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

AT THE

REGIONAL GAW STATION
PHA DIN
VIETNAM
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World Meteorological Organization

GLOBAL ATMOSPHERE WATCH

Empa Materials Science and Technology

WCC-Empa Report 22/5

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

Acknowledgements

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WCC-Empa Report 22/5

Contact Information:

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

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit by WCC-Empa[1] at the regional GAW station Pha Din (PDI), which is run by Hydro-Meteorological Observation Center (HYMOC) of the Vietnam Hydrological and Meteorological Administration (VNMHA), was conducted from 24 - 27 November 2022 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of all WCC-Empa audits and the corresponding audit reports is available from the WCC-Empa webpage (www.empa.ch/gaw). The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Dr Martin Steinbacher	Empa, Dübendorf, QA/SAC Switzerland
Mr Nguyen Nhat Anh	HYMOC, Technical Manager of environmental and climate observation network
Mr Vang A Phia	Pha Din station, North-West Regional Meteo-Hydrological Center Station manager and operator
Mr Vu Khac Minh	Maintenance company (Comtech)
Mr Vu Minh Hoang	Maintenance company (Comtech)
Mr Nguyen Minh Sang	HYMOC, Technician of meteorological, environmental and climate observation network
Mr Nguyen Quang Vinh	HYMOC, Technician of meteorological, environmental and climate observation network
Mr Truong Cong Dung	North-West Regional Meteo-Hydrological Center Technical manager

This report summarises the assessment of the Pha Din GAW station in general, as well as the surface ozone, methane, carbon dioxide, and carbon monoxide in particular.

The report is distributed to the Vietnam Hydrological and Meteorological Administration (VMHA), the station manager of Pha Din, the national focal point for GAW in Vietnam, and the World Meteorological Organization in Geneva. The report will be published as a WMO/GAW report and posted on the internet (www.empa.ch/web/s503/wcc-empa).

The recommendations found in this report are graded as minor, important and critical and are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Management and Operation

The station is operated and managed by the run by the Hydro-Meteorological Observation Center (HYMOC) of the Vietnam Hydrological and Meteorological Administration (VNMHA). The station is under the responsibility of the North-West Regional Meteo-Hydrological Center of Vietnam, and it is permanently staffed with a station operator. Maintenance and repair of instrument is outsourced to a private company (Comtech, http://vncomtech.com/, website currently not working).

> **Recommendation 1 (***, important, ongoing)**
> *VNMHA should explore all possibilities for training of station operators and scientists. Participation in GAWTEC as well as other training courses is highly recommended, and the knowledge needs to be shared within VNMHA/HYMOC.*

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

Measurements of surface ozone, carbon monoxide and greenhouse gases were established in 2014 as part of the Capacity Building and Twinning for Climate Observing Systems (CATCOS) project, which was financed by the Swiss Agency for Development and Cooperation (SDC) with MeteoSwiss as the coordinating partner. The implementation was made by the CATCOS project team and QA/SAC Switzerland.

Station Location and Access

PDI (21.5731°N, 103.5157°E, 1466 m a.s.l.) is located on a hilltop in the northwest of Vietnam on a mountain pass at the border of the Son La and Dien Bien provinces. The pass is embedded in a mountain chain with hills between 700 and 1600 m a.s.l., stretching from China into Vietnam in a northwest-to-southwest orientation. The surrounding of the station is mainly covered with forest, but the station itself is above the canopy. There are no residents at the station except for the station operators, and no relevant residential areas within 10–20 km except for sparse farmhouses. The location is adequate for the intended purpose. The station is accessible by road. More information is available from GAWSIS (https://gawsis.meteoswiss.ch) and from Bukowiecki et al. (2019).

Station Facilities and Infrastructure

The Pha Din station comprises a small laboratory, and basic offices, kitchen and sanitary facilities are available. Internet access is available with sufficient bandwidth (about 50 MPS up- and download). The facilities are sufficient to support the current measurement programme. However, more space is needed in case of an extension of the programme. The meteorological parameters are still manually recorded in 3 to 6-hourly intervals, and change to an automated system is recommended. Next to the laboratory, office and lodging facilities, a state-of-the-art weather radar on top of a 30 m tower is also operated.

> **Recommendation 2 (***, important, 2022)**
> *The availability of continuously meteorological data is important for the interpretation of the PDI measurements. The installation of an automated weather station is recommended.*

Measurement Programme

The PDI GAW station hosts a small measurement programme of observations of trace gases and aerosol properties that covers the most important parameters of the GAW programme. An overview on measured species is available from GAWSIS (https://gawsis.meteoswiss.ch/GAWSIS).

The information available from GAWSIS was reviewed as part of the audit. The last update was made in 2014, but the information was still mostly up-to-date. However, more details (e.g. instrument characteristics) should be added, and the list of station contacts needs to be revised.

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

Data Submission

As of November 2022, the following PDI data of the scope of the audit has been submitted to the World Data Centres:

VNMHA, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2014-2021)

VNMHA, submission to World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2014-2021), CO_2 (2014-2021), CO (2014-2021)

Data shown in this report was accessed on 25 November 2022. All data of the scope of the audit has been submitted with a submission delay of less than one year. Continuation of this timely submission practice is recommended.

