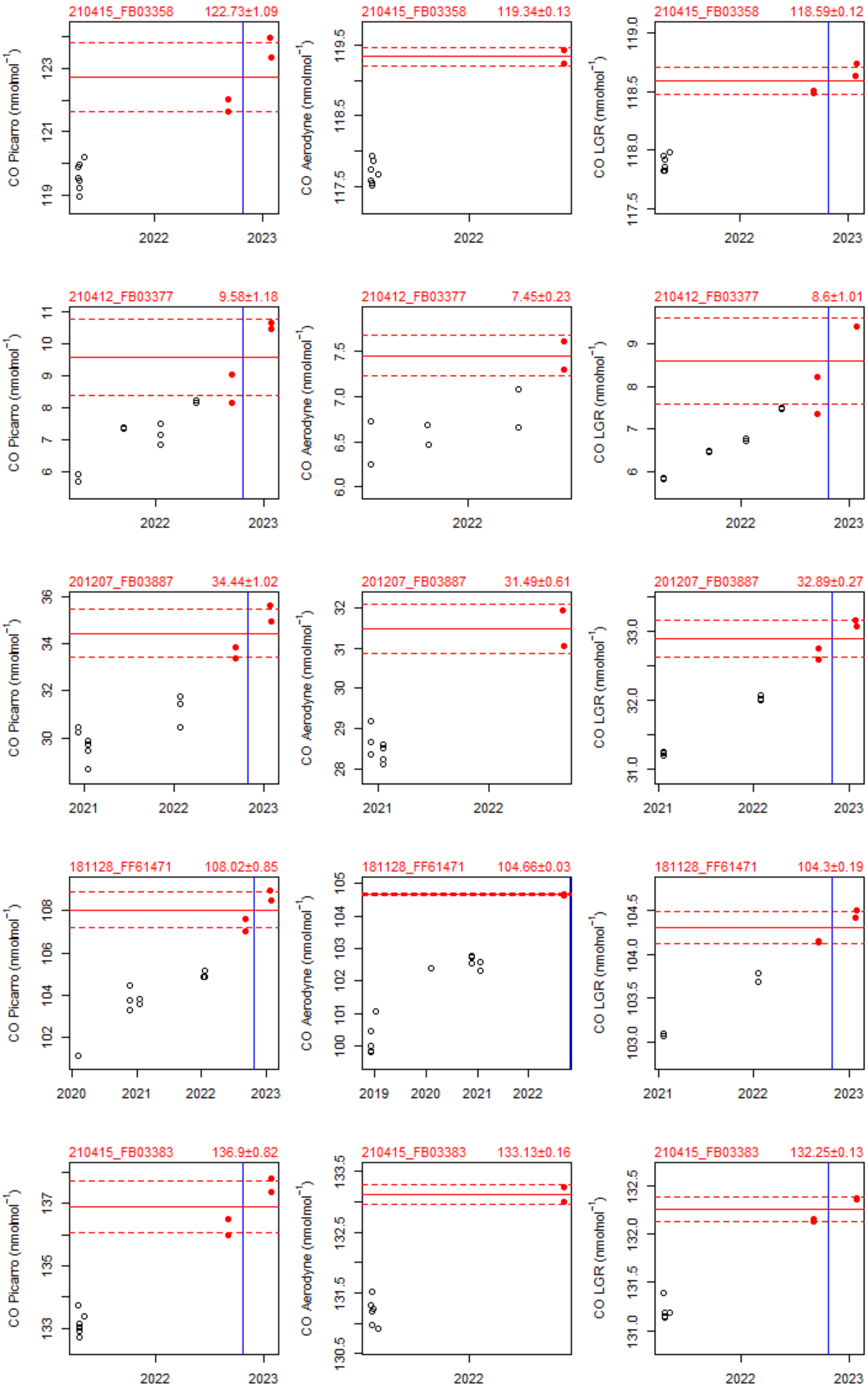

Figure 18. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points used to assign the values; the red dashed line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH_4 and CO_2, the Picarro G2401 SN #1467-CFKADS2098 was calibrated every 2210 min using one WCC-Empa TS as a working standard, and two TS as target tanks. Based on the working standard measurements, a loess fit drift correction was applied to the data as shown in the figure below. The maximum drift between two WS measurements was approximately 0.1 nmol mol^{-1} for CH_4 and 0.1 µmol mol^{-1} for CO_2. Most of the target cylinder measurements were within half of the WMO GAW compatibility goals.

