WCC-Empa Report 23/5

System and performance audit of Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide at the Global GAW Station Kennaook / Cape Grim, Australia, December 2023

Submitted to the World Meteorological Organization by
C. Zellweger, M. Steinbacher and L. Emmenegger
WMO World Calibration Centre WCC-Empa
Empa, Dübendorf, Switzerland

Acknowledgements

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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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1 Executive summary

The 4th WCC-Empa[1] system and performance audit at the Kennaook / Cape Grim global GAW station (CGO) was conducted from 4 to 7 December 2023 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 GAW Empa website. The following persons contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Ms Sarah Prior	Bureau of Meteorology, station manager, GAW country contact
Ms Cindy Spinks	Bureau of Meteorology, technical officer – logistics
Mr Jeremy Ward	Bureau of Meteorology, station operator
Mr Nigel Somerville	Bureau of Meteorology, station operator
Mr Stuart Baly	Bureau of Meteorology, station operator, IT
Ms Suzie Molloy	Kennaook / Cape Grim, station scientist (reactive gases)
Mr Paul Krummel	Kennaook / Cape Grim, station scientist (greenhouse gases)
Dr Ray Langenfelds	Kennaook / Cape Grim, station scientist (greenhouse gases)
Dr Zoë Loh	Kennaook / Cape Grim, station scientist (greenhouse gases)

This report summarises the evaluation of the Kennaook / Cape Grim GAW station in general and the measurements of surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide in particular.

The report will be distributed to the station manager of the Kennaook / Cape Grim GAW station, the national focal point for GAW in Australia, and 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 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.

2 Site description and operation

2.1 Station management

The Australian Bureau of Meteorology (BoM) funds and manages the CGO station and liaises with the World Meteorological Organization and the United Nations Environment Programme. Scientific research at the station is jointly managed by the BoM and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) - Environment. Other Australian and international research institutions contribute, notably the University of Southern Queensland, University of Wollongong and the Australian Nuclear Science and Technology Organisation (ANSTO).

Station management, senior scientists and other specialists provide advice on the overall programme. Principal investigators lead individual scientific programmes.

Further information is available on the BoM and CSIRO CGO websites.

2.2 Location and access

The CGO station (40.6822°S, 144.6883°E, 94 m above sea level) is located on a cliff near the northern end of the west coast of Tasmania, overlooking the Southern Ocean. The building sits on a small block surrounded by a 25 ha buffer zone. A small area within and adjacent to the building is leased to a telecommunications company, whose 80 m tower is used by the station. The buffer zone is surrounded by a 22,000 ha of land used for beef, dairy and wind farming. From the station, the clean air sector is 190-280 degrees. Winds from this sector occur about 35 % of the time. The station is supported by a BoM office at Smithton and CSIRO laboratories at Aspendale. Access to the site by road is possible throughout the year. Further information is available from GAWSIS.

2.3 Station facilities

CGO offers spacious laboratory and office facilities with high-speed internet access. These facilities include a large office space, a small dining room with a kitchen, and workshops. Basic accommodation is also available for visiting scientists. All laboratories are temperature controlled. CGO provides an ideal platform for ongoing atmospheric research. In addition to the large number of permanent measurements, space is available for campaign-based experiments.

2.4 Measurement programme

CGO hosts a comprehensive measurement programme covering all focal areas of the GAW programme. An overview of the measured species is available on GAWSIS. The activities of CGO are well embedded in national and international programmes, such as the Advanced Global Atmospheric Gases Experiment (AGAGE) and the NOAA Cooperative Air Sampling Network. A full list of collaborators and partnerships is available on the CSIRO website.

The information available on GAWSIS was reviewed as part of the audit. The last update was made by BoM in July 2022 and the information found on GAWSIS was largely up to date. However, some details on instrumentation and station contacts still need to be checked and corrected.

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

2.5 Data submission

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

CSIRO, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (1981-2022), four data sets.

CSIRO, submission to the WDCGG:
CH_4 flask data (1984-2023), CO_2 in-situ data (2004-2019), CO_2 flask data (1984-2023), N_2O flask data (1991-2023), CO flask data (1984-2023).

AGAGE in-situ data, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (1981-2023), three data sets, N_2O (1978-2023), three data sets, CO (1993-2023).

NOAA flask data, submission to WDCGG:
CH_4 (1984-2023), CO_2 (1990-2023), N_2O (1994-2023), two data sets, CO (1990-2023).

The data presented in this report were accessed on 8 March 2024. All data covered by the review were submitted with a submission delay of one to several years, depending on the parameter. It is recommended to continue the practice of timely submission of data.

> **Recommendation 2 (**, important, 2024)**
> *Most data have been submitted with a delay of less than one year. However, some recent data are not yet available from the data centres. It is recommended to submit the O_3 data for the period from 2017 onwards as soon as the final quality control has been completed. In addition, in-situ CO data should also be submitted as soon as possible.*

2.6 Data review

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

2.7 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.

2.8 Air inlet system

GHGs and CO are sampled from the CGO tower. The AGAGE multidetector gas chromatograph (GC-MD) and Picarro instruments are all on the same inlet. The inlet is a 1.5" Polypipe and runs from the 70 m height on the new tower to the bulkhead of the building, which is approximately 100 m long including the gantry. Inside the building there is then a run of about 50 m through a 1.5" Polypipe before it joins a 2" stainless steel manifold which runs through the main laboratory and is about 15 m long. One section of the manifold has 16 outlets, shown in Figure 1. The flow rate through the entire system is ~600 litres per minute. The flush pump that draws air through the entire system is a Vortex blower, model number VB001S.

The surface ozone air intake is located at the top of the laboratory building at a height of 10 m from the roof. It consists of a 10 m stainless steel tube with an inner diameter of 15 cm. The flow rate is ~220 litres per minute, and the Inlet is protected from rain and hail by an inverted stainless steel cup. Stainless steel wires inside the cup prevent bird nesting. The ozone instruments are connected by PTFE tubing (inner diameter 4 mm). The residence time is approximately 50 seconds. The ozone inlet has not been modified since the last WCC-Empa audit in 2016.

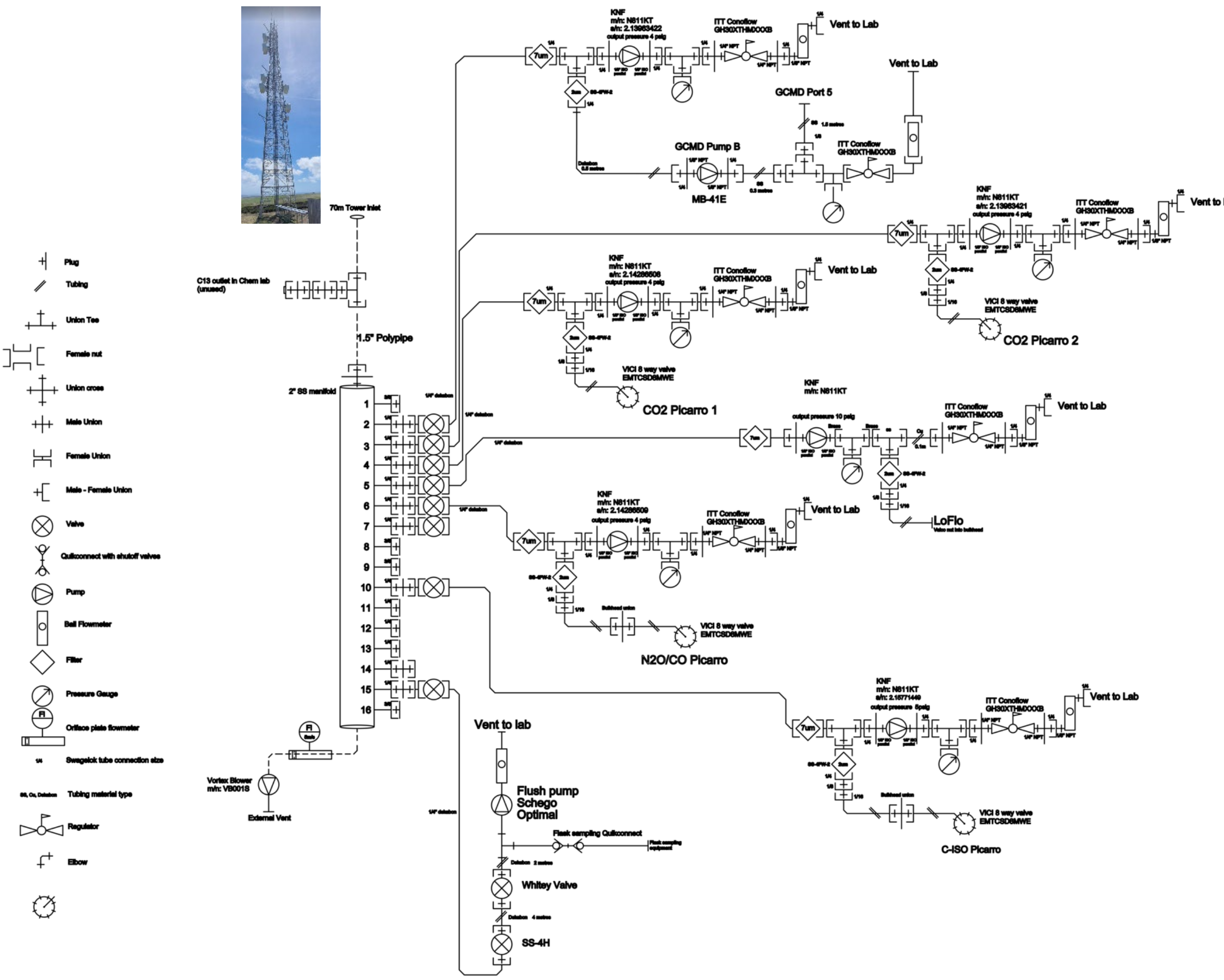

Figure 1. *Schematic overview of the plumbing and inlet system for the CGO CRDS and GC-MD instruments.*

3 Performance audit

3.1 Surface ozone measurements

Surface ozone measurements began at CGO in 1981, and continuous time series data have been available since then.

Instrumentation. At the time of the audit, two Thermo Scientific ozone analysers (models 49i and 49iQ) were available. The instruments are replaced every few years and the measurements are always redundant, with one instrument being considered as the main analyser (49i), and the newer instrument (49iQ) acting as a backup and usually becoming the main analyser when the older instrument is replaced.

Standards. Two Thermo Scientific 49i-PS ozone standards, both traceable to NIST SRP #21 of the New South Wales Office of Environment & Heritage, are available at CGO.

Data acquisition. A custom made Grafana data acquisition system developed by CGO is used to acquire ozone data and other ancillary instrument parameters via the TC/IP port of the analysers. 1-minute ozone data and ancillary parameters are stored in a database. The system also allows daily tasks such as zero / span checks and time synchronisation to be scheduled.

> **Recommendation 3 (*, minor, 2024)**
> *Zero and span checks are currently performed daily for 1 hour each. This results in a loss of data of 2 hours per day. It is recommended that the frequency and duration of these checks be reduced, for example to weekly zero and span checks of 15 minutes each.*

Intercomparison (performance audit). The Thermo Scientific CGO ozone analysers (OA) and calibrators (OC) 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 ranging from 0 to 250 nmol mol^{-1} for the analysers, and from 0 to 500 nmol mol^{-1} for the calibrators. 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 data were treated in the same way as ambient air measurements, and the following corrections were applied to the instrument readings based on the last calibration with the CGO ozone standard.

49i #CM16160046: Corrected O_3 = (instrument reading – 0.49 nmol mol^{-1}) / 0.973 (1)

49iQ #1191302833: Corrected O_3 = (instrument reading + 0.36 nmol mol^{-1}) / 0.958 (2)

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 1.1476x10^{-17} cm^2 (Hearn, 1961), the uncertainties reported below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #CM16160046 (BKG -0.5 nmol mol^{-1}, COEF 0.984):

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] - 0.11 nmol mol^{-1}) / 1.0014 (3)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt (0.29 nmol mol^{-1} + 2.07e-05 * X_{O3}^2) (4)

Thermo Scientific 49iQ #1191302833 (BKG +0.5 nmol mol^{-1}, COEF 0.978):

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] + 0.07 nmol mol^{-1}) / 1.0055 (5)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt (0.29 nmol mol^{-1} + 2.05e-05 * X_{O3}^2) (6)

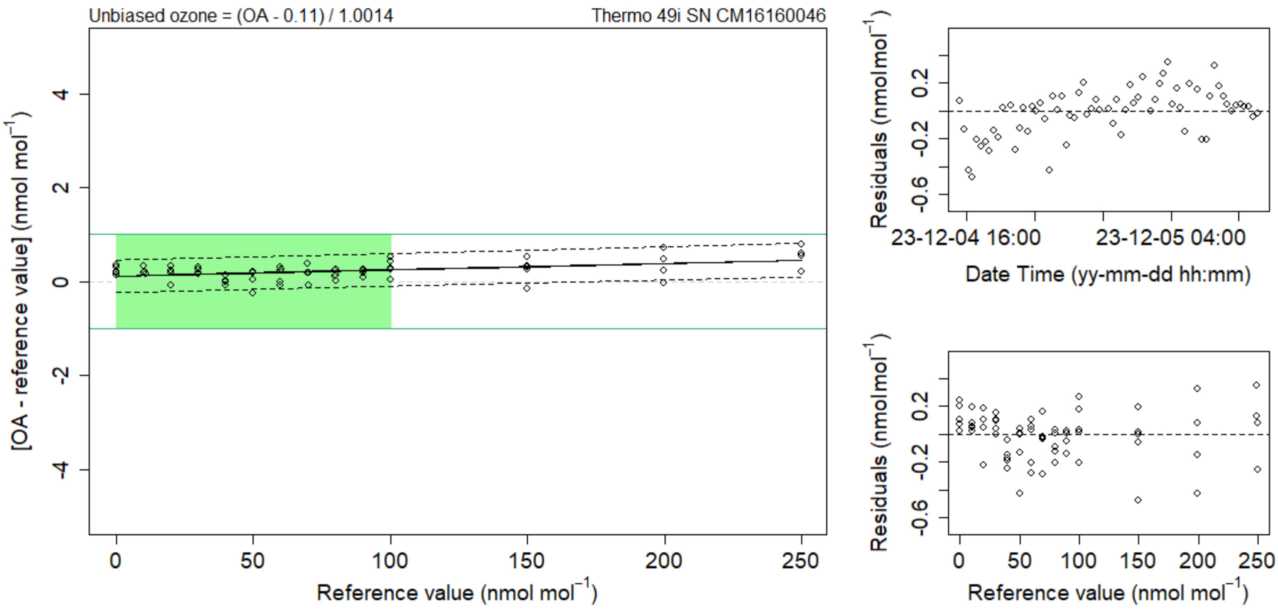

Figure 2. *Left: Bias of the CGO ozone analyser (Thermo Scientific 49i #CM16160046, BKG -0.5 nmol mol^{-1}, COEF 0.984) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

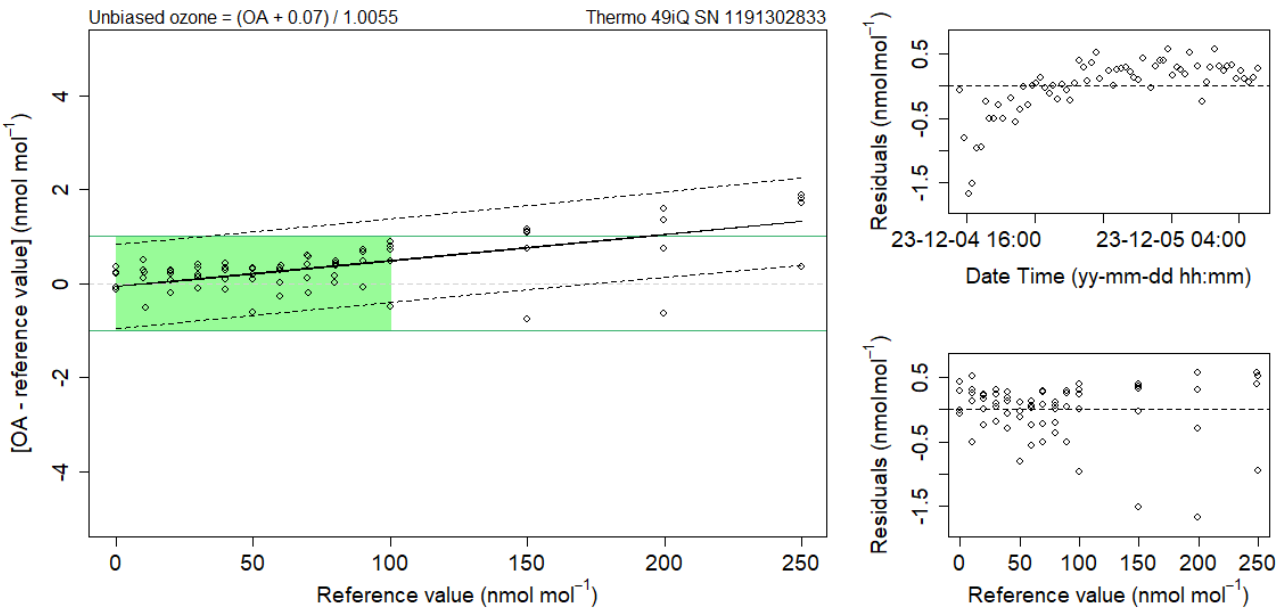

Figure 3. *Left: Bias of the CGO ozone analyser (Thermo Scientific 49iQ #1191302833, BKG +0.5 nmol mol^{-1}, COEF 0.978) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

Thermo Scientific 49i-PS #1180930024 (BKG 0.0 nmol mol^{-1}, COEF 0.988):

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OC] + 0.19 nmol mol^{-1}) / 0.99831 (7)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt (0.30 nmol mol^{-1} + 2.09e-05 * X_{O3}^2) (8)

Thermo Scientific 49i-PS #1315588104 (BKG 0.0 nmol mol^{-1}, COEF 1.035):

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OC] + 0.20 nmol mol^{-1}) / 1.0425 (9)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt (0.29 nmol mol^{-1} + 2.05e-05 * X_{O3}^2) (10)

The results of the comparisons can be summarised as follows:

Thermo Scientific 49i #CM16160046: The CGO main ozone analyser showed excellent agreement within the WMO/GAW DQOs after the correction based on the last calibration with the CGO ozone calibrator. The instrument is in good working condition, and no further action is required.

Thermo Scientific 49iQ #1191302833: This instrument is currently used as a backup analyser and also agreed within the DQOs. However, this instrument (49iQ series) showed significantly more instrumental noise compared to the 49i series instrument. This instrument should not be used to replace the Thermo Scientific 49i #CM16160046 as it would normally be the case under the CGO instrument rotation scheme. The following recommendations are made:

> **Recommendation 4 (**, important, 2024)**
> *The Thermo Scientific 49iQ #1191302833 is not performing well, and the cause needs to be identified. It is recommended that the analyser be returned to the manufacturer for inspection and repair.*
>
> **Recommendation 5 (**, important, before next instrument exchange)**
> *The Thermo Scientific 49iQ #1191302833 should not be used as a primary ozone analyser in its current condition. It is recommended to keep the 49i #CM16160046 as the primary analyser, and to replace the 49iQ instrument if its performance cannot be improved.*

Thermo Scientific 49i-PS #1180930024 and Thermo Scientific 49i-PS #1315588104: The CGO ozone calibrators have been compared to the WCC-Empa reference. The resulting calibration functions are within the uncertainties of the functions determined by the New South Wales Office of Environment & Heritage. The calibrators are used to calibrate the CGO analysers, and the instrument and data handling performed by CGO is fully adequate. No further recommendations are required.

In conclusion, CGO ozone measurements are within the WMO/GAW quality objectives, and the redundancy provided by backup instruments ensures the long-term quality of the data. It is recommended to continue with the current practice.

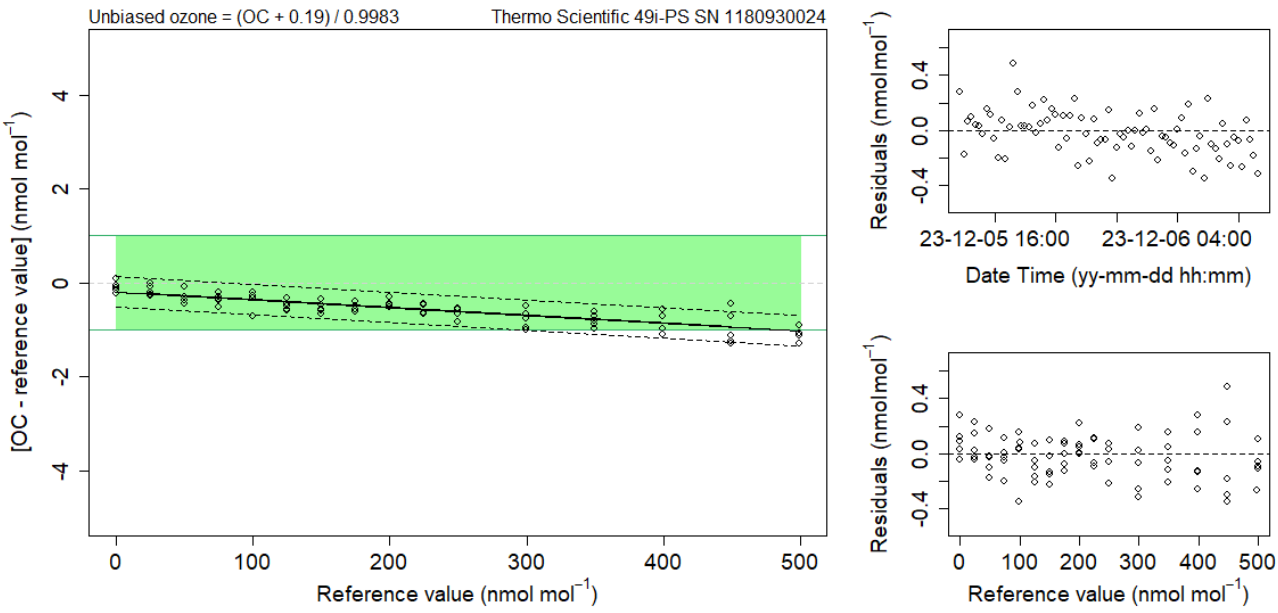

Figure 4. *Left: Bias of the CGO ozone calibrator (Thermo Scientific 49i-PS #1180930024, BKG 0.0 nmol mol^{-1}, COEF 0.988) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

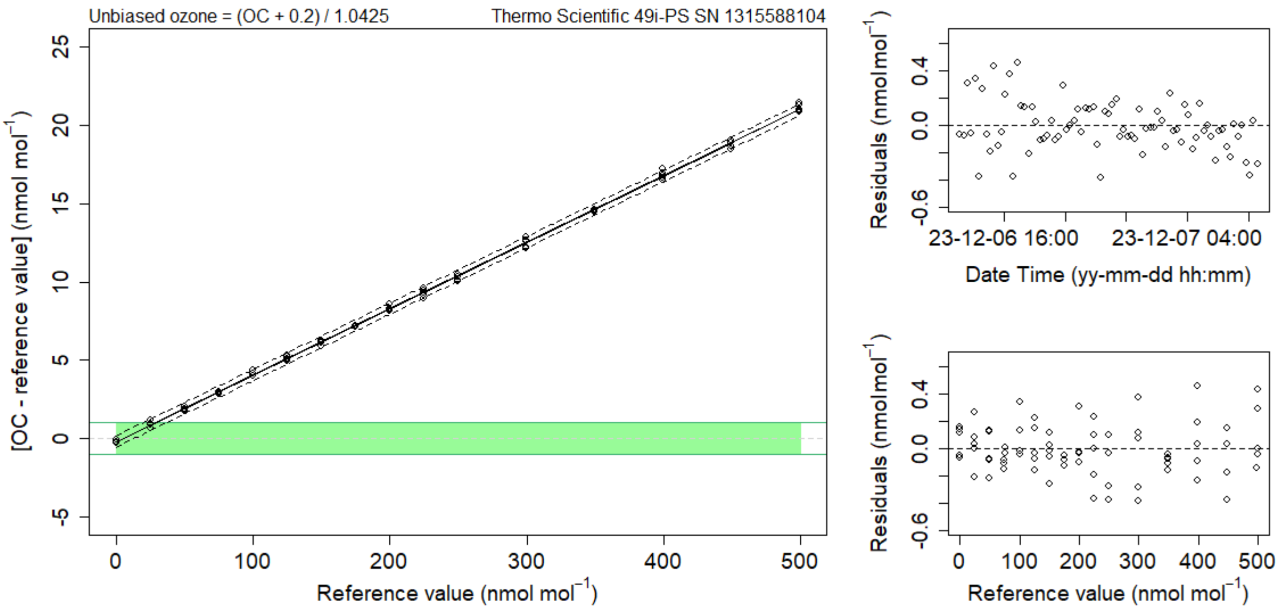

Figure 5. *Left: Bias of the CGO ozone calibrator (Thermo Scientific 49i-PS #1315588104, BKG 0.0 nmol mol^{-1}, COEF 1.003) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

3.2 Carbon monoxide measurements

Continuous measurements of CO at CGO started in 1993 using gas chromatography (GC) / mercuric oxide reduction detection (Reduction Gas Detector (RGD)), and continuous time series are available since then. While the GC systems are still in operation, several instruments based on spectroscopic methods have been added over time.

Instrumentation. The following instruments have been audited: Picarro G5310 (mid-IR CRDS) and the multidetector GC system (GC-MD). No dryer is used for the CRDS instrument. In addition to the audited instruments, CGO has an FTIR instrument that was not operational at the time of the audit.

Standards. Several in-house and NOAA CCL standards are available for the calibration of the CO instruments. CSIRO maintains its own CO calibration scale, and the data used for this audit were reported on the CSIRO-2020 CO calibration scale. This scale is related to the previously used CSIRO-1994 CO scale by a constant factor of 1.03 (i.e. CSIRO-2020 is exactly 3% higher than CSIRO-1994). The CSIRO-2020 scale is maintained using ~20 high pressure cylinder standards covering a CO range of ~29–487 nmol mol^{-1}. The long-term stability and internal consistency (i.e. relative mole fraction over the calibrated range) are defined by CSIRO's internal calibration systems and are completely independent of the WMO X2014A scale. However, the absolute level of the CSIRO-2020 scale is aligned with the WMO X2014A CO scale based on NOAA measurements of 8 of the CSIRO standards in 2015-16. Preliminary assessment of these data suggests that the scales are consistent to within ±1 nmol mol^{-1} over the calibrated range of the CSIRO scale.

Calibration. GC-MD: The calibration sequence for this instrument consists of alternating injections of air samples and a standard gas (tank at the time of the audit was J-261). Ambient air amount fractions are determined based on the average of the two bracketing standard runs. In addition, a series of calibration tanks are run to determine the non-linearity fits.

CRDS: One standard tank (UAN20230094 CC498977) is run once a day for 30 minutes. The first 10 minutes (sometimes more) of data from the standard runs are discarded and the remaining data are averaged. These daily runs are then used to assign amount fractions to the air data by interpolating between the daily standard runs. This essentially accounts for instrument drift. The instrument also has a dedicated target tank which is run daily. In addition, a dedicated suite of 3-4 calibration tanks (typically a low, mid and high tank) is available. These are run once a month in the following sequence: 3 x (30 min low-cal, 30 min air), 30 min standard, 30 min air, 3 x (30 min mid-cal, 30 min air), 3 x (30 min high-cal, 30 min air), 30 min standard. The aim of the calibration tank runs is to get a handle on the magnitude of the non-linearities, but so far none of these have been applied to the ambient air data.

Data acquisition. The GCWerks software is used to acquire, process and analyse the data for both the GC and spectroscopic instruments.