Data evaluation still relies on the support from external partners, and is done as part of the twinning between HYMOC and QA/SAC Switzerland. Responsibility for data analysis and data ownership needs to be transferred to HYMOC.

> **Recommendation 4 (***, critical, ongoing)**
> *HYMOC staffs needs to get more involved in the data validation process. HYMOC is further encouraged to actively use the available data for scientific purposes.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCRG and WDCGG was reviewed. Summary plots and a short description of the findings are presented in the Appendix.

Documentation

Information is entered in electronic log books (ELOG). Log books are available for all instruments. The electronic note books are stored locally on the data acquisition PC. It was noted that no backup was available. The instrument manuals are available at the site. The reviewed information was mostly comprehensive and up-to-date. However, the checklists for the ozone instrument were not filled in, and it was therefore not possible to identify the period when the issue with the pressure sensor has started. Most ancillary instrument parameters are continuously recorded by the data acquisition system, but not the pressure of the ozone instrument.

> **Recommendation 5 (***, important, ongoing)**
> *It is recommended to fill in the checklist for the ozone instrument on a weekly basis. All electronic log books need to be backed-up in regular intervals.*

Air Inlet System

Ozone: The air inlet is located 12 m above ground on top of a mast located north of the station building. It is protected against rain by a downward facing Teflon filter holder. The inlet line consists of a ~18 m long ¼ inch PFA tube, which goes directly to the ozone instrument. The flow rate in the line of approximately 1 l/min is controlled by the ozone analyser. The instrument is protected by a PTFE inlet filter. The residence time is approximately 14 seconds.

GHG and CO measurements: Same air intake location as for ozone. The inlet line is protected against rain by a downward filter holder. The inlet line consists of a ~18 m long ¼ inch Synflex-1300 tube, which goes directly to the valve box of the instrument. The flow rate in the line of approximately 4 l/min is controlled by an external pump. The instrument is protected by a stainless steel inlet filter. The residence time is approximately 5 seconds.

The inlet systems are adequate regarding material and residence times, and no change is required.

Data Acquisition

Currently, data of the gaseous species are stored on a commercial data acquisition system as hourly text files (Breitfuss GmbH; EasyComp and MKT/Anavis). These files contain all necessary ancillary information from the instruments, with the exception of the pressure sensor reading of the ozone instrument. Data transfer to Empa is operational. The automatic data transfer to VNMHA needs still to be established.

> **Recommendation 6 (***, important, 2023)**
> *An automatic data transfer to VNMHA should be established, which would serve as an off-site back-up of the data and which is a prerequisite for taking over the full data ownership and the processing of the data (see also recommendation 4).*

VNHMA has ambitious plans to install a network of up to 35 climate monitoring stations measuring trace gases and aerosols throughout the country. 7 of them are already deployed. While a common data flow to the VNHMA headquarters in Hanoi is in place for the newly established sites, Pha Din data are treated in an isolated fashion.

> **Recommendation 7 (***, important, 2023)**
> *VHNMA should make better use of the long-term experience gained at Pha Din when pursuing its extension plans towards a country-wide network of Pha Din-like monitoring stations. Pha Din could serve as a blueprint in terms of equipment, quality assurance, quality control and data processing.*

Surface Ozone Measurements

Surface ozone measurements at PDI were established in 2014 as part of the CATCOS project, and continuous time series are available since then.

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

Standards. No ozone standard is available. The instrument has only be calibrated before installation at WCC-Empa in 2012, and no further calibration have been made since then until the current audit.

> **Recommendation 8 (***, important, 2024)**
> *It is recommended to purchase an ozone calibrator with traceability to the WMO/GAW ozone reference for regular (at least yearly) checks of the instrument.*

Intercomparison (Performance Audit). The PDI analyser was compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}.

It was noted during the first comparison that the pressure sensor of the PDI analyser was not working. The reading showed constantly 999.9 mmHg, and consequently, the pressure compensation was not possible. The pressure in the measurement cells is a required variable for the determination of the sample's ozone mole fraction. The reason for the faulty pressure reading was identified after the initial comparison, and the broken interface board of the PDI Thermo 49i instrument was exchanged with the board of the WCC-Empa TS. A second comparison was made with the correct pressure readings for the PDI analyser. Due to the broken board, the pressure measurement of the WCC-Empa TS was not possible. The pressure of the TS was set to 643.0 mmHg, which was slightly below the ambient pressure of 644.6 mmHg (859 hPa). The ambient pressure was recorded, and the variability was ±2 hPa during the second comparison, leading to a slightly higher uncertainty in the reference values.

The result of the first and second comparisons are summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system. The following equations characterise the bias of instruments and the remaining uncertainty after compensation of the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the ozone absorption cross section of 11.476×10^{-18} cm^2 $molecule^{-1}$ (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #1205551879 (BKG 0.0 nmol mol^{-1}, SPAN 1.011), before replacement of the interface board:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.06 nmol mol^{-1}) / 0.6483 (1a)

