WCC-Empa Report 23/4

System and performance audit of Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide at the Regional GAW Station Baring Head, New Zealand, November 2023

Submitted to the World Meteorological Organization by

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1 Executive summary

The first WCC-Empa[1] system and performance audit at the Baring Head regional GAW station (BHD) took place from 27 to 30 November 2023, in accordance with the WMO/GAW quality assurance system (WMO, 2025). A list of all WCC-Empa audits and their respective reports can be found on the GAW-Empa website. The following persons contributed to this audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr Gordon Brailsford	NIWA, Station Manager
Dr Haeyoung Lee	NIWA, Atmospheric Scientist
Ms Sylvia Nichol	NIWA, Atmospheric Scientist

This report summarises the evaluation of the Baring Head GAW station in general, with a particular focus on the measurements of surface ozone, methane, carbon dioxide and carbon monoxide.

The report will be distributed to the station manager of the Baring Head GAW station, the National focal point for GAW in New Zealand and to the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and made available on the WCC-Empa website.

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

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

2 Site description and operation

2.1 Station management

The Baring Head Atmospheric Research Station has been in operation for over 50 years and is managed by the New Zealand National Institute of Water and Atmospheric Research (NIWA). The station is fully automated, and remote access to instruments and data is possible. Staff visit the site approximately weekly to maintain the equipment.

Further information about the station can be found on the GAWSIS and BHD websites.

2.2 Location and access

The Baring Head GAW station (41.40819°S, 174.8708°E, 85 m above sea level) was established in 1972 and is situated on a remote coastal cliff top on the south coast of New Zealand's North Island. It overlooks the South Pacific Ocean and is approximately 240 meters from the shoreline. The area between the station and the ocean comprises a strip of beach and a cliff face with sparse shrubby vegetation. Apart from a single residence to the north, there is no permanent habitation within a 3 km radius. The surrounding land is primarily used for low-density livestock farming. Wellington, a city with a population of around 380,000, is located 10 km to the northwest. Southerly wind episodes are prevalent and represent oceanic air from the south of New Zealand.

The site is fully adequate for a regional GAW station, and the air masses measured at BHD are usually representative of the unpolluted Southern Hemisphere (SH). Further information is available from the GAWSIS and BHD websites.

2.3 Station facilities

The laboratory of the BHD station is located in a concrete building and provides a small space for instruments. A second container provides a small office space. There is very limited space, and it is difficult to install additional instruments. The measurement building is air-conditioned, but the temperature can vary significantly. During the current audit, the temperature ranged from 18 to 24 °C and exhibited a pronounced diurnal cycle.

In conclusion, the BHD infrastructure is suitable for supporting the current measurements. The following recommendation is made for the facilities:

> **Recommendation 1 (**, important, when the measurement programme is expanded)**
> *The current situation is acceptable for the equipment in use. However, space is tight and needs to be increased if the measurement programme is expanded.*

2.4 Measurement programme

The measurement programme of BHD focuses on greenhouse and reactive gases. BHD has the longest CO_2 time series of the SH and is considered the main site for surface GHG measurements in New Zealand by NIWA. The Lauder GAW station, located further south, has a more extensive measurement programme with a focus on column observations, but does not prioritise GHG measurements. Together, BHD and Lauder provide complementary observations that strengthen New Zealand's contribution to the GAW network by covering both surface and column measurements across a range of atmospheric constituents. The scope and programme of the BHD station are fully adequate for a GAW regional station and, in fact, sufficient to meet the requirements of a GAW Global Observatory. BHD also maintains active collaborations with over seven international partners, covering both greenhouse gases and reactive gases, including their tracers. This underscores BHD's strong integration within the international scientific community and its significance in global atmospheric research.

Information available on GAWSIS was reviewed and updated during the audit. Updates are made regularly, and it is recommended that this practice continues.

2.5 Data management and data processing

Data from all analysers is acquired on a custom-made data acquisition system based on LabVIEW. This data, along with the raw data from the GHG analyser, is automatically transferred to NIWA and stored on a Unix machine that is regularly backed up by NIWA's IT department. Data processing is carried out at NIWA using R scripts.

2.6 Data submission

As of September 2025, the following BHD data within the scope of the audit were available at the World Data Centres:

NIWA data submitted to the World Data Centre for Reactive Gases (WDCRG):
O_3, three data sets:

1991-2021: https://doi.org/10.48597/APBU-HUQH
2005-2021: https://doi.org/10.48597/YAN5-YXBK (only minimum and maximum of hourly values)
2022-2023: https://doi.org/10.48597/MY4E-5ZG4

NIWA flask data, submitted to the World Data Centre for Greenhouse Gases (WDCGG):
CO (1998-2024), CH_4 (1989-2024)

NIWA in-situ data, submitted to the World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2016-2024), CO_2 (1972-2024)

NOAA flask data, submitted to the World Data Centre for Greenhouse Gases (WDCGG):
CO (1999-2023), CH_4 (1999-2024), CO_2 (1999-2024)

The data presented in this report were accessed on 10 September 2025.

Continuous CO data has not yet been submitted.

> **Recommendation 2 (**, important, 2025)**
> *Most data has been submitted with a delay of less than two years, but continuous CO data is not yet available. It is recommended that the CO time series is submitted too.*

2.7 Data review

As part of the system audit, the data available at WDCRG within the scope of WCC-Empa was reviewed. Summary graphs and a brief description of the findings can be found in the Appendix.

It was noted that the ozone data for 2022 and 2023 was lower than in previous years. This is most likely due to the faulty solenoid valve.

> **Recommendation 3 (***, critical, 2025)**
> *It is recommended that the ozone time series of ~2019 to 2023 is reviewed to check for a potential lower reading due to the faulty valve. If any irregularities are observed, the data should be corrected, if possible, or flagged as questionable or invalid.*

2.8 Documentation

Logbooks and check lists are available in electronic form (GHG and CO), or as handwritten notes (O_3). Instrument manuals are available on site. The information provided was comprehensive and up to date.

2.9 Air inlet system

GHGs and CO are sampled from a mast attached to the BHD measurement building (see picture on the right). Ambient air is drawn through a 6 mm Synflex-1300 line from a height of 10 m above ground. A diaphragm pump and a tee fitting control the air flow, sending ~230 ml/min to the analyser and ~3 l/min for purging. To remove water vapour, the air passes through three drying stages: a glass fridge trap at 2–6 °C and a stainless steel trap in a cryogenic ethanol bath at -80 °C, then a second smaller cryogenic trap for both the air sample and the standard tanks. This reduces the water content to approximately 1 µmol mol^{-1}. See Brailsford et al. (2012) for more details.

Ozone is sampled from the same mast using a dedicated 13 m PFA line. The airflow is controlled by the instrument (about 1 l/min) and the analyser is protected by a PTFE filter upstream of the analyser.

The inlet systems are adequate for the intended purpose.

3 Performance audit

3.1 Surface ozone measurements

Surface ozone measurements began at BHD in 1991, and continuous time series data are available since then.

Instrumentation. At the time of the audit, a Thermo Scientific ozone analyser (model 49i) was available. A backup instrument was available at NIWA headquarters, but it was out of order at the time of the audit.

Standards. BHD is equipped with a Teledyne API M700E dynamic dilution calibrator (manufactured in 2008). The instrument has an analogue output, and only the display readings are considered when it is used to calibration the ozone analyser.

> **Recommendation 4 (**, important, 2026)**
> *The current ozone calibration system has reached the end of its expected lifetime. It is therefore recommended that a newer ozone calibrator is purchased and that traceability is established to a NIST Standard Reference Photometer (SRP).*

Data acquisition. The data are downloaded using Thermo iPort software. The data are stored as 5-minute averages for ozone data only, and as hourly averages for ozone and ancillary data. When calibrations are being run, the data are stored as 1-minute averages.

Intercomparison (performance audit). The Thermo Scientific ozone analyser and calibrator of BHD were compared to the WCC-Empa Thermo Scientific 49i-PS ozone Travelling Standard (TS) with traceability to SRP#15. The internal ozone generator of the TS was used to generate a random sequence of ozone levels from 0 to 250 nmol mol^{-1}. The results of the comparisons are summarised below in relation to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). Data were collected using the WCC-Empa data acquisition system (Thermo instruments) and a National Instruments NI USB-6210 USB multifunction I/O device (Teledyne API M700E).

A significant deviation was found during the initial comparison of the BHD Thermo ozone analyser. The problem was identified as a leaking solenoid valve. Before the final comparison, the solenoid valve was replaced with one from an old analyser. However, this valve was dirty and not working properly, and, although the results improved, they did not meet the DQOs.

> **Recommendation 5 (***, critical, 2025)**
> *The BHD ozone analyser needs to be repaired. Given the age of the instrument, replacing it with a new one should also be considered.*

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.

BHD analyser Thermo Scientific 49i #1152220033 (BKG -0.1 nmol mol^{-1}, COEF 0.997), initial comparison, leaking solenoid valve:

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] – 0.05 nmol mol^{-1}) / 0.8856 (1)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt ((0.54 nmol mol^{-1})^2+ 2.06e-05 * X_{O3}^2) (2)

BHD analyser Thermo Scientific 49i #1152220033 (BKG -0.1 nmol mol^{-1}, COEF 0.997), final comparison after valve replacement:

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OA] + 0.31 nmol mol^{-1}) / 0.9712 (3)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt ((0.54 nmol mol^{-1})^2 + 2.06e-05 * X_{O3}^2) (4)

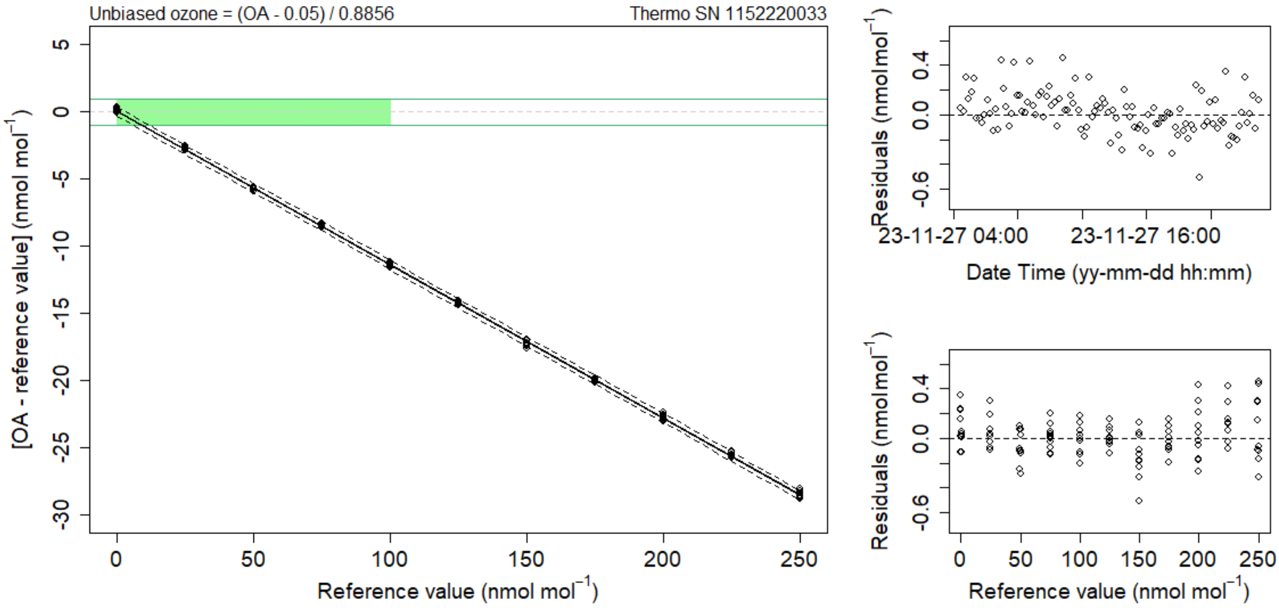

Figure 1. *Left: Bias of the BHD ozone analyser (Thermo Scientific 49i #1152220033, BKG -0.1 nmol mol^{-1}, COEF 0.997, initial comparison, leaking solenoid valve) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given 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).*

After the initial comparison, the broken solenoid valve was replaced and the instrument was again compared to the TS. The results were as follows:

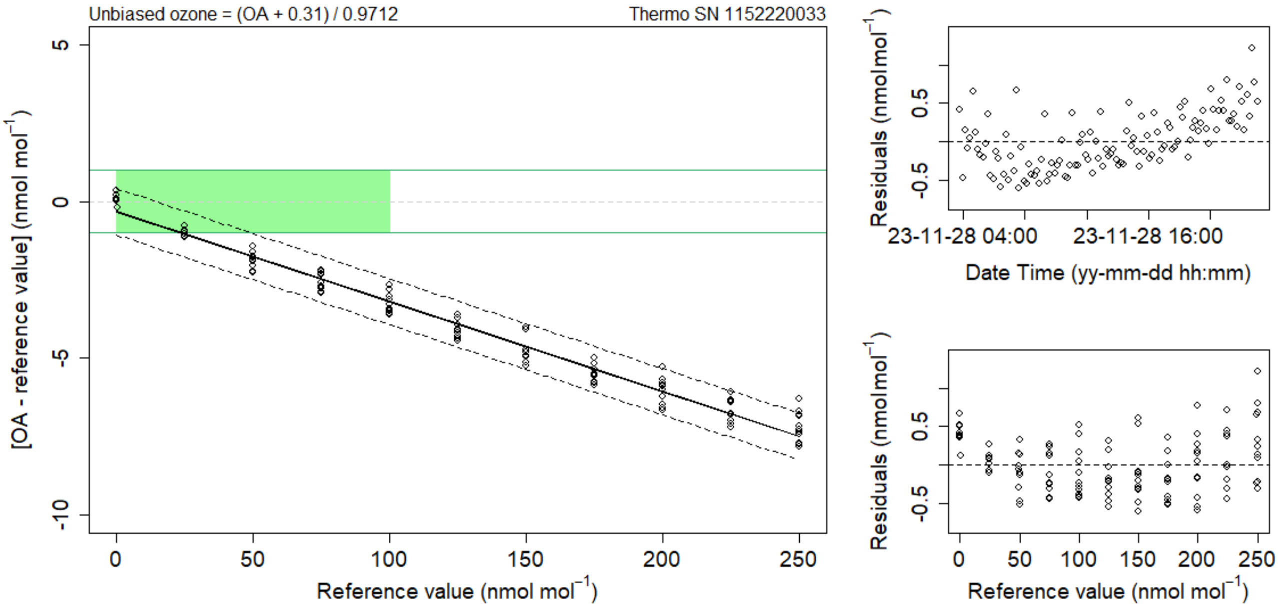

Figure 2. *Left: Bias of the BHD ozone analyser (Thermo Scientific 49i #1152220033, BKG -0.1 nmol mol⁻¹, COEF 0.997, final comparison after valve replacement) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. 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).*

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

The BHD Thermo Scientific 49i #1152220033 had a faulty solenoid valve, which was replaced with an old but functioning valve during the audit. Nevertheless, the instrument produced lower readings and requires a full service or replacement (see the above recommendation).

BHD calibrator Teledyne API M700E #528 (BKG 1.1 nmol mol^{-1}, SPAN 0.992):

Unbiased O_3 amount fraction X_{O3} (nmol mol^{-1}): X_{O3} = ([OC] – 1.14 nmol mol^{-1}) / 1.0068 (5)

Standard uncertainty u_{O3} (nmol mol^{-1}): u_{O3} = sqrt ((0.54 nmol mol^{-1})^2 + 2.08e-05 * X_{O3}^2) (6)

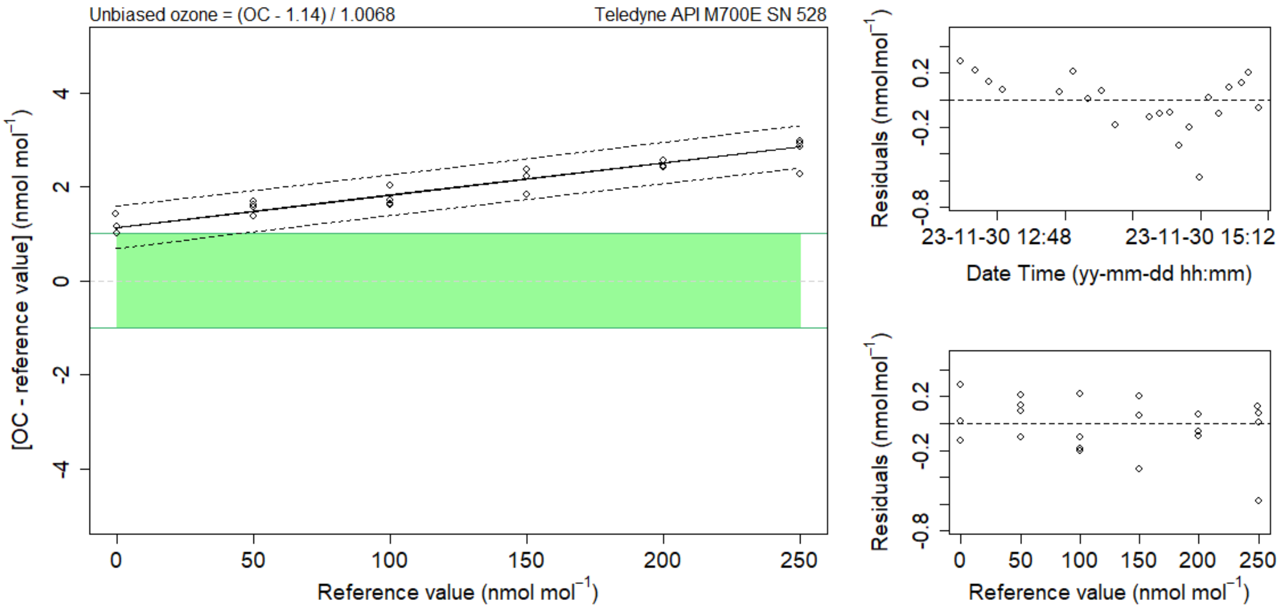

Figure 3. *Left: Bias of the BHD ozone calibrator (Teledyne API M700E #528, BKG 1.1 nmol mol^{-1}, SPAN 0.992) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount 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).*

The results of the BHD ozone calibrator comparison can be summarised as follows:

The BHD Teledyne API M700E #528 ozone calibrator produced slightly higher readings than the WCC-Empa reference instrument. This discrepancy can be corrected using the above calibration function. The instrument appears to be in good working condition. However, the calibrator is over 15 years old, so repairing it in the event of a failure might be difficult. Therefore, it should be considered replacing it with a newer model.