Intercomparison (performance audit). The comparison consisted of repeated challenges of the CGO 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 Figures 6 to 8 with respect to the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020):

Picarro G5310 #5066-DAS-JKADS5075:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 0.03 nmol mol^{-1}) / 1.0318 (11)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (7.3 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (12)

GC-MD (CGO):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 3.07 nmol mol^{-1}) / 0.97276 (13)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (63.4 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (14)

The TS were sent to the GASLAB at CSIRO following the audit at CGO and were also analysed there on the GC-RGD system. The following results were obtained:

GC-RGD (GASLAB, CSIRO):

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 3.66 nmol mol^{-1}) / 0.99224 (15)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (16.4 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (16)

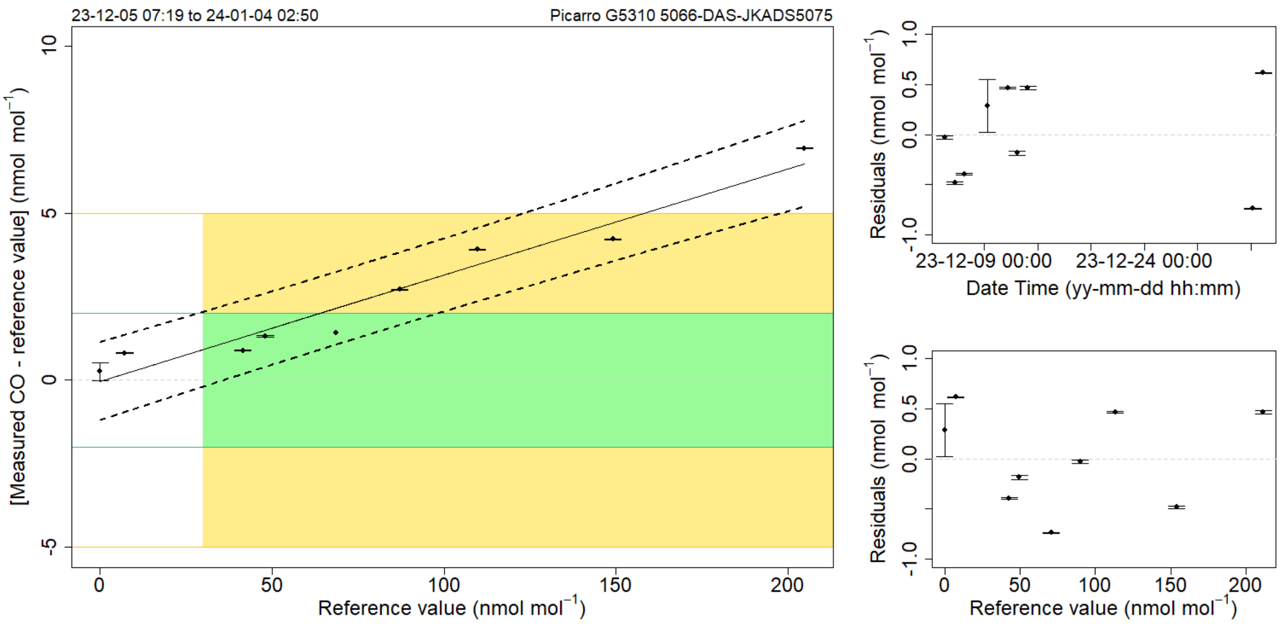

Figure 6. *Left: Bias of the PICARRO G5310 #5066-DAS-JKADS5075 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

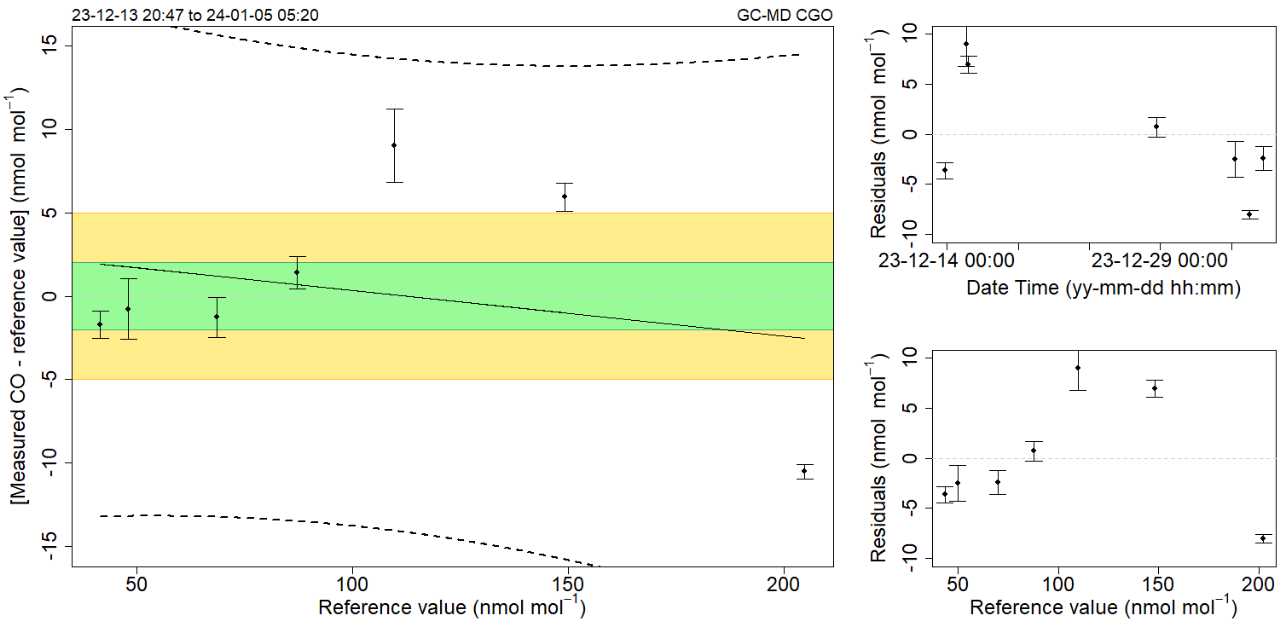

Figure 7. *Left: Bias of the CGO GC-MD carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

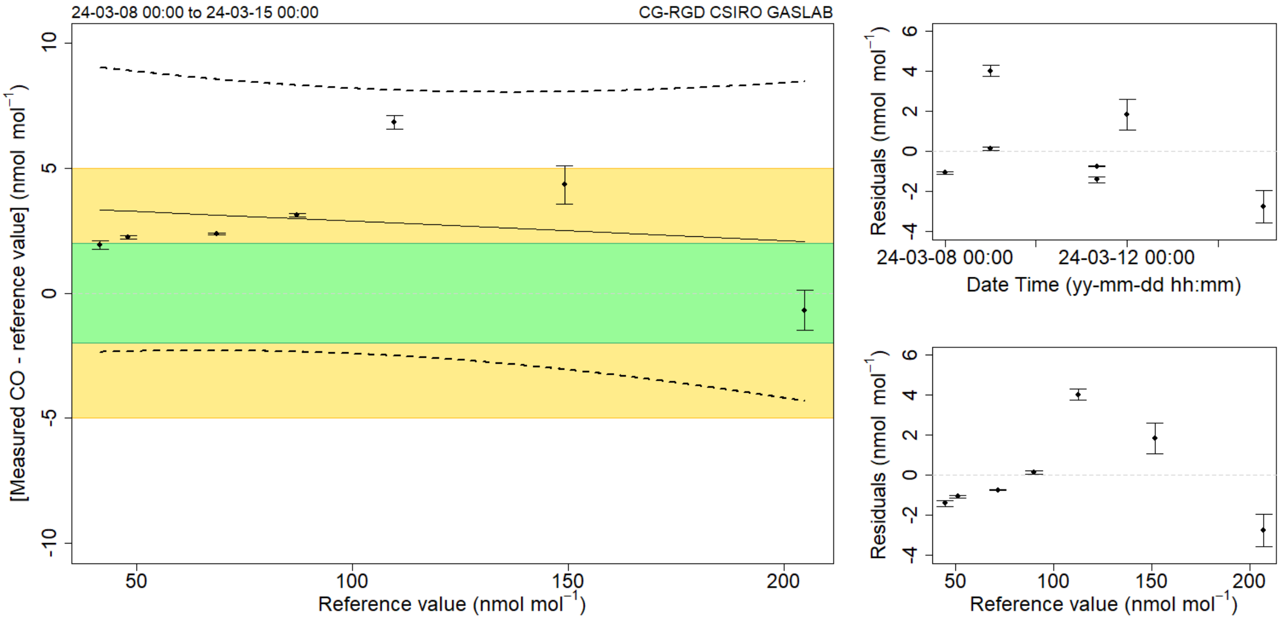

Figure 8. *Left: Bias of the CSIRO GASLAB GC-RGD carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement 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 CGO. 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 agreement between the CGO and the WCC-Empa measurements was relatively good at low amount fractions below 100 nmol mol^{-1}. Above this level, the agreement was worse and not consistent between the different instruments, which needs further attention. It is recommended to further investigate the cause of the bias between the different instruments.

Recommendation 6 (*, minor, 2024)
It is recommended to characterise the CO linearity of the CRDS and GC-MD instruments between 0 and 300 (GC) and 0 and 1000 nmol mol^{-1} (CRDS).

3.3 Methane measurements

Continuous measurements of CH_4 at CGO started in 1986 using GC / Flame Ionisation Detection (FID). A GC system is still in operation but the measurements are now also made by CRDS.

Instrumentation. The following instrumentation was audited: Picarro G2301 (near-IR CRDS) and the GC-MD. No dryer is used for the CRDS instrument. In addition to the audited instruments, CGO is equipped with a backup Picarro G2301 analyser and an FTIR instrument that was not operational at the time of the audit.

Standards and calibration. See CO, with the following exceptions: The standards used for the CRDS instruments were UAN20220577 CC745343 (Picarro G2301 #1151-CFADS2263) and UAN20230096 CB11466 (Picarro G2301 #2121-CFADS2386). CGO methane data are reported on the WMO-X2004A calibration scale for the CRDS instruments and the Tohoku University CH_4 gravimetric scale (TU-1987) for the GC-MD instruments.

Data acquisition. See CO.

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

The following equation characterises the instrument bias. The results are further illustrated in Figures 9 to 11 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G2301 #1151-CFADS2263:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 0.32 nmol mol^{-1}) / 1.0004 (17)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.1 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (18)

GC-MD (CGO):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 + 1.11 nmol mol^{-1}) / 1.0015 (19)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.5 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (20)

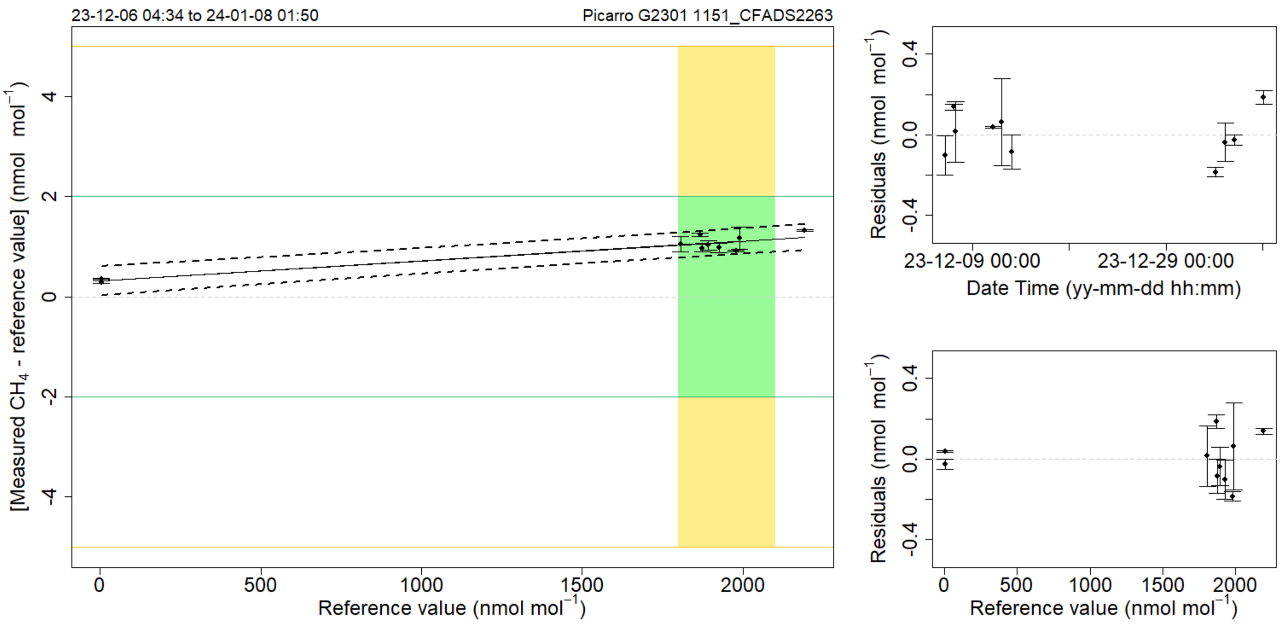

Figure 9. *Left: Bias of the Picarro G2301 #1151-CFADS2263 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

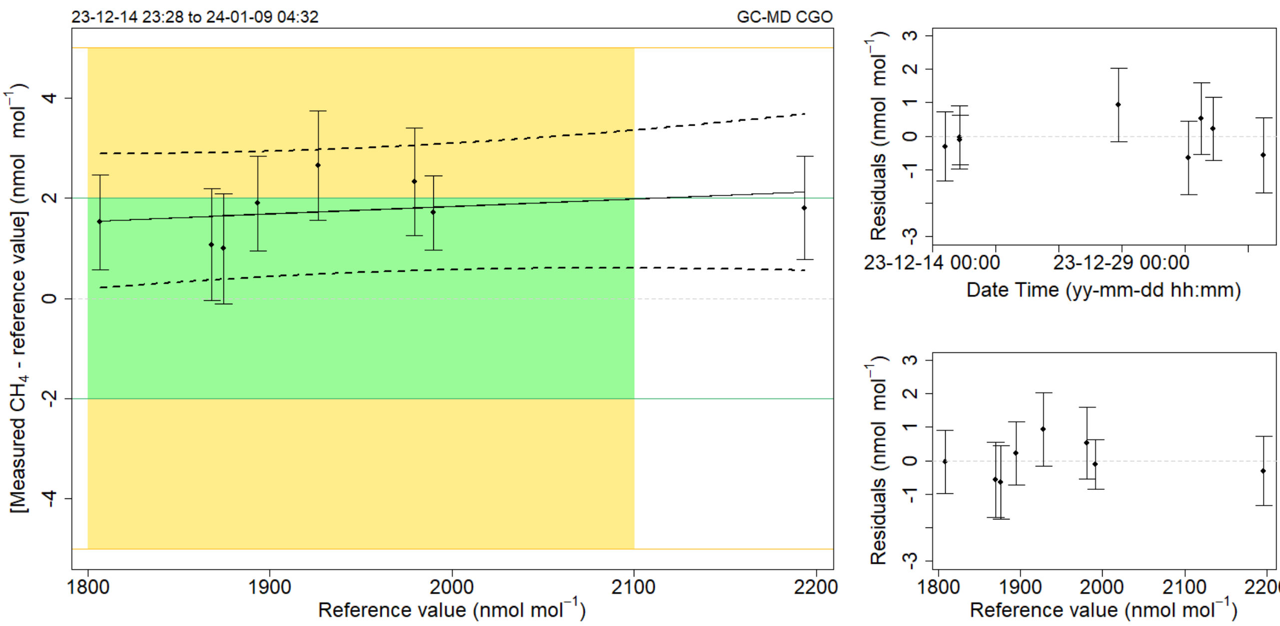

Figure 10. *Left: Bias of the CGO GC-MD instrument with respect to the WMO-X2004A CH_4 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The TS were sent to the GASLAB at CSIRO following the audit at CGO and were also analysed there on the GC with Flame Ionisation Detector (FID) system. The following results were obtained:

GC-FID (GASLAB, CSIRO):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.56 nmol mol^{-1}) / 0.9988 (21)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (1.2 nmol mol^{-1} + 1.30e-07 * X_{CH4}^2) (22)

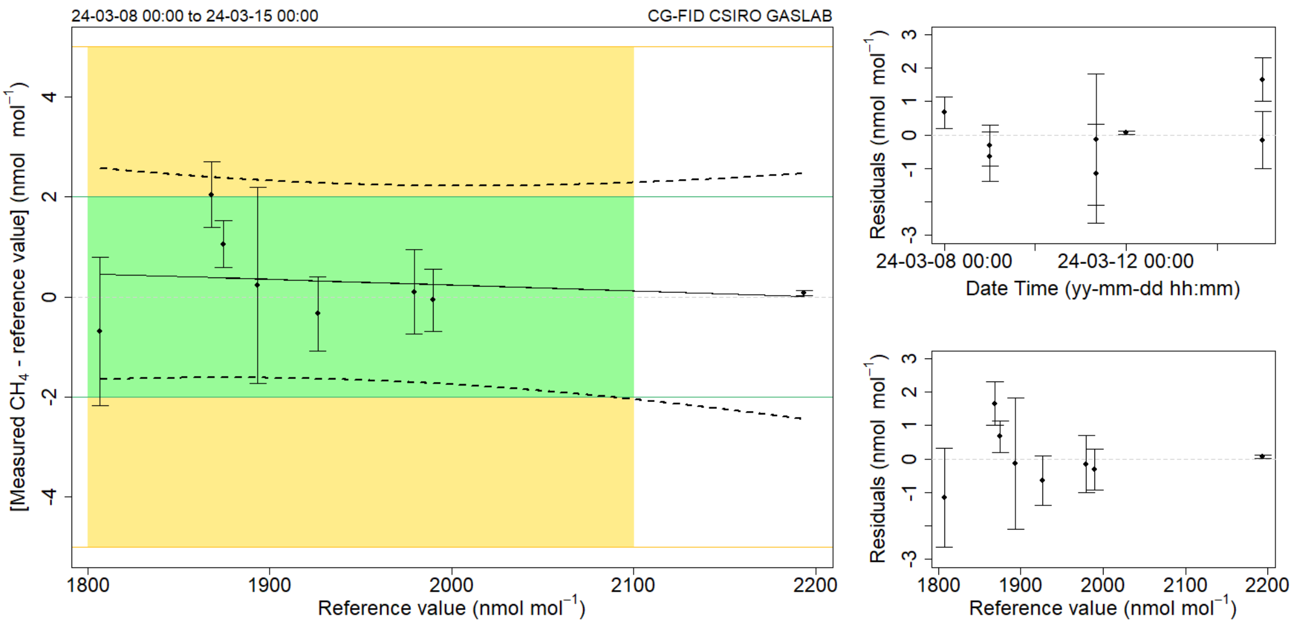

Figure 11. *Left: Bias of the CSIRO GASLAB GC-FID methane instrument with respect to the WMO-X2004A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

Excellent agreement, well within the WMO/GAW network compatibility goal, was found for all instruments 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 at this time.

3.4 Carbon dioxide measurements

Continuous measurements of CO_2 at CGO started in 1976 using the NDIR technique. Since then, several instruments based on spectroscopic methods have been added.

Instrumentation. The following instrument has been audited: Picarro G2301 (near-IR CRDS). No dryer is used for the CRDS instrument. In addition to the audited instruments, CGO has a backup Picarro G2301 analyser and an FTIR instrument that was not operational at the time of the audit.

Standards and calibration. See CH_4, with the following exception: The WMO-X2019 calibration scale is used to report CO_2 data.

Data acquisition. See CH_4.

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

The following equations characterise the instrument bias. The result is further illustrated in Figures 12 and 13 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G2301 #1151-CFADS2263:

Unbiased CO_2 mixing ratio: X_{CO2} (μmol mol^{-1}) = (CO_2 + 0.40 μmol mol^{-1}) / 0.0010 (23)

Remaining standard uncertainty: u_{CO2} (μmol mol^{-1}) = sqrt (0.00 μmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (24)

The TS were sent to the GASLAB at CSIRO following the audit at CGO and were also analysed there on the GC-FID system. The following results were obtained:

GC-FID (CSIRO GASLAB):

Unbiased CO_2 mixing ratio: X_{CO2} (μmol mol^{-1}) = (CO_2 - 0.32 μmol mol^{-1}) / 0.9990 (25)

Remaining standard uncertainty: u_{CO2} (μmol mol^{-1}) = sqrt (0.02 μmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (26)

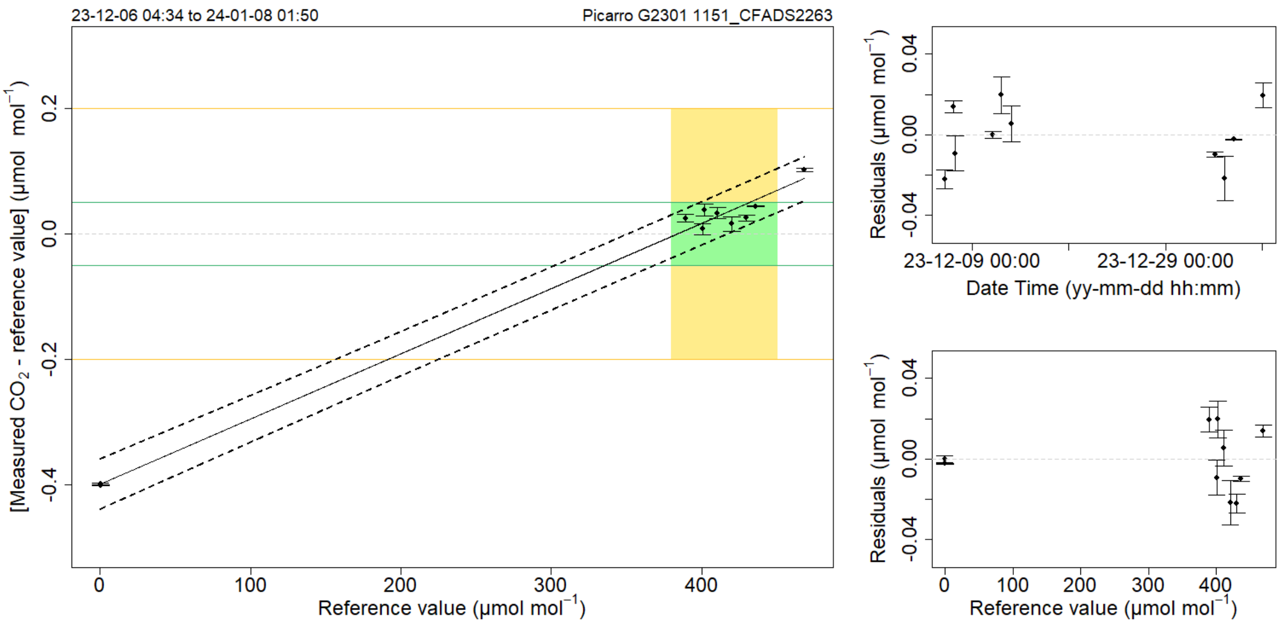

Figure 12. *Left: Bias of the Picarro G2301 #1151-CFADS2263 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

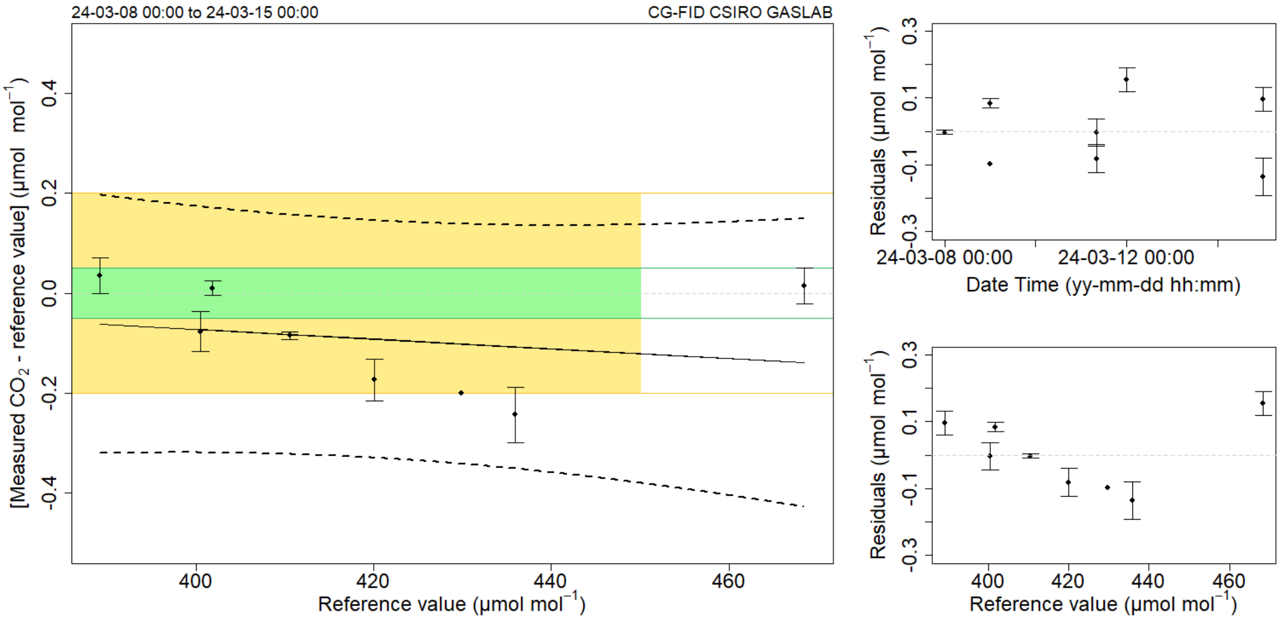

Figure 13. *Left: Bias of the CSIRO GASLAB GC-FID instrument with respect to the WMO-X2019 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

The result was within the WMO/GAW network compatibility goal in the relevant CO_2 range for the main CGO instrument. The bias showed a small dependence on the amount fraction with an offset of about -0.4 μmol mol^{-1} at zero. This could be due to small inconsistencies in the standards available at CGO. However, due to the good results in the relevant amount fraction range, no further action is required at this time.

The CSIRO GASLAB GC-FID showed slightly higher bias and uncertainties compared to the CGO CRDS system, which is to be expected. The results were within the extended WMO/GAW compatibility goals. No further action is required.

3.5 Nitrous oxide measurements

Continuous measurements of N_2O at CGO started in 1978 using a GC with Electron Capture Detection (ECD) technique. A GC is still in operation but measurements are now also made by a mid-IR CRDS instrument.

Instrumentation. The following instrumentation has been audited: Picarro G5310 (mid-IR CRDS) and the GC-MD. The air is dried for the GC system, but no dryer is used for the CRDS instrument. In addition to the audited instruments, CGO has an FTIR instrument that was not operational at the time of the audit.

Standards and calibration. See CH_4, with the following exception: The WMO-X2006A (CRDS instrument) and the SIO-2016 (GC-MD) calibration scales are used for reporting N_2O data.

Data acquisition. See CH_4.

Intercomparison (performance audit). The comparison involved repeated challenges of the CGO instruments with randomly selected N_2O levels from travelling standards.