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

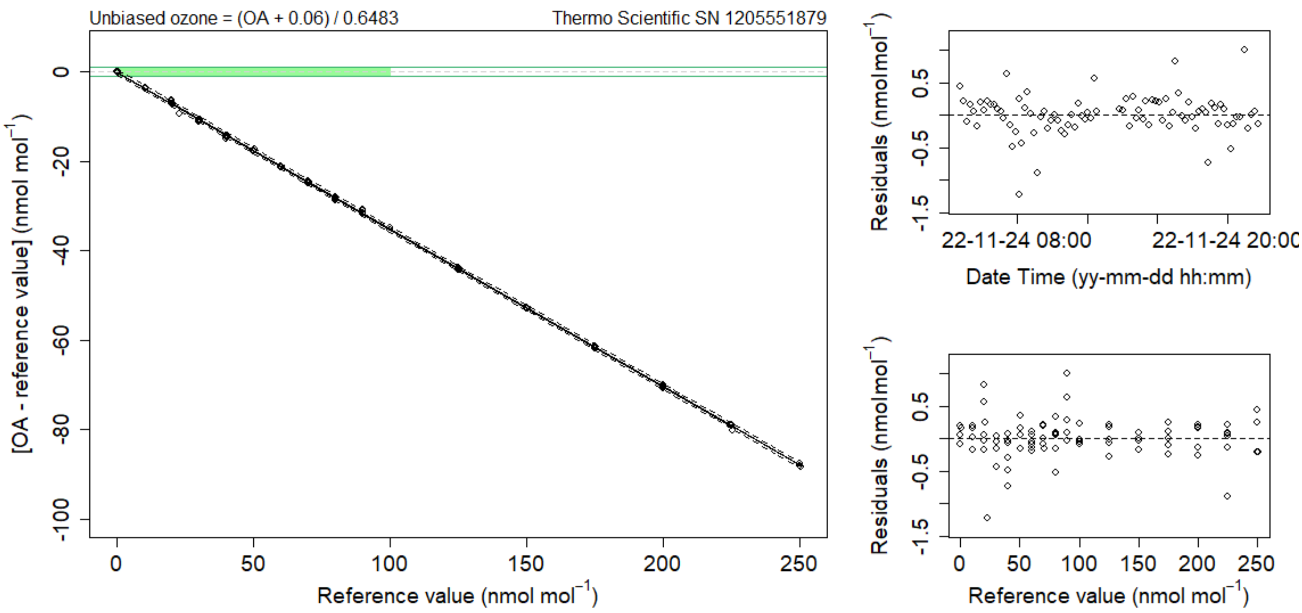

Figure 1. *Left: Bias of the PDI ozone analyser (Thermo Scientific 49i #1205551879, BKG -0.0 nmol mol^{-1}, COEF 1.011, initial condition, unrepaired) with respect to the SRP as a function of mole fraction. Each point represents the average of ten 40 second averages at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

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

A large bias was observed due to the wrong pressure value of the PDI ozone analyser. The value was fixed at 999.9 mmHg due to the broken interface board. The ambient pressure was 644.6 mmHg during the comparison. The cell pressure is usually a few mm Hg below ambient pressure. The bias can therefore entirely be explained by the pressure reading difference, and the calibration of the analyser itself is still valid.

To confirm this, a second comparison was made with swapped interface boards of the PDI analyser and the WCC-Empa TS. The pressure in the measurement cell of the TS is normally also slightly below ambient pressure, and to account for this, the pressure in the TS was set to a fixed value of 643.0 mmHg (ambient 645.4 mmHg). The result after swapping the interface board and using a fixed pressure value in the TS, was as follows:

Thermo Scientific 49i #1205551879 (BKG 0.0 nmol mol^{-1}, SPAN 1.011), after replacement of the interface board:

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.47 nmol mol^{-1}) / 1.0060 (1c)