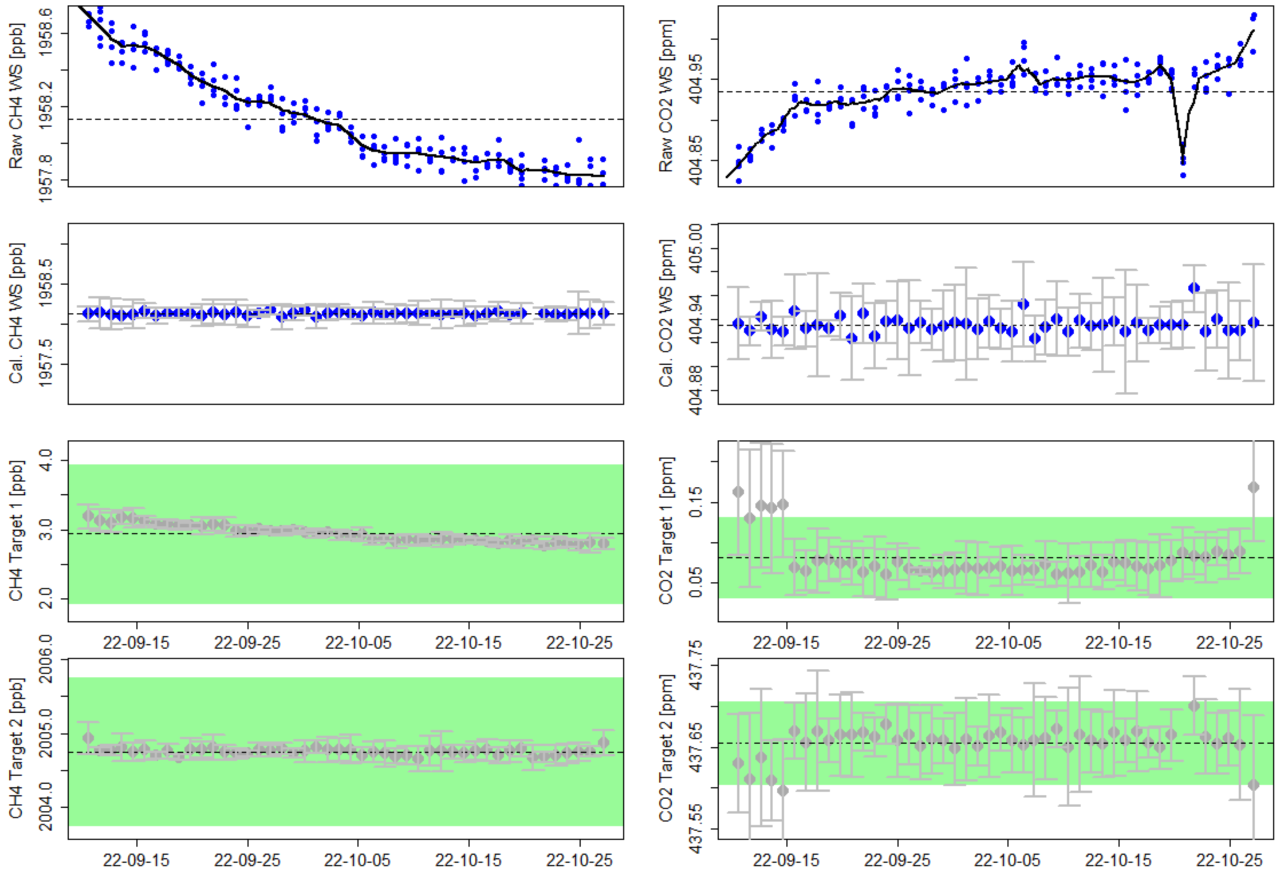

Figure 19. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The top panel shows the raw 1 min values of the working standard and the loess fit (black line) used to account for the drift. The second panel shows the variation of the WS after application of the drift correction. The lower two most panels show 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 2210 minutes using three WCC-Empa TS as a working standards. Based on the working standard measurements, a a loess fit drift correction was first applied to the data, as shown in the figure below.

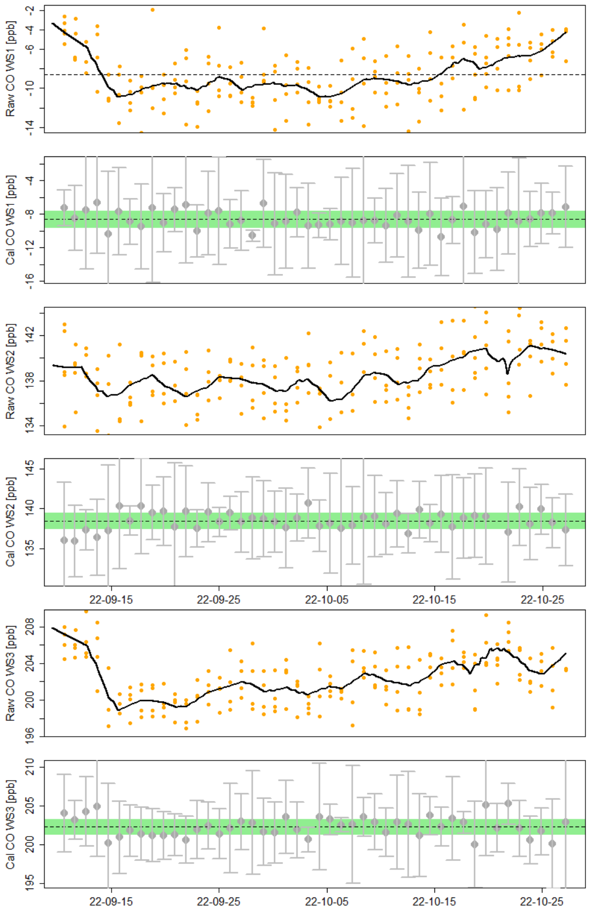

Figure 20. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show the raw 1 min values of the working standards and the loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in 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 data from the working standards was then used to calculate calibrated CO data, as shown in the figure below.