The following equations characterise the instrument bias. The results are further illustrated in Figures 14 to 16 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

Picarro G5310 #5066-DAS-JKADS5075:

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 1.83 nmol mol^{-1}) / 1.0055 (27)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.05 nmol mol^{-1} + 1.01e-04 * X_{N2O}^2) (28)

GC-MD (CGO):

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 11.18 nmol mol^{-1}) / 1.0337 (29)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.07 nmol mol^{-1} + 1.01e-04 * X_{N2O}^2) (30)

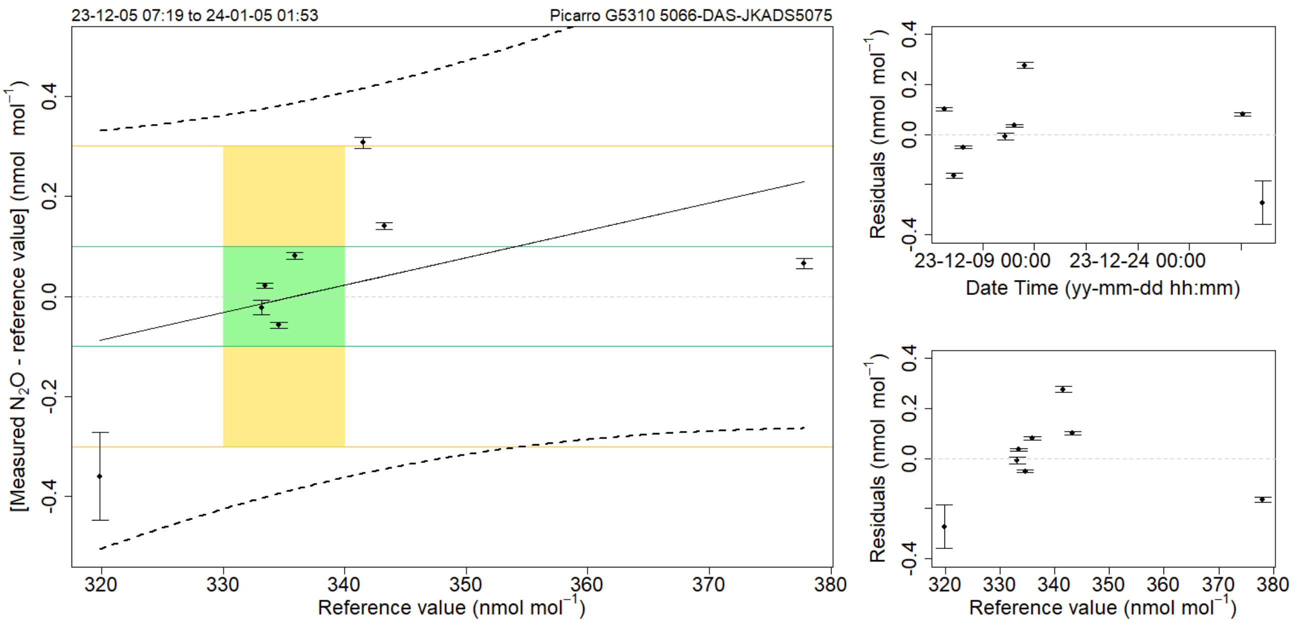

Figure 14. *Left: Bias of the CGO Picarro G5310 #5066-DAS-JKADS5075 nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

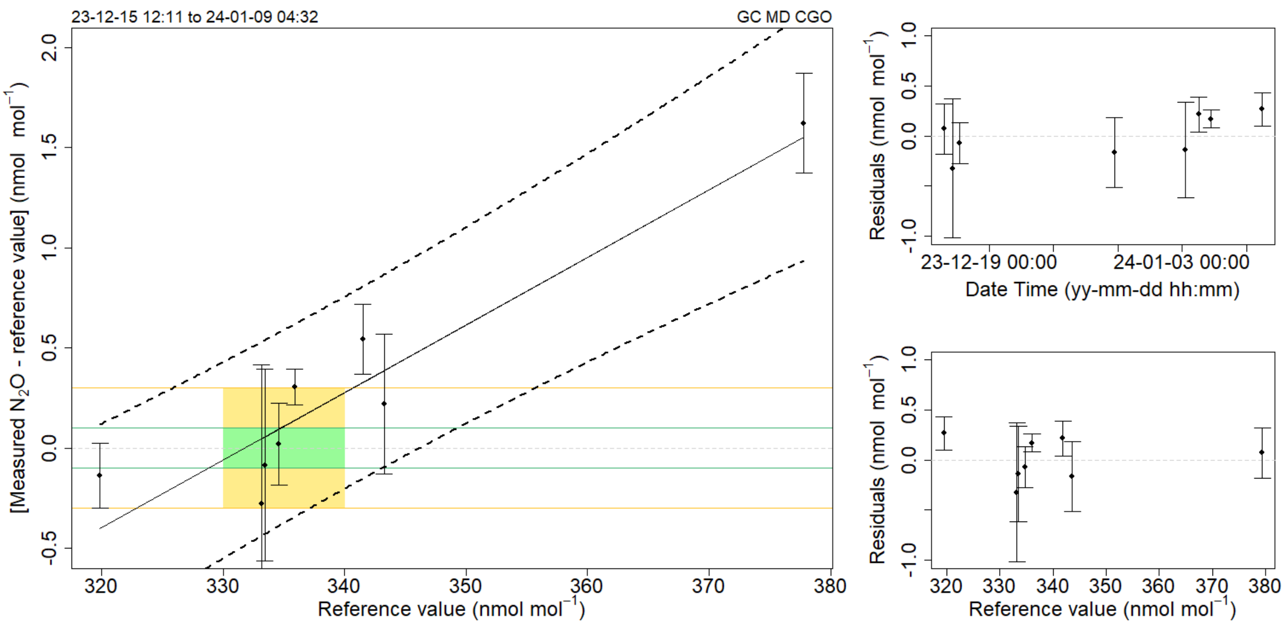

Figure 15. *Left: Bias of the CGO GC-MD nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. 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 CGO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The TS were sent to the GASLAB at CSIRO following the audit at CGO and were also analysed there on the GC-ECD system. The following results were obtained:

GC-ECD (CSIRO GASLAB):

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 0.81 nmol mol^{-1}) / 1.0019 (31)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.01 nmol mol^{-1} + 1.01e-04 * X_{N2O}^2) (32)

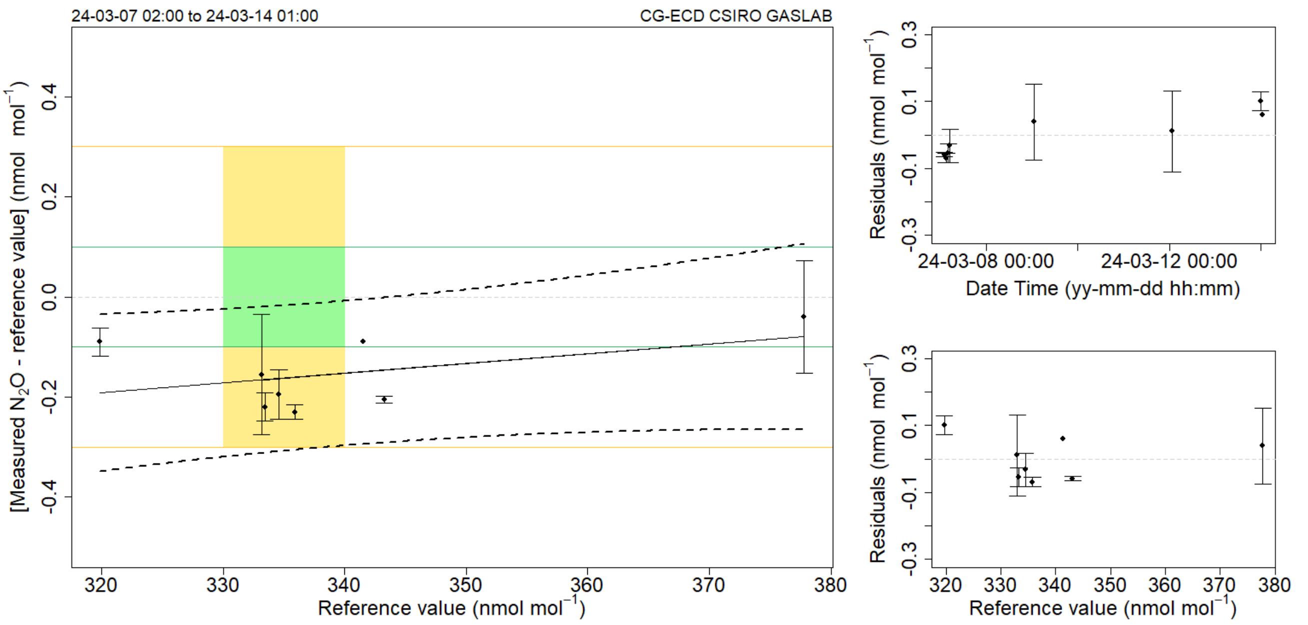

Figure 16. *Left: Bias of the CSIRO GASLAB GC-ECD nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement 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 CGO. 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:

Good agreement within the WMO/GAW compatibility goal was found in the relevant range of ambient air amount fractions for the CRDS instrument. However, the deviations exceeded the network compatibility goals for amount fractions below and above the currently relevant range. The following recommendation is therefore made:

> **Recommendation 7 (*, minor, 2024)**
> *It is recommended to characterise the N_2O linearity of the CRDS and GC-MD instruments.*

The deviations were slightly larger for the GC-MD instruments, which can be explained by the poorer performance of the GC/ECD technique compared to the mid-IR CRDS and the different calibration scales.

4 Comparison of CGO performance audit results with other stations

This section compares the results of the CGO performance audit with other station audits conducted by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO, but is also applicable to other compounds. Essentially, the bias in the middle of the relevant amount fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant amount fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone the amount fraction range of 0-100 nmol mol^{-1} was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 17 shows the bias vs. slope of the WCC-Empa performance audits by for O_3, and Figure 18 for CO, CH_4, CO_2, and N_2O. 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 CGO audit are shown as coloured dots in Figures 17 and 18.

For the surface ozone analysers, the results were within the DQOs. The results of the ozone calibrators are not shown in the plots because the bias of the instruments is corrected when they are used. The WMO/GAW network compatibility goals were also met for all audited CH_4 instruments, while the CO_2 comparison slightly exceeded the WMO/GAW network compatibility for the Southern Hemisphere (SH). The CO and N_2O comparisons were within the extended WMO/GAW network compatibility goals for the GC-MD instruments. The Picarro G5310 N_2O measurements were within the WMO/GAW network compatibility goals, but the CO measurements of this instrument did not meet the goal. It should be noted, however, that CO was within the network compatibility goal for the background levels of CO in the SH.

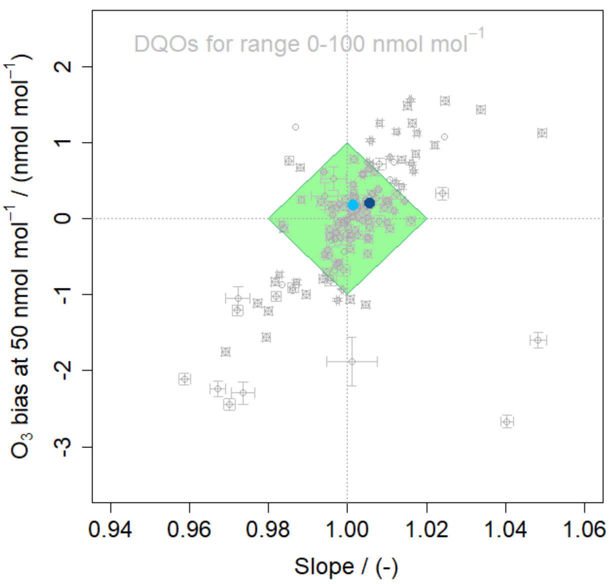

Figure 17. *O_3 bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show CGO results (light blue: 49i #CM16160046, dark blue: 49iQ #1191302833). The uncertainty bars refer to the standard uncertainty. The green area corresponds to the WMO/GAW DQOs for ozone.*

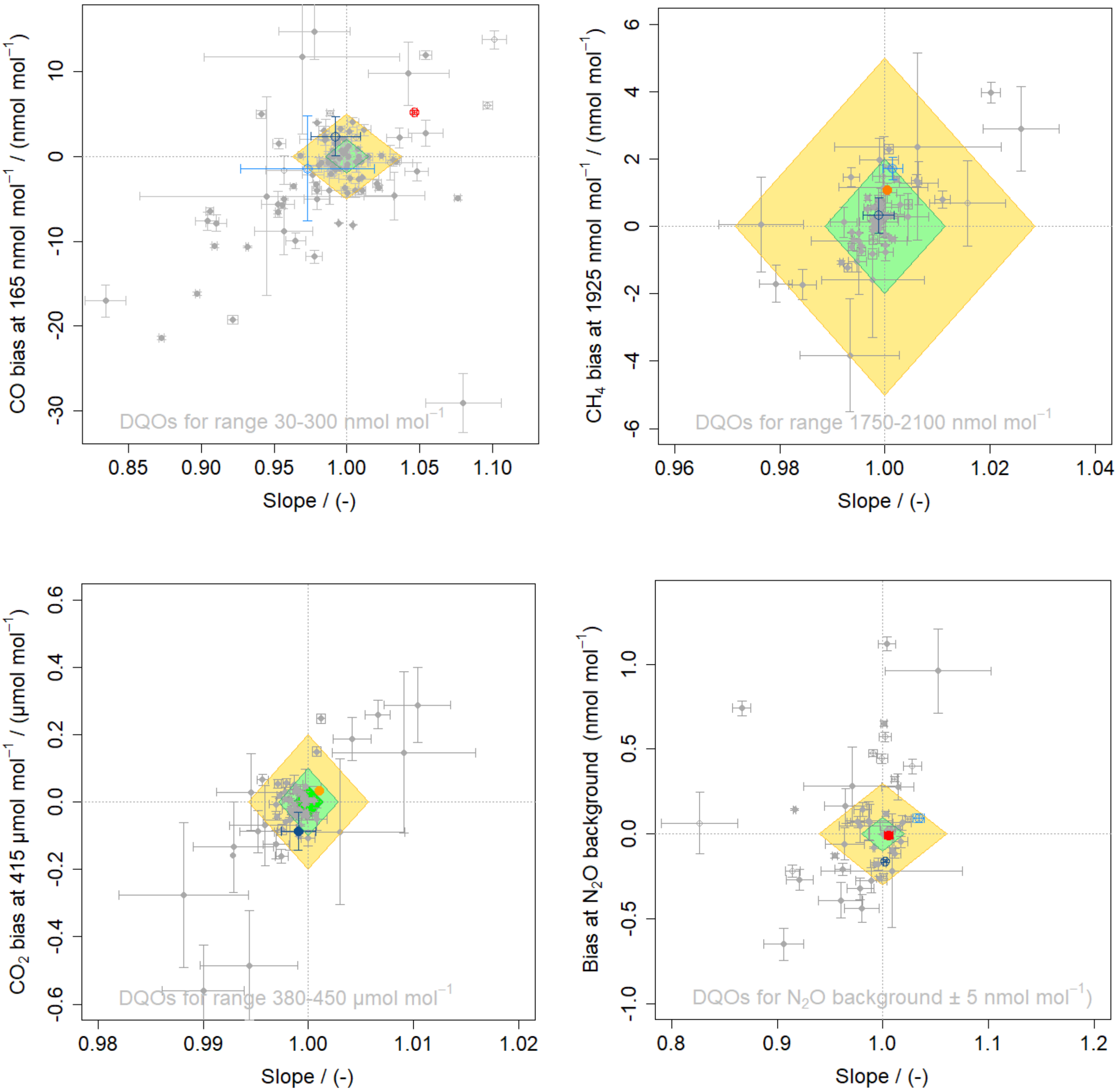

Figure 18. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show CGO and CSIRO GASLAB results (red: Picarro G5310, orange: Picarro G2301, light blue: CGO GC-MD, dark blue: CSIRO GASLAB GC). 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, shades for southern and northern hemisphere 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). Both Kennaook / Cape Grim GAW CRDS instruments and the AGAGE CGO GC-MD were compared to the TI between 6 December 2023 and 6 February 2024. The TI was connected to an independent inlet line leading to the same inlet location as for the CGO analysers. The TI sampled air in the following sequence: 3125 min of ambient air from the independent inlet by 60 min measurement of three standard gases, each for 20 min. The sample air was dried using a Nafion dryer (model MD-070-48S-4) 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 (Zellweger et al., 2012; Rella et al., 2013) was applied to the CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The CGO data were processed by the CGO station staff.

Figures 19 to 25 show the comparison of hourly CO, CH_4, and CO_2 measurements between the WCC-Empa TI and the CGO instruments. 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. Injections from the GC-MD instrument were compared with 1-min data from the WCC-Empa TI. Ambient air comparisons are shown for both CGO Picarro G2301 instruments, as the main analyser failed during the comparison period.

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

5.1 Carbon monoxide

CGO ambient air CRDS measurements were about 5 nmol mol^{-1} higher compared to WCC-Empa. This is approximately 3 nmol mol^{-1} higher than the bias of the TS comparison in the corresponding amount fraction range. A slightly better agreement within the extended WMO/GAW network compatibility goal was observed between the CGO GC-MD instrument and the WCC-Empa TI. The temporal variation was mostly well captured by all instruments.

> **Recommendation 8 (**, important, 2024)**
> *WCC-Empa recommends testing and characterising the internal water vapour correction of the Picarro G5310 instrument, which may be a potential source of the larger bias observed in the ambient air comparison.*

5.2 Methane

Good agreement within the WMO/GAW network compatibility goals was found between the TI and both the CGO CRDS and GC-MD instruments, confirming the results of the travelling standard comparisons. The temporal variability was mostly well captured by all instruments and the inter-instrument variability was small.

5.3 Carbon dioxide

On average, the agreement between the WCC-Empa TI and the CGO instruments was just within the WMO/GAW compatibility goal for the main CRDS instrument (-0.04 µmol mol^{-1}), while the bias of the backup instrument (-0.07 µmol mol^{-1}) slightly exceeded the goals for the SH (0.05 µmol mol^{-1}). However, both instruments showed significant periods within the time series where the discrepancy was larger than the WMO/GAW compatibility goal. The temporal variability was well captured by all instruments, and no significant dependence of the bias on the amount fraction was observed.

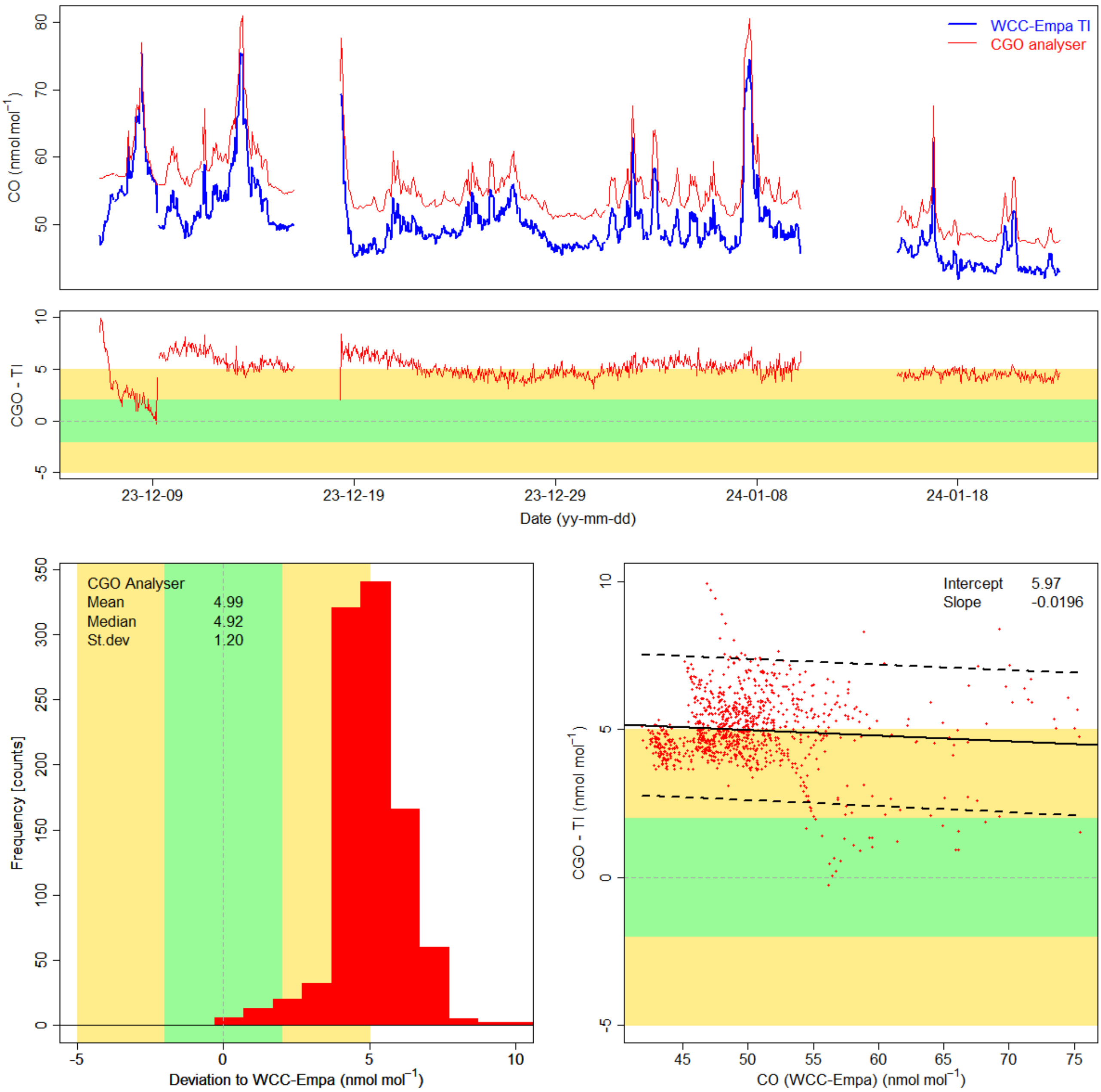

Figure 19. *Top: Comparison of the Picarro G5310 #5066-DAS-JKADS5075 with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G5310 #5066-DAS-JKADS5075 analyser compared to the WCC-Empa TI. Bottom right: CGO 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.*

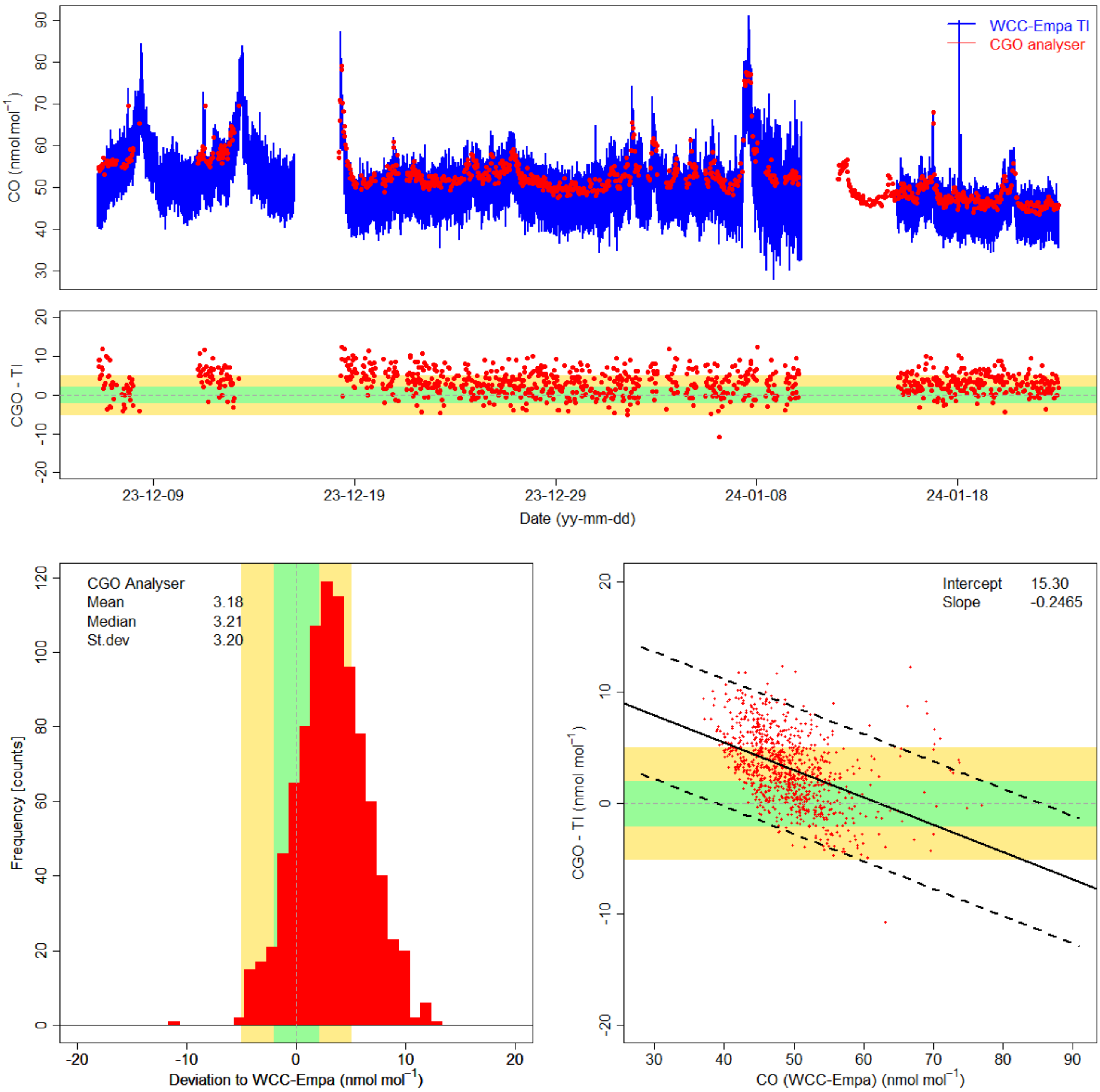

Figure 20. *Top: Comparison of CGO GC-MD with the WCC-Empa travelling instrument for CO. Time series based on 1-min data (WCC-Empa) and individual GC measurements (CGO) and the difference between the CGO GC-MD instrument and the TI are shown. Bottom left: CO deviation histograms for the CGO GC-MD compared to the WCC-Empa TI. Bottom right: CGO GC-MD bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