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

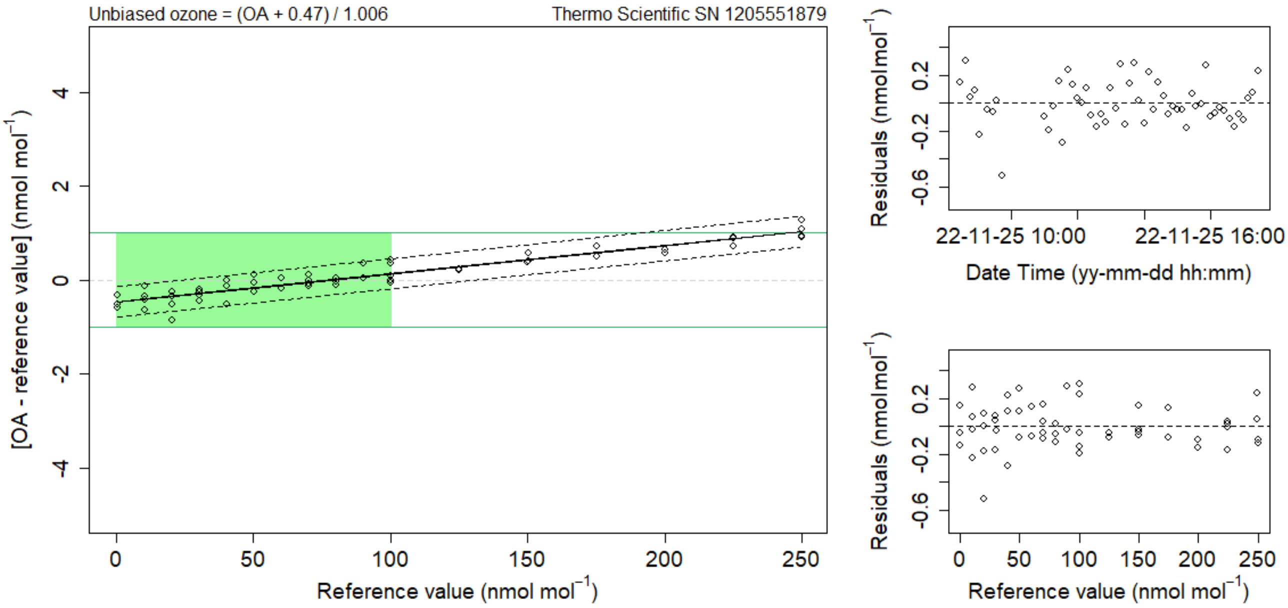

Figure 2. *Left: Bias of the PDI ozone analyser (Thermo Scientific 49i #1205551879, BKG -0.0 nmol mol^{-1}, COEF 1.011, final condition, replaced interface board) with respect to the SRP as a function of mole fraction. Each point represents the average of ten 40 second averages at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

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

Agreement within the WMO/GAW DQOs was found after the replacement of the interface board of the PDI ozone analyser. The results confirms that the initial calibration of the instrument made at WCC-Empa at the beginning of the CATCOS project remains still valid. However, the PDI time series needs to be thoroughly re-analysed to identify the point in time when the interface board failed. To do so, historic data should be compared with most likely unbiased data right after the audit. Several months of data following the audit should be used to identify any systematic biases for certain periods of the previous data. Daily or even monthly aggregates should be compared to minimize the effect of short term variability. Furthermore, the ozone instrument is reaching the end of its expected lifetime, and replacement should be considered.

Recommendation 9 (*, critical, 2023)**
All ozone data needs to be re-analysed. The time of the interface board failure needs to be identified, and data of the corresponding time period needs to be flagged as invalid.

Recommendation 10 (, important, 2023)**
Replacement of the PDI ozone instrument should be considered. This needs to be included the budgetary planning of the PDI station.

After the comparison, WCC-Empa donated the interface board of its travelling standard. Thus, the functional interface board remained in the Pha Din ozone analyser after the second comparison to ensure correct measurements also after the audit.

Carbon Monoxide Measurements

Carbon monoxide measurements at PDI were established in 2014 as part of the CATCOS project, and continuous time series are available since then.

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

Standards. At the time of the audit, two NOAA laboratory standards and seven working standards provided by WCC-Empa were available at PDI. An overview of the available standards is shown in Table 8 in the Appendix.

Calibrations schemes with the following sequence were/are implemented:

Before the current audit:

Air-WS-Air-WS-Air-WS-LS1-LS2-LS3-Air-WS-Air-WS-Air-WS-LS1-Air-WS.
Standards (LS: laboratory standards, WS: working standards) were measured for 20 min, and air for 1500 min. The first five minutes after a change were rejected.

After the current audit:

Air-WS-Air-WS-Air-WS-LS1-LS2-LS3-LS4-Air-WS-Air-WS-Air-WS-LS1-Air-WS.
Standards are measured for 20 min, and air for 1500 min. The first eight minutes after a change are rejected. Compared to the previous sequence, additional measurements of an almost CO-free (0.58 nmol mol^{-1}) LS (pure nitrogen, quality 6.0) and a LS containing high CO (3.97 µmol mol^{-1} and ambient CH_4 and CO_2 mole fractions) are made for the calibration of CO.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PDI instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The TS were analysed twice: The first comparison was made using the calibration standards that were available before the current audit (Table 1), and the second comparison was made after the implementation of the new calibration scheme (Table 2).

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

Cylinder ID	CH_4 (X2004A) (nmol mol^{-1})	CO_2(X2019) (µmol mol^{-1})	CO (X2014A) (nmol mol^{-1})	Calibration gas for
CC726879	479.35	2015.99	481.27	CH_4, CO_2, CO
CB09677	373.76	1773.84	145.42	CH_4, CO_2, CO
120315_CB08982	287.57	1888.78	171.3	CH_4, CO_2, CO

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

Cylinder ID	CH_4 (X2004A) (nmol mol^{-1})	CO_2(X2019) (µmol mol^{-1})	CO (X2014A) (nmol mol^{-1})	Calibration gas for
CC726879	479.35	2015.99	481.27	CH_4, CO_2
CB09677	373.76	1773.84	145.42	CH_4, CO_2
201209_CC726929	388.69	2036.03	3970.6	CH_4, CO_2, CO
220815_CC749996	0.05	0.16	0.58	CO

The following equations characterise the instrument bias. The result is further illustrated in Figures 3 and 4 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1145-CFKADS2028, first comparison:

Unbiased CO mixing ratio:	X_{CO} (nmol mol^{-1}) = (CO + 5.72 nmol mol^{-1}) / 1.0102	(2a)
Remaining standard uncertainty:	u_{CO} (nmol mol^{-1}) = sqrt (1.3 nmol mol^{-1} + 1.01e-04 * X_{CO}^2)	(2b)