> **Recommendation 6 (*, minor, 2026)**
> *The Teledyne API M700E #528 ozone calibrator has reached the end of its expected lifetime. It is recommended that a new ozone calibrator is purchased to replace it within the next few years.*

3.2 Carbon monoxide measurements

Continuous measurements of CO at BHD started in 2000 and continuous data are available since then.

Instrumentation. BHD is equipped with a Picarro G2401 CRDS analyser and a custom-made gas distribution system for the calibration of the instrument. The sample air is dried with a cryogenic trap (-80°C).

Standards. A large number of standards are available at the BHD station. At the time of the audit, five reference standards from the GAW Central Calibration Laboratory (CCL) were used to calibrate the BHD instrument. Working standards and a target cylinder, which are made from BHD air using a RIX compressor, are also available. Table 9 in the Appendix provides an overview of the available standard gases.

Calibration. A comprehensive calibration using all CCL gases is nominally performed every 2 weeks to characterise the detector response and the amount fractions of the working standards. More details of the calibration procedure can be found in Brailsford et al. (2012).

Data acquisition. The data acquisition of the GHG and CO measurements is performed by a custom-built system programmed in LabVIEW. One-minute time resolution is available for all data. Furthermore, the internal data acquisition of the CRDS analyser is also available, and the highest resolution (1-2 s resolution) raw data files are stored. This data is currently being used for further processing.

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

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

Picarro G2401 #2444-CFKADS2209:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 1.22 nmol mol^{-1}) / 1.0097 (7)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt ((3.0 nmol mol^{-1})^2 + 1.01e-04 * X_{CO}^2) (8)

The results of the comparison can be summarised as follows:

The BHD measurements agreed well with the WCC-Empa reference within the relevant amount fraction range. However, a larger deviation was observed at high CO levels. It should be noted that this is outside the calibrated range of the instrument. Due to the good agreement, no further action is required.

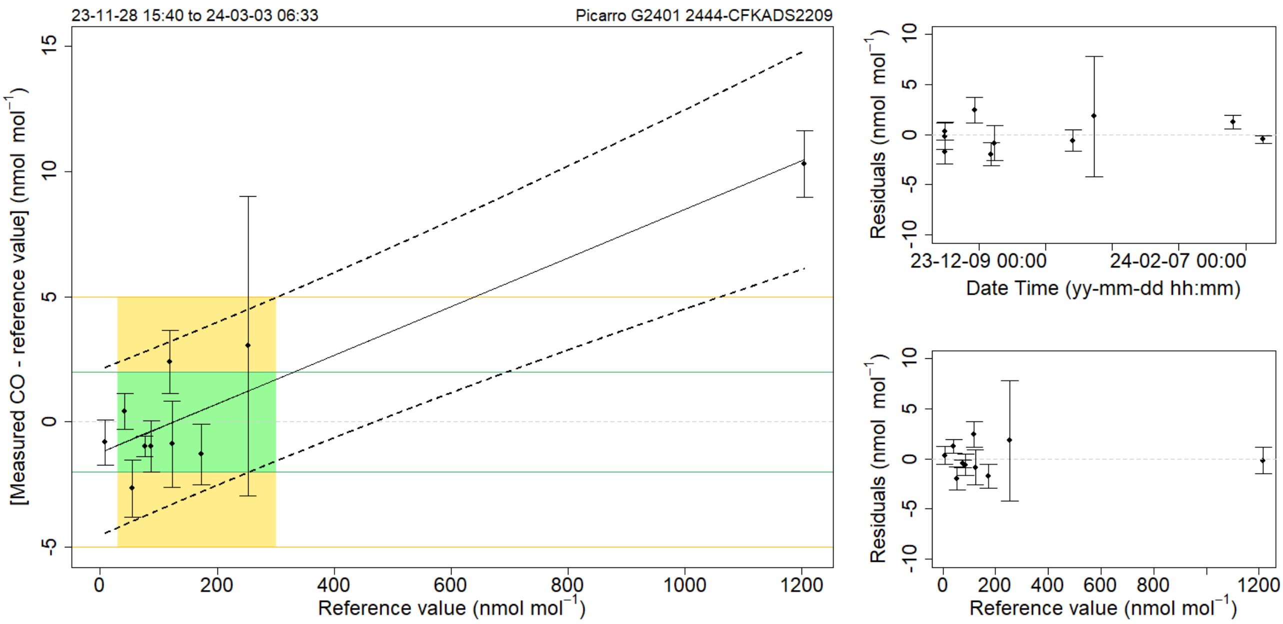

Figure 4. *Left: Bias of the PICARRO G2401 #2444-CFKADS2209 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation 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 BHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

3.3 Methane measurements

Continuous measurements of CH_4 at BHD started in 2016 with using a CRDS instrument, and CH_4 data are available since April 2016.

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

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

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

Picarro G2401 #2444-CFKADS2209:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 2.18 nmol mol^{-1}) / 0.9987 (9)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt ((3.94 nmol mol^{-1})^2+ 1.30e-07 * $X_{CH4}{}^2$) (10)

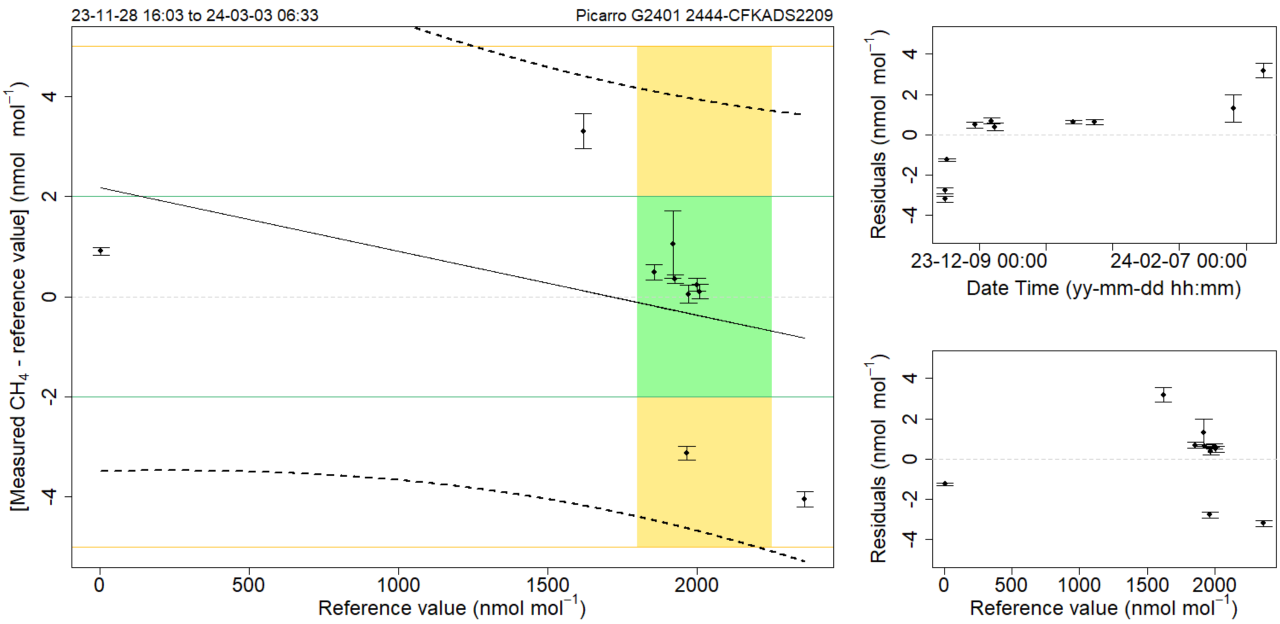

Figure 5. *Left: Bias of the Picarro G2401 #2444-CFKADS2209 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual 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 BHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The results of the comparison can be summarised as follows:

On average, good agreement with the WMO/GAW network compatibility goal was found within the relevant range of amount fractions. However, it should be noted that a few of the travelling standard comparisons showed larger deviations. This was most likely due to flow issues during the comparison, which should not occur during routine operation of the BHD system. The good overall results indicate that the entire system, including the calibration procedures and the standard gases, is adequate, and that no further action is required at this time.

3.4 Carbon dioxide measurements

Continuous measurements of CO_2 at BHD started in December 1972 using NDIR technique (Brailsford et al., 2012). This is the longest CO_2 data series in the Southern Hemisphere. Continuous CO_2 data are available from the WDCGG from 1978 onwards.

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

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

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

Picarro G2401 #2444-CFKADS2209:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 1.35 µmol mol^{-1}) / 0.9967 (11)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt ((0.81 µmol mol^{-1})^2 + 3.28e-8 * X_{CO2}^2) (12)

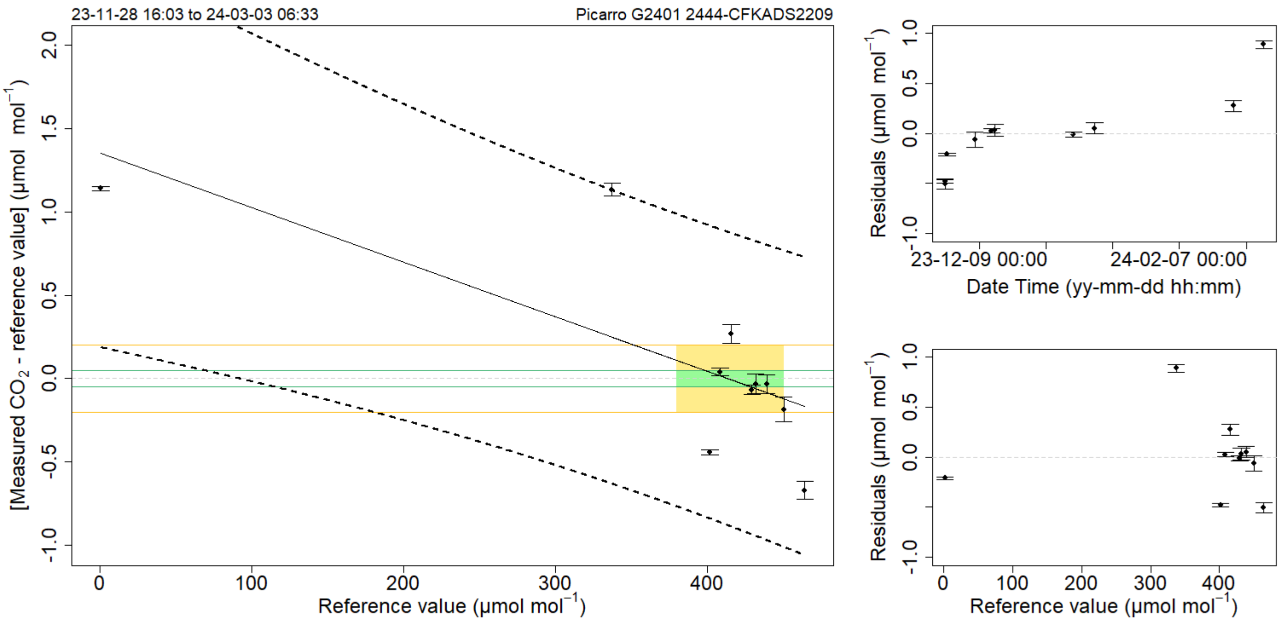

Figure 6. *Left: Bias of the Picarro G2401 #2444-CFKADS2209 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement 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 BHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The results of the comparison can be summarised as follows:

On average, BHD CO_2 measurements agreed within the extended WMO/GAW compatibility goals with the WCC-Empa reference values. The flow issues described above for CH_4 also impacted the CO_2 analysis. These issues should not be present during the normal operation of the BHD CO_2 instrument. Therefore, the observed bias should not be used to apply corrections.

4 Comparison of BHD performance audit results with other stations

This section compares the results of the BHD 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, 2024) for CO_2, CH_4, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone, the amount fraction range of 0--100 nmol mol^{-1} was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 7 shows the bias vs. slope of the WCC-Empa performance audits for O_3, CO, CH_4 and CO_2. The grey dots show all comparisons made during the WCC-Empa audits for the main station analysers but exclude cases with known instrumental problems. Where an adjustment was made during an audit, only the final comparison is shown. The results of the current BHD audit are shown as coloured dots in Figure 7.

The BHD surface ozone analyser did not comply with the DQOs, although better results were obtained after replacing the broken solenoid valve. The instrument needs servicing and must be recalibrated afterwards. The BHD ozone calibrator reading was slightly higher than that of the WCC-Empa reference instrument.

The WMO/GAW network compatibility goals were met for CH_4, and CO was within the extended network compatibility goal. However, the CO_2 comparison slightly exceeded the extended Southern Hemisphere (SH) WMO/GAW network compatibility goal. It should be noted that this was likely caused by flow issues during the comparison of the travelling standards.

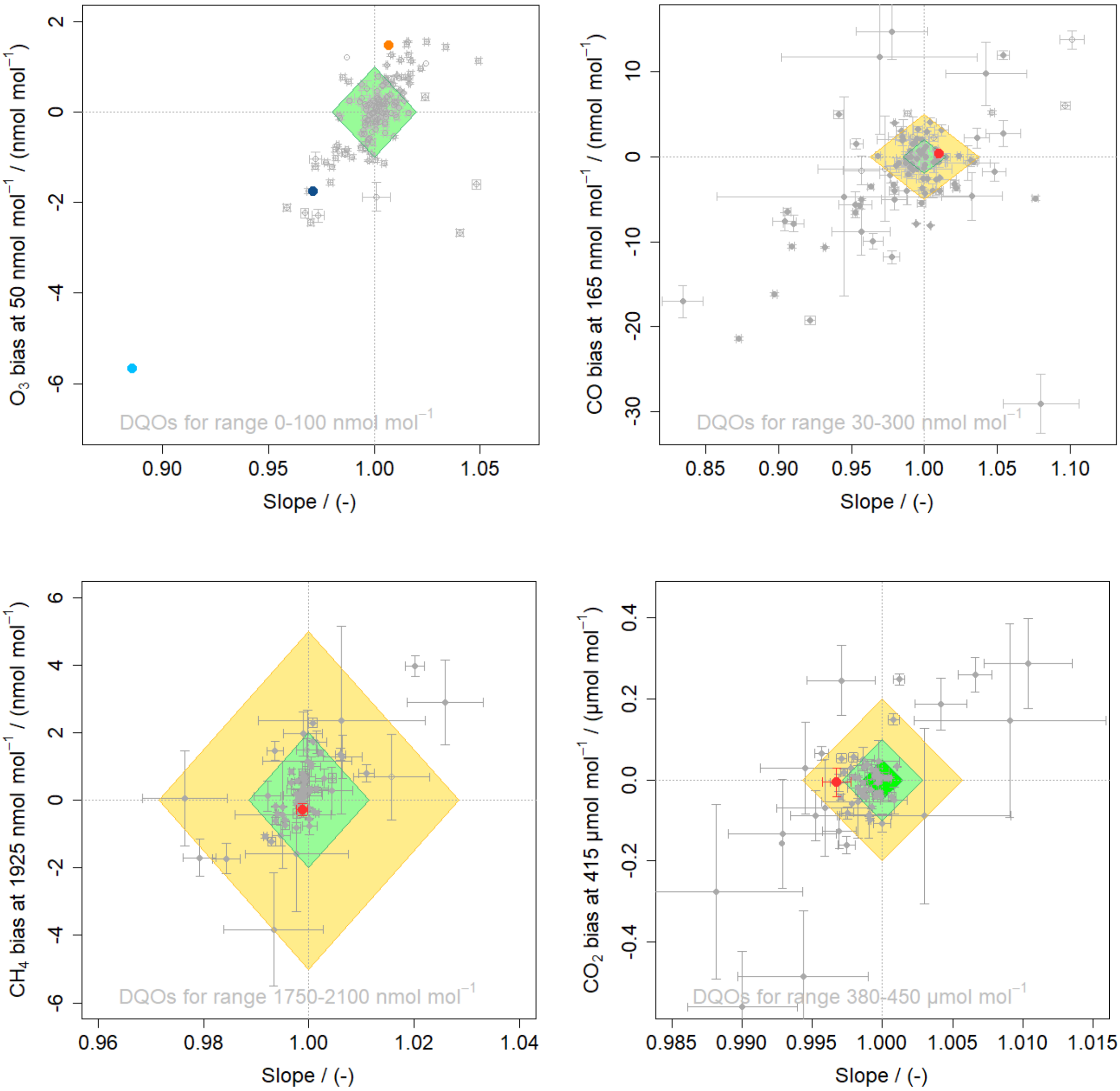

Figure 7. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show BHD results (light blue: BHD Thermo 49iQ, initial comparison with broken solenoid valve, dark blue: BHD Thermo 49i, final comparison, orange: BHD API M700E calibrator, red: Picarro G2401). Filled symbols refer to a comparison with the same calibration scale at the station and at the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green, 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 using a WCC-Empa travelling instrument (TI) (Picarro G2401 #1497-CFKADS2098). It should be noted that the TI experienced a number of issues during the comparison campaign that necessitated the involvement of Picarro support. The TI's laser parameters were adjusted several times during this period and the instrument experienced prolonged periods of downtime due to these issues. Therefore, the data presented here should be interpreted with caution, as potential bias from the TI cannot be ruled out.