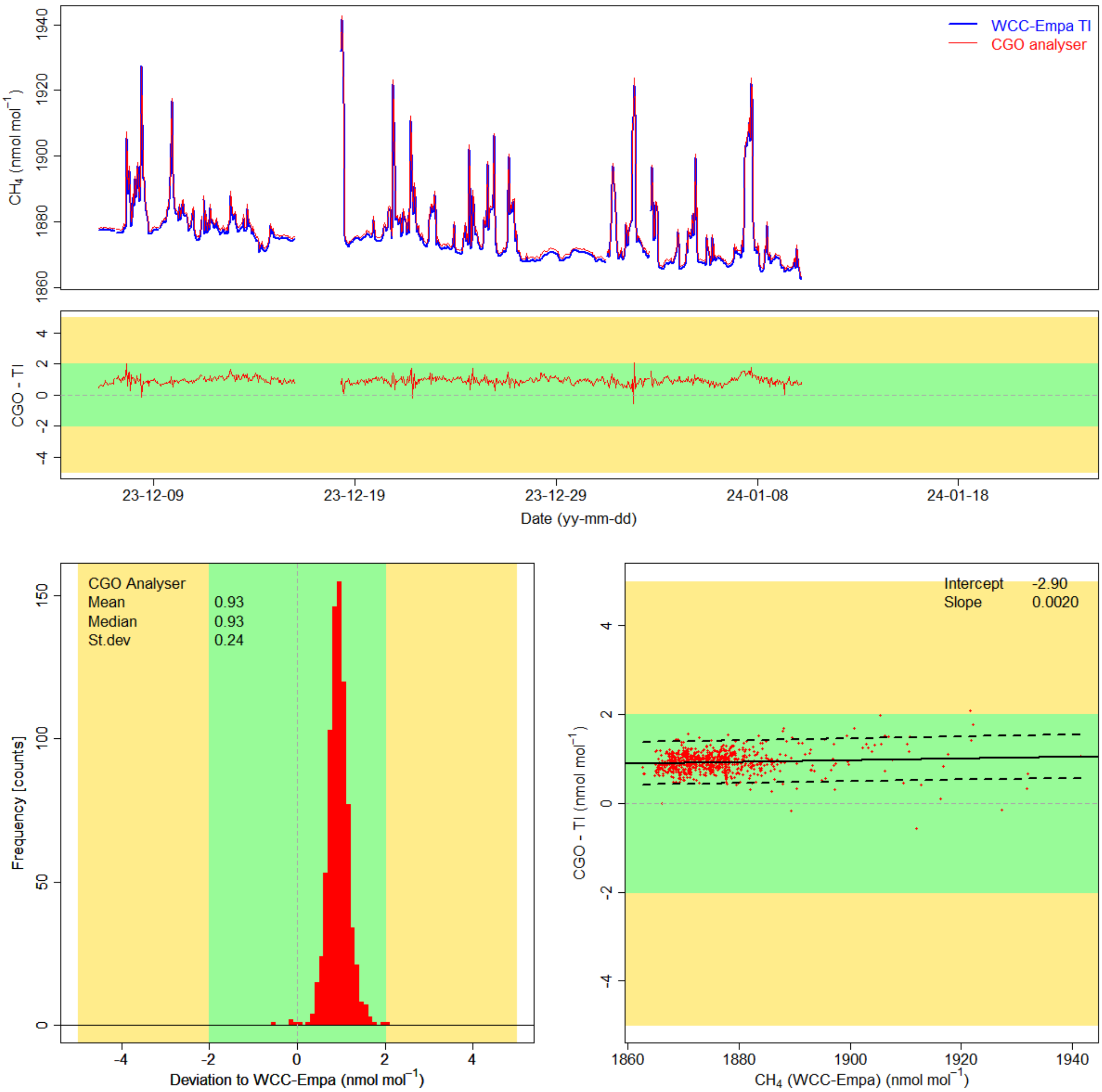

Figure 21. *Top: Comparison of the G2301 #1151-CFADS2263 analyser (main instrument) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CH_4 deviation histograms for the G2301 #1151-CFADS2263 analyser compared to the WCC-Empa TI. Bottom right: CGO 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.*

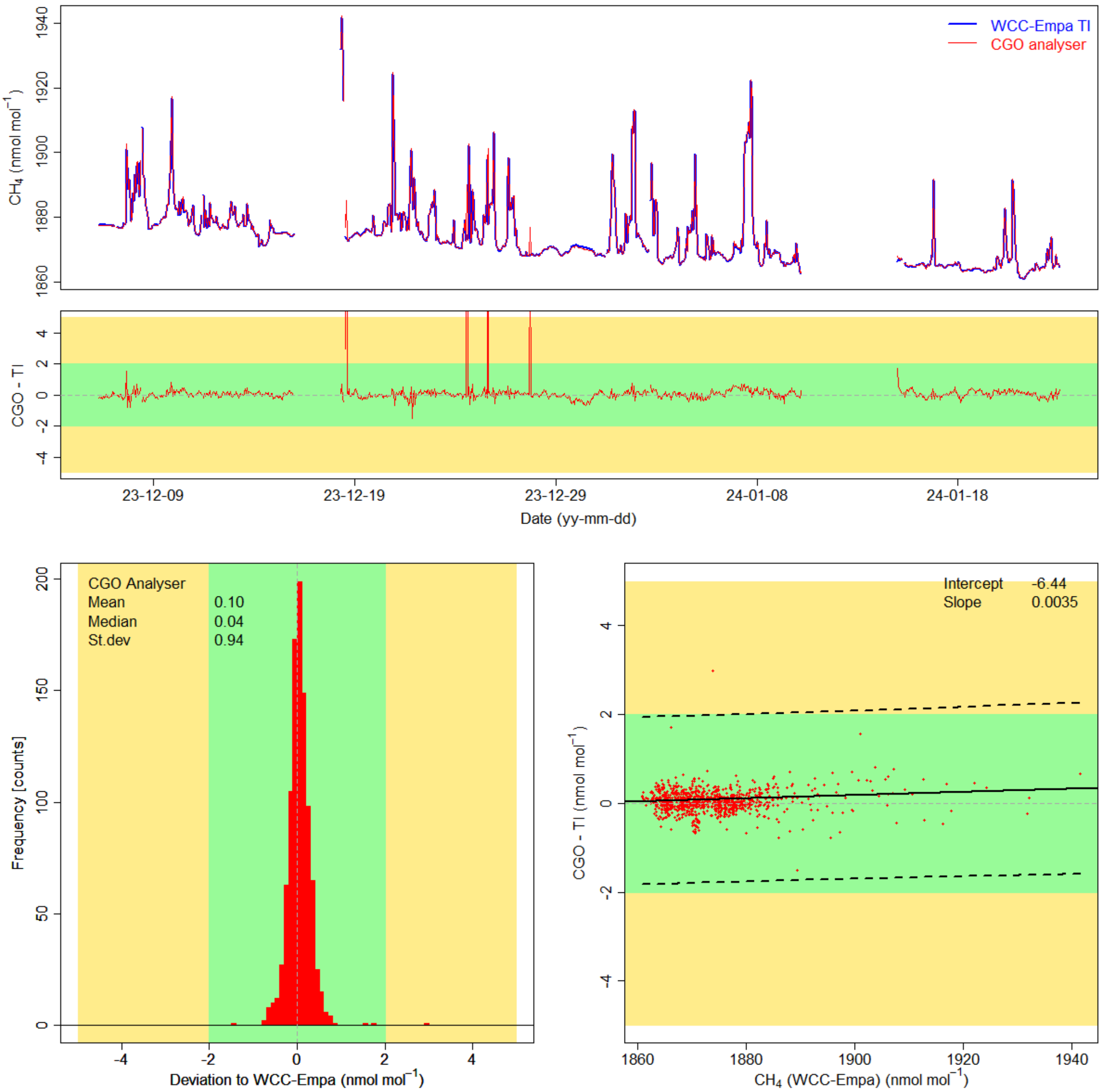

Figure 22. *Top: Comparison of the G2301 #2121-CFADS2386 analyser (backup instrument) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CH_4 deviation histograms for the G2301 #2121-CFADS2386 analyser compared to the WCC-Empa TI. Bottom right: CGO 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.*

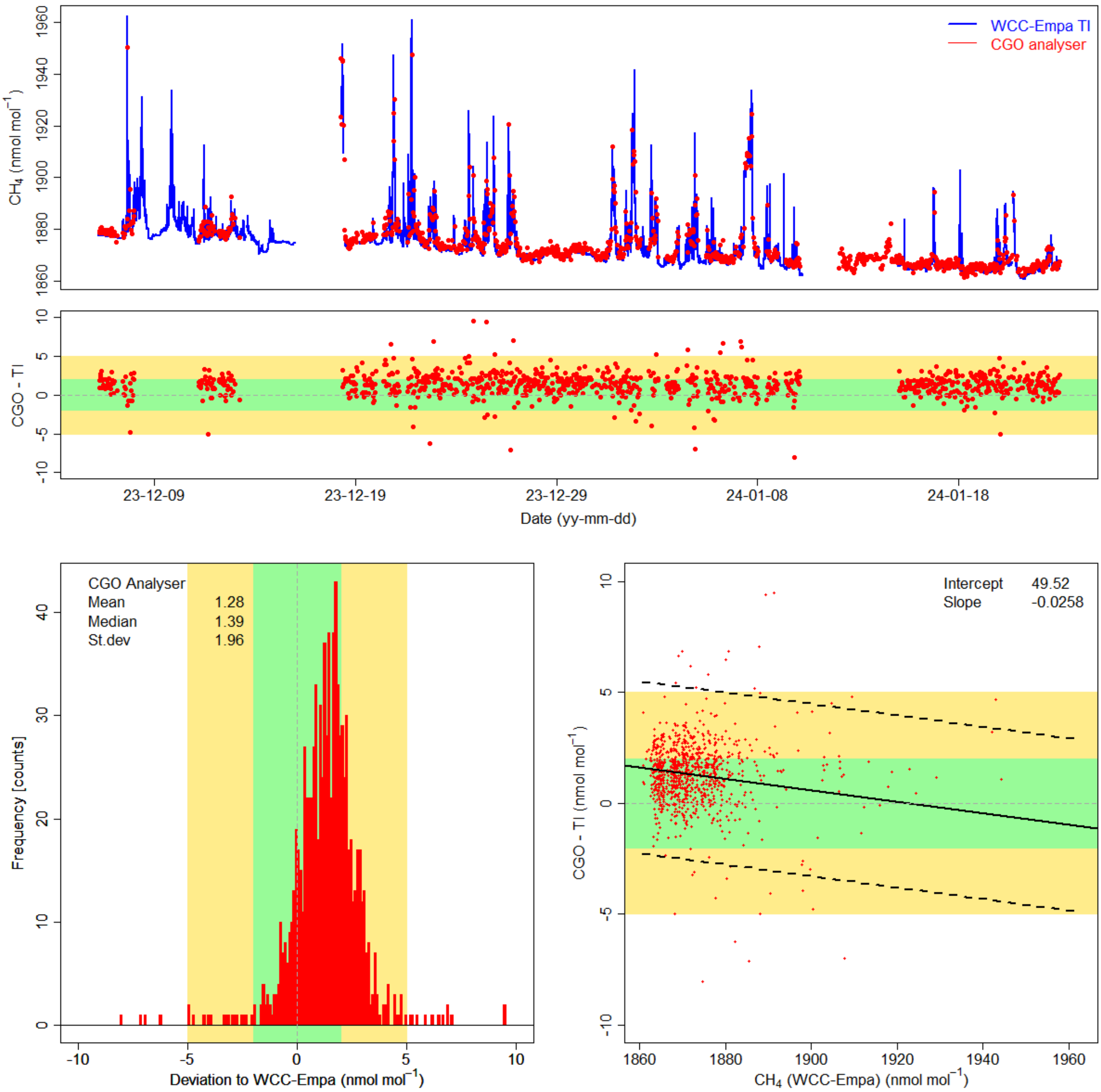

Figure 23. *Top: Comparison of CGO GC-MD with the WCC-Empa travelling instrument for CH_4. Time series based on 1-min data (WCC-Empa) and individual GC measurements (CGO) and the difference between the CGO GC-MD instrument and the TI are shown. Bottom left: CO deviation histograms for the CGO GC-MD compared to the WCC-Empa TI. Bottom right: CGO GC-MD bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

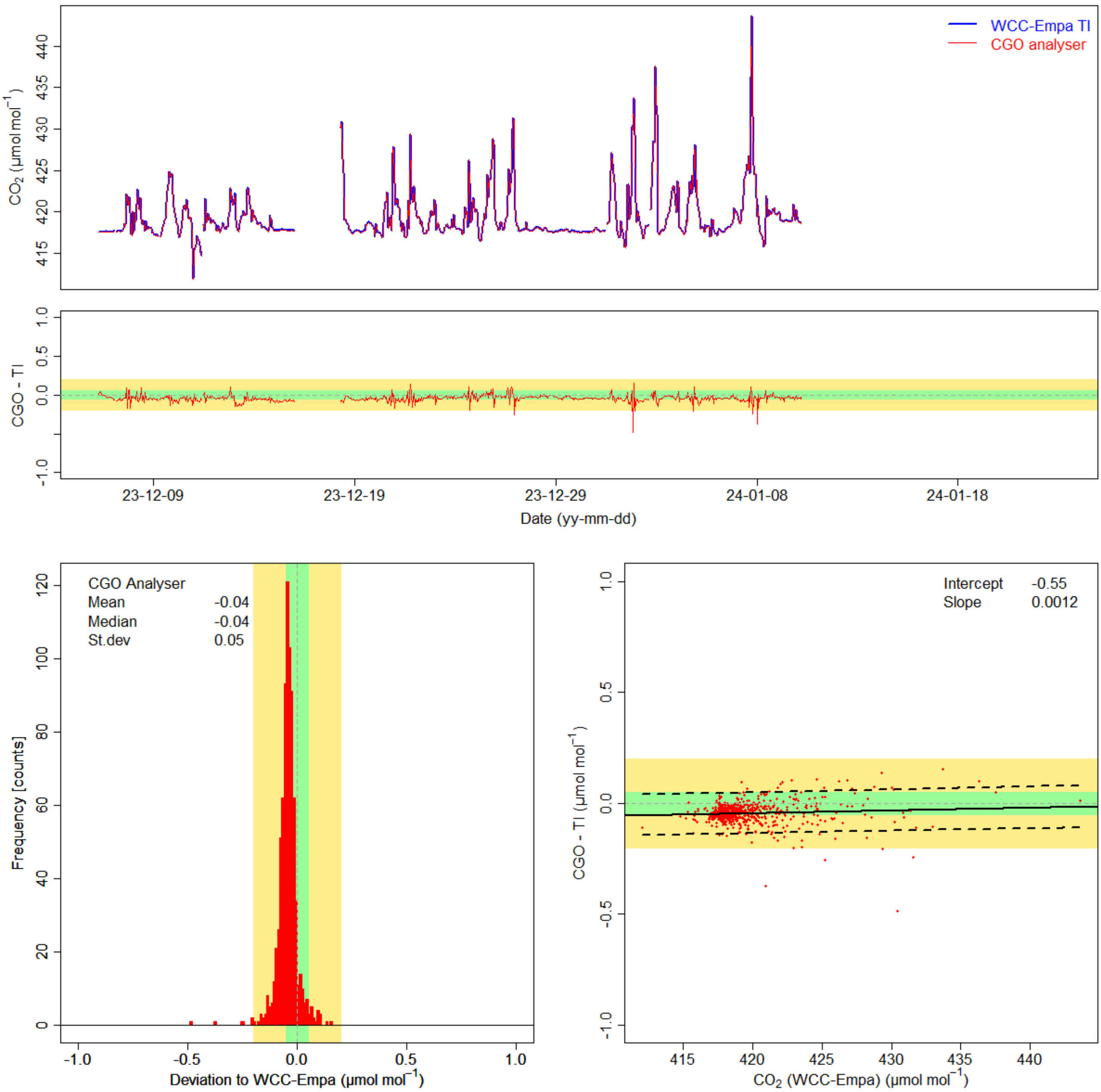

Figure 24. *Top: Comparison of the G2301 #1151-CFADS2263 analyser (main instrument) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO_2 deviation histograms for the Picarro G2301 #1151-CFADS2263 analyser compared to the WCC-Empa TI. Bottom right: CGO instrument bias as a function of the CO_2 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

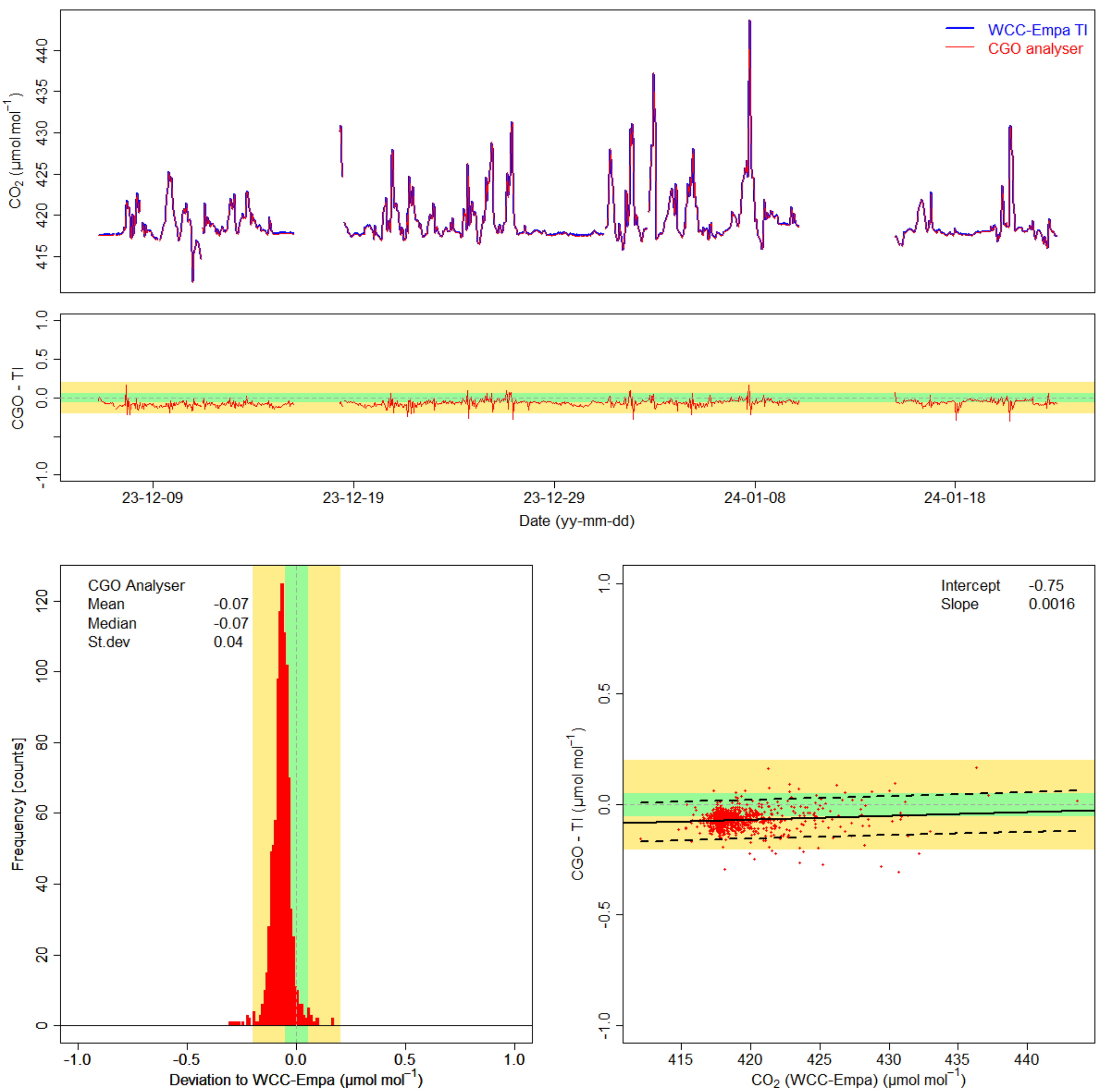

Figure 25. *Top: Comparison of the G2301 #2121-CFADS2386 analyser (backup instrument) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO_2 deviation histograms for the Picarro G2301 #2121-CFADS2386 analyser compared to the WCC-Empa TI. Bottom right: CGO instrument bias as a function of the CO_2 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

6 Conclusions

The Kennaook / Cape Grim Global GAW Station provides a comprehensive research infrastructure that supports a wide range of ongoing observations in all WMO/GAW focal areas and enables various research projects. The station's GAW activities are well integrated into national and international research networks, establishing it as a major contributor to the WMO/GAW programme. As such, the continuation of the Kennaook / Cape Grim measurement series is vital for GAW. The station facilitates advanced research through its in-depth monitoring of atmospheric constituents and its consistently high data quality over many decades.

Most of the measurements were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant range of amount fractions. Therefore, due to the good results of the comparisons and the well-established and fully appropriate operational procedures, only few recommendations were made.

Table 1 summarises the results of the performance audit with travelling standards and the ambient air comparison in relation to the WMO/GAW compatibility goals.

Table 1. *Summary of the performance audit and parallel measurement results at Kennaook / Cape Grim. 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 exceeding the compatibility goals.*

Compound / Instrument	**Range**	**Unit**	**CGO within DQO/eDQO**
O_3 (Thermo Scientific 49i #CM16160046)	0 -100	nmol mol^{-1}	✓ (green)
O_3 (Thermo Scientific 49iQ #1191302833)	0 -100	nmol mol^{-1}	✓ (green)
CO (Picarro G5310 #5066-DAS-JKADS5075)	30 - 300	nmol mol^{-1}	✗
CO (Picarro G5310 #5066-DAS-JKADS5075), parallel measurements	NA	nmol mol^{-1}	✓ (orange)
CO (CGO GC-MD)	30 - 300	nmol mol^{-1}	✓ (orange)
CO (CGO GC-MD), parallel measurements	NA	nmol mol^{-1}	✓ (orange)
CO (CSIRO GC-RGD)	30 - 300	nmol mol^{-1}	✓ (orange)
CH_4 (Picarro G2301 #1151-CFADS2263)	1750 - 2100	nmol mol^{-1}	✓ (green)
CH_4 (Picarro G2301 #1151-CFADS2263), parallel measurements	NA	nmol mol^{-1}	✓ (green)
CH_4 (CGO GC-MD)	1750 - 2100	nmol mol^{-1}	✓ (green)
CH_4 (CGO GC-MD), parallel measurements	NA	nmol mol^{-1}	✓ (green)
CH_4 (CSIRO GC-FID)	1750 - 2100	nmol mol^{-1}	✓ (green)
CH_4 (Picarro G2301 #2121-CFADS2386), parallel measurements	NA	nmol mol^{-1}	✓ (green)
CO_2 (Picarro G2301 #1151-CFADS2263)	380 - 450	µmol mol^{-1}	✓ (orange)
CO_2 (Picarro G2301 #1151-CFADS2263), parallel measurements	NA	µmol mol^{-1}	✓ (green)
CO_2 (Picarro G2401 #2121-CFADS2386), parallel measurements	NA	µmol mol^{-1}	✓ (orange)
CO_2 (CSIRO GC-FID)	380 - 450	µmol mol^{-1}	✓ (orange)
N_2O (Picarro G5310 #5066-DAS-JKADS5075)	330 - 340	nmol mol^{-1}	✓ (green)
N_2O (CGO GC-MD)	330 - 340	nmol mol^{-1}	✓ (orange)
N_2O (CSIRO GC-ECD)	330 - 340	nmol mol^{-1}	✓ (orange)

7 Summary ranking of the Kennaook / Cape Grim GAW station

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme
Access	(5)	Year-round access
Facilities		
Laboratory and office space	(5)	Fully adequate, with space for additional research campaigns
Internet access	(5)	High-speed connection
Air Conditioning	(5)	Air conditioned, temperature fluctuations of less than 1°C
Power supply	(5)	Reliable and stable, backup system
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(5)	Fully adequate inlet systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2 Picarro G2301	(5)	State of the art instrumentation
N_2O/CO Picarro G5310	(5)	State of the art instrumentation
Standards		
O_3	(5)	Transfer standards with SRP traceability on site
CO, CO_2, CH_4	(5)	Full traceability to the WMO/GAW reference. Different scales in use, ongoing comparisons.
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(5)	Skilled staff, appropriate procedures
Data submission WDCRG	(3)	Ozone data is available up to 2017, new data needs to be submitted
Data submission WDCGG	(4)	Most data were submitted timely, a few data series with a delay of more than 2 years

#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 completion date.

#	Recommendation	Priority	Significance	Date
1	It is recommended that GAWSIS is updated annually or when there are major changes. Some of the reviewed information needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface.	Medium	Important	Ongoing
2	Most data have been submitted with a delay of less than one year. However, some recent data is not yet available on the data centres. It is recommended to submit the O_3 data for the period from 2017 onwards as soon as the final quality control has been completed. In addition, in-situ CO data should also be submitted as soon as possible.	Medium	Important	2024
3	Thermo Scientific 49iQ #1191302833 is not performing well, and the cause needs to be identified. It is recommended that the analyser be returned to the manufacturer for inspection and repair.	Medium	Important	2024
4	The Thermo Scientific 49iQ #1191302833 should not be used as a primary ozone analyser in its current condition. It is recommended to keep the 49i #CM16160046 as the main analyser, and to replace the 49iQ instrument if its performance cannot be improved.	Medium	Important	Before next instrument change
5	It is recommended to characterise the CO linearity of the CRDS and GC-MD instruments between 0 and 300 (GC) and 0 and 1000 nmol mol-1 (CRDS).	Low	Minor	2024
6	It is recommended to characterise the N_2O linearity of the CRDS and GC-MD instruments.	Low	Minor	2024
7	WCC-Empa recommends testing and characterising the internal water vapour correction of the Picarro G5310 instrument, which may be a potential source of the larger bias observed in the ambient air comparison.	Medium	Important	2024

A2. Data review

The following figures show summary plots of CGO data obtained from WDCRG and WDCGG on 18 September 2024. The plots show time series of hourly data, frequency distribution and diurnal and seasonal variations.

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

Surface ozone:

The in-situ O_3 data submitted by CSIRO is shown in the figure below. The three available data sets have been merged to produce this figure.

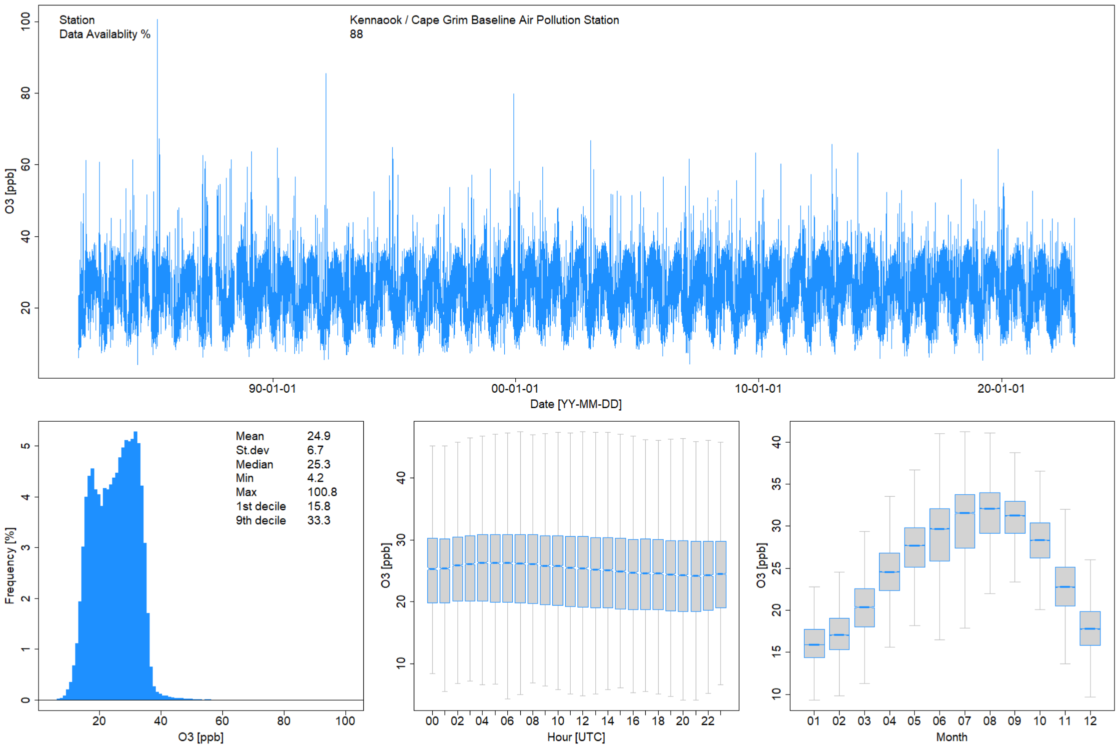

Figure 26. *WDCRG O_3 data for the period 1981 to 2022. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- The datasets look good in terms of amount fraction, trend, seasonal and diurnal variation.

Carbon monoxide:

The in-situ CO data submitted by AGAGE, CSIRO and NOAA are shown in the figures below.