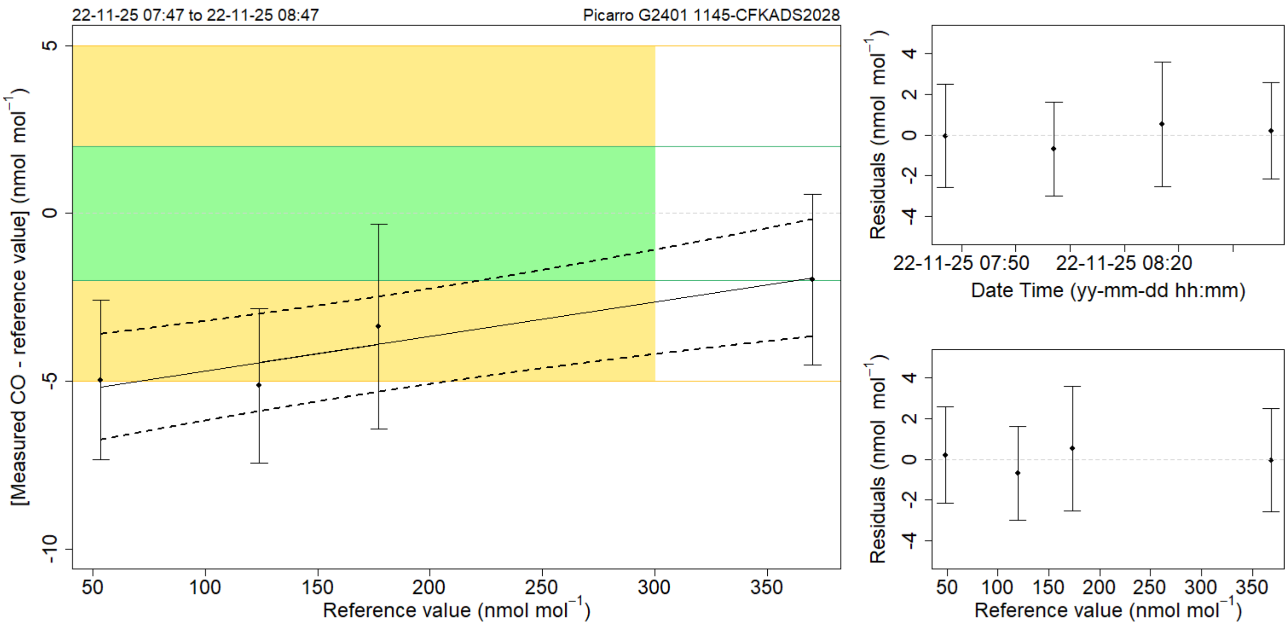

Figure 3. *Left: Bias of the PDI Picarro G2401 #1145-CFKADS2028 carbon monoxide instrument (initial comparison) with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for PDI. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #1145-CFKADS2028, second comparison:

Unbiased CO mixing ratio:	X_{CO} (nmol mol^{-1}) = (CO + 0.67 nmol mol^{-1}) / 0.9951	(2c)
Remaining standard uncertainty:	u_{CO} (nmol mol^{-1}) = sqrt (1.1 nmol mol^{-1} + 1.01e-04 * X_{CO}^2)	(2d)

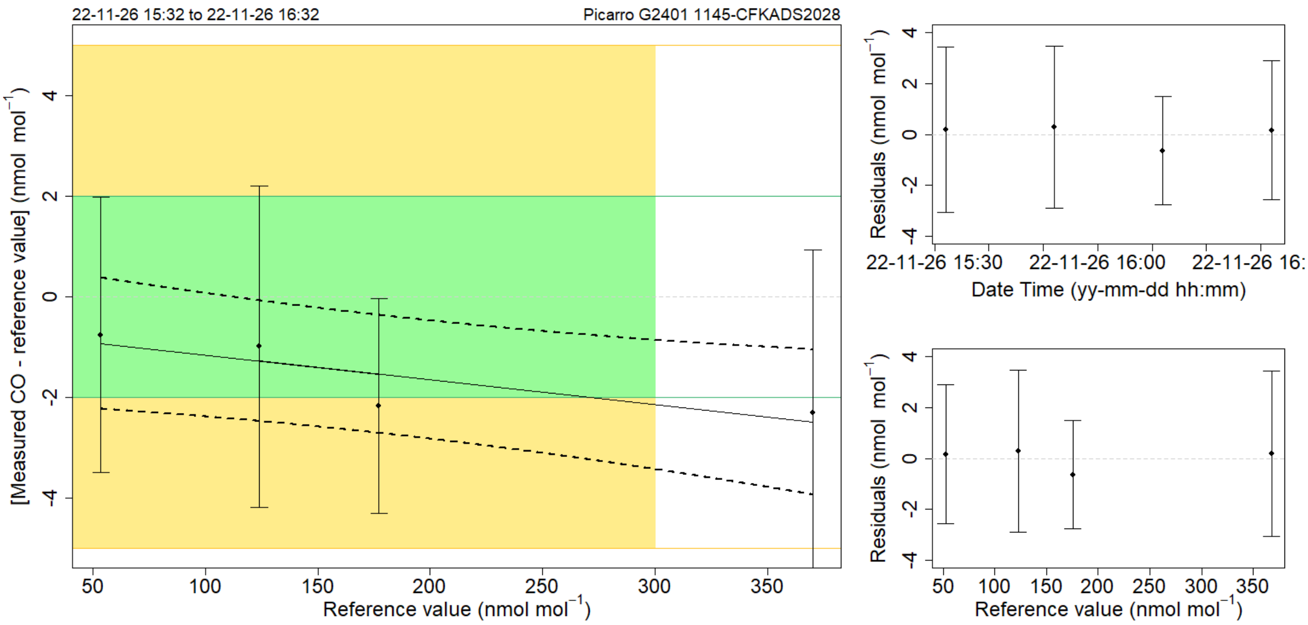

Figure 4. *Same as above, for the second comparison.*

The results of the comparisons can be summarised as follows:

The agreement between the PDI CO analyser significantly improved after the implementation of the new calibration scheme using standards with very low and high amount fractions for the calibration. A part of the bias during the first comparison with the previous calibration scheme can be most likely attributed to instability (drift) issues of the CO mole fractions in the laboratory standards since CO mole fractions are known to be prone to growth in the cylinders. It was noticed that the PDI CRDS instrument showed a relatively high short term noise for CO, which is exceeding the instrument specifications of 10 nmol mol^{-1}. Therefore, instrument replacement should be foreseen in the near future.

> **Recommendation 11 (**, important, 2023)**
> *Replacement of the PDI CRDS instrument will be necessary in the near future due to the age of the instrument. This needs to be included in the budgetary planning for the PDI station.*

Methane Measurements

See the section on carbon monoxide measurements above for instrumentation, standards and comparison procedure. Like for CO, a different set of standards was for the second comparison, which corresponds to the set of standards used operationally after the audit. However, the pure nitrogen standard is not used for CH_4 calibration and no particularly high CH_4 standard is applied as the high CO standard contains close to ambient CH_4 mole fractions

The following equations characterise the instrument bias. The result is further illustrated in Figures 5 and 6 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1145-CFKADS2028, first comparison:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 4.97 nmol mol^{-1}) / 0.9977 (3a)

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

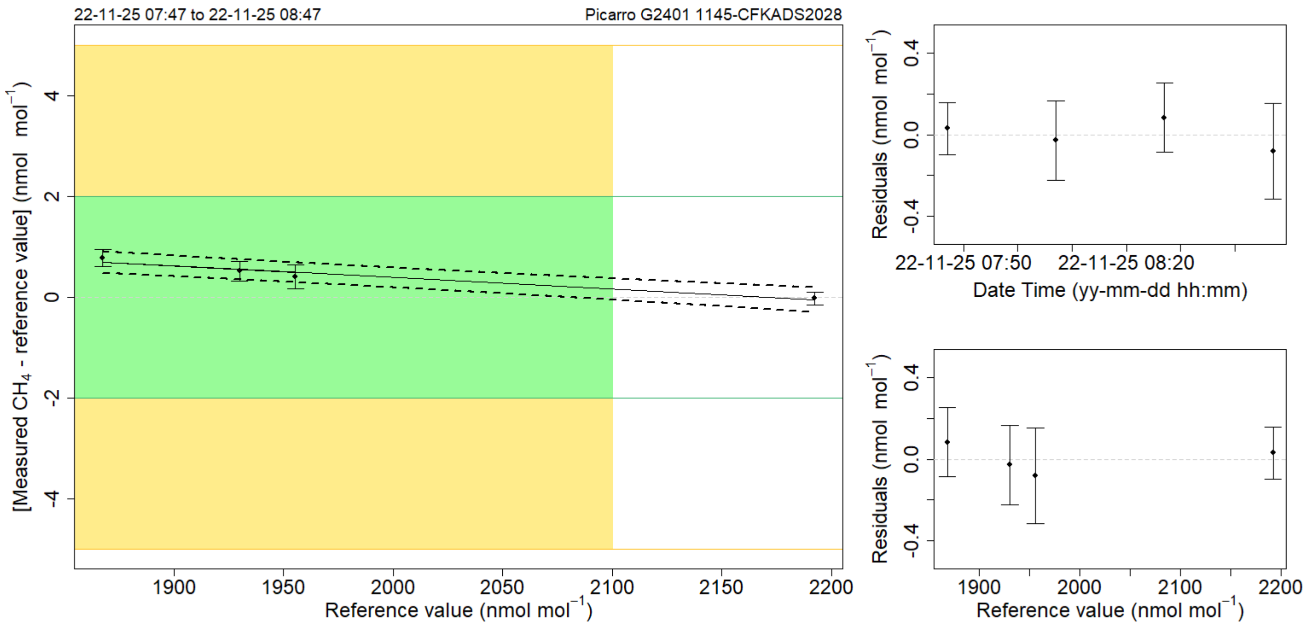

Figure 5. *Left: Bias of the Picarro G2401 #1145-CFKADS2028 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for PDI. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #1145-CFKADS2028, second comparison:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 4.15 nmol mol^{-1}) / 0.9979 (3c)