The BHD CRDS instrument was compared with the TI between 11 January and 6 March 2024. The TI was connected to an independent inlet line leading to the same inlet location as the BHD analyser. The TI sampled air in the following sequence: 3210 min ambient air from the independent inlet, followed by 75 min of measuring three standard gases, each for 25 minutes. The sample air was dried using a Nafion dryer (Perma Pure model PD-50T-12MPS) in reflux mode, with the Picarro pump providing the vacuum for the purge air stream. To account for the residual effect of water vapour, the internal Picarro correction function (Rella et al., 2013; Zellweger et al., 2012) was applied to the CO_2 and CH_4 data of the TI. Details of the TI calibration can be found in the Appendix. The results of the ambient air comparison are presented below. The BHD data were processed by NIWA.

Figures 8 to 10 show the comparison of hourly CO, CH_4 and CO_2 measurements between the TI and the BHD instrument. The hourly averages were calculated based on one minute data, provided that data was available simultaneously from both the BHD station analyser and the TI.

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

5.1 Carbon monoxide

On average, the bias between the BHD ambient air measurements and the WCC-Empa TI was within the extended WMO/GAW compatibility goal. However, the bias varied considerably over time. While good agreement was observed during some periods, biases exceeding 10 nmol mol^{-1} were evident during others. Issues with the instruments, particularly the WCC-TI, cannot be ruled out as the cause of the bias. The results should therefore be treated with care.

5.2 Methane

Good agreement was found between the TI and the BHD instrument, mostly within the WMO/GAW network compatibility goals, confirming the results of the travelling standard comparisons. Both instruments captured the temporal variability well.

5.3 Carbon dioxide

The agreement between the TI and BHD instruments exceeded the extended WMO/GAW network compatibility goal (median -0.51 µmol mol^{-1}) and was not consistent over time. Furthermore, the bias exhibited a distinct diurnal cycle in part. Some of the bias may have been caused by instrumental issues, but the impact of the BHD drying system cannot be ruled out either.

Recommendation 7 (*, minor, 2026)
It is recommended to assess and optimise the flushing time of the smaller cryogenic trap at BHD. The observed differences in gas measurements, particularly the lower quality of CO_2 compared to CH_4 and CO, suggest that incomplete flushing may lead to residual contamination. Alternatively, it should be considered to upgrade to a Nafion drying system. This technology enables the same treatment for both sample air and calibration gas. Furthermore, it has proven to be highly reliable at many GAW stations.

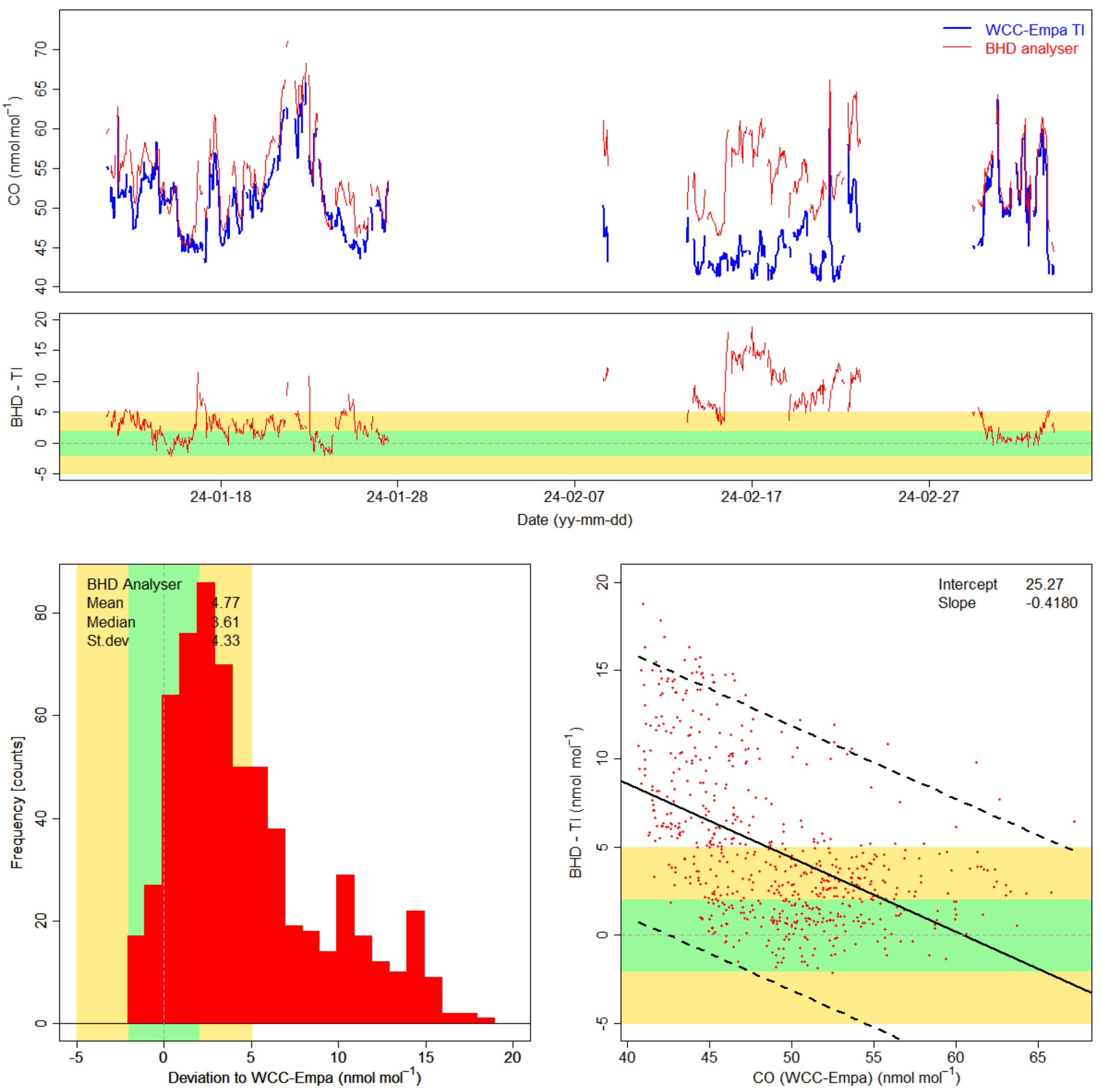

Figure 8. *Top: Comparison of the Picarro G2401 #2444-CFKADS2209 with the travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G2401 #2444-CFKADS2209 analyser compared to the WCC-Empa TI. Bottom right: BHD instrument bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

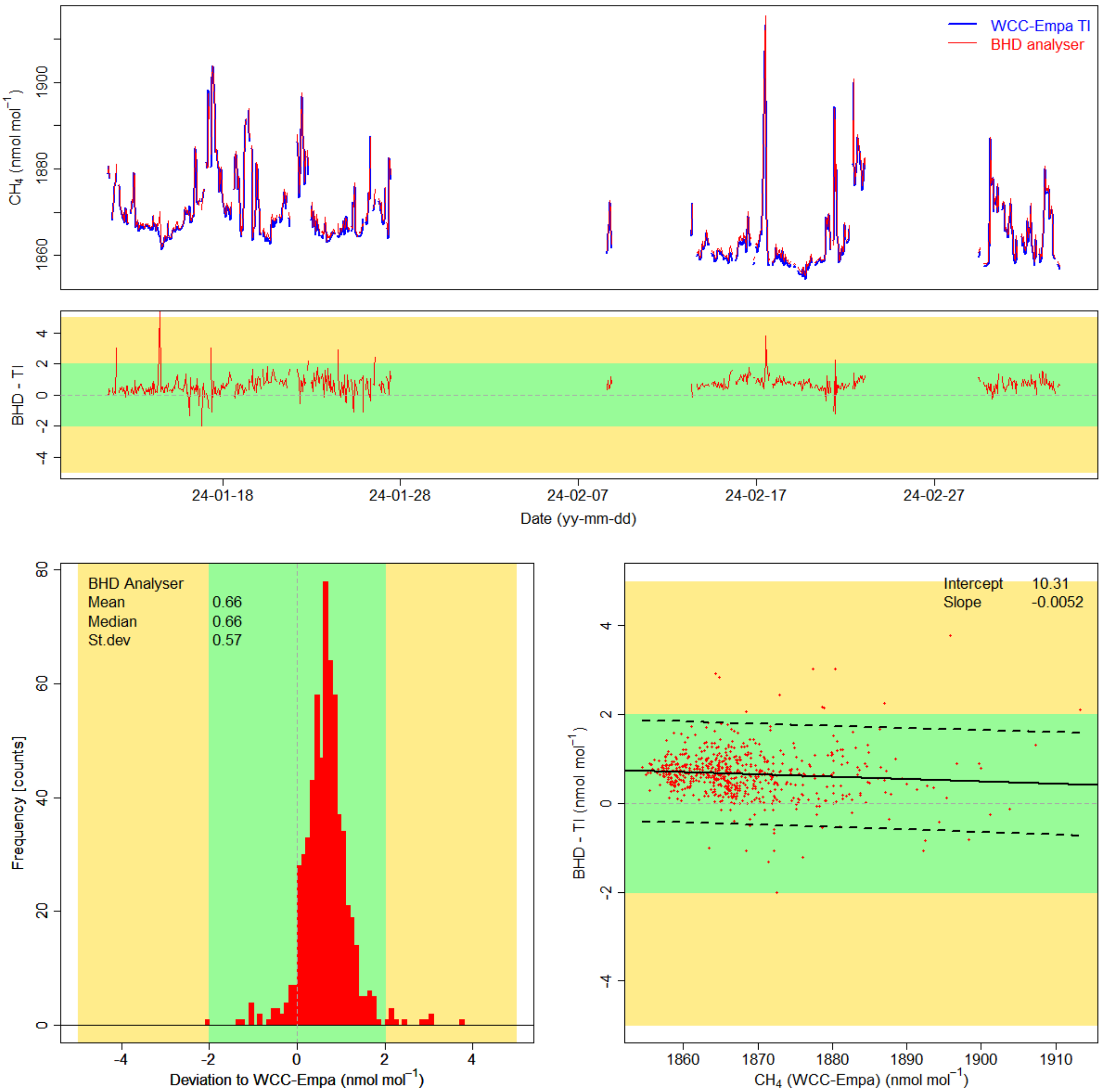

Figure 9. *Top: Comparison of the G2401 #2444-CFKADS2209 analyser (main instrument) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CH_4 deviation histograms for the G2401 #2444-CFKADS2209 analyser compared to the WCC-Empa TI. Bottom right: BHD instrument bias as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

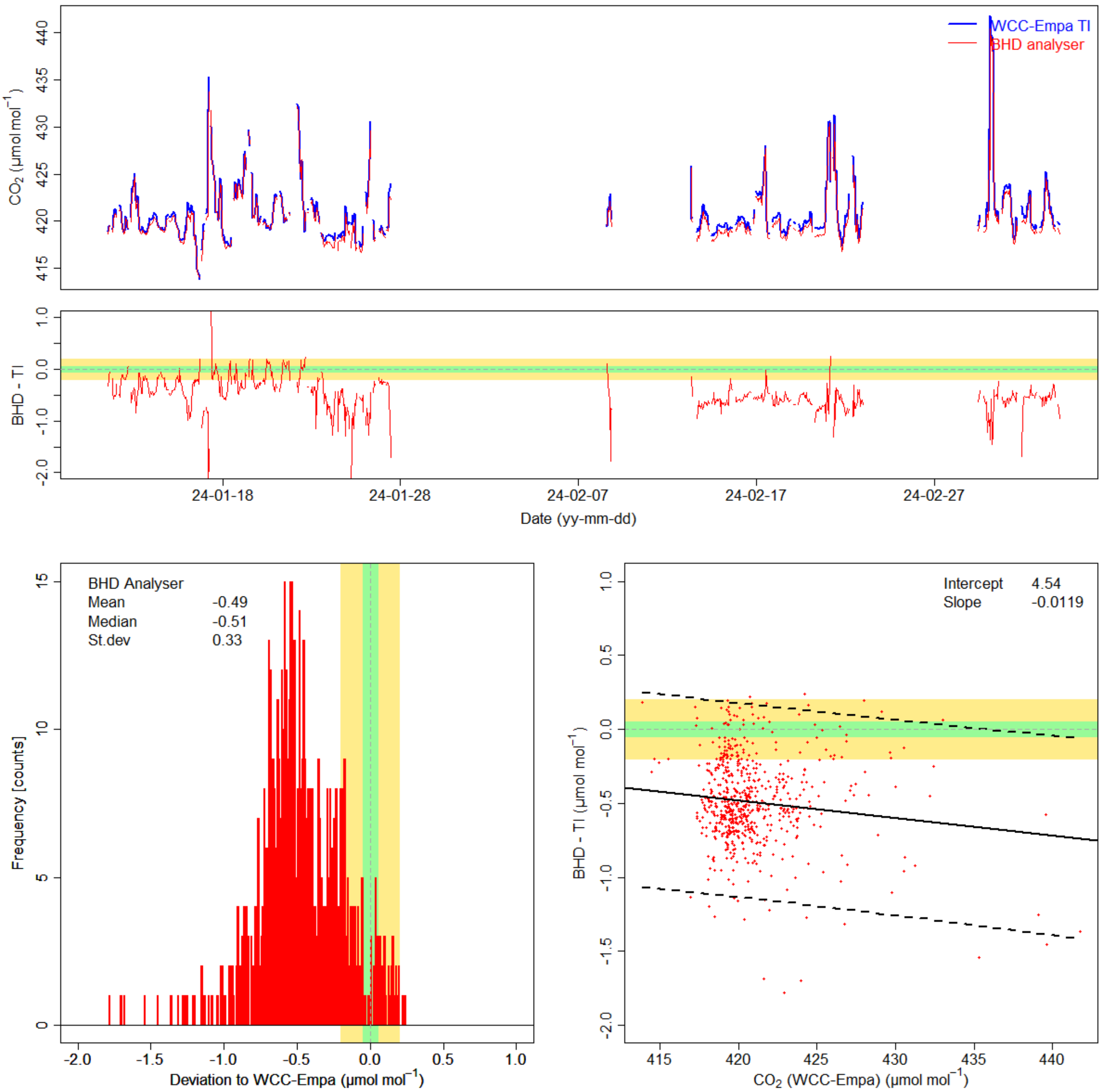

Figure 10. *Top: Comparison of the G2401 #2444-CFKADS2209 analyser (main instrument) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO_2 deviation histograms for the Picarro G2401 #2444-CFKADS2209 analyser compared to the WCC-Empa TI. Bottom right: BHD instrument bias as a function of the CH_4 amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

6 Conclusions

The Baring Head GAW regional station has the longest continuous CO_2 time series in the Southern Hemisphere and has expanded its measurement programme in recent years. Although BHD contributes to the GAW programme as a regional station, its location enables it to monitor changes in unpolluted southern hemisphere air.

The continuation of the Baring Head measurement series is critically important to the GAW programme. Maintaining the long-term time series of CO_2 and ozone - already spanning several decades - is essential to ensure the integrity and continuity of atmospheric monitoring.

The GHG measurements evaluated were of sufficient quality and mostly met the WMO/GAW network compatibility or extended goals within the relevant amount fraction range. However, the observed bias of CO_2 measurements was slightly larger than the extended WMO/GAW network compatibility goal. Some of this bias may be due to flow control issues during the comparisons, meaning the observed biases represent an upper limit and the actual measurements are more likely to comply with the WMO/GAW compatibility goals.