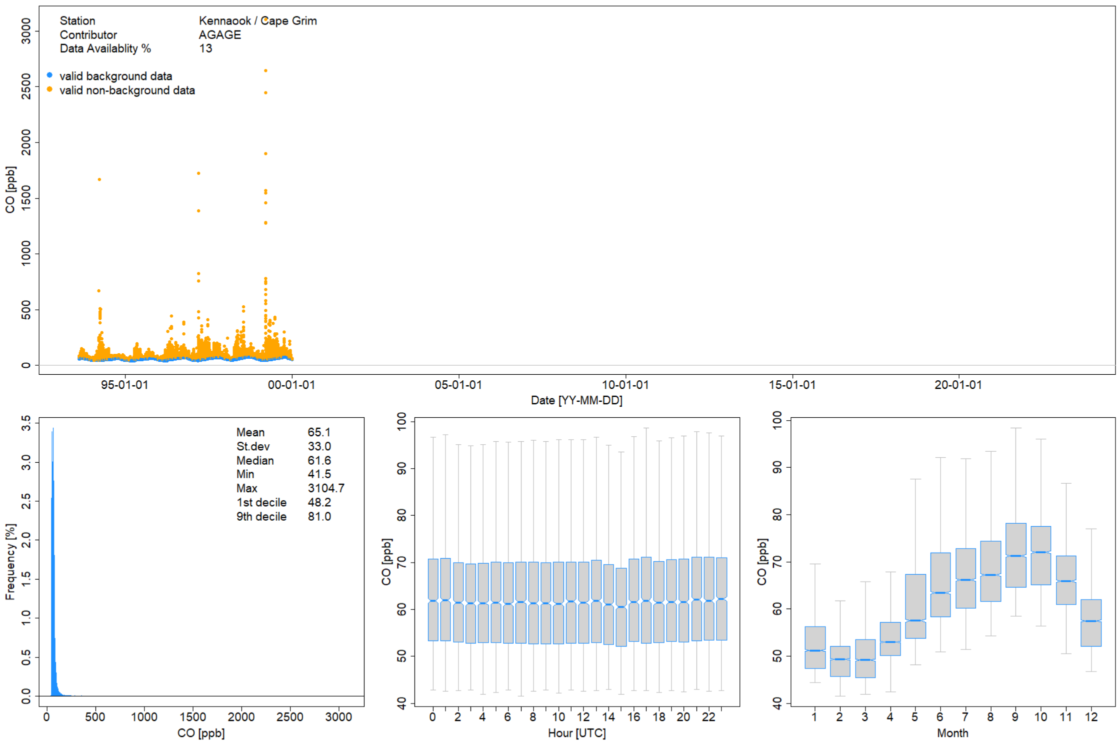

Figure 27. *CGO in-situ CO data (GC-MD) (1993-2023) provided by AGAGE. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

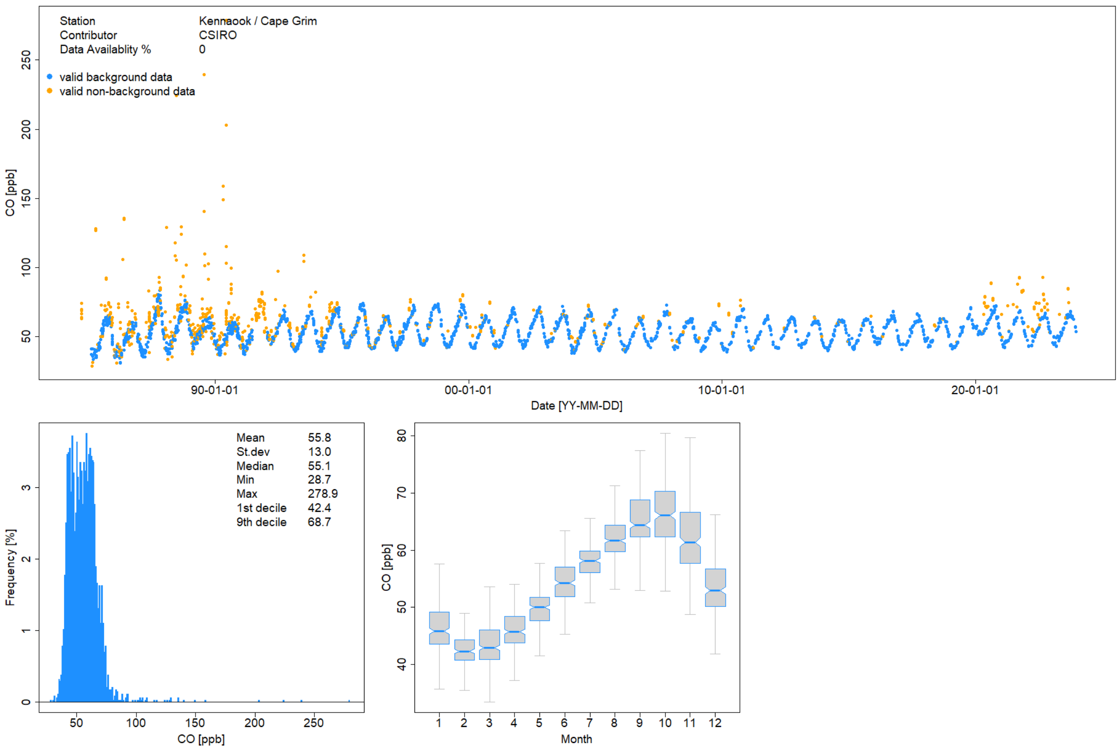

Figure 28. *CGO CO flask data (1984-2023) submitted to WDCGG by CSIRO. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

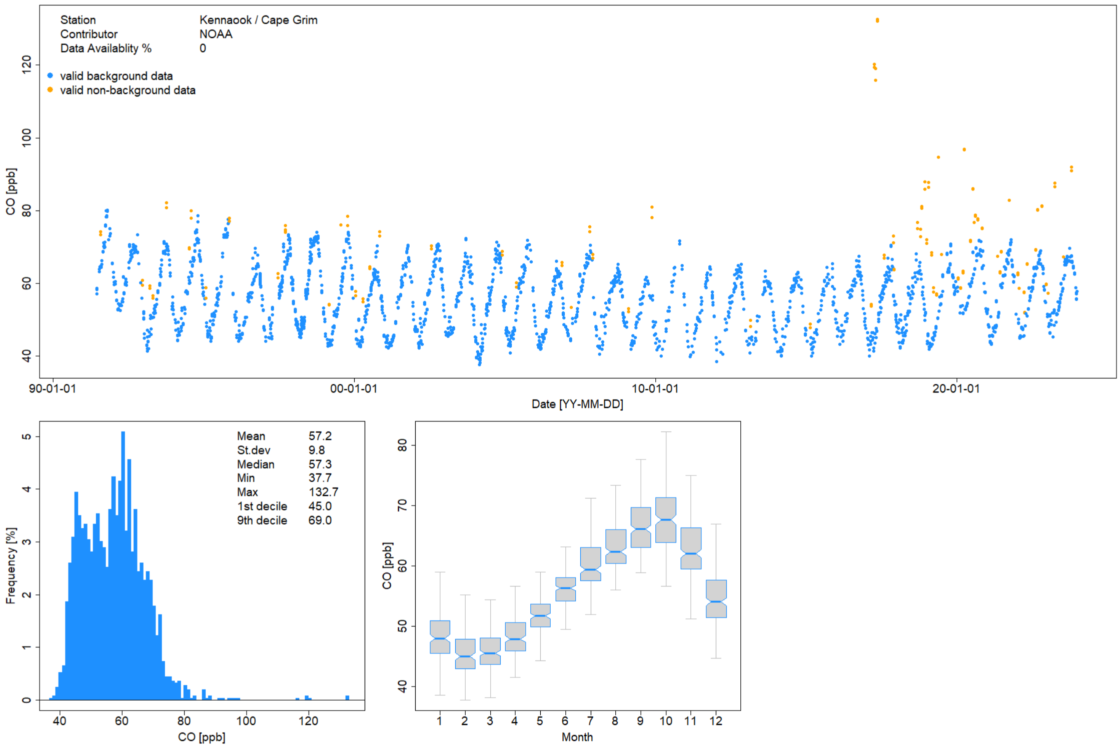

Figure 29. *CGO CO flask data (1990-2023) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- Valid data in the AGAGE in-situ data set ends in 1999. Data from 1999 onwards need to be submitted after quality control.
- Both the CSIRO and NOAA CO flask data series look sound in terms of amount fraction, trend and seasonal variation.
- The temporal distribution of the valid non-background data is highly variable for the NOAA data set and the occurrence of such data has increased again in recent years. A similar increase is also observed in the CSIRO flask data. It should be investigated whether this is related to a change in sampling strategy or an increase in pollution episodes.

Methane:

The in-situ CH_4 data submitted by AGAGE is shown in the figures below.

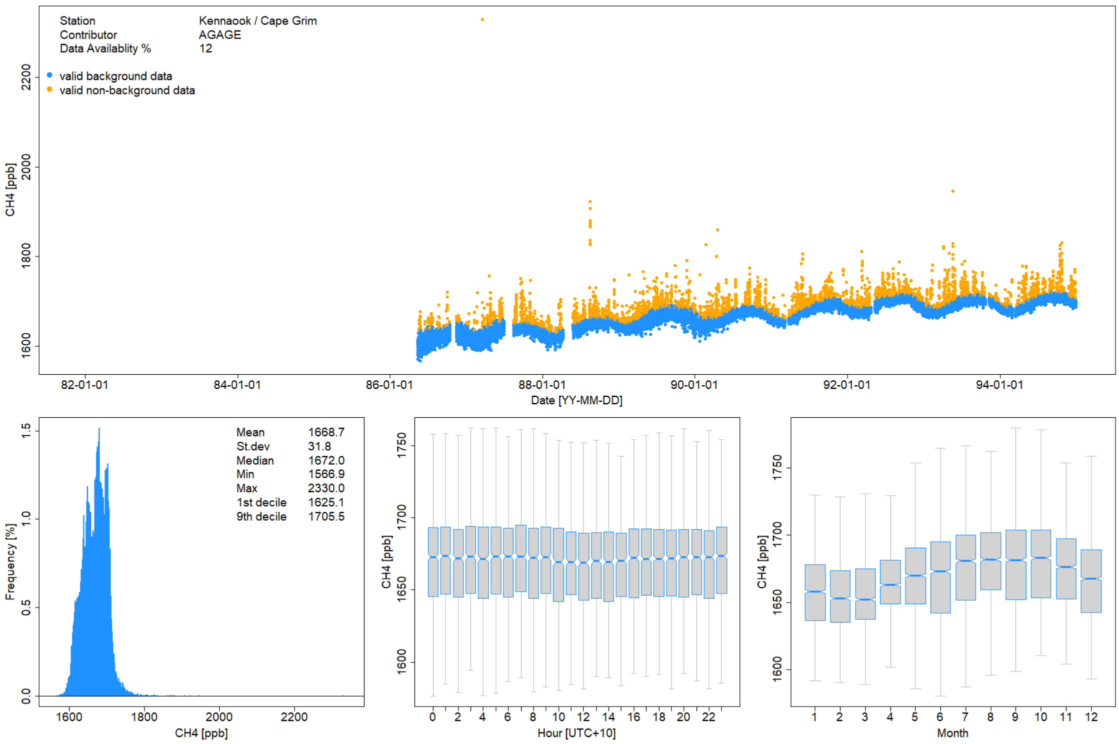

Figure 30. *CGO in-situ CH_4 data (GC-MD) (1981-1994) provided by AGAGE. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

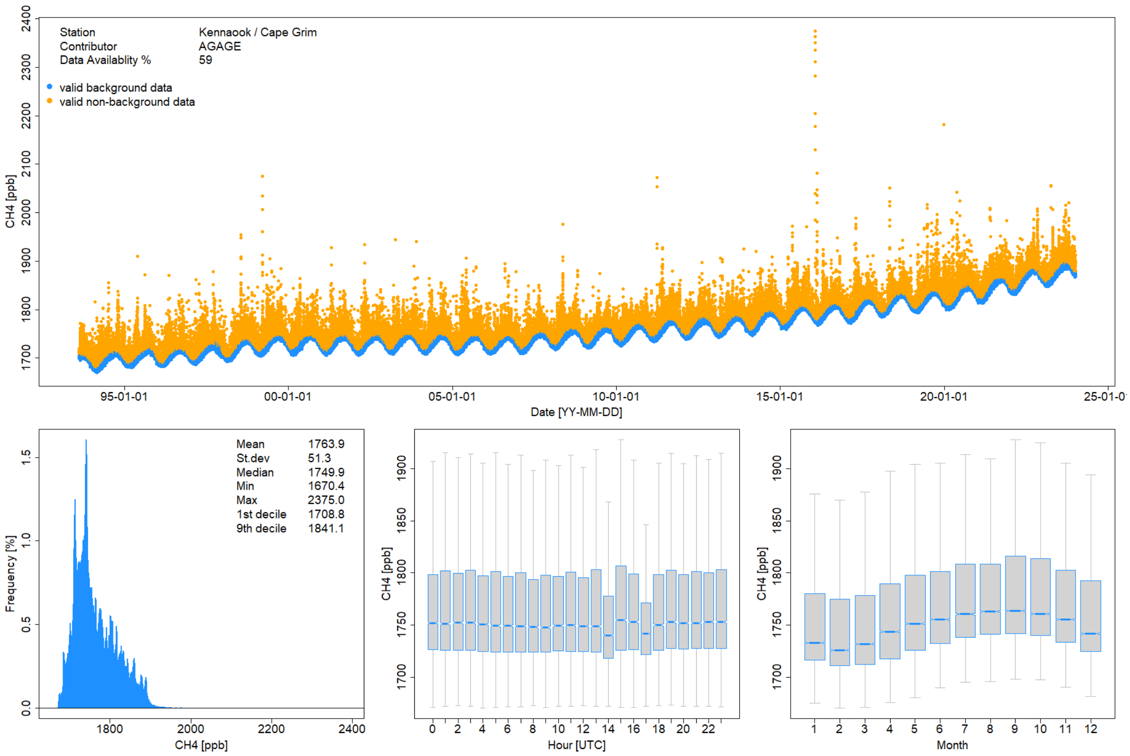

Figure 31. *CGO in-situ CH_4 data (GC-MD) (1993-2023) provided by AGAGE. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

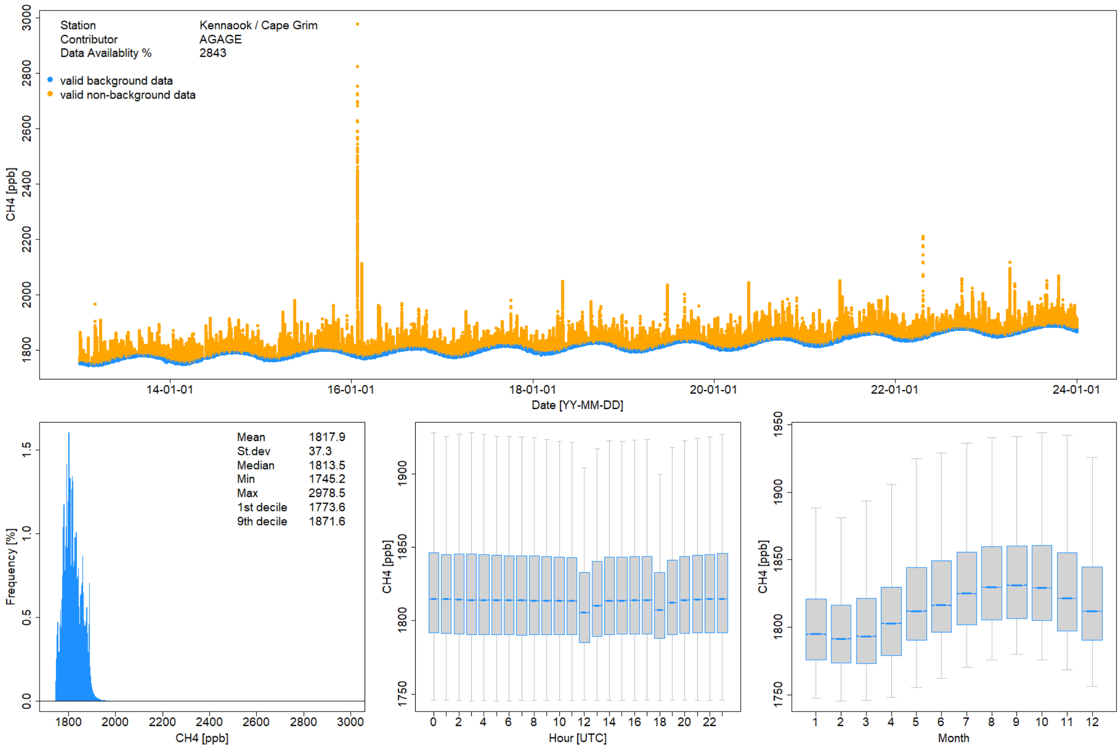

Figure 32. *CGO in-situ CH_4 data (Picarro) (2013-2023) provided by AGAGE. All valid data are shown. Top: Time series, 1-minute averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

The CH_4 flask data submitted by CSIRO and NOAA is shown below.

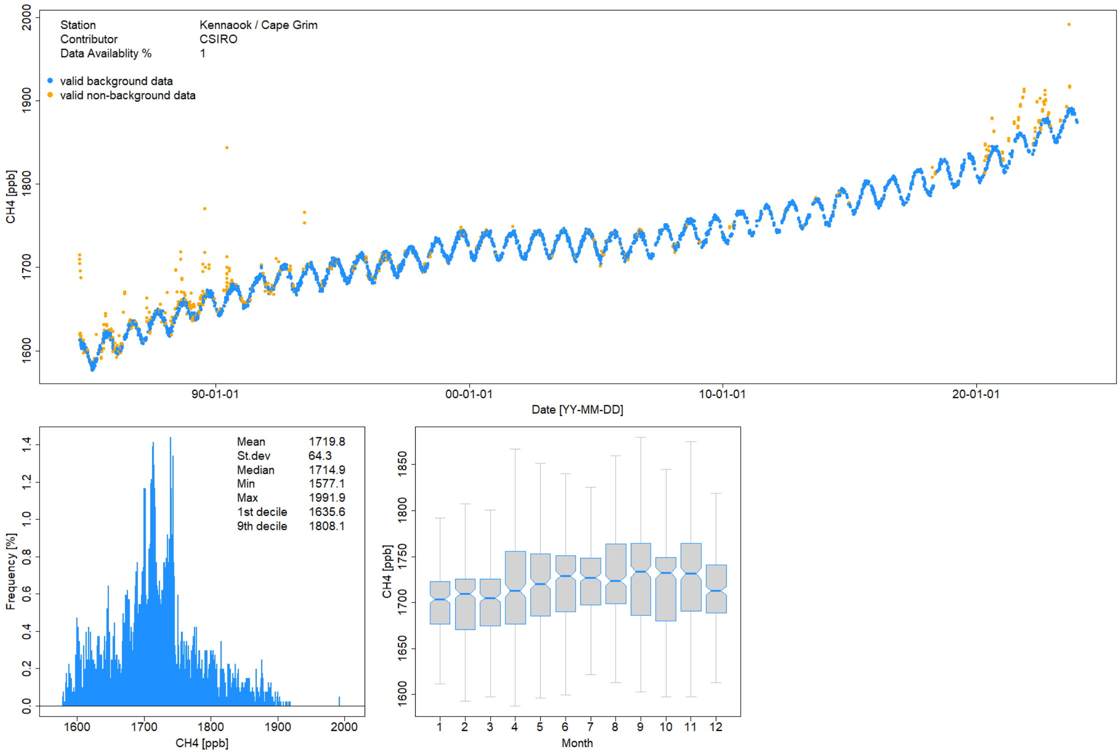

Figure 33. *CGO CH_4 flask data (1984-2023) submitted to WDCGG by CSIRO. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

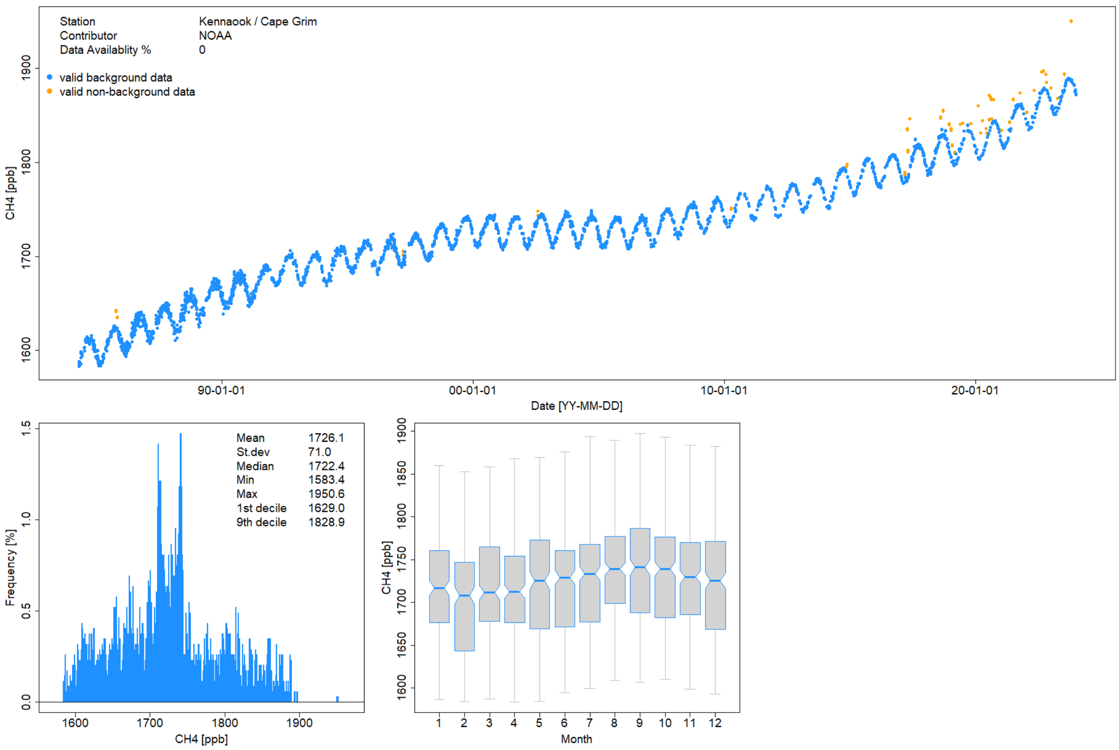

Figure 34. *CGO CH_4 flask data (1984-2023) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- All CH_4 data sets look sound in terms of amount fraction, trend, seasonal and diurnal variation.
- The comment on the frequency of valid non-background data made for CO measurements also applies to CH_4.

Carbon dioxide:

The in-situ CO_2 data submitted by CSIRO (LoFlo Mk2 NDIR instrument) is shown in the figures below.

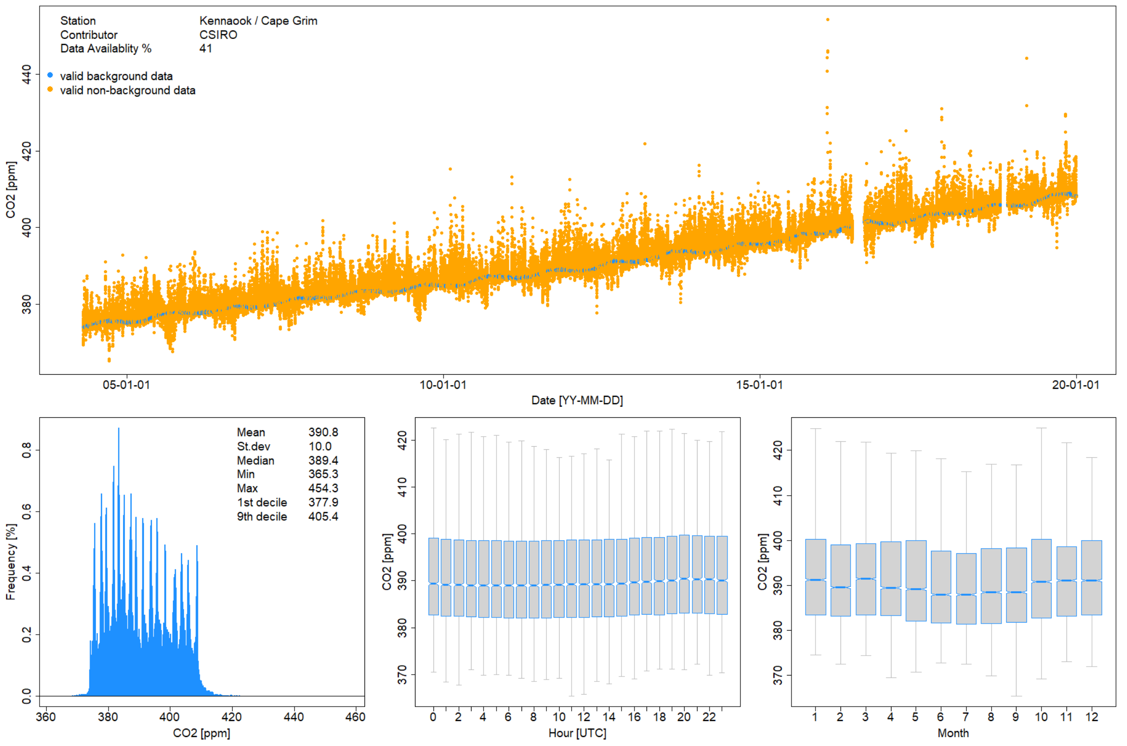

Figure 35. *CGO in-situ CO_2 data (LoFlo Mk2 NDIR instrument) (2004-2019) provided by CSIRO. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

The CO_2 flask data submitted by CSIRO and NOAA is shown below.