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

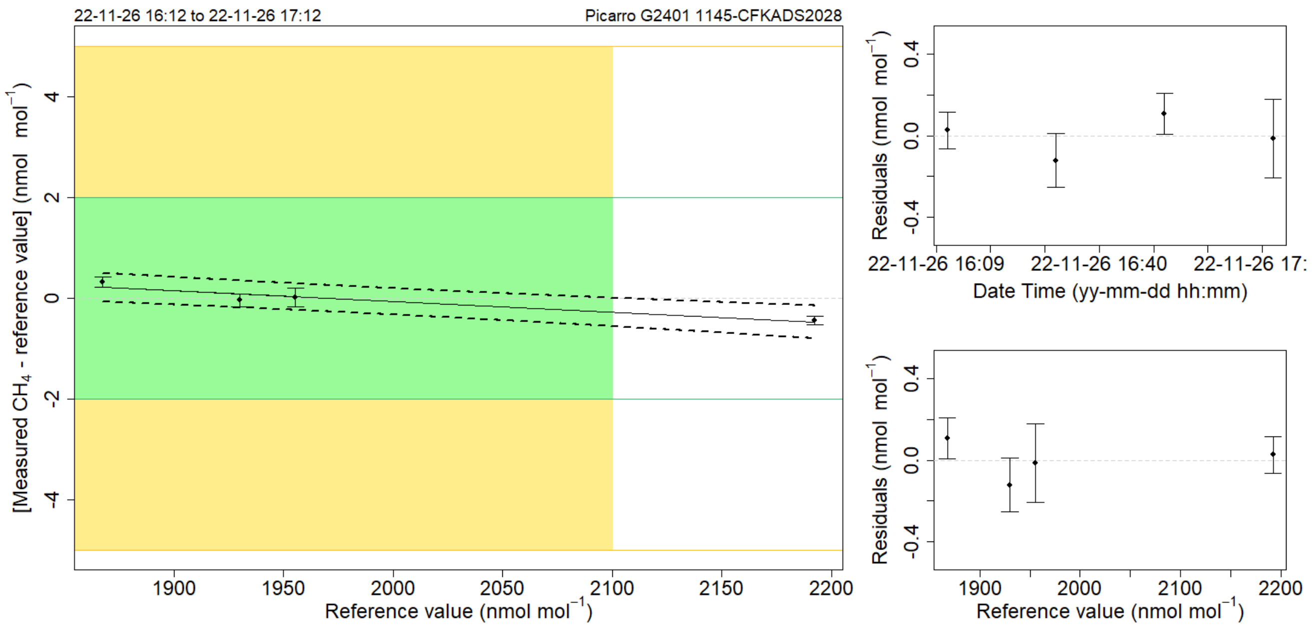

Figure 6. *Same as above, second comparison.*

The result of the comparison can be summarised as follows:

Excellent agreement well within the WMO/GAW compatibility goal was found for both comparisons. However, a slight dependence of the bias on the amount fraction was observed.

> **Recommendation 12 (*, minor, 2023)**
> *The CRDS measurement technique shows a linear response for CH_4 in the amount fraction range from at least 0 to 5000 nmol mol^{-1}. It should be considered to include CH_4 free air (or N_2 6.0) in the calibration scheme to compensate for a zero offset. The same standard as for the CO zero calibration can be used.*

Carbon Dioxide Measurements

See the section on carbon monoxide measurements above for instrumentation, standards and comparison procedure. Like for CO, a different set of standards was for the second comparison, which corresponds to the set of standards used operationally after the audit. However, the pure nitrogen standard is not used for CO_2 calibration and no particularly high CO_2 standard is applied as the high CO standard contains close to ambient CO_2 mole fractions

The following equations characterise the instrument bias. The result is further illustrated in Figures 7 and 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #1145-CFKADS2028, first comparison:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 + 0.07 µmol mol^{-1}) / 1.00020 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.001 µmol mol^{-1} + 3.28e-8 * $X_{CO2}{}^2$) (4b)