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 results of the performance audit and parallel measurement in Baring Head. A tick mark in the table indicates that the compatibility goal (green) or the extended compatibility goal (orange) was met on average, and ✗ indicates results exceeding the compatibility goals.*

Compound / Instrument	Range	Unit	BHD within DQO/eDQO
O_3 (Thermo Scientific 49i #1152220033), BHD, broken solenoid valve	0 -100	nmol mol^{-1}	✗
O_3 (Thermo Scientific 49i #1152220033), BHD, after repair	0 -100	nmol mol^{-1}	✗
CO (Picarro G2401 #2444-CFKADS2209)	30 - 300	nmol mol^{-1}	✓
CO (Picarro G2401 #2444-CFKADS2209), parallel measurements	NA	nmol mol^{-1}	✓
CH_4 (Picarro G2401 #2444-CFKADS2209)	1750 - 2100	nmol mol^{-1}	✓
CH_4 (Picarro G2401 #2444-CFKADS2209), parallel measurements	NA	nmol mol^{-1}	✓
CO_2 (Picarro G2401 #2444-CFKADS2209)	380 - 450	µmol mol^{-1}	✓
CO_2 (Picarro G2401 #2444-CFKADS2209), parallel measurements	NA	µmol mol^{-1}	(✗)*

* Bias was most likely overestimated due to instrumental issues during the comparison.

7 Summary ranking of the Baring Head GAW station

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme focused on in-situ observations (GHGs, reactive gases, aerosols)
Access	(5)	Year-round access
Facilities		
Laboratory and office space	(3)	Adequate, with very limited space for additional research campaigns
Internet access	(5)	High speed connection
Air Conditioning	(4)	Air-conditioning runs continuously, temperature normally between 22-23°C, was 18-24°C during the audit
Power supply	(5)	Mains-powered with UPS and battery backup, ensuring over 7 hours of runtime during outages
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(5)	Skilled and motivated staff with long-term experience
Air Inlet System	(4)	Adequate air inlet systems
Instrumentation		
Ozone (Themo Scientific 49i)	(2)	Instrument needs service
CH_4/CO_2/CO Picarro G2401	(5)	State of the art instrumentation
Standards		
O_3 (Teledyne API M700E)	(3)	Working, but needs to be replaced
CO, CO_2, CH_4	(5)	CCL standards
Data Management		
Data acquisition	(5)	Fully adequate systems
Data processing	(4)	Qualified staff, appropriate procedures
Data submission to WDCRG	(4)	Timely submission, but in-situ CO data has not been submitted
Data submission to WDCGG	(5)	Timely data submission

#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	The current situation is acceptable for the equipment in use. However, space is tight and needs to be increased if the measurement programme is expanded.	Medium	Important	When the measurement programme is expanded
2	Most data has been submitted with a delay of less than two years, but continuous CO data is not yet available. It is recommended that the CO time series is submitted too.	Medium	Important	2025
3	It is recommended that the ozone time series of ~2019 to 2023 is reviewed to check for a potential lower reading due to the faulty valve. If any irregularities are observed, the data should be corrected, if possible, or flagged as questionable or invalid.	High	Critical	2025
4	The current ozone calibration system has reached the end of its expected lifetime. It is therefore recommended that a newer ozone calibrator is purchased and that traceability is established to a NIST Standard Reference Photometer (SRP).	Medium	Important	2026
5	The BHD ozone analyser needs to be repaired. Given the age of the instrument, replacing it with a new one should also be considered.	High	Critical	2025
6	The Teledyne API M700E #528 ozone calibrator has reached the end of its expected lifetime. It is recommended that a new ozone calibrator is purchased to replace it within the next few years.	Low	Minor	2026
7	It is recommended to assess and optimise the flushing time of the smaller cryogenic trap at BHD. The observed differences in gas measurements, particularly the lower quality of CO_2 compared to CH_4 and CO, suggest that incomplete flushing may lead to residual contamination. Alternatively, it should be considered to upgrade to a Nafion drying system. This technology enables the same treatment for both sample air and calibration gas. Furthermore, it has proven to be highly reliable at many GAW stations.	Low	Minor	2026

A2. Data review

The following figures show summary plots of BHD data obtained from WDCRG and WDCGG on 23 May 2025. The plots show time series of hourly data, frequency distribution and diurnal and seasonal variations.

Surface ozone submitted by NIWA:

The two data sets of BHD O_3 data from the WDCRG are shown in the figures below.

- Both data sets are looking good in terms of amount fraction, diurnal and seasonal variation and trend.
- However, the data from 2022 to 2023 are on average about 13 lower compared to the previous data. This is in good agreement with the low readings found during the performance audit. Most likely, this data is affected by the faulty valve.

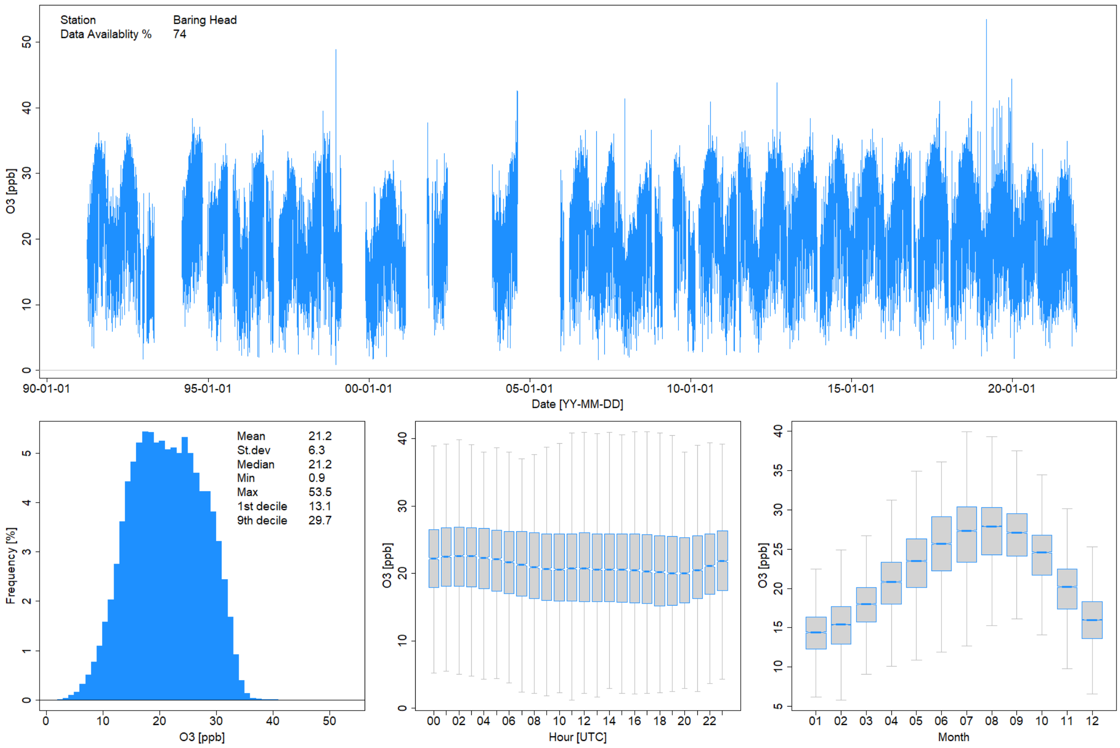

Figure 11. *WDCRG O_3 data for the period 1991 to 2021. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

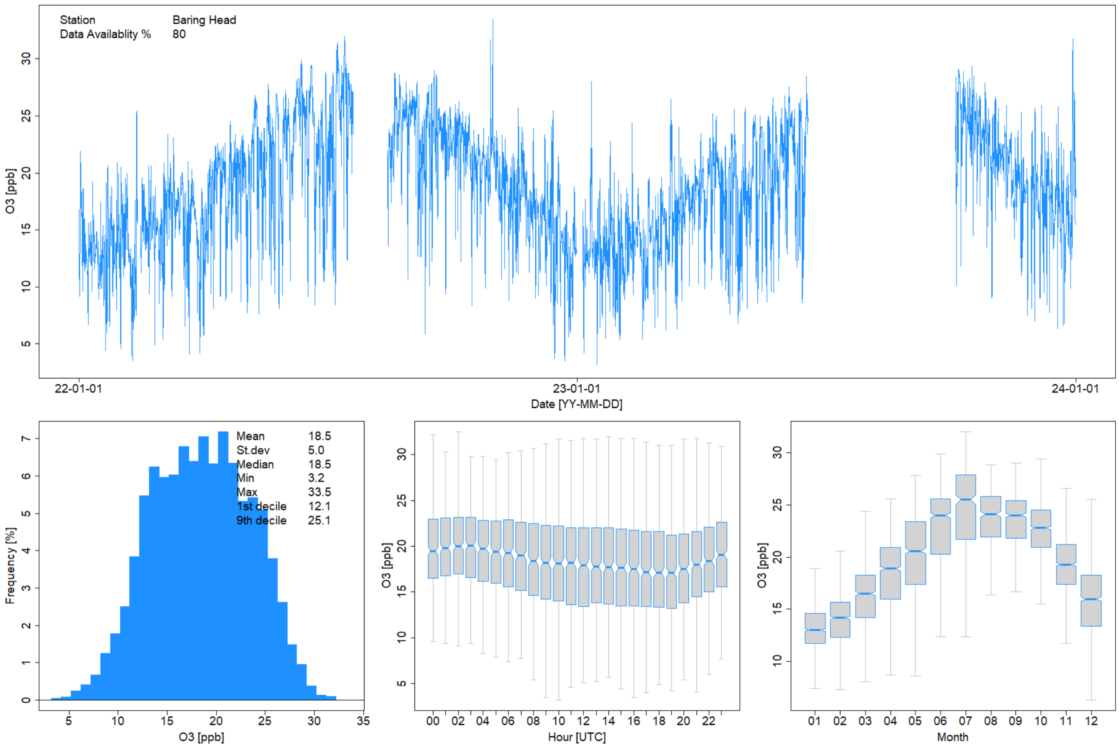

Figure 12. *WDCRG O_3 data set for the period 2022 to 2023. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

CO data submitted by NIWA and NOAA:

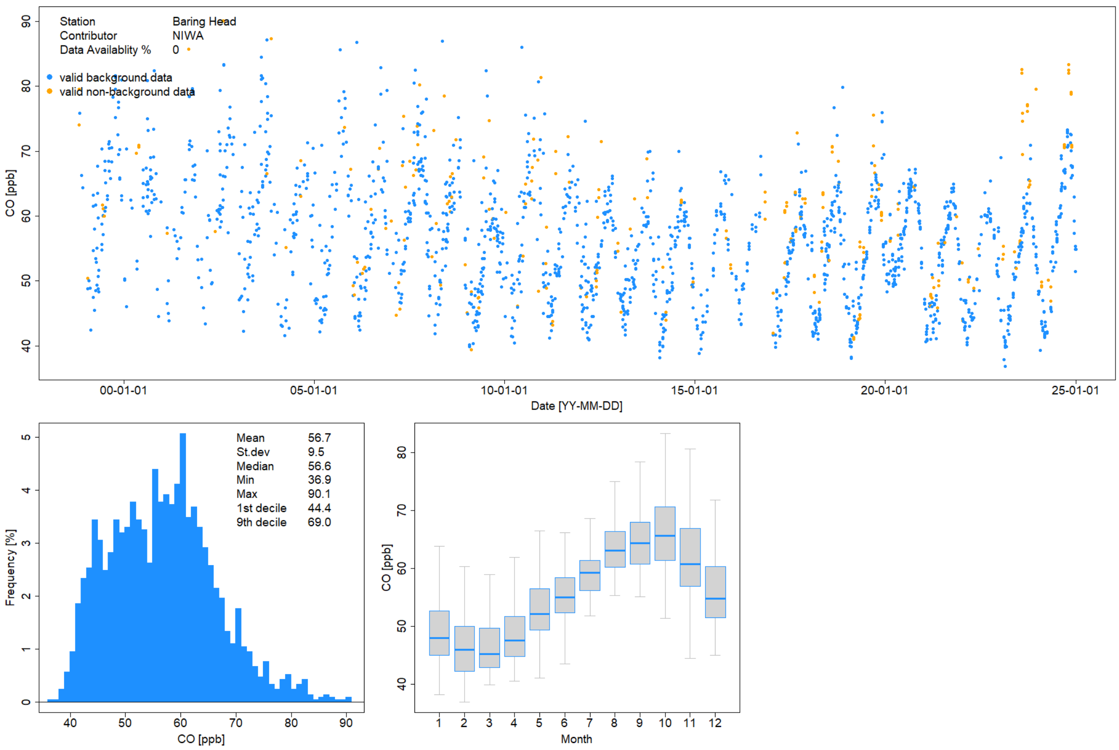

Figure 13. *BHD CO flask data (1998-2024) submitted to WDCGG by NIWA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

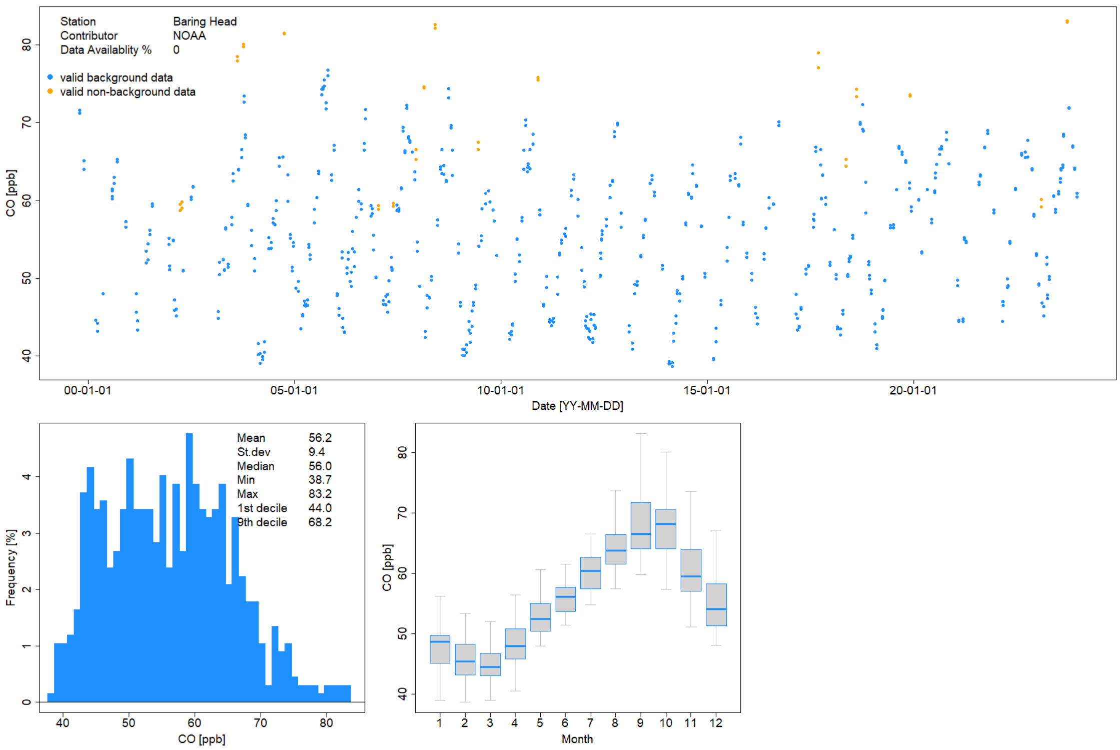

Figure 14. *BHD CO flask data (1999-2023) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

CH_4 data submitted by NIWA and NOAA:

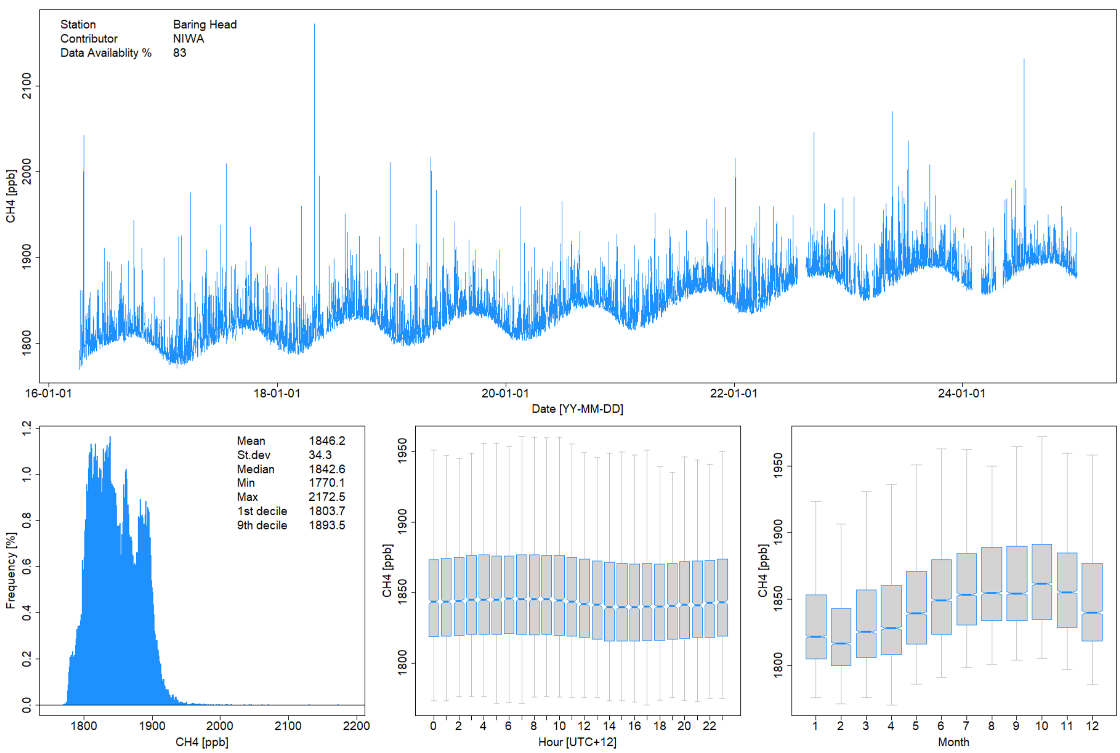

Figure 15. *BHD in-situ CH_4 data (2016-2024) accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, right: diurnal variation; the horizontal blue line denotes to the median and the blue boxes the inter-quartile range.*