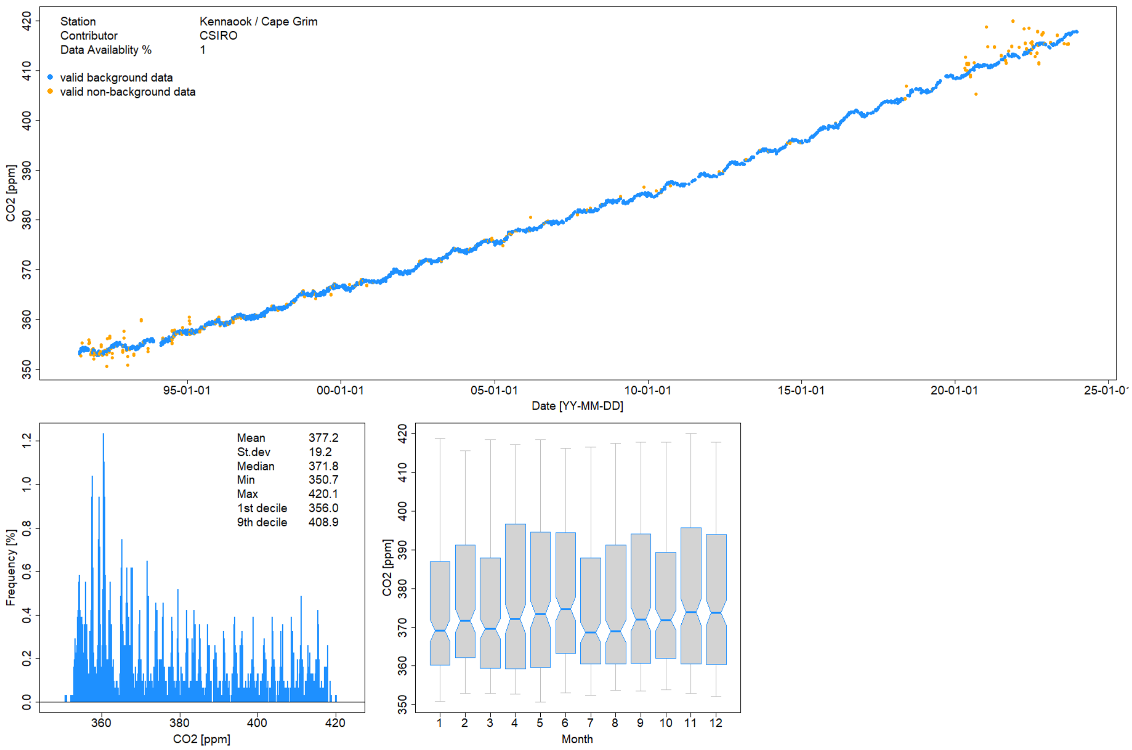

Figure 36. *CGO CO_2 flask data (1984-2023) submitted to WDCGG by CSIRO. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

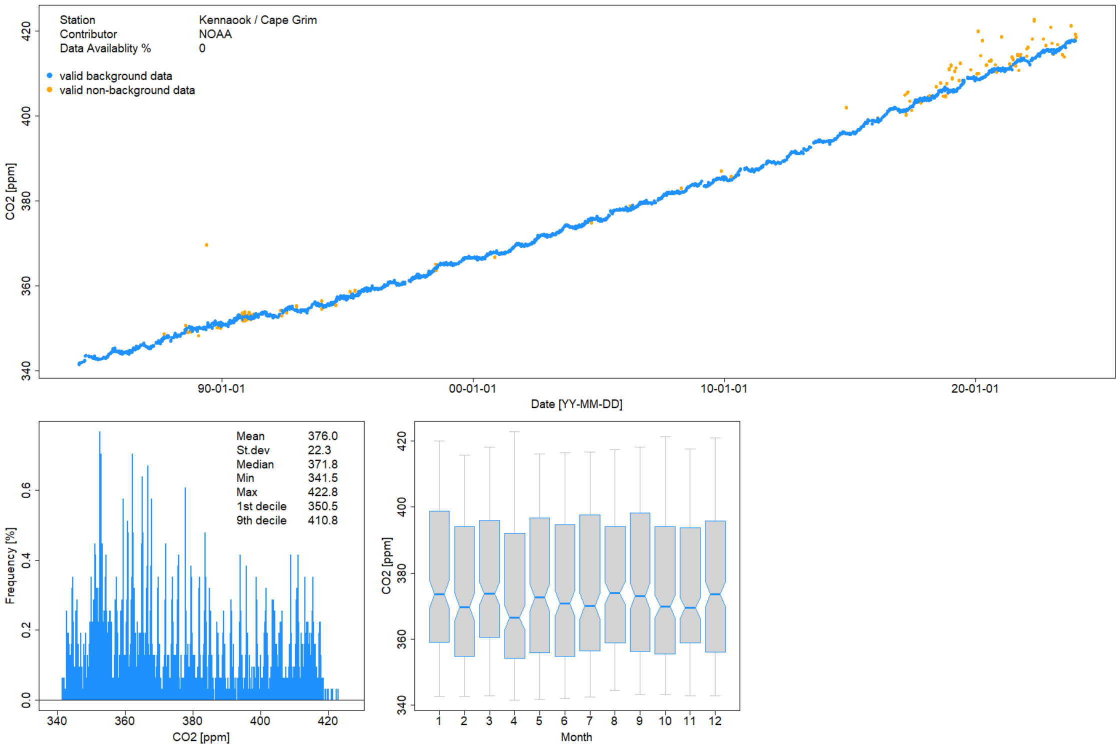

Figure 37. *CGO CO_2 flask data (1990-2023) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- All CO_2 data sets look sound in terms of amount fraction, trend, seasonal and diurnal variation.
- The comment on the frequency of valid non-background data made for CO measurements also applies for CO_2.

Nitrous oxide:

The in-situ N_2O data submitted by AGAGE (GC-MD instrument) is shown in the figures below.

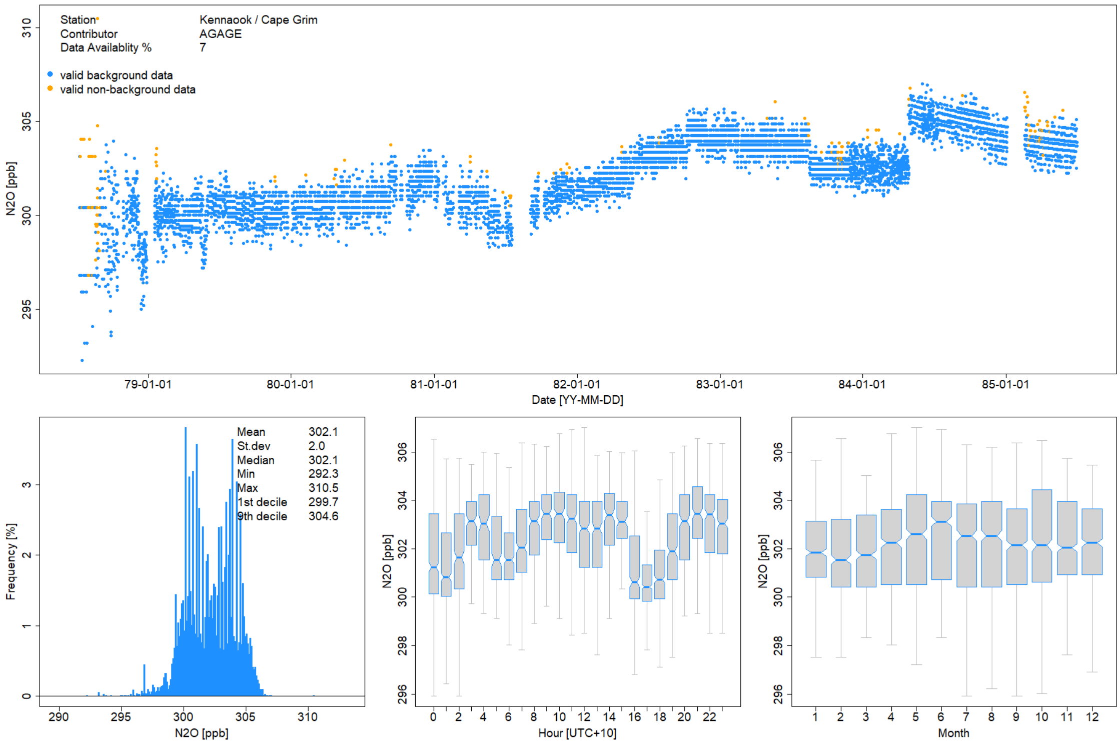

Figure 38. *CGO in-situ N_2O data (GC-MD) (1978-1985) provided by AGAGE. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

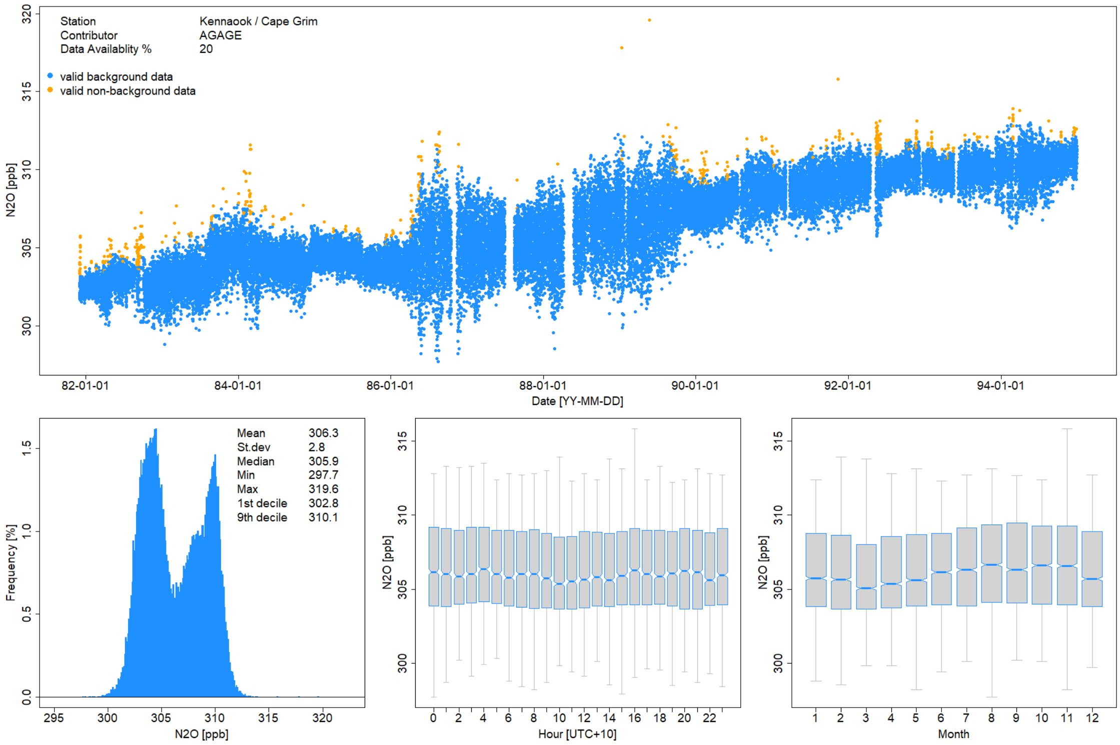

Figure 39. *CGO in-situ N_2O data (GC-MD) (1981-1994) provided by AGAGE. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

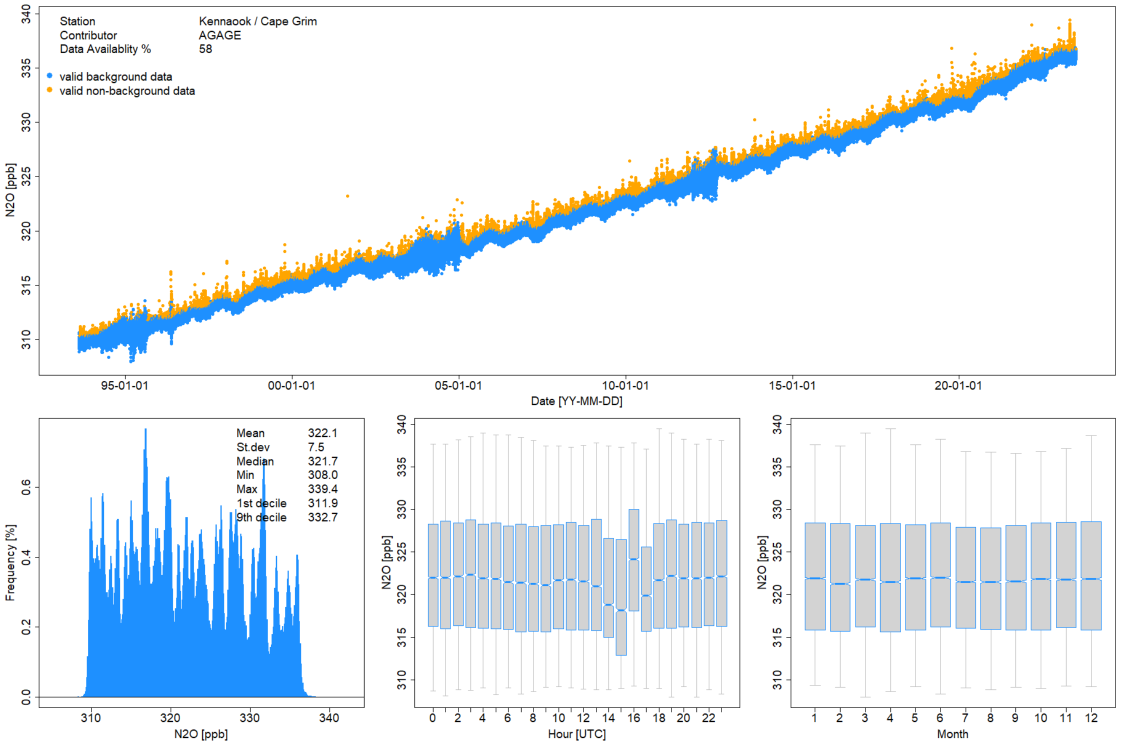

Figure 40. *CGO in-situ N_2O data (GC-MD) (1993-2023) provided by AGAGE. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

The N_2O flask data submitted by CSIRO and NOAA is shown below.

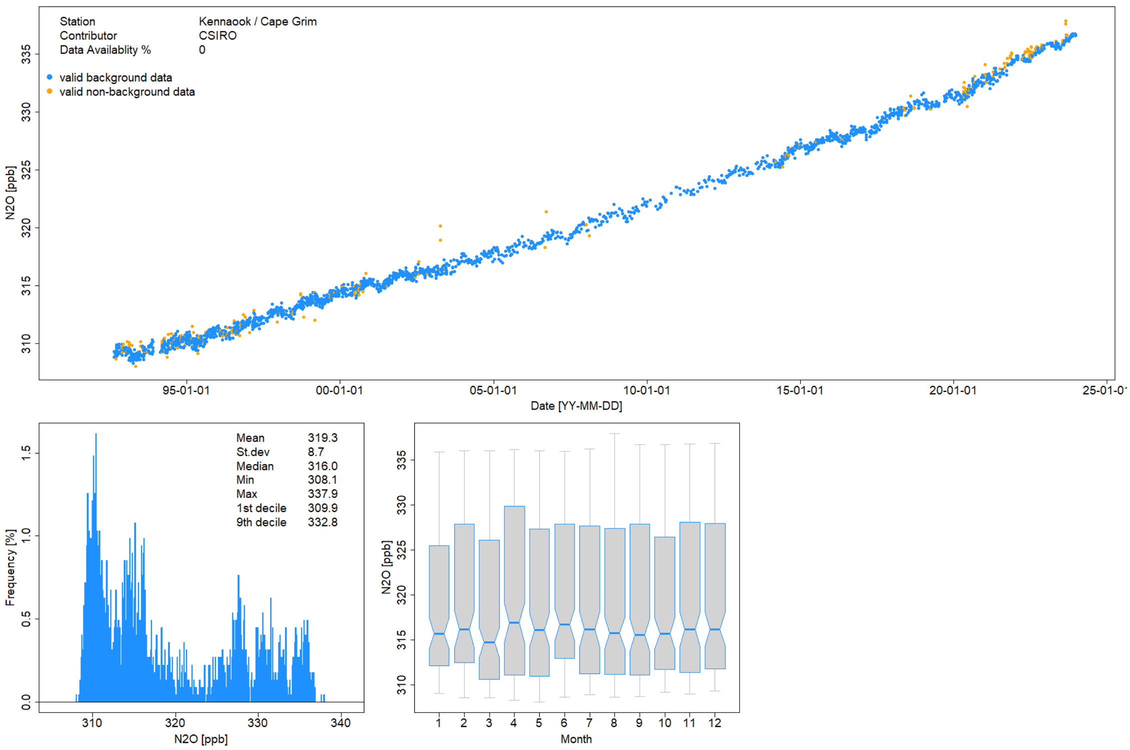

Figure 41. *CGO N_2O flask data (1991-2023) submitted to WDCGG by CSIRO. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

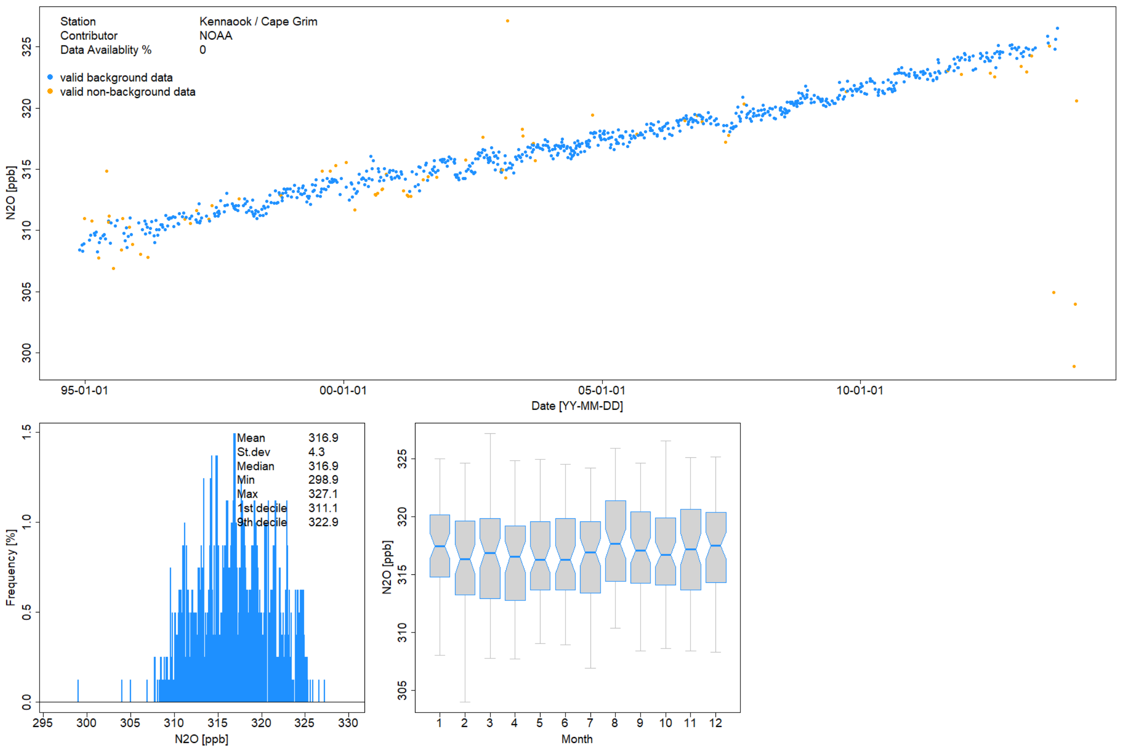

Figure 42. *CGO N_2O flask data (1994-2014) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

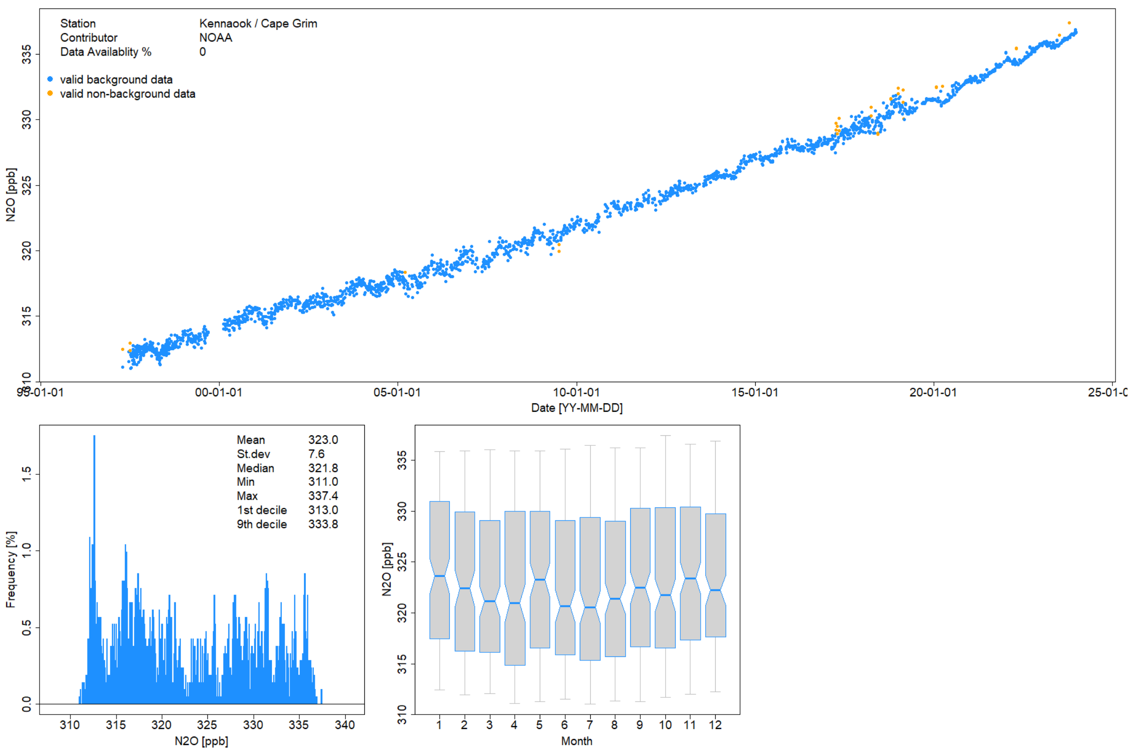

Figure 43. *CGO N_2O flask data (1996-2023) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- All N_2O data sets look generally sound in terms of amount fraction, trend, seasonal and diurnal variations.

- Data from earlier periods appear to be more variable due to the larger measurement uncertainties at that time.
- The AGAGE in-situ data for the period from 1993-2022 show a few periods with much higher variability, and lower than expected values during these periods are flagged as valid background data.

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 2 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 CGO data acquisition systems.

Table 2. *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)	Ambient 1002.5; TS 1003.3 (no adjustment was made)
Main CGO ozone analyser (OA)	
Model, S/N	Thermo Scientific 49i #CM16160046
Principle	UV absorption
Settings	BKG -0.5 nmol mol^{-1}, COEF 0.984
Pressure readings (hPa)	Ambient 1002.1; OA 996.5 (no adjustment was made)
Backup CGO ozone analyser (OA)	
Model, S/N	Thermo Scientific 49iQ #1191302833
Principle	UV absorption
Settings	BKG +0.5 nmol mol^{-1}, COEF 0.978
Pressure readings (hPa)	Ambient 1002.1; OA 1006.7 (no adjustment was made)
Main CGO ozone calibrator (OC)	
Model, S/N	Thermo Scientific 49i-PS #1180930024
Principle	UV absorption
Settings	BKG 0.0 nmol mol^{-1}, COEF 0.988
Pressure readings (hPa)	Ambient 1001.3; OA 998.1 (no adjustment was made)
Backup CGO ozone calibrator (OC)	
Model, S/N	Thermo Scientific 49i-PS #1315588104
Principle	UV absorption
Settings	BKG 0.0 nmol mol^{-1}, COEF 1.035
Pressure readings (hPa)	Ambient 1007.7; OC 1005.0 (no adjustment was made)

Results

Each ozone level was measured for ten 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 as given in Table 2 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment was applied as for the ambient air analysis.
The results of the assessment are shown in the following table (individual measurement points) and are also presented in the Executive Summary.

Table 3. *Comparison of the main CGO ozone analyser (OA) Thermo Scientific 49i #CM16160046 (BKG -0.0 nmol mol*$^{-1}$*, COEF 0.984) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2023-12-04 15:35	0.07	0.21	0.26	0.27	0.19	NA
2023-12-04 15:50	50.01	0.10	50.06	0.11	0.05	0.10
2023-12-04 16:05	199.72	0.14	199.68	0.25	-0.04	-0.02
2023-12-04 16:20	149.87	0.17	149.71	0.31	-0.16	-0.11
2023-12-04 16:35	99.96	0.06	100.00	0.20	0.04	0.04
2023-12-04 16:50	249.66	0.12	249.86	0.21	0.20	0.08
2023-12-04 17:05	20.12	0.18	20.03	0.34	-0.09	-0.45
2023-12-04 17:20	70.01	0.08	69.93	0.25	-0.08	-0.11
2023-12-04 17:35	89.95	0.09	90.04	0.23	0.09	0.10
2023-12-04 17:50	40.06	0.11	40.04	0.23	-0.02	-0.05
2023-12-04 18:05	10.70	0.76	10.84	0.68	0.14	1.31
2023-12-04 18:35	30.06	0.11	30.25	0.21	0.19	0.63
2023-12-04 18:50	59.95	0.05	59.87	0.31	-0.08	-0.13
2023-12-04 19:05	79.89	0.16	79.98	0.40	0.09	0.11
2023-12-04 19:20	0.21	0.21	0.34	0.19	0.13	NA
2023-12-04 19:35	199.76	0.17	199.99	0.39	0.23	0.12
2023-12-04 19:50	99.88	0.14	100.16	0.35	0.28	0.28
2023-12-04 20:05	30.05	0.14	30.20	0.29	0.15	0.50
2023-12-04 20:20	10.13	0.34	10.31	0.33	0.18	1.78
2023-12-04 20:35	149.84	0.07	150.10	0.51	0.26	0.17
2023-12-04 20:50	50.01	0.08	49.77	0.39	-0.24	-0.48
2023-12-04 21:05	20.05	0.15	20.29	0.17	0.24	1.20
2023-12-04 21:20	79.94	0.13	80.16	0.47	0.22	0.28
2023-12-04 21:35	60.02	0.05	60.32	0.14	0.30	0.50
2023-12-04 21:50	40.00	0.11	39.92	0.11	-0.08	-0.20
2023-12-04 22:05	69.91	0.13	70.08	0.33	0.17	0.24
2023-12-04 22:20	89.96	0.11	90.15	0.48	0.19	0.21
2023-12-04 22:35	249.65	0.12	250.24	0.46	0.59	0.24
2023-12-04 22:50	0.10	0.14	0.41	0.12	0.31	NA
2023-12-04 23:05	69.97	0.09	70.15	0.13	0.18	0.26
2023-12-04 23:20	149.82	0.11	150.15	0.34	0.33	0.22
2023-12-04 23:35	249.71	0.13	250.24	0.20	0.53	0.21
2023-12-04 23:50	50.01	0.14	50.19	0.33	0.18	0.36
2023-12-05 00:20	99.89	0.05	100.16	0.11	0.27	0.27
2023-12-05 00:35	79.95	0.05	80.08	0.19	0.13	0.16
2023-12-05 00:50	10.34	0.38	10.54	0.68	0.20	1.93
2023-12-05 01:05	40.07	0.14	40.06	0.22	-0.01	-0.02

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
2023-12-05 01:20	89.97	0.11	90.20	0.19	0.23	0.26
2023-12-05 01:35	20.02	0.20	20.34	0.26	0.32	1.60
2023-12-05 01:50	60.04	0.22	60.29	0.39	0.25	0.42
2023-12-05 02:05	30.03	0.12	30.27	0.25	0.24	0.80
2023-12-05 02:20	0.07	0.13	0.42	0.20	0.35	NA
2023-12-05 02:50	50.03	0.18	50.21	0.17	0.18	0.36
2023-12-05 03:05	199.77	0.15	200.24	0.36	0.47	0.24
2023-12-05 03:20	149.82	0.11	150.33	0.24	0.51	0.34
2023-12-05 03:35	99.90	0.05	100.41	0.27	0.51	0.51
2023-12-05 03:50	249.62	0.11	250.41	0.27	0.79	0.32
2023-12-05 04:05	20.05	0.28	20.24	0.18	0.19	0.95
2023-12-05 04:20	69.94	0.15	70.31	0.40	0.37	0.53
2023-12-05 04:35	89.94	0.14	90.20	0.28	0.26	0.29
2023-12-05 04:50	40.04	0.02	40.06	0.26	0.02	0.05
2023-12-05 05:05	10.09	0.12	10.41	0.17	0.32	3.17
2023-12-05 05:35	30.04	0.05	30.34	0.19	0.30	1.00
2023-12-05 05:50	60.01	0.17	60.00	0.23	-0.01	-0.02
2023-12-05 06:05	79.95	0.05	79.97	0.21	0.02	0.03
2023-12-05 06:20	0.14	0.26	0.35	0.10	0.21	NA
2023-12-05 06:35	199.81	0.05	200.51	0.16	0.70	0.35
2023-12-05 06:50	99.89	0.10	100.32	0.14	0.43	0.43
2023-12-05 07:05	30.02	0.12	30.27	0.43	0.25	0.83
2023-12-05 07:20	10.10	0.22	10.28	0.26	0.18	1.78
2023-12-05 07:35	149.83	0.08	150.15	0.20	0.32	0.21
2023-12-05 07:50	50.04	0.09	50.26	0.35	0.22	0.44
2023-12-05 08:05	19.99	0.09	20.18	0.11	0.19	0.95
2023-12-05 08:20	79.96	0.14	80.21	0.31	0.25	0.31
2023-12-05 08:35	59.99	0.12	60.22	0.18	0.23	0.38
2023-12-05 08:50	40.02	0.12	40.15	0.28	0.13	0.32
2023-12-05 09:05	70.00	0.05	70.19	0.23	0.19	0.27