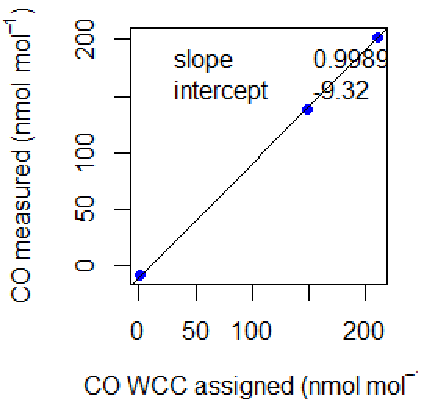

Figure 21. *CO calibration function based on the average values of the drift corrected working standard measurements.*

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LIST OF ABBREVIATIONS

AERONET	Aerosol Robotic Network
a.s.l	above sea level
ATC	Atmosphere Thematic Centre
BIRA	Royal Belgian Institute for Space Aeronomy
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
eDQO	Extended Data Quality Objective
FCL	Flask and Calibration Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
IR	Infrared
LS	Laboratory Standard
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
ML	Mobile Laboratory
NA	Not Applicable
NDACC	Network for the Detection of Atmospheric Composition Change
NOAA	National Oceanic and Atmospheric Administration
RUN	La Réunion GAW Station
SHADOZ	Southern Hemisphere Additional Ozonesondes
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