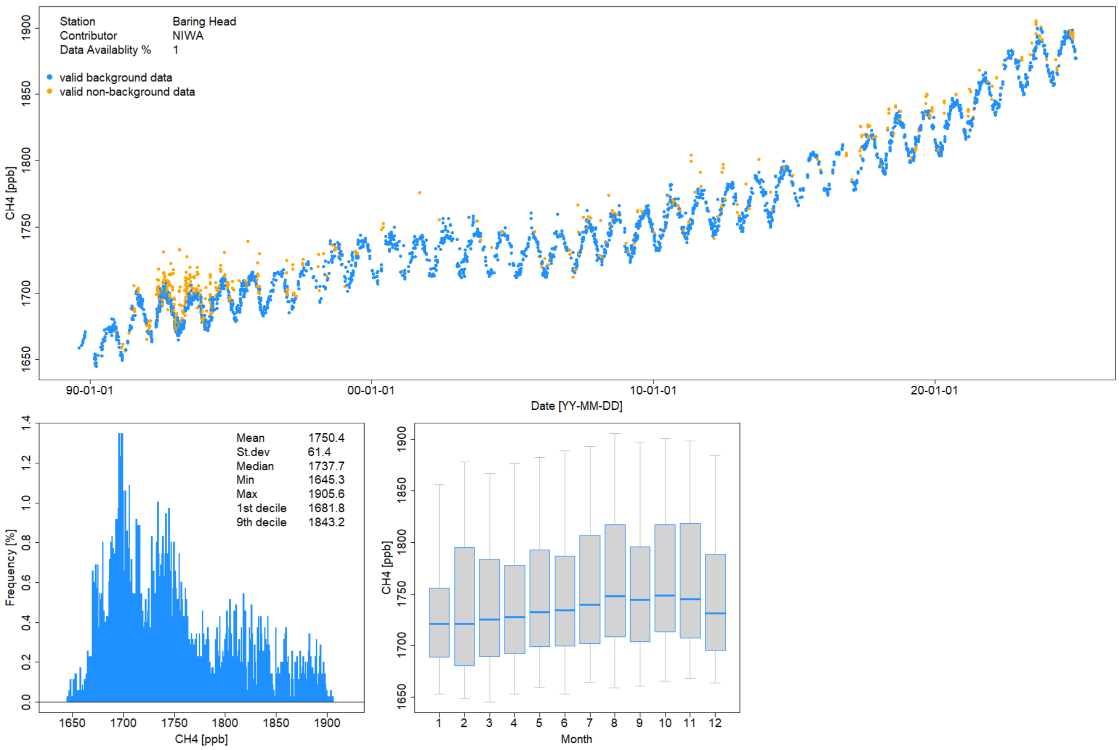

Figure 16. *BHD CH_4 flask data (1989-2024) submitted to WDCGG by NIWA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

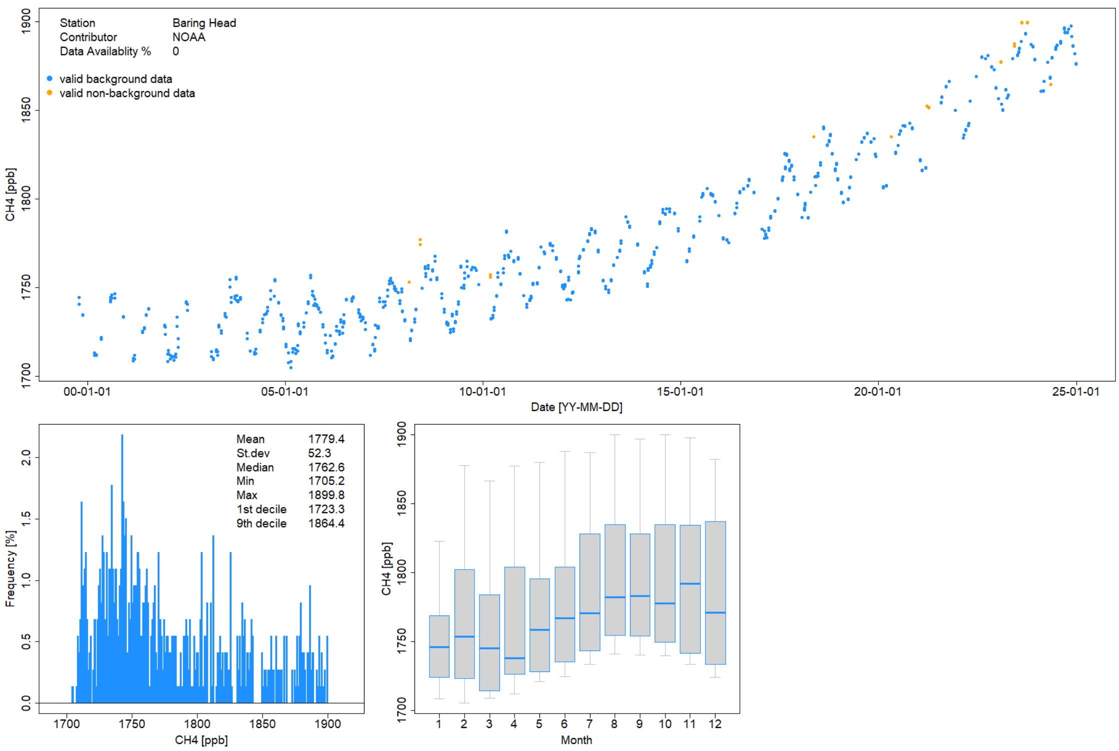

Figure 17. *BHD CH_4 flask data (1999-2024) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

CO_2 data submitted by NIWA and NOAA:

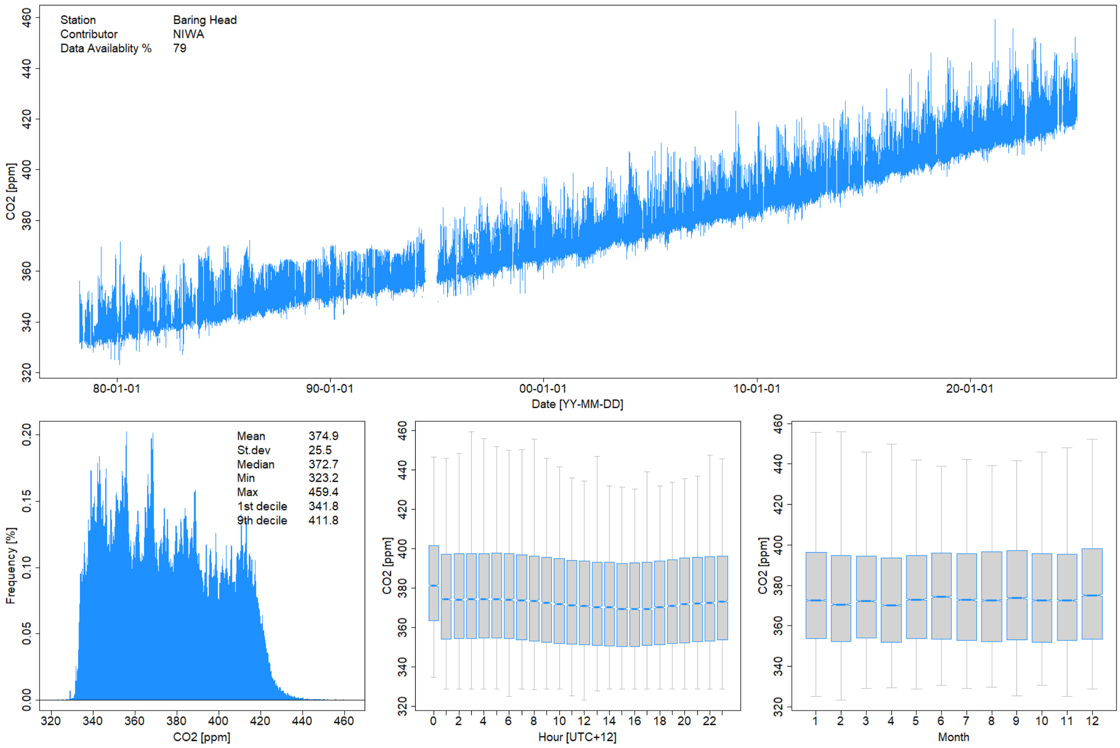

Figure 18. *BHD in-situ CO_2 data (1978-2024) accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, right: diurnal variation; the horizontal blue line denotes to the median and the blue boxes the inter-quartile range.*

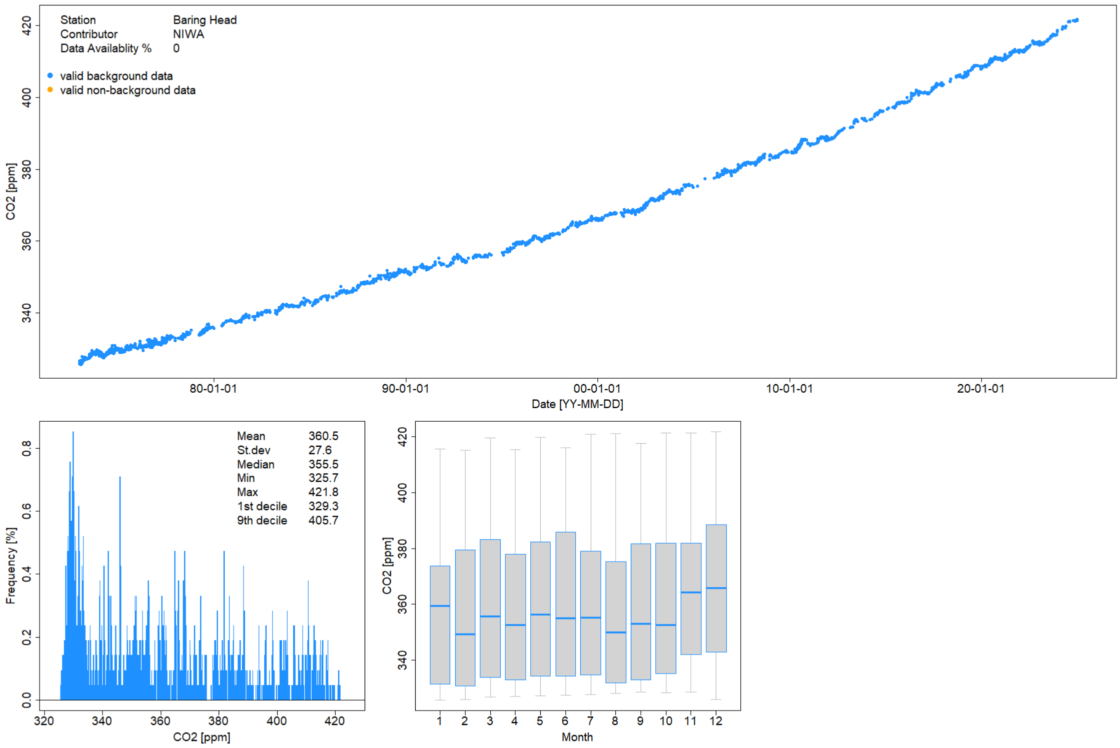

Figure 19. *BHD in-situ steady interval event CO_2 data (1972-2024) accessed from WDCGG. Top: Time series, steady interval event data. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

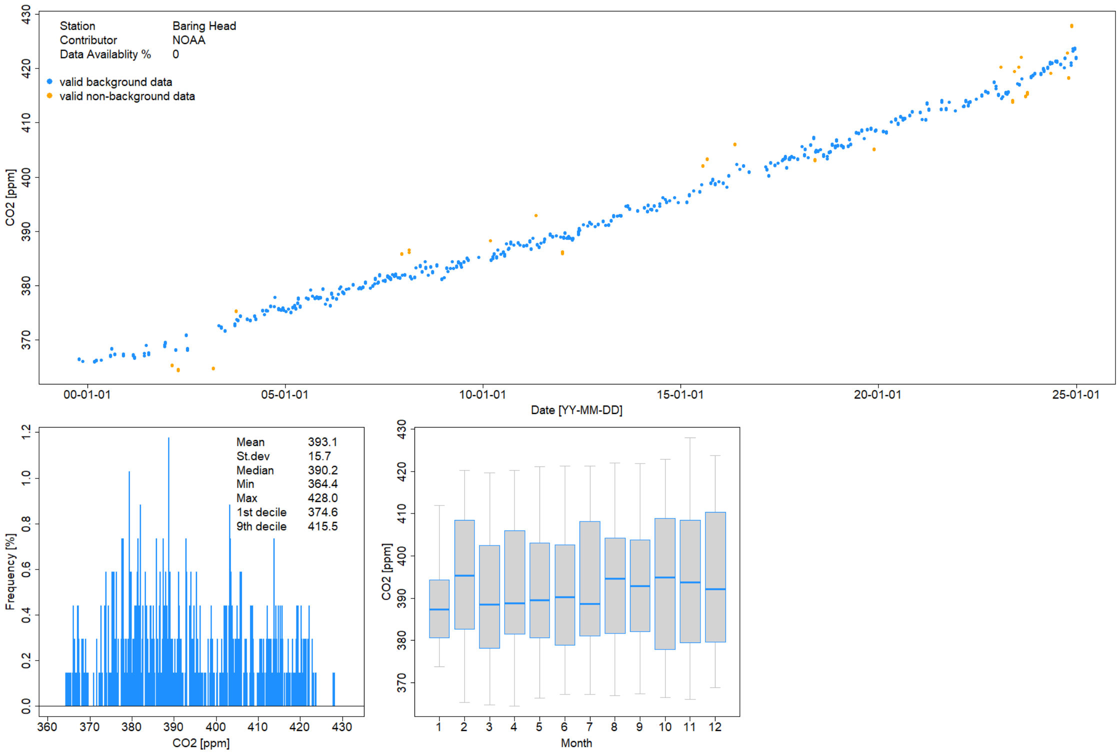

Figure 20. *BHD CO_2 flask data (1999-2024) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median and the blue boxes the interquartile range.*

NIWA GHG and CO data:

- Data set looks sound in terms of mole fraction, trend, seasonal and diurnal variation.

NOAA GHG and CO flask data:

- The data set looks sound in terms of mole fraction, trend, seasonal and diurnal variations.

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 random sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}. Zero air was generated using a custom-built zero air generator (Nafion dryer, Purafil, activated charcoal). The TS was connected to the station 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 evaluation were recorded by the WCC-Empa and BHD data acquisition systems.