Table 4. *Comparison of the CGO ozone analyser (OA) Thermo Scientific 49iQ #1191302833 (BKG +0.5 nmol mol^{-1}, COEF 0.978) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
2023-12-04 15:35	0.07	0.21	-0.07	0.05	-0.14	NA
2023-12-04 15:50	50.01	0.10	49.40	0.11	-0.61	-1.22
2023-12-04 16:05	199.72	0.14	199.08	0.18	-0.64	-0.32
2023-12-04 16:20	149.87	0.17	149.11	0.08	-0.76	-0.51
2023-12-04 16:35	99.96	0.06	99.47	0.07	-0.49	-0.49
2023-12-04 16:50	249.66	0.12	250.02	0.12	0.36	0.14
2023-12-04 17:05	20.12	0.18	19.92	0.05	-0.20	-0.99
2023-12-04 17:20	70.01	0.08	69.82	0.05	-0.19	-0.27
2023-12-04 17:35	89.95	0.09	89.88	0.09	-0.07	-0.08
2023-12-04 17:50	40.06	0.11	39.92	0.13	-0.14	-0.35
2023-12-04 18:05	10.70	0.76	10.18	0.18	-0.52	-4.86
2023-12-04 18:35	30.06	0.11	29.96	0.03	-0.10	-0.33

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2023-12-04 18:50	59.95	0.05	59.67	0.03	-0.28	-0.47
2023-12-04 19:05	79.89	0.16	79.89	0.07	0.00	0.00
2023-12-04 19:20	0.21	0.21	0.14	0.02	-0.07	NA
2023-12-04 19:35	199.76	0.17	200.49	0.18	0.73	0.37
2023-12-04 19:50	99.88	0.14	100.36	0.06	0.48	0.48
2023-12-04 20:05	30.05	0.14	30.19	0.05	0.14	0.47
2023-12-04 20:20	10.13	0.34	10.24	0.13	0.11	1.09
2023-12-04 20:35	149.84	0.07	150.58	0.07	0.74	0.49
2023-12-04 20:50	50.01	0.08	50.10	0.04	0.09	0.18
2023-12-04 21:05	20.05	0.15	20.10	0.03	0.05	0.25
2023-12-04 21:20	79.94	0.13	80.11	0.12	0.17	0.21
2023-12-04 21:35	60.02	0.05	60.31	0.08	0.29	0.48
2023-12-04 21:50	40.00	0.11	40.09	0.05	0.09	0.23
2023-12-04 22:05	69.91	0.13	70.01	0.17	0.10	0.14
2023-12-04 22:20	89.96	0.11	90.44	0.06	0.48	0.53
2023-12-04 22:35	249.65	0.12	251.37	0.11	1.72	0.69
2023-12-04 22:50	0.10	0.14	0.32	0.03	0.22	NA
2023-12-04 23:05	69.97	0.09	70.38	0.03	0.41	0.59
2023-12-04 23:20	149.82	0.11	150.94	0.17	1.12	0.75
2023-12-04 23:35	249.71	0.13	251.53	0.10	1.82	0.73
2023-12-04 23:50	50.01	0.14	50.34	0.08	0.33	0.66
2023-12-05 00:20	99.89	0.05	100.61	0.11	0.72	0.72
2023-12-05 00:35	79.95	0.05	80.32	0.05	0.37	0.46
2023-12-05 00:50	10.34	0.38	10.58	0.19	0.24	2.32
2023-12-05 01:05	40.07	0.14	40.49	0.03	0.42	1.05
2023-12-05 01:20	89.97	0.11	90.69	0.06	0.72	0.80
2023-12-05 01:35	20.02	0.20	20.28	0.04	0.26	1.30
2023-12-05 01:50	60.04	0.22	60.42	0.12	0.38	0.63
2023-12-05 02:05	30.03	0.12	30.22	0.04	0.19	0.63
2023-12-05 02:20	0.07	0.13	0.43	0.06	0.36	NA
2023-12-05 02:50	50.03	0.18	50.22	0.17	0.19	0.38
2023-12-05 03:05	199.77	0.15	201.11	0.06	1.34	0.67
2023-12-05 03:20	149.82	0.11	150.96	0.07	1.14	0.76
2023-12-05 03:35	99.90	0.05	100.78	0.08	0.88	0.88
2023-12-05 03:50	249.62	0.11	251.49	0.08	1.87	0.75
2023-12-05 04:05	20.05	0.28	20.27	0.08	0.22	1.10
2023-12-05 04:20	69.94	0.15	70.54	0.05	0.60	0.86
2023-12-05 04:35	89.94	0.14	90.62	0.05	0.68	0.76
2023-12-05 04:50	40.04	0.02	40.37	0.07	0.33	0.82
2023-12-05 05:05	10.09	0.12	10.60	0.05	0.51	5.05
2023-12-05 05:35	30.04	0.05	30.44	0.04	0.40	1.33
2023-12-05 05:50	60.01	0.17	60.03	0.16	0.02	0.03
2023-12-05 06:05	79.95	0.05	80.38	0.05	0.43	0.54
2023-12-05 06:20	0.14	0.26	0.35	0.06	0.21	NA
2023-12-05 06:35	199.81	0.05	201.41	0.11	1.60	0.80
2023-12-05 06:50	99.89	0.10	100.68	0.02	0.79	0.79
2023-12-05 07:05	30.02	0.12	30.34	0.06	0.32	1.07
2023-12-05 07:20	10.10	0.22	10.39	0.04	0.29	2.87

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2023-12-05 07:35	149.83	0.08	150.91	0.10	1.08	0.72
2023-12-05 07:50	50.04	0.09	50.35	0.05	0.31	0.62
2023-12-05 08:05	19.99	0.09	20.26	0.07	0.27	1.35
2023-12-05 08:20	79.96	0.14	80.44	0.02	0.48	0.60
2023-12-05 08:35	59.99	0.12	60.31	0.10	0.32	0.53
2023-12-05 08:50	40.02	0.12	40.31	0.17	0.29	0.72
2023-12-05 09:05	70.00	0.05	70.58	0.08	0.58	0.83

Table 5. *Comparison of the CGO ozone analyser (OA) Thermo Scientific 49i-PS #1180930024 (BKG 0.0 nmol mol^{-1}, COEF 0.988) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2023-12-05 13:44	0.15	0.24	0.23	0.09	0.08	NA
2023-12-05 13:59	50.08	0.08	49.63	0.31	-0.45	-0.90
2023-12-05 14:14	199.81	0.06	199.35	0.25	-0.46	-0.23
2023-12-05 14:29	149.76	0.09	149.42	0.21	-0.34	-0.23
2023-12-05 14:44	99.90	0.11	99.58	0.19	-0.32	-0.32
2023-12-05 14:59	249.65	0.07	249.08	0.18	-0.57	-0.23
2023-12-05 15:14	25.04	0.12	24.78	0.10	-0.26	-1.04
2023-12-05 15:29	349.46	0.12	348.85	0.20	-0.61	-0.17
2023-12-05 15:44	224.69	0.07	224.24	0.14	-0.45	-0.20
2023-12-05 15:59	499.22	0.08	498.14	0.40	-1.08	-0.22
2023-12-05 16:14	74.93	0.11	74.41	0.16	-0.52	-0.69
2023-12-05 16:29	174.80	0.05	174.39	0.16	-0.41	-0.23
2023-12-05 16:44	124.85	0.09	124.25	0.23	-0.60	-0.48
2023-12-05 16:59	299.58	0.09	298.92	0.15	-0.66	-0.22
2023-12-05 17:14	449.33	0.09	448.88	0.22	-0.45	-0.10
2023-12-05 17:29	399.41	0.05	398.83	0.05	-0.58	-0.15
2023-12-05 17:44	0.16	0.23	0.01	0.11	-0.15	NA
2023-12-05 17:59	99.88	0.05	99.56	0.21	-0.32	-0.32
2023-12-05 18:14	25.02	0.19	24.81	0.23	-0.21	-0.84
2023-12-05 18:29	50.02	0.13	49.93	0.30	-0.09	-0.18
2023-12-05 18:44	149.83	0.04	149.36	0.21	-0.47	-0.31
2023-12-05 18:59	349.48	0.09	348.75	0.32	-0.73	-0.21
2023-12-05 19:14	199.78	0.04	199.48	0.21	-0.30	-0.15
2023-12-05 19:29	124.89	0.06	124.56	0.22	-0.33	-0.26
2023-12-05 19:44	399.43	0.07	398.72	0.19	-0.71	-0.18
2023-12-05 19:59	74.95	0.07	74.75	0.17	-0.20	-0.27
2023-12-05 20:14	174.85	0.09	174.24	0.18	-0.61	-0.35
2023-12-05 20:29	499.23	0.08	498.31	0.19	-0.92	-0.18
2023-12-05 20:44	249.63	0.04	248.96	0.12	-0.67	-0.27
2023-12-05 20:59	224.68	0.07	224.22	0.13	-0.46	-0.20
2023-12-05 21:14	449.30	0.14	448.58	0.26	-0.72	-0.16
2023-12-05 21:29	299.58	0.08	298.63	0.21	-0.95	-0.32
2023-12-05 21:44	0.26	0.28	0.15	0.03	-0.11	NA
2023-12-05 21:59	50.01	0.13	49.71	0.14	-0.30	-0.60
2023-12-05 22:14	149.77	0.08	149.11	0.44	-0.66	-0.44

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2023-12-05 22:29	99.94	0.11	99.66	0.31	-0.28	-0.28
2023-12-05 22:44	499.26	0.13	498.14	0.29	-1.12	-0.22
2023-12-05 22:59	299.60	0.06	298.85	0.24	-0.75	-0.25
2023-12-05 23:14	224.72	0.06	224.09	0.26	-0.63	-0.28
2023-12-05 23:29	24.99	0.10	24.90	0.12	-0.09	-0.36
2023-12-05 23:44	449.36	0.11	448.07	0.36	-1.29	-0.29
2023-12-05 23:59	399.38	0.08	398.40	0.35	-0.98	-0.25
2023-12-06 00:14	74.93	0.10	74.58	0.22	-0.35	-0.47
2023-12-06 00:29	124.87	0.06	124.43	0.34	-0.44	-0.35
2023-12-06 00:44	174.82	0.06	174.34	0.25	-0.48	-0.27
2023-12-06 00:59	349.50	0.11	348.60	0.38	-0.90	-0.26
2023-12-06 01:14	199.76	0.10	199.24	0.15	-0.52	-0.26
2023-12-06 01:29	0.19	0.18	0.12	0.06	-0.07	NA
2023-12-06 01:44	50.05	0.17	49.76	0.29	-0.29	-0.58
2023-12-06 01:59	199.74	0.09	199.22	0.29	-0.52	-0.26
2023-12-06 02:14	149.90	0.11	149.30	0.05	-0.60	-0.40
2023-12-06 02:29	99.89	0.06	99.69	0.30	-0.20	-0.20
2023-12-06 02:44	249.58	0.10	248.76	0.31	-0.82	-0.33
2023-12-06 02:59	25.05	0.16	24.77	0.09	-0.28	-1.12
2023-12-06 03:14	349.53	0.12	348.71	0.35	-0.82	-0.23
2023-12-06 03:29	224.69	0.06	224.04	0.16	-0.65	-0.29
2023-12-06 03:44	499.23	0.14	498.09	0.33	-1.14	-0.23
2023-12-06 03:59	74.94	0.04	74.63	0.22	-0.31	-0.41
2023-12-06 04:14	174.76	0.12	174.36	0.23	-0.40	-0.23
2023-12-06 04:29	124.92	0.09	124.36	0.17	-0.56	-0.45
2023-12-06 04:44	299.60	0.07	299.10	0.16	-0.50	-0.17
2023-12-06 04:59	449.29	0.03	448.05	0.10	-1.24	-0.28
2023-12-06 05:14	399.41	0.10	398.42	0.28	-0.99	-0.25
2023-12-06 05:29	0.26	0.21	0.03	0.10	-0.23	NA
2023-12-06 05:44	99.92	0.07	99.22	0.30	-0.70	-0.70
2023-12-06 05:59	25.10	0.09	25.10	0.20	0.00	0.00
2023-12-06 06:14	50.02	0.10	49.65	0.21	-0.37	-0.74
2023-12-06 06:29	149.82	0.05	149.25	0.29	-0.57	-0.38
2023-12-06 06:44	349.53	0.14	348.55	0.22	-0.98	-0.28
2023-12-06 06:59	199.77	0.08	199.30	0.10	-0.47	-0.24
2023-12-06 07:14	124.87	0.06	124.38	0.18	-0.49	-0.39
2023-12-06 07:29	399.35	0.10	398.24	0.19	-1.11	-0.28
2023-12-06 07:44	74.94	0.03	74.58	0.13	-0.36	-0.48
2023-12-06 07:59	174.82	0.06	174.26	0.14	-0.56	-0.32
2023-12-06 08:14	499.15	0.08	497.86	0.25	-1.29	-0.26
2023-12-06 08:29	249.70	0.06	249.17	0.14	-0.53	-0.21
2023-12-06 08:44	224.71	0.10	224.07	0.25	-0.64	-0.28
2023-12-06 08:59	449.35	0.05	448.23	0.23	-1.12	-0.25
2023-12-06 09:14	299.56	0.09	298.55	0.07	-1.01	-0.34

Table 6. *Comparison of the CGO ozone calibrator (OC) Thermo Scientific 49i-PS # 1315588104 (BKG -0.4 nmol mol⁻¹, COEF 1.003) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2023-12-06 13:06	0.16	0.13	-0.09	0.08	-0.25	NA
2023-12-06 13:21	50.04	0.13	51.90	0.20	1.86	3.72
2023-12-06 13:36	199.75	0.09	208.34	0.10	8.59	4.30
2023-12-06 13:51	149.81	0.06	155.92	0.27	6.11	4.08
2023-12-06 14:06	99.94	0.09	104.32	0.20	4.38	4.38
2023-12-06 14:21	249.67	0.07	259.70	0.23	10.03	4.02
2023-12-06 14:36	25.15	0.13	26.29	0.26	1.14	4.53
2023-12-06 14:51	349.47	0.04	364.04	0.17	14.57	4.17
2023-12-06 15:06	224.75	0.07	233.90	0.11	9.15	4.07
2023-12-06 15:21	499.27	0.09	520.70	0.30	21.43	4.29
2023-12-06 15:36	74.93	0.10	77.76	0.17	2.83	3.78
2023-12-06 15:51	174.80	0.02	181.97	0.13	7.17	4.10
2023-12-06 16:06	124.84	0.06	130.16	0.04	5.32	4.26
2023-12-06 16:21	299.57	0.08	312.47	0.19	12.90	4.31
2023-12-06 16:36	449.34	0.04	467.85	0.18	18.51	4.12
2023-12-06 16:51	399.37	0.07	416.58	0.22	17.21	4.31
2023-12-06 17:06	0.11	0.14	0.06	0.09	-0.05	NA
2023-12-06 17:21	99.95	0.12	104.13	0.24	4.18	4.18
2023-12-06 17:36	24.98	0.09	25.63	0.23	0.65	2.60
2023-12-06 17:51	50.00	0.09	52.06	0.22	2.06	4.12
2023-12-06 18:06	149.87	0.08	156.06	0.23	6.19	4.13
2023-12-06 18:21	349.45	0.10	363.99	0.23	14.54	4.16
2023-12-06 18:36	199.75	0.08	207.93	0.35	8.18	4.10
2023-12-06 18:51	124.86	0.06	129.89	0.22	5.03	4.03
2023-12-06 19:06	399.43	0.07	416.22	0.16	16.79	4.20
2023-12-06 19:21	74.96	0.08	77.84	0.16	2.88	3.84
2023-12-06 19:36	174.79	0.04	181.93	0.21	7.14	4.08
2023-12-06 19:51	499.31	0.06	520.60	0.25	21.29	4.26
2023-12-06 20:06	249.66	0.09	260.03	0.14	10.37	4.15
2023-12-06 20:21	224.73	0.05	234.07	0.21	9.34	4.16
2023-12-06 20:36	449.33	0.08	468.24	0.32	18.91	4.21
2023-12-06 20:51	299.55	0.06	312.18	0.16	12.63	4.22
2023-12-06 21:06	0.19	0.16	-0.05	0.16	-0.24	NA
2023-12-06 21:21	50.03	0.18	52.09	0.19	2.06	4.12
2023-12-06 21:36	149.89	0.05	156.18	0.27	6.29	4.20
2023-12-06 21:51	99.91	0.09	104.09	0.12	4.18	4.18
2023-12-06 22:06	499.20	0.05	520.06	0.41	20.86	4.18
2023-12-06 22:21	299.53	0.04	311.67	0.31	12.14	4.05
2023-12-06 22:36	224.72	0.07	234.16	0.17	9.44	4.20
2023-12-06 22:51	25.07	0.23	26.02	0.21	0.95	3.79
2023-12-06 23:06	449.41	0.05	468.44	0.14	19.03	4.23
2023-12-06 23:21	399.36	0.07	416.31	0.11	16.95	4.24
2023-12-06 23:36	74.93	0.05	77.83	0.05	2.90	3.87
2023-12-06 23:51	124.87	0.12	129.94	0.15	5.07	4.06
2023-12-07 00:06	174.77	0.13	181.91	0.30	7.14	4.09
2023-12-07 00:21	349.49	0.06	364.06	0.23	14.57	4.17

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OC (nmol mol^{-1})	sdOC (nmol mol^{-1})	OC-TS (nmol mol^{-1})	OC-TS (%)
2023-12-07 00:36	199.70	0.04	207.88	0.11	8.18	4.10
2023-12-07 00:51	0.04	0.17	-0.04	0.11	-0.08	NA
2023-12-07 01:06	50.05	0.09	51.76	0.34	1.71	3.42
2023-12-07 01:21	199.71	0.05	207.97	0.39	8.26	4.14
2023-12-07 01:36	149.86	0.11	156.01	0.08	6.15	4.10
2023-12-07 01:51	99.91	0.09	103.94	0.22	4.03	4.03
2023-12-07 02:06	249.66	0.15	260.15	0.56	10.49	4.20
2023-12-07 02:21	25.05	0.12	25.95	0.19	0.90	3.59
2023-12-07 02:36	349.52	0.12	364.01	0.47	14.49	4.15
2023-12-07 02:51	224.70	0.20	234.27	0.44	9.57	4.26
2023-12-07 03:06	499.26	0.08	520.23	0.16	20.97	4.20
2023-12-07 03:21	75.01	0.05	77.96	0.25	2.95	3.93
2023-12-07 03:36	174.79	0.04	181.89	0.11	7.10	4.06
2023-12-07 03:51	124.84	0.12	130.09	0.31	5.25	4.21
2023-12-07 04:06	299.54	0.10	312.14	0.30	12.60	4.21
2023-12-07 04:21	449.33	0.07	468.04	0.20	18.71	4.16
2023-12-07 04:36	399.42	0.06	416.09	0.24	16.67	4.17
2023-12-07 04:51	-0.01	0.17	-0.05	0.09	-0.04	NA
2023-12-07 05:06	99.94	0.06	103.94	0.19	4.00	4.00
2023-12-07 05:21	25.05	0.14	25.92	0.14	0.87	3.47
2023-12-07 05:36	49.98	0.07	51.82	0.10	1.84	3.68
2023-12-07 05:51	149.84	0.03	155.75	0.24	5.91	3.94
2023-12-07 06:06	349.49	0.07	364.09	0.25	14.60	4.18
2023-12-07 06:21	199.76	0.14	208.01	0.30	8.25	4.13
2023-12-07 06:36	124.87	0.06	129.82	0.15	4.95	3.96
2023-12-07 06:51	399.42	0.05	415.95	0.19	16.53	4.14
2023-12-07 07:06	75.00	0.10	77.99	0.37	2.99	3.99
2023-12-07 07:21	174.78	0.06	181.92	0.24	7.14	4.09
2023-12-07 07:36	499.28	0.08	520.28	0.22	21.00	4.21
2023-12-07 07:51	249.66	0.06	259.79	0.43	10.13	4.06
2023-12-07 08:06	224.66	0.01	233.64	0.17	8.98	4.00
2023-12-07 08:21	449.34	0.07	468.26	0.26	18.92	4.21
2023-12-07 08:36	299.59	0.05	311.83	0.26	12.24	4.09

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 6 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 shown in the Executive Summary, and the individual measurements of the TS are shown in the following tables.

Table 7. *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G5310 #5066-DAS-JKADS5075 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 (%)
(24-01-05 01:53:00)	150601_FA02493	1319.8	0.8	1379.1	1.6	3	59.4	4.5
(23-12-06 06:25:00)	171124_FA02786	150.0	0.2	153.3	0.0	3	3.3	2.2
(23-12-11 04:37:00)	181128_FF61471	111.5	1.1	113.6	0.0	3	2.1	1.9
(23-12-09 06:38:00)	220124_FA02773	-0.1	0.4	0.3	0.3	5	0.4	NA
(24-01-04 02:50:00)	230424_FB03894	6.9	0.7	7.9	0.0	3	1.0	14.3
(23-12-12 01:53:00)	230425_FB03853	49.8	0.2	49.3	0.0	3	-0.5	-1.0
(23-12-07 03:22:00)	230425_FB03865	43.0	0.4	42.4	0.0	3	-0.6	-1.4
(24-01-03 03:29:20)	230425_FB03911	70.4	0.4	69.9	0.0	3	-0.4	-0.6
(23-12-05 07:19:20)	230426_FB03904	89.2	0.2	89.8	0.0	3	0.6	0.7
(23-12-13 02:36:00)	230427_FB03918	206.6	0.4	211.8	0.0	3	5.2	2.5

Table 8. *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the CGO GC-MD instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(23-12-15 12:11:48)	171124_FA02786	149.1	4.3	155.1	0.8	24	5.9	4.0
(23-12-15 08:35:16)	181128_FF61471	109.7	3.2	118.7	2.2	11	9.0	8.2
(24-01-03 06:18:00)	230425_FB03853	48.0	2.8	47.2	1.8	14	-0.8	-1.6
(23-12-13 20:47:04)	230425_FB03865	41.5	2.4	39.8	0.8	29	-1.7	-4.1
(24-01-05 05:20:00)	230425_FB03911	68.5	2.3	67.3	1.2	14	-1.3	-1.8
(23-12-28 17:32:39)	230426_FB03904	87.1	2.7	88.5	1.0	17	1.4	1.6
(24-01-04 06:39:00)	230427_FB03918	204.8	2.4	194.3	0.4	14	-10.5	-5.1

Table 9. *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the GASLAB GC-RGD 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 (%)
(24-03-15 00:00:00)	230427_FB03918	204.8	2.4	204.2	0.8	3	-0.7	-0.3
(24-03-12 00:00:00)	171124_FA02786	149.1	4.3	153.4	0.8	2	4.3	2.9
(24-03-09 00:00:00)	181128_FF61471	109.7	3.2	116.5	0.3	2	6.8	6.2
(24-03-09 00:00:00)	230426_FB03904	87.1	2.7	90.3	0.1	2	3.1	3.6
(24-03-11 08:00:00)	230425_FB03911	68.5	2.3	70.9	0.0	3	2.4	3.5
(24-03-08 00:00:00)	230425_FB03853	48.0	2.8	50.2	0.1	2	2.2	4.7
(24-03-11 08:00:00)	230425_FB03865	41.5	2.4	43.4	0.2	3	1.9	4.6

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 6 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 shown 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 G2301 #1151-CFADS2263 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 (%)
(24-01-08 01:50:00)	150601_FA02493	1868.06	0.06	1869.30	0.04	3	1.24	0.07
(23-12-07 02:11:00)	171124_FA02786	2193.71	0.08	2195.03	0.02	3	1.32	0.06
(23-12-12 01:24:00)	181128_FF61471	1989.77	0.09	1990.94	0.22	3	1.17	0.06
(23-12-11 03:41:00)	220124_FA02773	3.07	0.08	3.43	0.00	2	0.36	11.73
(24-01-05 01:29:00)	230424_FB03894	2.90	0.04	3.19	0.02	3	0.29	10.00
(23-12-13 01:51:00)	230425_FB03853	1874.49	0.08	1875.46	0.08	3	0.97	0.05
(23-12-07 06:34:00)	230425_FB03865	1806.76	0.11	1807.80	0.15	3	1.04	0.06
(24-01-04 03:25:00)	230425_FB03911	1893.39	0.08	1894.42	0.09	3	1.03	0.05
(23-12-06 04:34:00)	230426_FB03904	1926.38	0.07	1927.36	0.10	3	0.98	0.05
(24-01-03 02:30:00)	230427_FB03918	1979.28	0.06	1980.19	0.02	3	0.91	0.05

Table 11. *CH_4 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the CGO GC-MD 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 (%)
(24-01-09 04:32:04)	150601_FA02493	1868.06	0.06	1869.13	1.12	14	1.07	0.06
(23-12-14 23:28:25)	171124_FA02786	2193.71	0.08	2195.51	1.03	22	1.80	0.08
(23-12-16 04:08:00)	181128_FF61471	1989.77	0.09	1991.48	0.74	14	1.71	0.09
(24-01-03 06:18:00)	230425_FB03853	1874.49	0.08	1875.48	1.10	14	0.99	0.05
(23-12-16 02:46:33)	230425_FB03865	1806.76	0.11	1808.28	0.94	20	1.52	0.08
(24-01-05 05:20:00)	230425_FB03911	1893.39	0.08	1895.28	0.94	14	1.89	0.10
(23-12-28 17:32:39)	230426_FB03904	1926.38	0.07	1929.03	1.09	17	2.65	0.14
(24-01-04 06:39:00)	230427_FB03918	1979.28	0.06	1981.61	1.08	14	2.33	0.12

Table 12. *CH_4 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the GASLAB GC-FID 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 (%)
(24-03-15 00:00:00)	150601_FA02493	1868.06	0.06	1870.11	0.66	2	2.05	0.11
(24-03-15 00:00:00)	230427_FB03918	1979.28	0.06	1979.38	0.85	3	0.10	0.01
(24-03-12 00:00:00)	171124_FA02786	2193.71	0.08	2193.79	0.06	2	0.08	0.00
(24-03-09 00:00:00)	181128_FF61471	1989.77	0.09	1989.70	0.62	2	-0.07	0.00
(24-03-09 00:00:00)	230426_FB03904	1926.38	0.07	1926.05	0.74	2	-0.34	-0.02
(24-03-11 08:00:00)	230425_FB03911	1893.39	0.08	1893.62	1.96	3	0.23	0.01
(24-03-08 00:00:00)	230425_FB03853	1874.49	0.08	1875.55	0.47	2	1.06	0.06
(24-03-11 08:00:00)	230425_FB03865	1806.76	0.11	1806.07	1.48	3	-0.69	-0.04

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

Table 13. *CO_2 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2301 #1151-CFADS2263 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 (%)
(24-01-08 01:50:00)	150601_FA02493	389.21	0.03	389.24	0.01	3	0.03	0.01
(23-12-07 02:11:00)	171124_FA02786	468.52	0.03	468.62	0.00	3	0.10	0.02
(23-12-12 01:24:00)	181128_FF61471	401.89	0.02	401.93	0.01	3	0.04	0.01
(23-12-11 03:41:00)	220124_FA02773	0.12	0.02	-0.28	0.00	2	-0.40	NA
(24-01-05 01:29:00)	230424_FB03894	0.39	0.02	-0.01	0.00	3	-0.40	NA
(23-12-13 01:51:00)	230425_FB03853	410.57	0.01	410.60	0.01	3	0.03	0.01
(23-12-07 06:34:00)	230425_FB03865	400.50	0.03	400.51	0.01	3	0.01	0.00
(24-01-04 03:25:00)	230425_FB03911	420.09	0.02	420.11	0.01	3	0.02	0.00
(23-12-06 04:34:00)	230426_FB03904	429.84	0.04	429.87	0.00	3	0.03	0.01
(24-01-03 02:30:00)	230427_FB03918	435.96	0.03	436.00	0.00	3	0.04	0.01

Table 14. *CO_2 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the CSIRO GASLAB GC-FID 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 (%)
(24-03-15 00:00:00)	150601_FA02493	389.21	0.03	389.24	0.04	2	0.04	0.01
(24-03-15 00:00:00)	230427_FB03918	435.96	0.03	435.72	0.06	3	-0.24	-0.06
(24-03-12 00:00:00)	171124_FA02786	468.52	0.03	468.53	0.04	2	0.01	0.00
(24-03-09 00:00:00)	181128_FF61471	401.89	0.02	401.90	0.01	2	0.01	0.00
(24-03-09 00:00:00)	230426_FB03904	429.84	0.04	429.64	0.00	2	-0.20	-0.05
(24-03-11 08:00:00)	230425_FB03911	420.09	0.02	419.92	0.04	3	-0.17	-0.04
(24-03-08 00:00:00)	230425_FB03853	410.57	0.01	410.48	0.01	2	-0.08	-0.02
(24-03-11 08:00:00)	230425_FB03865	400.50	0.03	400.42	0.04	3	-0.08	-0.02

A7. Nitrous oxide 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 6 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 shown in the Executive Summary, and the individual measurements of the TS are presented in the following tables.