Table 2. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG +0.0, COEF 0.991
Pressure readings (hPa)	Ambient 1001.0; TS 1001.1 No adjustments were made
BHD ozone analyser (OA)	
Model, S/N	Thermo Scientific 49i #1152220033
Principle	UV absorption
Settings	Initial: BKG -0.1 nmol mol^{-1}, COEF 0.997
Pressure readings (hPa)	Ambient 1001.0; OA 1000.6 No adjustments were made
BHD ozone calibrator (OC)	
Model, S/N	Teledyne API M700E #528
Principle	UV absorption
Settings	BKG +1.1 nmol mol^{-1}, SPAN 0.992
Pressure readings (hPa)	Ambient 1003.8; OC 1005.8 No adjustments were 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 given in Table 2 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) before 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 BHD ozone analyser (OA) Thermo Scientific 49i #1152220033 (BKG -0.1 nmol mol⁻¹, COEF 0.997, initial comparison) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2023-11-27 04:28	0.23	0.18	0.30	0.12	0.07	NA
2023-11-27 04:38	50.00	0.09	44.36	0.39	-5.64	-11.28
2023-11-27 04:48	200.00	0.06	177.48	0.22	-22.52	-11.26
2023-11-27 04:58	150.00	0.06	133.02	0.10	-16.98	-11.32
2023-11-27 05:08	100.03	0.06	88.82	0.21	-11.21	-11.21
2023-11-27 05:18	249.99	0.09	221.74	0.16	-28.25	-11.30
2023-11-27 05:28	74.95	0.12	66.40	0.19	-8.55	-11.41
2023-11-27 05:38	24.99	0.08	22.15	0.11	-2.84	-11.36
2023-11-27 05:48	175.02	0.04	154.99	0.20	-20.03	-11.44
2023-11-27 05:58	125.06	0.08	110.80	0.22	-14.26	-11.40
2023-11-27 06:08	225.07	0.09	199.50	0.16	-25.57	-11.36
2023-11-27 06:18	0.37	0.17	0.39	0.12	0.02	NA
2023-11-27 06:28	74.96	0.06	66.31	0.14	-8.65	-11.54
2023-11-27 06:38	149.97	0.05	132.91	0.19	-17.06	-11.38
2023-11-27 06:48	50.02	0.06	44.24	0.16	-5.78	-11.56
2023-11-27 06:58	250.04	0.06	221.93	0.26	-28.11	-11.24
2023-11-27 07:08	200.05	0.07	177.43	0.15	-22.62	-11.31
2023-11-27 07:18	99.97	0.04	88.66	0.04	-11.31	-11.31
2023-11-27 07:28	25.04	0.12	22.14	0.22	-2.90	-11.58
2023-11-27 07:38	174.99	0.02	155.04	0.13	-19.95	-11.40
2023-11-27 07:48	224.99	0.06	199.73	0.12	-25.26	-11.23
2023-11-27 07:58	124.96	0.09	110.88	0.13	-14.08	-11.27
2023-11-27 08:08	0.16	0.15	0.35	0.13	0.19	NA
2023-11-27 08:18	150.00	0.04	132.93	0.12	-17.07	-11.38
2023-11-27 08:28	25.01	0.10	22.23	0.17	-2.78	-11.12
2023-11-27 08:38	175.00	0.03	155.13	0.53	-19.87	-11.35
2023-11-27 08:48	200.00	0.09	177.61	0.29	-22.39	-11.19
2023-11-27 08:58	50.02	0.13	44.42	0.12	-5.60	-11.20
2023-11-27 09:08	75.01	0.04	66.48	0.11	-8.53	-11.37
2023-11-27 09:18	224.94	0.12	199.42	0.41	-25.52	-11.35
2023-11-27 09:28	100.06	0.10	88.85	0.18	-11.21	-11.20
2023-11-27 09:38	124.99	0.07	110.72	0.11	-14.27	-11.42
2023-11-27 09:48	249.95	0.08	221.56	0.30	-28.39	-11.36
2023-11-27 09:58	-0.01	0.22	0.27	0.13	0.28	NA
2023-11-27 10:08	49.97	0.09	44.38	0.29	-5.59	-11.19
2023-11-27 10:18	199.99	0.08	177.27	0.26	-22.72	-11.36
2023-11-27 10:28	150.01	0.07	132.82	0.24	-17.19	-11.46
2023-11-27 10:38	100.01	0.05	88.74	0.15	-11.27	-11.27
2023-11-27 10:48	250.03	0.06	221.95	0.14	-28.08	-11.23
2023-11-27 10:58	75.02	0.05	66.53	0.28	-8.49	-11.32
2023-11-27 11:08	24.96	0.14	22.20	0.10	-2.76	-11.06
2023-11-27 11:18	175.03	0.09	155.22	0.28	-19.81	-11.32
2023-11-27 11:28	124.98	0.07	110.83	0.19	-14.15	-11.32
2023-11-27 11:38	225.00	0.07	199.61	0.15	-25.39	-11.28
2023-11-27 11:48	0.22	0.12	0.28	0.13	0.06	NA
2023-11-27 11:58	74.97	0.02	66.33	0.19	-8.64	-11.52

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 (%)
2023-11-27 12:08	150.00	0.10	132.72	0.35	-17.28	-11.52
2023-11-27 12:18	50.02	0.04	44.24	0.08	-5.78	-11.56
2023-11-27 12:28	249.99	0.05	221.75	0.25	-28.24	-11.30
2023-11-27 12:38	199.98	0.04	177.14	0.38	-22.84	-11.42
2023-11-27 12:48	99.97	0.08	88.61	0.10	-11.36	-11.36
2023-11-27 12:58	24.96	0.08	22.24	0.11	-2.72	-10.90
2023-11-27 13:08	175.04	0.08	155.13	0.09	-19.91	-11.37
2023-11-27 13:18	225.01	0.06	199.45	0.22	-25.56	-11.36
2023-11-27 13:28	125.04	0.04	110.88	0.28	-14.16	-11.32
2023-11-27 13:38	0.21	0.08	0.26	0.05	0.05	NA
2023-11-27 13:48	150.01	0.06	132.67	0.14	-17.34	-11.56
2023-11-27 13:58	25.02	0.17	22.25	0.11	-2.77	-11.07
2023-11-27 14:08	175.05	0.09	155.05	0.19	-20.00	-11.43
2023-11-27 14:18	200.04	0.11	177.05	0.24	-22.99	-11.49
2023-11-27 14:28	50.03	0.11	44.08	0.37	-5.95	-11.89
2023-11-27 14:38	75.01	0.12	66.68	0.39	-8.33	-11.11
2023-11-27 14:48	224.98	0.08	199.36	0.13	-25.62	-11.39
2023-11-27 14:58	100.00	0.05	88.60	0.16	-11.40	-11.40
2023-11-27 15:08	124.98	0.07	110.80	0.18	-14.18	-11.35
2023-11-27 15:18	250.01	0.02	221.36	0.13	-28.65	-11.46
2023-11-27 15:28	0.20	0.06	0.12	0.31	-0.08	NA
2023-11-27 15:38	49.95	0.06	44.20	0.13	-5.75	-11.51
2023-11-27 15:48	200.01	0.06	176.92	0.14	-23.09	-11.54
2023-11-27 15:58	149.95	0.12	132.72	0.27	-17.23	-11.49
2023-11-27 16:08	99.97	0.10	88.59	0.28	-11.38	-11.38
2023-11-27 16:18	250.01	0.07	221.16	0.16	-28.85	-11.54
2023-11-27 16:28	74.99	0.03	66.52	0.50	-8.47	-11.29
2023-11-27 16:38	25.00	0.19	22.12	0.14	-2.88	-11.52
2023-11-27 16:48	174.99	0.08	154.95	0.12	-20.04	-11.45
2023-11-27 16:58	124.97	0.04	110.71	0.24	-14.26	-11.41
2023-11-27 17:08	224.98	0.05	199.27	0.32	-25.71	-11.43
2023-11-27 17:18	0.26	0.19	0.30	0.11	0.04	NA
2023-11-27 17:28	75.00	0.05	66.49	0.11	-8.51	-11.35
2023-11-27 17:38	150.01	0.08	132.59	0.16	-17.42	-11.61
2023-11-27 17:48	49.97	0.09	44.20	0.06	-5.77	-11.55
2023-11-27 17:58	250.05	0.06	221.33	0.05	-28.72	-11.49
2023-11-27 18:08	199.97	0.08	177.20	0.17	-22.77	-11.39
2023-11-27 18:18	99.98	0.11	88.47	0.04	-11.51	-11.51
2023-11-27 18:28	24.97	0.15	22.09	0.21	-2.88	-11.53
2023-11-27 18:38	175.00	0.03	154.84	0.18	-20.16	-11.52
2023-11-27 18:48	225.00	0.07	199.23	0.09	-25.77	-11.45
2023-11-27 18:58	124.97	0.05	110.61	0.19	-14.36	-11.49
2023-11-27 19:08	0.07	0.18	0.35	0.13	0.28	NA
2023-11-27 19:18	149.99	0.07	132.37	0.15	-17.62	-11.75
2023-11-27 19:28	25.01	0.10	22.40	0.16	-2.61	-10.44
2023-11-27 19:38	175.02	0.07	154.96	0.18	-20.06	-11.46
2023-11-27 19:48	200.01	0.05	177.13	0.08	-22.88	-11.44
2023-11-27 19:58	49.95	0.07	44.39	0.13	-5.56	-11.13

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 (%)
2023-11-27 20:08	75.01	0.11	66.41	0.18	-8.60	-11.47
2023-11-27 20:18	224.96	0.06	199.40	0.27	-25.56	-11.36
2023-11-27 20:28	99.97	0.03	88.48	0.24	-11.49	-11.49
2023-11-27 20:38	124.99	0.11	110.70	0.31	-14.29	-11.43
2023-11-27 20:48	250.01	0.05	221.41	0.27	-28.60	-11.44
2023-11-27 20:58	0.00	0.06	0.40	0.21	0.40	NA
2023-11-27 21:08	49.96	0.03	44.05	0.41	-5.91	-11.83
2023-11-27 21:18	199.93	0.07	176.95	0.38	-22.98	-11.49
2023-11-27 21:28	150.00	0.06	132.72	0.12	-17.28	-11.52
2023-11-27 21:38	100.00	0.07	88.41	0.16	-11.59	-11.59
2023-11-27 21:48	249.99	0.08	221.36	0.13	-28.63	-11.45
2023-11-27 21:58	74.99	0.08	66.49	0.11	-8.50	-11.33
2023-11-27 22:08	24.90	0.13	22.41	0.27	-2.49	-10.00
2023-11-27 22:18	174.96	0.07	154.94	0.17	-20.02	-11.44
2023-11-27 22:28	124.98	0.06	110.74	0.11	-14.24	-11.39
2023-11-27 22:38	225.03	0.05	199.50	0.31	-25.53	-11.35
2023-11-27 22:48	0.26	0.12	0.18	0.12	-0.08	NA
2023-11-27 22:58	74.92	0.09	66.52	0.23	-8.40	-11.21

Table 4. *Comparison of the BHD ozone analyser (OA) Thermo Scientific 49i #1152220033 (BKG -0.1 nmol mol^{-1}, COEF 0.997, final comparison) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2023-11-28 03:46	0.17	0.06	0.26	0.15	0.09	NA
2023-11-28 03:56	50.06	0.05	47.84	0.13	-2.22	-4.43
2023-11-28 04:06	199.99	0.14	194.08	0.33	-5.91	-2.96
2023-11-28 04:16	150.00	0.08	145.28	0.36	-4.72	-3.15
2023-11-28 04:26	99.99	0.06	96.85	0.18	-3.14	-3.14
2023-11-28 04:36	249.98	0.06	243.13	0.14	-6.85	-2.74
2023-11-28 04:46	75.02	0.08	72.67	0.16	-2.35	-3.13
2023-11-28 04:56	24.95	0.07	23.82	0.13	-1.13	-4.53
2023-11-28 05:06	175.00	0.08	169.49	0.19	-5.51	-3.15
2023-11-28 05:16	125.00	0.09	120.89	0.31	-4.11	-3.29
2023-11-28 05:26	225.01	0.09	218.20	0.16	-6.81	-3.03
2023-11-28 05:36	0.15	0.12	0.19	0.06	0.04	NA
2023-11-28 05:46	75.00	0.08	72.10	0.15	-2.90	-3.87
2023-11-28 05:56	150.02	0.05	144.91	0.18	-5.11	-3.41
2023-11-28 06:06	50.00	0.04	48.12	0.14	-1.88	-3.76
2023-11-28 06:16	250.03	0.06	242.31	0.15	-7.72	-3.09
2023-11-28 06:26	200.02	0.05	193.36	0.47	-6.66	-3.33
2023-11-28 06:36	100.01	0.08	96.39	0.16	-3.62	-3.62
2023-11-28 06:46	25.00	0.09	24.05	0.16	-0.95	-3.80
2023-11-28 06:56	175.01	0.07	169.16	0.06	-5.85	-3.34
2023-11-28 07:06	224.98	0.04	218.00	0.18	-6.98	-3.10
2023-11-28 07:16	124.99	0.08	120.71	0.23	-4.28	-3.42
2023-11-28 07:26	0.04	0.06	0.39	0.26	0.35	NA
2023-11-28 07:36	150.03	0.06	144.80	0.16	-5.23	-3.49

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 (%)
2023-11-28 07:46	24.97	0.09	23.87	0.10	-1.10	-4.41
2023-11-28 07:56	174.96	0.06	169.10	0.23	-5.86	-3.35
2023-11-28 08:06	200.02	0.03	193.42	0.19	-6.60	-3.30
2023-11-28 08:16	49.96	0.05	47.92	0.16	-2.04	-4.08
2023-11-28 08:26	74.97	0.06	72.08	0.19	-2.89	-3.85
2023-11-28 08:36	224.99	0.09	217.76	0.17	-7.23	-3.21
2023-11-28 08:46	100.04	0.07	96.47	0.14	-3.57	-3.57
2023-11-28 08:56	125.02	0.06	120.56	0.09	-4.46	-3.57
2023-11-28 09:06	249.96	0.09	242.22	0.16	-7.74	-3.10
2023-11-28 09:16	0.19	0.07	0.22	0.04	0.03	NA
2023-11-28 09:26	49.98	0.07	47.73	0.25	-2.25	-4.50
2023-11-28 09:36	200.02	0.09	193.52	0.10	-6.50	-3.25
2023-11-28 09:46	149.96	0.07	145.05	0.21	-4.91	-3.27
2023-11-28 09:56	100.00	0.05	96.40	0.24	-3.60	-3.60
2023-11-28 10:06	250.01	0.05	242.20	0.11	-7.81	-3.12
2023-11-28 10:16	75.00	0.06	72.28	0.14	-2.72	-3.63
2023-11-28 10:26	24.97	0.07	23.96	0.17	-1.01	-4.04
2023-11-28 10:36	175.01	0.09	169.21	0.48	-5.80	-3.31
2023-11-28 10:46	125.01	0.05	120.63	0.10	-4.38	-3.50
2023-11-28 10:56	225.00	0.06	217.90	0.18	-7.10	-3.16
2023-11-28 11:06	0.07	0.06	0.13	0.11	0.06	NA
2023-11-28 11:16	74.95	0.07	72.18	0.30	-2.77	-3.70
2023-11-28 11:26	149.95	0.07	145.03	0.19	-4.92	-3.28
2023-11-28 11:36	49.93	0.07	48.17	0.34	-1.76	-3.52
2023-11-28 11:46	250.03	0.05	242.61	0.19	-7.42	-2.97
2023-11-28 11:56	199.96	0.04	193.72	0.12	-6.24	-3.12
2023-11-28 12:06	100.00	0.09	96.58	0.18	-3.42	-3.42
2023-11-28 12:16	24.98	0.07	24.08	0.10	-0.90	-3.60
2023-11-28 12:26	174.98	0.09	169.22	0.22	-5.76	-3.29
2023-11-28 12:36	225.05	0.07	218.27	0.31	-6.78	-3.01
2023-11-28 12:46	125.00	0.07	120.88	0.20	-4.12	-3.30
2023-11-28 12:56	0.12	0.17	0.19	0.10	0.07	NA
2023-11-28 13:06	149.92	0.08	144.97	0.19	-4.95	-3.30
2023-11-28 13:16	25.00	0.03	23.87	0.09	-1.13	-4.52
2023-11-28 13:26	174.95	0.08	169.42	0.08	-5.53	-3.16
2023-11-28 13:36	200.02	0.08	193.79	0.28	-6.23	-3.11
2023-11-28 13:46	49.97	0.07	48.12	0.15	-1.85	-3.70
2023-11-28 13:56	74.98	0.08	72.28	0.21	-2.70	-3.60
2023-11-28 14:06	225.00	0.07	217.91	0.30	-7.09	-3.15
2023-11-28 14:16	99.99	0.08	96.53	0.15	-3.46	-3.46
2023-11-28 14:26	124.94	0.07	120.73	0.22	-4.21	-3.37
2023-11-28 14:36	250.00	0.06	242.64	0.14	-7.36	-2.94
2023-11-28 14:46	0.06	0.11	0.25	0.17	0.19	NA
2023-11-28 14:56	49.95	0.07	48.16	0.14	-1.79	-3.58
2023-11-28 15:06	200.05	0.05	194.04	0.09	-6.01	-3.00
2023-11-28 15:16	150.00	0.05	145.24	0.07	-4.76	-3.17
2023-11-28 15:26	100.04	0.05	96.53	0.13	-3.51	-3.51
2023-11-28 15:36	250.01	0.10	242.83	0.14	-7.18	-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 (%)
2023-11-28 15:46	74.97	0.11	72.37	0.32	-2.60	-3.47
2023-11-28 15:56	24.98	0.13	24.03	0.15	-0.95	-3.80
2023-11-28 16:06	174.99	0.11	169.43	0.25	-5.56	-3.18
2023-11-28 16:16	124.94	0.07	120.86	0.06	-4.08	-3.27
2023-11-28 16:26	224.98	0.10	218.57	0.40	-6.41	-2.85
2023-11-28 16:36	0.33	0.19	0.14	0.15	-0.19	NA
2023-11-28 16:46	74.99	0.05	72.27	0.05	-2.72	-3.63
2023-11-28 16:56	150.00	0.13	145.27	0.20	-4.73	-3.15
2023-11-28 17:06	49.92	0.04	48.12	0.07	-1.80	-3.61
2023-11-28 17:16	250.01	0.07	242.74	0.44	-7.27	-2.91
2023-11-28 17:26	199.99	0.05	194.11	0.06	-5.88	-2.94
2023-11-28 17:36	99.96	0.08	96.67	0.48	-3.29	-3.29
2023-11-28 17:46	24.94	0.18	23.85	0.21	-1.09	-4.37
2023-11-28 17:56	174.95	0.05	169.61	0.33	-5.34	-3.05
2023-11-28 18:06	225.02	0.08	218.68	0.09	-6.34	-2.82
2023-11-28 18:16	125.05	0.09	121.45	0.42	-3.60	-2.88
2023-11-28 18:26	-0.02	0.13	0.19	0.09	0.21	NA
2023-11-28 18:36	149.94	0.07	145.12	0.35	-4.82	-3.21
2023-11-28 18:46	24.99	0.14	23.98	0.26	-1.01	-4.04
2023-11-28 18:56	174.96	0.07	169.80	0.40	-5.16	-2.95
2023-11-28 19:06	199.97	0.05	194.17	0.17	-5.80	-2.90
2023-11-28 19:16	49.99	0.09	48.38	0.13	-1.61	-3.22
2023-11-28 19:26	75.03	0.09	72.79	0.15	-2.24	-2.99
2023-11-28 19:36	225.01	0.07	218.64	0.03	-6.37	-2.83
2023-11-28 19:46	100.02	0.15	96.99	0.21	-3.03	-3.03
2023-11-28 19:56	125.01	0.07	121.07	0.48	-3.94	-3.15
2023-11-28 20:06	250.00	0.08	243.17	0.16	-6.83	-2.73
2023-11-28 20:16	0.04	0.17	0.14	0.12	0.10	NA
2023-11-28 20:26	49.97	0.10	48.38	0.17	-1.59	-3.18
2023-11-28 20:36	200.01	0.04	194.35	0.16	-5.66	-2.83
2023-11-28 20:46	149.93	0.08	145.84	0.22	-4.09	-2.73
2023-11-28 20:56	100.00	0.09	97.21	0.28	-2.79	-2.79
2023-11-28 21:06	250.00	0.04	243.29	0.14	-6.71	-2.68
2023-11-28 21:16	75.00	0.07	72.80	0.15	-2.20	-2.93
2023-11-28 21:26	25.00	0.09	24.23	0.12	-0.77	-3.08
2023-11-28 21:36	174.94	0.07	169.95	0.48	-4.99	-2.85
2023-11-28 21:46	125.00	0.07	121.30	0.13	-3.70	-2.96
2023-11-28 21:56	225.01	0.06	218.94	0.13	-6.07	-2.70
2023-11-28 22:06	0.05	0.13	0.26	0.13	0.21	NA
2023-11-28 22:16	74.94	0.06	72.63	0.19	-2.31	-3.08
2023-11-28 22:26	149.99	0.11	145.97	0.25	-4.02	-2.68
2023-11-28 22:36	50.01	0.08	48.59	0.14	-1.42	-2.84
2023-11-28 22:46	250.04	0.05	243.74	0.31	-6.30	-2.52
2023-11-28 22:56	200.04	0.07	194.74	0.16	-5.30	-2.65
2023-11-28 23:06	99.99	0.04	97.31	0.17	-2.68	-2.68