Results

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

Table 15. *N_2O aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G5310 #5066-DAS-JKADS5075 instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (µmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(24-01-05 01:53:00)	150601_FA02493	319.86	0.05	319.50	0.09	3	-0.36	-0.11
(23-12-06 06:25:00)	171124_FA02786	377.82	0.09	377.89	0.01	3	0.07	0.02
(23-12-11 04:37:00)	181128_FF61471	333.15	0.04	333.13	0.01	3	-0.02	-0.01
(23-12-12 01:53:00)	230425_FB03853	333.41	0.04	333.43	0.01	3	0.02	0.01
(23-12-07 03:22:00)	230425_FB03865	334.57	0.07	334.51	0.01	3	-0.06	-0.02
(24-01-03 03:29:20)	230425_FB03911	335.87	0.05	335.95	0.01	3	0.08	0.02
(23-12-05 07:19:20)	230426_FB03904	343.24	0.04	343.38	0.01	3	0.14	0.04
(23-12-13 02:36:00)	230427_FB03918	341.50	0.05	341.81	0.01	3	0.31	0.09

Table 16. *N_2O aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the CGO GC-MD instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (µmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(24-01-09 04:32:04)	150601_FA02493	319.86	0.05	319.72	0.16	14	-0.14	-0.04
(23-12-15 12:11:48)	171124_FA02786	377.82	0.09	379.44	0.25	24	1.62	0.43
(23-12-16 04:08:00)	181128_FF61471	333.15	0.04	332.87	0.69	14	-0.28	-0.08
(24-01-03 06:18:00)	230425_FB03853	333.41	0.04	333.32	0.48	14	-0.09	-0.03
(23-12-16 17:26:57)	230425_FB03865	334.58	0.04	334.60	0.21	20	0.02	0.01
(24-01-05 05:20:00)	230425_FB03911	335.87	0.05	336.18	0.09	14	0.31	0.09
(23-12-28 17:32:39)	230426_FB03904	343.24	0.04	343.46	0.35	17	0.22	0.06
(24-01-04 06:39:00)	230427_FB03918	341.50	0.05	342.04	0.17	14	0.54	0.16

Table 17. *N_2O aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the CSIRO GASLAB GC-ECD instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (µmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(24-03-14 00:00:00)	150601_FA02493	319.86	0.05	319.77	0.03	2	-0.09	-0.03
(24-03-14 01:00:00)	230427_FB03918	341.50	0.05	341.41	0.00	2	-0.09	-0.03
(24-03-09 01:00:00)	171124_FA02786	377.82	0.09	377.78	0.11	2	-0.04	-0.01
(24-03-12 01:30:00)	181128_FF61471	333.15	0.04	333.00	0.12	2	-0.15	-0.05
(24-03-07 02:00:00)	230426_FB03904	343.24	0.04	343.03	0.01	2	-0.21	-0.06
(24-03-07 03:00:00)	230425_FB03911	335.87	0.05	335.64	0.01	2	-0.23	-0.07
(24-03-07 04:00:00)	230425_FB03853	333.41	0.04	333.19	0.03	2	-0.22	-0.07
(24-03-07 05:00:00)	230425_FB03865	334.57	0.07	334.38	0.05	2	-0.19	-0.06
(24-03-14 00:00:00)	150601_FA02493	319.86	0.05	319.77	0.03	2	-0.09	-0.03

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 18. The TS passed the pre-audit evaluation criteria defined for maximum acceptable bias (Klausen et al., 2003) (see Figure 44). 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 33). The uncertainty of the TS (Equation 34) was previously estimated (see equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] + 0.09\ \text{nmol mol}^{-1}) / 1.0017 \quad (33)$$

$$u_{TS}\ (\text{nmol mol}^{-1}) = \text{sqrt}\,((0.43\ \text{nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (34)$$

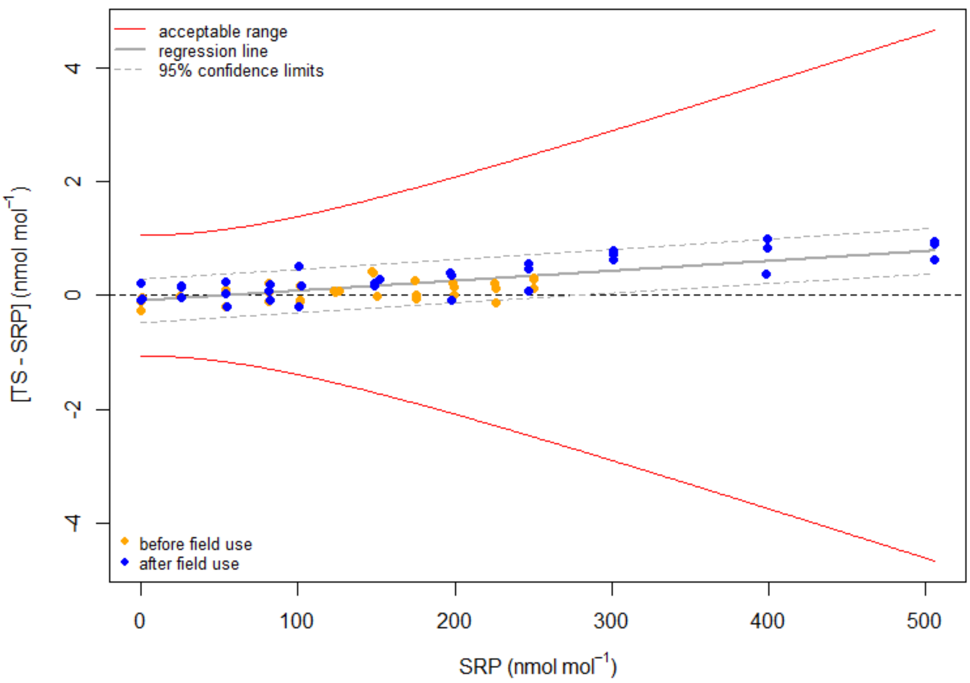

Figure 44. *Deviations between Traveling Standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS in the field.*

Table 18. *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})
2023-08-09	1	125	126.11	0.19	126.19	0.20
2023-08-09	1	0	0.02	0.17	-0.24	0.24
2023-08-09	1	55	54.21	0.28	54.31	0.29
2023-08-09	1	200	199.66	0.12	199.67	0.24
2023-08-09	1	100	101.24	0.11	101.14	0.23
2023-08-09	1	250	250.06	0.25	250.34	0.16
2023-08-09	1	150	150.36	0.14	150.35	0.23
2023-08-09	1	225	226.21	0.21	226.09	0.32
2023-08-09	1	175	175.49	0.24	175.49	0.31
2023-08-09	1	80	81.18	0.33	81.40	0.25
2023-08-09	1	25	24.67	0.15	24.66	0.17
2023-08-09	2	150	147.20	0.27	147.62	0.17
2023-08-09	2	100	101.07	0.16	100.99	0.19
2023-08-09	2	25	24.80	0.34	24.80	0.21
2023-08-09	2	250	250.19	0.36	250.31	0.36
2023-08-09	2	225	226.14	0.22	226.27	0.21
2023-08-09	2	175	175.45	0.30	175.40	0.24
2023-08-09	2	0	0.06	0.33	-0.04	0.17
2023-08-09	2	125	123.24	0.22	123.31	0.16
2023-08-09	2	200	198.83	0.29	199.05	0.22
2023-08-09	2	80	81.24	0.19	81.29	0.19
2023-08-09	2	55	54.17	0.06	53.98	0.24
2023-08-09	3	200	199.75	0.17	199.89	0.15
2023-08-09	3	250	250.54	0.19	250.84	0.26
2023-08-09	3	80	81.22	0.41	81.13	0.31
2023-08-09	3	25	24.76	0.21	24.75	0.28
2023-08-09	3	125	123.62	0.18	123.69	0.17
2023-08-09	3	0	0.11	0.33	0.07	0.17
2023-08-09	3	150	147.77	0.14	148.17	0.22
2023-08-09	3	55	54.08	0.36	54.17	0.21
2023-08-09	3	175	174.73	0.15	174.99	0.28
2023-08-09	3	225	225.34	0.20	225.55	0.24
2023-08-09	3	100	101.32	0.24	101.50	0.15
2024-04-30	4	150	148.62	0.42	148.84	0.28
2024-04-30	4	400	399.03	0.39	399.41	0.34
2024-04-30	4	80	81.54	0.33	81.62	0.15
2024-04-30	4	100	100.47	0.50	100.28	0.15
2024-04-30	4	200	197.57	0.29	197.93	0.33
2024-04-30	4	0	0.10	0.31	0.01	0.17
2024-04-30	4	245	247.10	0.31	247.57	0.22
2024-04-30	4	55	53.59	0.36	53.84	0.22
2024-04-30	4	300	301.38	0.22	302.17	0.20
2024-04-30	4	505	506.12	0.35	506.76	0.37
2024-04-30	4	25	25.31	0.38	25.47	0.27
2024-04-30	5	25	25.79	0.36	25.76	0.24

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2024-04-30	5	55	54.34	0.30	54.15	0.25
2024-04-30	5	150	149.09	0.28	149.27	0.26
2024-04-30	5	80	81.89	0.18	82.09	0.27
2024-04-30	5	100	100.40	0.18	100.92	0.27
2024-04-30	5	300	301.37	0.45	302.00	0.31
2024-04-30	5	0	0.16	0.33	0.10	0.25
2024-04-30	5	200	197.53	0.50	197.45	0.21
2024-04-30	5	245	246.74	0.31	247.30	0.38
2024-04-30	5	400	399.84	0.43	400.83	0.23
2024-04-30	5	505	505.65	0.38	506.55	0.47
2024-04-30	6	0	-0.01	0.46	0.20	0.52
2024-04-30	6	245	247.26	0.42	247.34	0.29
2024-04-30	6	55	53.67	0.24	53.69	0.29
2024-04-30	6	505	506.12	0.65	507.07	0.32
2024-04-30	6	100	101.73	0.32	101.90	0.24
2024-04-30	6	80	82.12	0.42	82.04	0.40
2024-04-30	6	25	25.73	0.17	25.87	0.20
2024-04-30	6	300	301.39	0.33	302.12	0.42
2024-04-30	6	400	399.45	0.55	400.29	0.32
2024-04-30	6	200	196.81	0.18	197.22	0.28
2024-04-30	6	150	151.76	0.38	152.05	0.45

#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 was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL through travelling standards and by addition of new laboratory standards from the CCL. For the assignment of the amount fractions to the TS, the following calibration scales were used:

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

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

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

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

Table 19 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 20, and Figure 45 shows the analysis of the TS over time.

Table 19. *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 20. *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	Press. (psi)	CH_4 (P) (nmol mol^{-1})	sd	CO_2 (P) (µmol mol^{-1})	sd	N_2O (L) (nmol mol^{-1})	sd	CO (P) (nmol mol^{-1})	sd
150601_FA02493	1030	1868.06	0.06	389.21	0.03	319.86	0.05	1318.64	2.39
171124_FA02786	1300	2193.71	0.08	468.52	0.03	377.82	0.09	149.11	4.30
181128_FF61471	1200	1989.77	0.09	401.89	0.02	333.15	0.04	109.68	3.24
220124_FA02773	1410	3.07	0.08	0.12	0.02	11.67	2.78	-0.30	0.90
230424_FB03894	1260	2.90	0.04	0.39	0.02	15.72	0.77	7.11	1.03
230425_FB03853	1800	1874.49	0.08	410.57	0.01	333.41	0.04	48.00	2.80
230425_FB03865	1590	1806.76	0.11	400.50	0.03	334.57	0.07	41.50	2.36
230425_FB03911	1420	1893.39	0.08	420.09	0.02	335.87	0.05	68.52	2.27
230426_FB03904	1690	1926.38	0.07	429.84	0.04	343.24	0.04	87.13	2.72
230427_FB03918	1480	1979.28	0.06	435.96	0.03	341.50	0.05	204.83	2.39

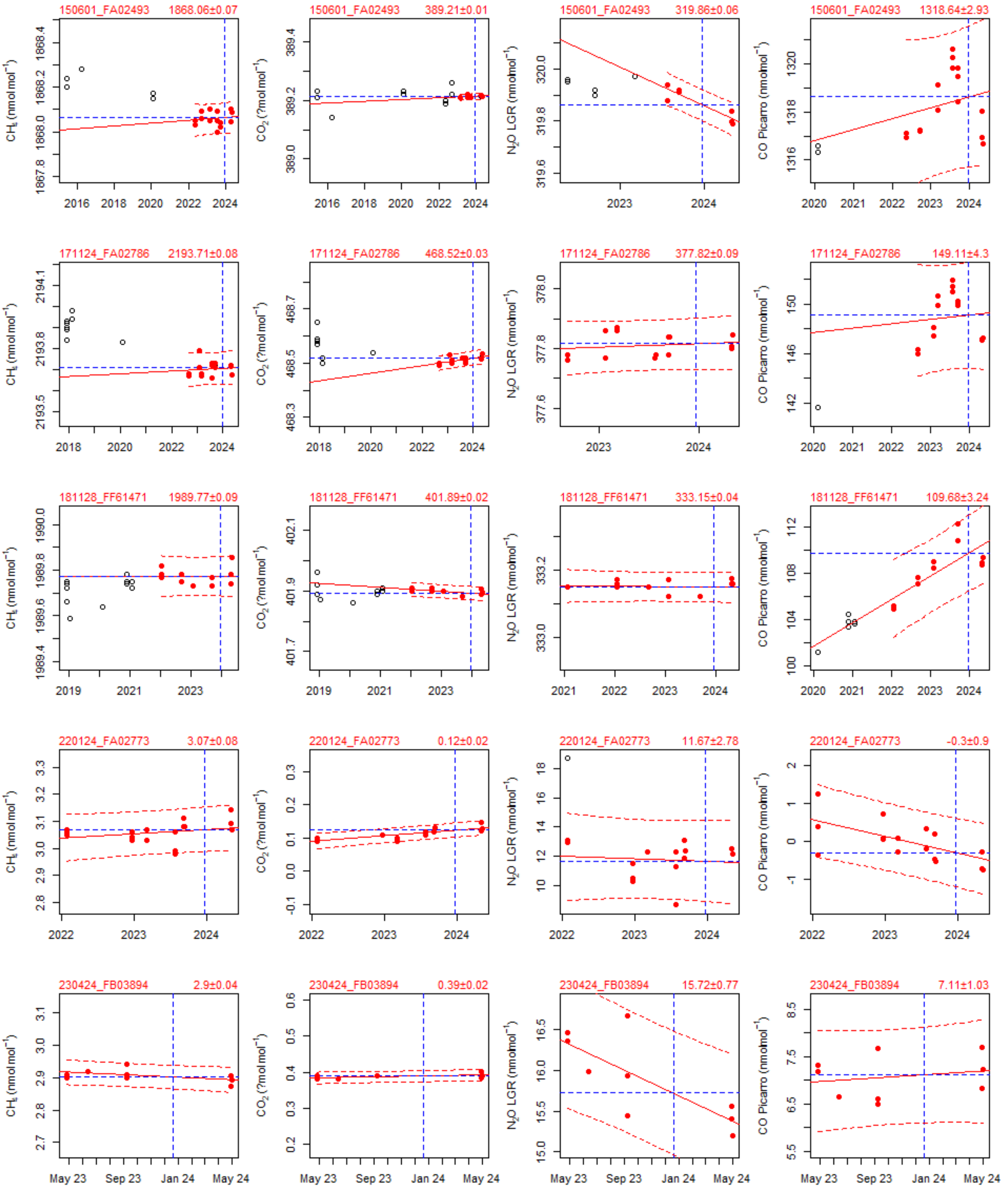

Figure 45. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, N_2O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the audit date.*

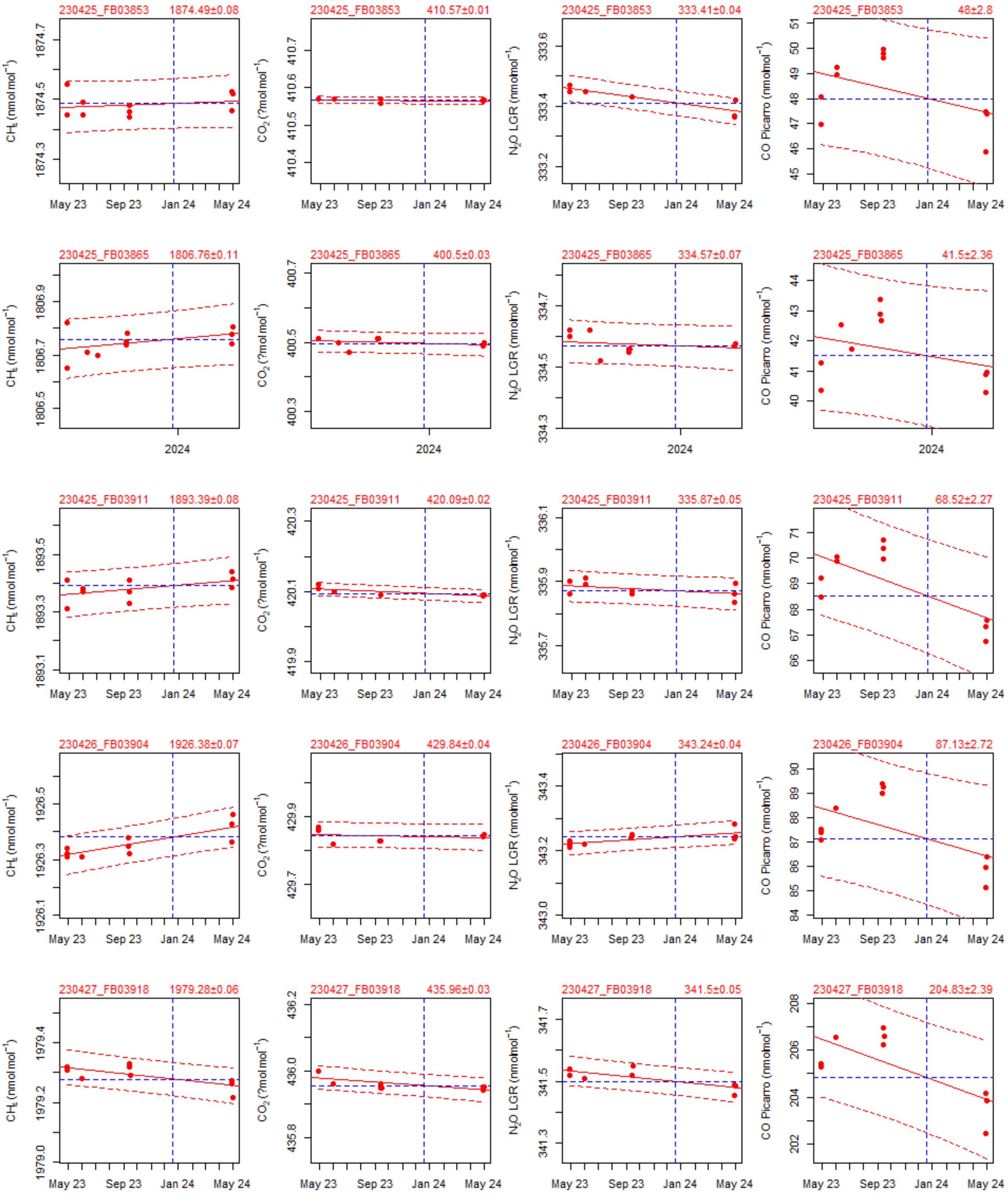

Figure 46. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, N_2O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard 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 3125 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 0.3 nmol mol^{-1} for CH_4 and 0.05 µmol mol^{-1} for CO_2. Almost all target cylinder measurements were within half of the WMO GAW compatibility goals.

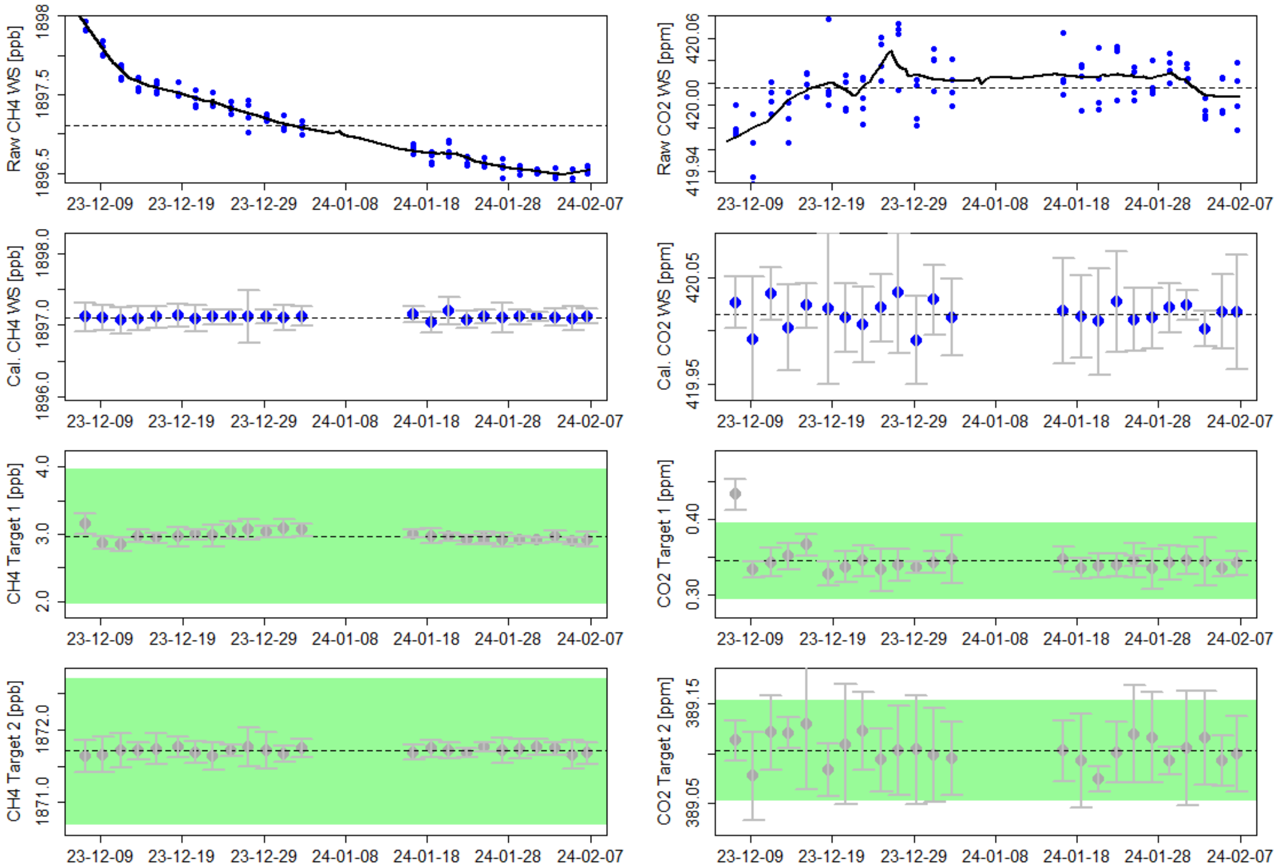

Figure 47. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The top panel shows the raw 1 min values of the working standard and the Loess fit (black line) used to account for the drift. The second panel shows the variation of the WS after application of the drift correction. The bottom panel shows the results from the two target cylinders. Individual points in the three lower panels are 5-minute averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 3125 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.

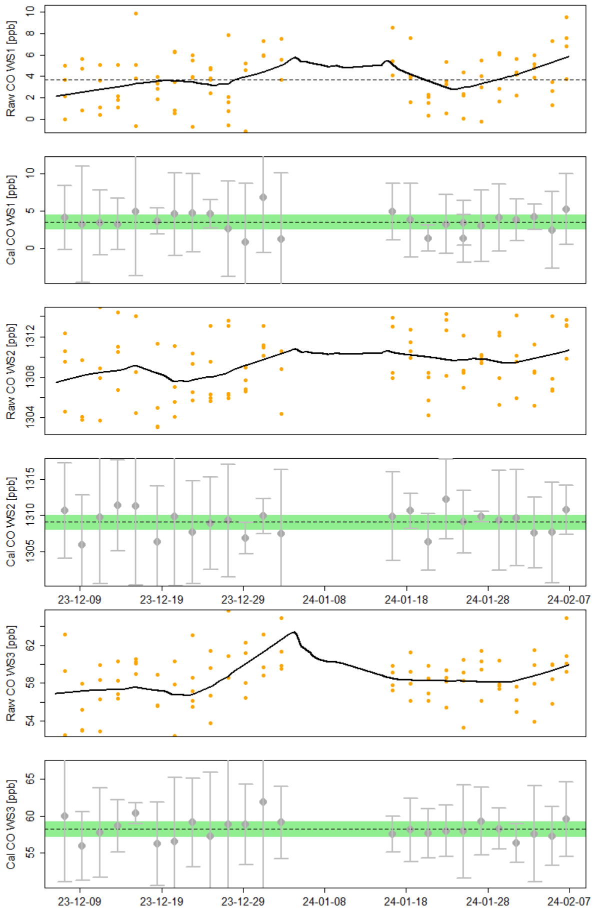

Figure 48. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show the raw 1 min values of the working standards and the Loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in 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.

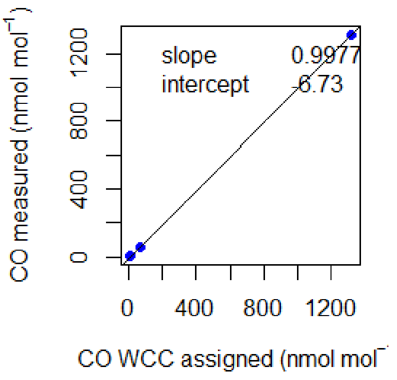

Figure 49. *CO calibration function based on the average values of the drift corrected working standard measurements.*

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List of abbreviations

ANSTO	Australia's Nuclear Science and Technology Organisation
BKG	Background
BoM	Australian Bureau of Meteorology
CCL	Central Calibration Laboratory
CGO	Kennaook / Cape Grim GAW Station
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
CSIRO	Commonwealth Scientific and Industrial Research Organisation
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
GC	Gas Chromatograph
GC-MD	Multidetector GC
GHG	Greenhouse Gases
IR	Infrared
LGR	Los Gatos Research
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
RGD	Reduction Gas Detector
SH	Southern Hemisphere
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