Table 5. *Comparison of the BHD ozone calibrator (OC) Teledyne API M700E #528 (BKG 1.1 nmol mol^{-1}, SPAN 0.992) 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 (%)
2023-11-30 12:22	-0.14	0.04	1.29	0.17	1.43	NA
2023-11-30 12:32	99.99	0.08	102.03	0.13	2.04	2.04
2023-11-30 12:42	49.98	0.04	51.59	0.41	1.61	3.22
2023-11-30 12:52	250.01	0.13	252.94	0.04	2.93	1.17
2023-11-30 13:32	149.96	0.06	152.18	0.34	2.22	1.48
2023-11-30 13:42	50.24	0.49	51.93	1.31	1.69	3.36
2023-11-30 13:52	250.01	0.05	252.86	0.23	2.85	1.14
2023-11-30 14:02	199.98	0.07	202.55	0.09	2.57	1.29
2023-11-30 14:12	100.00	0.06	101.63	0.23	1.63	1.63
2023-11-30 14:36	0.00	0.12	1.00	0.09	1.00	NA
2023-11-30 14:43	49.98	0.05	51.36	0.16	1.38	2.76
2023-11-30 14:50	199.97	0.05	202.38	0.23	2.41	1.21
2023-11-30 14:57	150.05	0.06	151.87	0.18	1.82	1.21
2023-11-30 15:04	99.93	0.06	101.55	0.18	1.62	1.62
2023-11-30 15:11	250.04	0.06	252.32	0.66	2.28	0.91
2023-11-30 15:18	-0.03	0.09	1.12	0.15	1.15	NA
2023-11-30 15:25	99.94	0.03	101.66	0.29	1.72	1.72
2023-11-30 15:32	49.96	0.03	51.54	0.30	1.58	3.16
2023-11-30 15:41	249.96	0.01	252.93	0.21	2.97	1.19
2023-11-30 15:46	149.95	0.11	152.32	0.29	2.37	1.58
2023-11-30 15:53	199.99	0.07	202.44	0.09	2.45	1.23

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

Table 6. *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2444-CFKADS2209 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 (%)
(23-11-28 15:40:06)	150819_FA02464	172.9	4.3	171.6	1.2	10	-1.3	-0.8
(23-11-28 16:03:27)	230424_FB03860	1205.1	1.2	1215.4	1.3	9	10.3	0.9
(23-11-28 19:39:30)	230424_FB03892	8.4	0.7	7.6	0.9	14	-0.8	-9.6
(24-02-23 05:09:00)	220817_FA02770	42.3	3.2	42.8	0.7	30	0.4	1.0
(24-01-12 12:25:56)	230427_FA02479	252.7	1.3	255.7	6.0	34	3.0	1.2
(23-12-07 14:23:30)	220927_FA02769	119.7	3.5	122.1	1.3	14	2.4	2.0
(24-03-03 06:33:15)	171122_FA02788	76.2	2.5	75.3	0.4	8	-1.0	-1.3
(23-12-13 14:35:12)	220927_FA01469	123.1	3.7	122.2	1.7	20	-0.9	-0.7
(23-12-12 15:42:26)	171122_FA02785	55.5	3.3	52.9	1.1	23	-2.7	-4.8
(24-01-06 05:37:42)	230426_FB03910	87.5	1.8	86.5	1.0	34	-1.0	-1.1

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

Table 7. *CH_4 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2444-CFKADS2209 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(23-11-28 16:45:45)	150819_FA02464	1965.93	0.30	1962.80	0.13	4	-3.13	-0.16
(23-11-28 16:03:27)	230424_FB03860	2361.61	0.06	2357.57	0.15	9	-4.04	-0.17
(23-11-29 05:42:00)	230424_FB03892	2.84	0.08	3.75	0.08	4	0.91	32.04
(24-02-23 05:09:00)	220817_FA02770	1918.92	0.09	1919.96	0.68	30	1.04	0.05
(24-01-12 12:25:56)	230427_FA02479	1999.97	0.08	2000.21	0.12	34	0.24	0.01
(23-12-07 14:23:30)	220927_FA02769	2009.69	0.09	2009.79	0.15	14	0.10	0.00
(24-03-03 06:33:15)	171122_FA02788	1619.02	0.14	1622.32	0.35	8	3.30	0.20
(23-12-13 14:35:12)	220927_FA01469	1971.50	0.11	1971.55	0.17	20	0.05	0.00
(23-12-12 15:42:26)	171122_FA02785	1856.36	0.14	1856.85	0.16	23	0.49	0.03
(24-01-06 05:37:42)	230426_FB03910	1926.67	0.11	1927.02	0.08	34	0.35	0.02

A6. Carbon dioxide comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before and after the audit. The WCC-Empa travelling standards are 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 presented in the Executive Summary, and the individual measurements of the TS are presented in the following table.

Table 8. *CO_2 aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2444-CFKADS2209 instrument (AL) with the WCC-Empa TS (WMO-X2019 CO_2 scale).*

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(23-11-28 16:45:45)	150819_FA02464	401.69	0.05	401.25	0.01	4	-0.44	-0.11
(23-11-28 16:03:27)	230424_FB03860	464.36	0.02	463.69	0.05	9	-0.67	-0.14
(23-11-29 05:42:00)	230424_FB03892	0.38	0.02	1.52	0.01	4	1.14	NA
(24-02-23 05:09:00)	220817_FA02770	415.72	0.06	415.99	0.06	30	0.27	0.06
(24-01-12 12:25:56)	230427_FA02479	439.13	0.04	439.10	0.05	34	-0.03	-0.01
(23-12-07 14:23:30)	220927_FA02769	450.38	0.06	450.20	0.08	14	-0.18	-0.04
(24-03-03 06:33:15)	171122_FA02788	337.28	0.05	338.41	0.04	8	1.13	0.34
(23-12-13 14:35:12)	220927_FA01469	431.93	0.04	431.90	0.06	20	-0.03	-0.01
(23-12-12 15:42:26)	171122_FA02785	408.45	0.11	408.49	0.02	23	0.04	0.01
(24-01-06 05:37:42)	230426_FB03910	429.48	0.07	429.41	0.03	34	-0.07	-0.02

A7. Calibration Standards for CO, CH_4 and CO_2

Table 9 provides an overview the standard gases available for calibration of the CO, CH_4 and CO_2 instruments.

Table 9 *BHD calibration standards as of November 2023.*

Cylinder ID	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2 (X2019) (µmol mol^{-1})	Usage
CA03758	91.92	1883.94	404.22	Laboratory standard (CCL)
CA08128	82.59	1938.82	441.53	Laboratory standard (CCL)
CC311714	152.7	1913.38	406.49	Laboratory standard (CCL)
ND05874	53.36	1803.91	388.74	Laboratory standard (CCL)
ND05876	179.23	1939.56	411.42	Laboratory standard (CCL)

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 #1171430027, BKG 0.0, COEF 0.991

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

$$X_{TS} \text{ (nmol mol}^{-1}\text{)} = ([TS] - 0.01 \text{ nmol mol}^{-1}) / 1.0000 \quad (13)$$

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

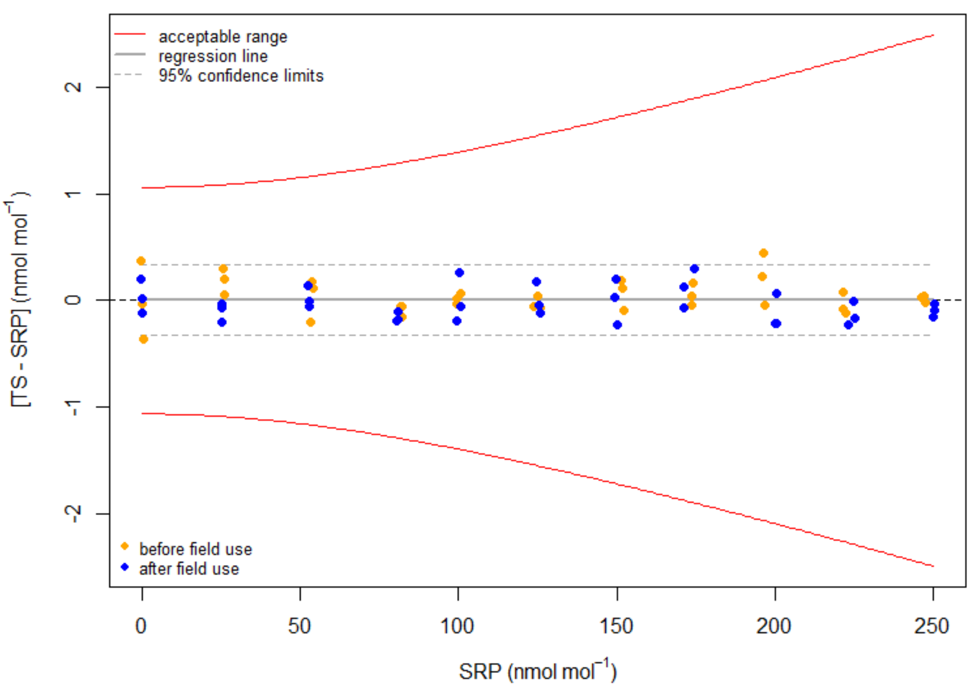

Figure 21. *Deviations between Traveling Standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS in the field.*

***Table 10**. 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})
2023-10-25	1	55	53.34	0.42	53.14	0.43
2023-10-25	1	150	151.77	0.40	151.88	0.34
2023-10-25	1	0	-0.05	0.11	-0.08	0.09
2023-10-25	1	245	246.37	0.23	246.40	0.34
2023-10-25	1	195	196.13	0.37	196.36	0.19
2023-10-25	1	80	81.82	0.40	81.77	0.24
2023-10-25	1	25	25.77	0.41	25.97	0.11
2023-10-25	1	100	99.53	0.30	99.55	0.16
2023-10-25	1	125	125.03	0.41	125.07	0.17
2023-10-25	1	175	173.62	0.33	173.67	0.25
2023-10-25	1	220	221.73	0.32	221.65	0.16
2023-10-25	2	80	82.16	0.39	82.01	0.24
2023-10-25	2	150	152.22	0.38	152.13	0.26
2023-10-25	2	25	25.89	0.22	25.94	0.14
2023-10-25	2	245	247.32	0.26	247.37	0.29
2023-10-25	2	195	196.43	0.32	196.88	0.15
2023-10-25	2	0	0.37	0.24	0.01	0.16
2023-10-25	2	125	123.89	0.31	123.83	0.21
2023-10-25	2	175	173.97	0.24	174.13	0.24
2023-10-25	2	220	222.22	0.25	222.10	0.18
2023-10-25	2	55	53.72	0.36	53.90	0.21
2023-10-25	2	100	100.45	0.22	100.52	0.13
2023-10-25	3	250	247.66	0.37	247.64	0.30
2023-10-25	3	195	196.95	0.35	196.91	0.19
2023-10-25	3	25	25.54	0.18	25.85	0.14
2023-10-25	3	125	125.62	0.51	125.55	0.14
2023-10-25	3	0	-0.29	0.34	0.09	0.08
2023-10-25	3	100	99.57	0.48	99.54	0.14
2023-10-25	3	55	54.09	0.35	54.20	0.18
2023-10-25	3	220	221.55	0.68	221.63	0.30
2023-10-25	3	175	173.48	0.49	173.44	0.20
2023-10-25	3	150	151.34	0.25	151.53	0.17
2023-10-25	3	80	81.98	0.26	81.93	0.25
2024-03-27	4	0	-0.24	0.41	-0.04	0.11
2024-03-27	4	80	80.86	0.24	80.76	0.30
2024-03-27	4	225	223.34	0.44	223.11	0.29
2024-03-27	4	55	52.51	0.44	52.65	0.20
2024-03-27	4	170	171.38	0.58	171.31	0.35
2024-03-27	4	125	125.82	0.27	125.70	0.16
2024-03-27	4	25	25.17	0.39	25.14	0.08
2024-03-27	4	150	150.10	0.46	149.88	0.44
2024-03-27	4	100	100.63	0.36	100.58	0.19
2024-03-27	4	250	250.25	0.24	250.21	0.27
2024-03-27	4	200	200.34	0.28	200.41	0.15
2024-03-27	5	55	52.77	0.26	52.72	0.21

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2024-03-27	5	125	124.52	0.31	124.69	0.14
2024-03-27	5	175	174.34	0.11	174.64	0.17
2024-03-27	5	80	80.56	0.26	80.37	0.24
2024-03-27	5	100	100.03	0.30	100.29	0.12
2024-03-27	5	250	249.82	0.31	249.66	0.17
2024-03-27	5	25	25.23	0.29	25.03	0.11
2024-03-27	5	225	225.46	0.34	225.30	0.19
2024-03-27	5	200	200.01	0.23	199.79	0.15
2024-03-27	5	0	0.10	0.28	-0.02	0.10
2024-03-27	5	150	149.95	0.87	150.15	0.71
2024-03-27	6	150	149.38	0.56	149.42	0.18
2024-03-27	6	55	52.95	0.29	52.94	0.14
2024-03-27	6	80	80.75	0.28	80.57	0.09
2024-03-27	6	125	125.22	0.38	125.17	0.13
2024-03-27	6	170	171.04	0.25	171.17	0.19
2024-03-27	6	200	200.34	0.27	200.12	0.17
2024-03-27	6	0	-0.07	0.37	-0.05	0.20
2024-03-27	6	225	224.65	0.22	224.64	0.17
2024-03-27	6	250	250.46	0.27	250.37	0.16
2024-03-27	6	25	25.06	0.31	24.99	0.10
2024-03-27	6	100	99.60	0.27	99.41	0.16

#The level is only indicative.

A9. WCC-Empa GHG and CO traveling standards

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

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

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

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

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

Table 11 gives an overview of the WCC-Empa laboratory standards 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 12 and Figure 21 shows the analysis of the TS over time.

Table 11. *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 12. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, N_2O and CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (L) Los Gatos.*

TS	Pressure (psi)	CH_4 (P) (nmol mol^{-1})	sd	CO_2 (P) (µmol mol^{-1})	sd	N_2O (L) (nmol mol^{-1})	sd	CO (P) (nmol mol^{-1})	sd
150819_FA02464	1610	1965.93	0.30	401.69	0.05	329.13	0.04	172.93	4.32
171122_FA02785	1090	1856.36	0.14	408.45	0.11	341.84	0.06	55.53	3.33
171122_FA02788	1100	1619.02	0.14	337.28	0.05	283.90	0.19	76.24	2.49
220817_FA02770	1700	1918.92	0.09	415.72	0.06	340.39	0.12	42.34	3.20
220927_FA01469	1500	1971.50	0.11	431.93	0.04	334.31	0.12	123.07	3.70
220927_FA02769	1050	2009.69	0.09	450.38	0.06	337.45	0.03	119.66	3.47
230424_FB03860	2030	2361.61	0.06	464.36	0.02	355.96	0.21	1205.07	1.20
230424_FB03892	1890	2.84	0.08	0.38	0.02	14.04	3.13	8.44	0.73
230426_FB03910	1670	1926.67	0.11	429.48	0.07	342.04	0.08	87.46	1.75
230427_FA02479	1790	1999.97	0.08	439.13	0.04	341.42	0.05	252.70	1.27

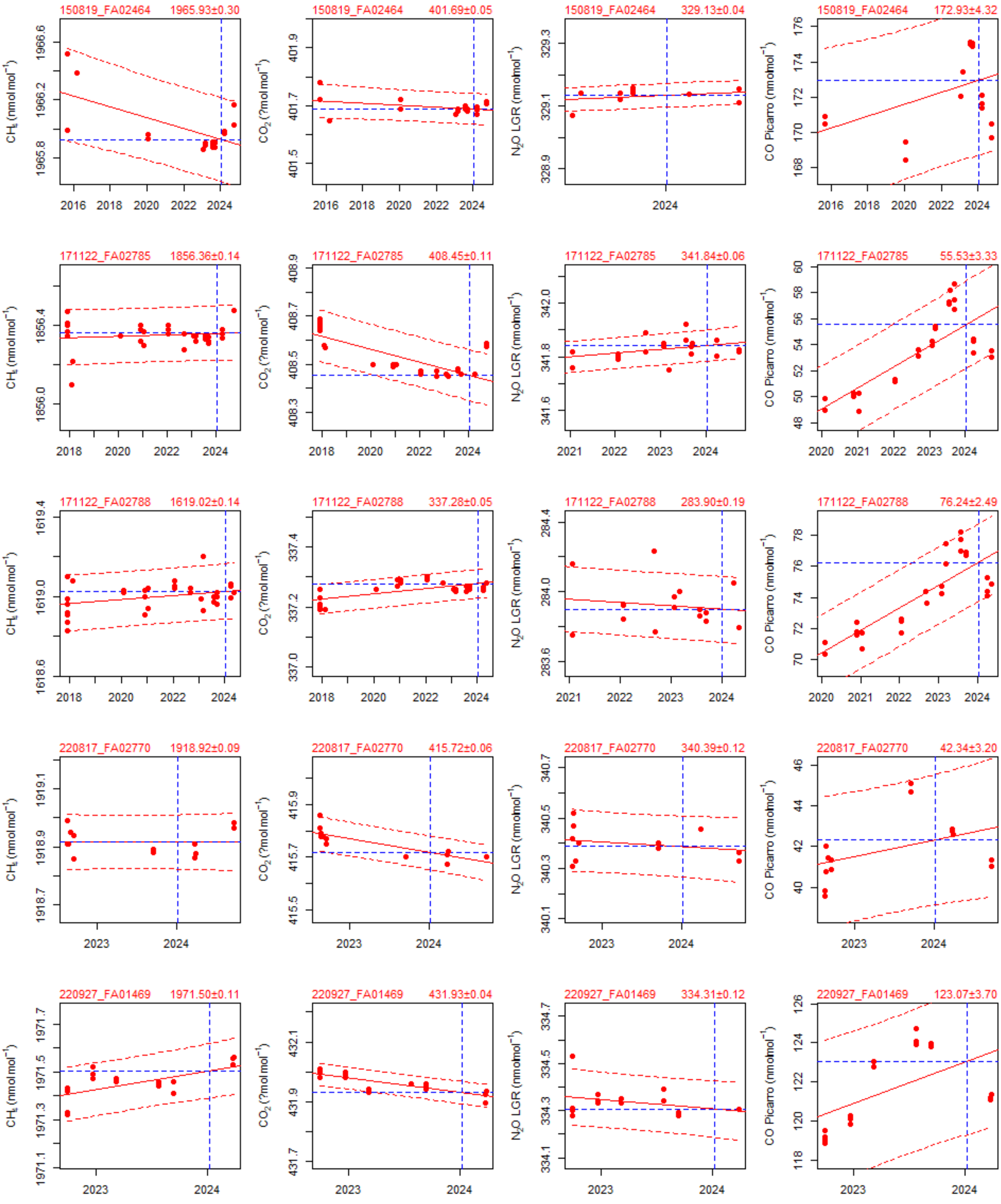

Figure 22. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, N_2O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the audit date.*

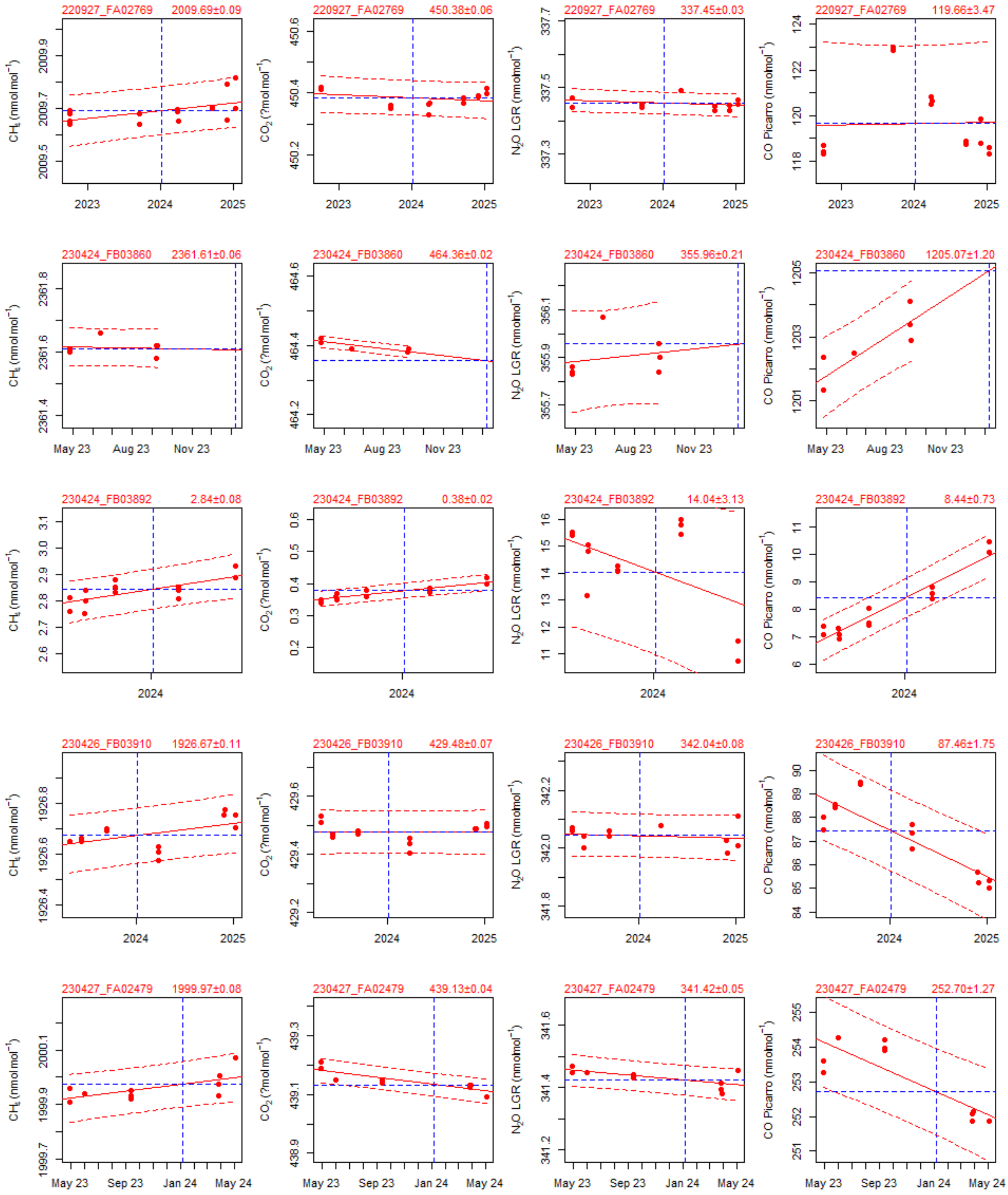

Figure 23. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, N_2O and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the audit date.*

A10. Calibration of the 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 3285 minutes using one WCC-Empa TS as the working standard and two TS as target tanks. Based on the working standard measurements, a Loess fit drift correction was applied to the data as shown in the figure below. For the continuously running instrument, the maximum drift between two WS measurements was approximately 0.5 nmol mol^{-1} for CH_4 and 0.1 µmol mol^{-1} for CO_2. Most of the target cylinder measurements were within half of the WMO GAW compatibility goals.

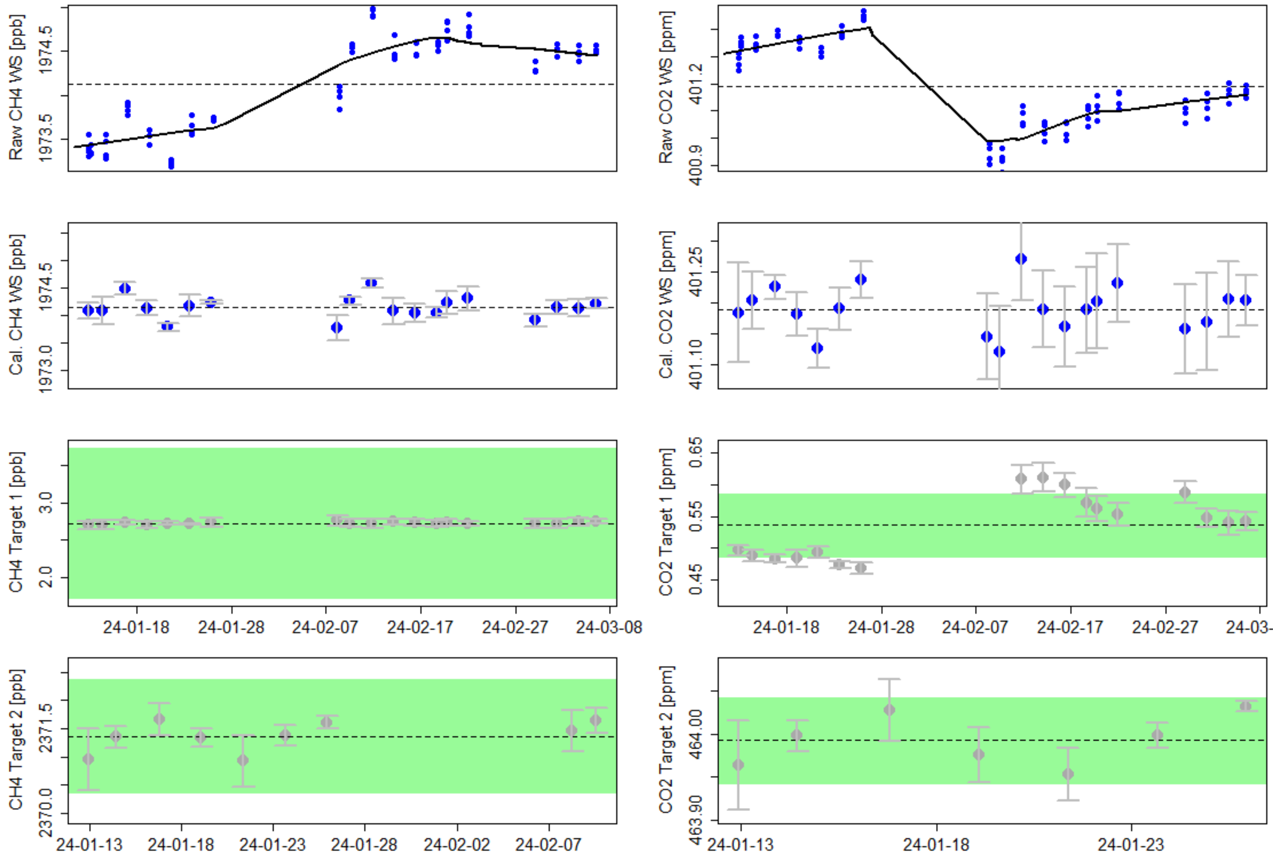

Figure 24. *CH_4 (left panel) and CO_2 (right panel) calibrations of the TI. The top panel shows the raw 1 min values of the working standard and the Loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The bottom panel 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 3285 minutes using three WCC-Empa TS as working standards. Based on the working standard measurements, a Loess fit drift correction was first applied to the data, as shown in the figure below.

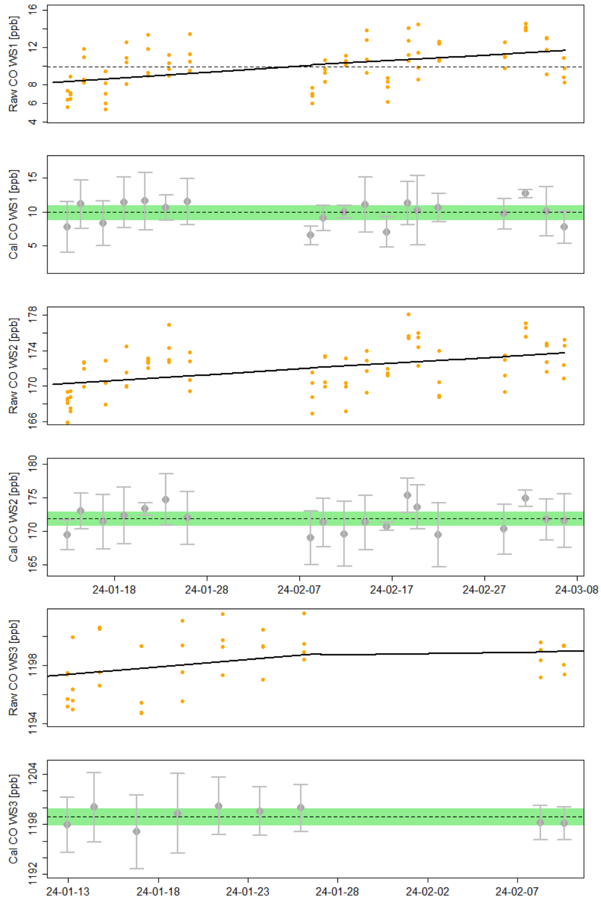

Figure 25. *CO calibrations of the TI. The panels with the orange dots show the raw 1 min values of the working standards and the Loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in these panels 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.

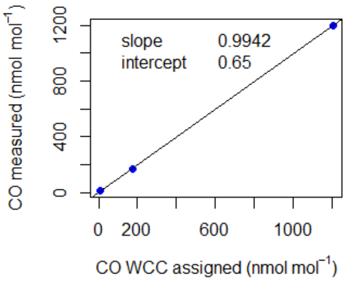

Figure 26. *CO calibration function based on the average values of the drift corrected working standard measurements.*

References

Brailsford, G. W., Stephens, B. B., Gomez, A. J., Riedel, K., Mikaloff Fletcher, S. E., Nichol, S. E., and Manning, M. R.: Long-term continuous atmospheric CO_2 measurements at Baring Head, New Zealand, Atmos. Meas. Tech., 5, 3109-3117, 10.5194/amt-5-3109-2012, 2012.

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, Journal Of Geophysical Research-Atmospheres, 110, Article D18306, 2005.

Empa: Standard Operating Procedure (SOP), Measurement uncertainty of ozone measuring instruments and standards, 7th Edition from 13 February 2014 (available in German), Empa, Laboratory for Air Pollution / Environmental Technology, 2014.

Hall, B. D., Crotwell, A. M., Kitzis, D. R., Mefford, T., Miller, B. R., Schibig, M. F., and Tans, P. P.: Revision of the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) CO_2 calibration scale, Atmos. Meas. Tech., 14, 3015-3032, 10.5194/amt-14-3015-2021, 2021.

Hearn, A. G.: Absorption of ozone in ultra-violet and visible regions of spectrum, Proceedings of the Physical Society of London, 78, 932-&, 10.1088/0370-1328/78/5/340, 1961.

Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, Journal of Geophysical Research-Atmospheres, 108, 4622, doi:4610.1029/2003JD003710, 2003.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech., 6, 837-860, 10.5194/amt-6-837-2013, 2013.

WMO: Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland, 2007.

WMO: Guidelines for Continuous Measurements of Ozone in the Troposphere, WMO TD No. 1110, GAW Report No. 209, World Meteorological Organization, Geneva, Switzerland, 2013.

WMO: Twenty-first WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2022), Wageningen, The Netherlands, 19–21 September 2022, GAW Report No. 292, World Meteorological Organization, Geneva, Switzerland, 2024.

WMO: WMO Global Atmosphere Watch (GAW) Science and Implementation Plan: 2024–2027, GAW Report No. 312. , World Meteorological Organization, Geneva, Switzerland, 2025.

Zellweger, C., Steinbacher, M., and Buchmann, B.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, Atmos. Meas. Tech., 5, 2555-2567, 10.5194/amt-5-2555-2012, 2012.

Zellweger, C., Steinbrecher, R., Laurent, O., Lee, H., Kim, S., Emmenegger, L., Steinbacher, M., and Buchmann, B.: Recent advances in measurement techniques for atmospheric carbon monoxide and nitrous oxide observations, Atmos. Meas. Tech., 12, 5863-5878, 10.5194/amt-12-5863-2019, 2019.

Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M., Kozlova, E., Spain, T. G., Steinbacher, M., van der Schoot, M. V., and Buchmann, B.: Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, Atmos. Meas. Tech., 9, 4737-4757, 10.5194/amt-9-4737-2016, 2016.

List of abbreviations

BKG	Background
BHD	Baring Head GAW Station
CCL	Central Calibration Laboratory
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
eDQO	Extended Data Quality Objective
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
IR	Infrared
LGR	Los Gatos Research
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NIWA	New Zealand National Institute of Water and Atmospheric Research
NOAA	National Oceanic and Atmospheric Administration
QA/SAC	Quality Assurance/Science Activity Centre
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