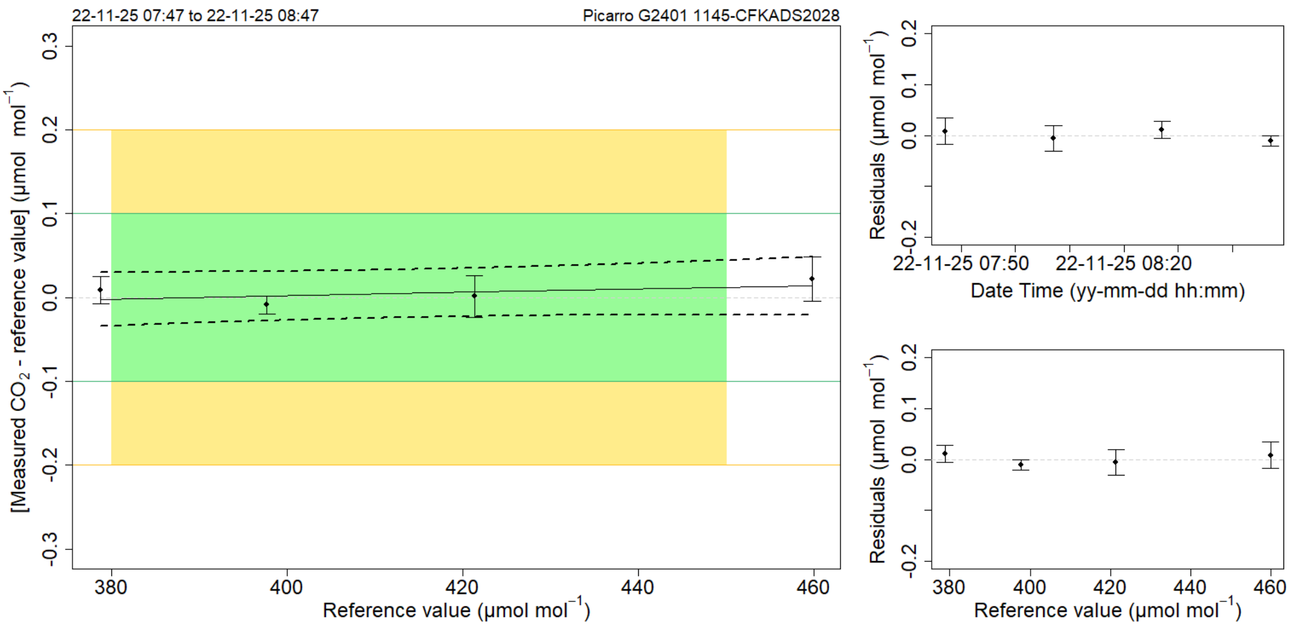

Figure 7. *Left: Bias of the Picarro G2401 #1145-CFKADS2028 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for PDI. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #1145-CFKADS2028, second comparison:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 - 0.24 µmol mol^{-1}) / 0.99944 (4c)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.001 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (4d)

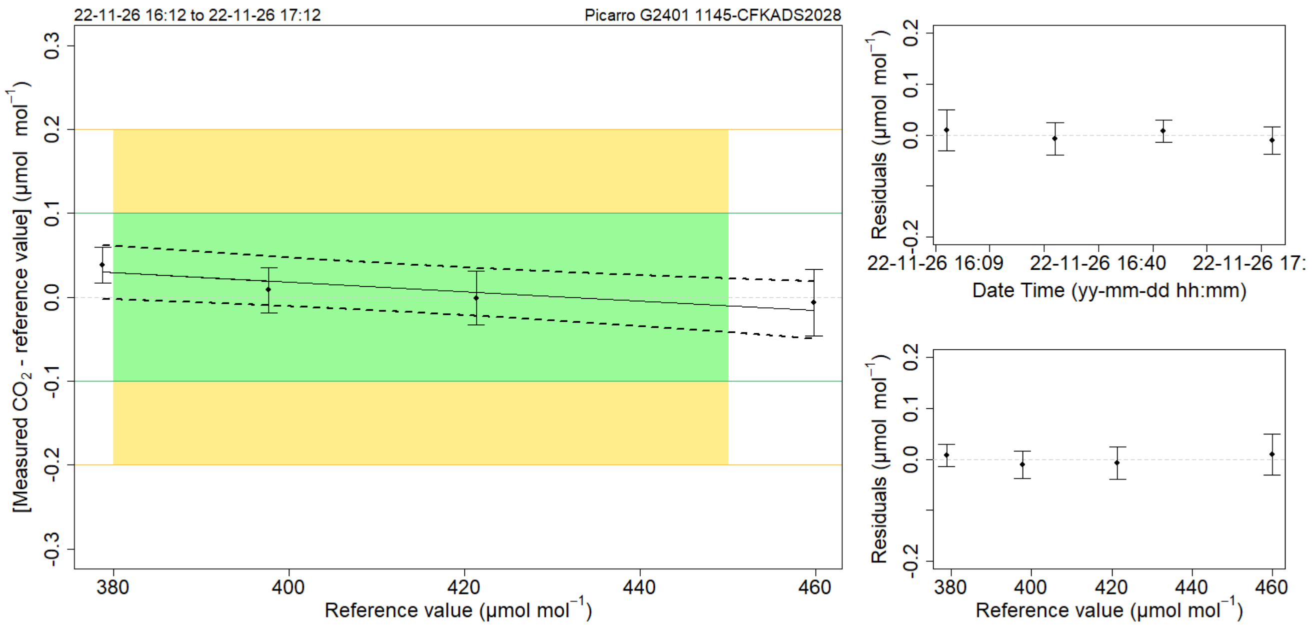

Figure 8. *Same as above, for the second comparison.*

The result of the comparison can be summarised as follows:

The Pha Din GAW CRDS instrument showed agreement within the WMO/GAW network compatibility goal. Therefore, no further action is required.

PDI PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the PDI performance audit to other station audits made by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO and N_2O, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions usually found in unpolluted air masses. For surface ozone the mole fraction range of 0-100 ppb was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 9 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, CO, CH_4, and CO_2. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current PDI audit are shown as coloured dots in Figure 9, and are also summarised in Table 3. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 3.

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

Table 3. *PDI performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5th and 6th columns show the percentage of all WCC-Empa audits until November 2022 within these criteria since 1996 (O_3), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound / Instrument	**Range**	**Unit**	**PDI within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs**[1]
O_3 (Thermo 49i (BKG 0.0, SPAN 1.011), initial	0 -100	nmol mol^{-1}	✗	65	NA
O_3 (Thermo 49i (BKG 0.0, SPAN 1.011), final	0 -100	nmol mol^{-1}	✓	65	NA
CO (Picarro G2401) 1st comparison	30 - 300	nmol mol^{-1}	✗	19	50
CO (Picarro G2401) 2nd comparison	30 - 300	nmol mol^{-1}	✓	19	50
CH_4 (Picarro G2401) 1st comparison	1750 - 2100	nmol mol^{-1}	✓	76	94
CH_4 (Picarro G2401) 2nd comparison	1750 - 2100	nmol mol^{-1}	✓	76	94
CO_2 (Picarro G2401) 1st comparison	380 - 450	µmol mol^{-1}	✓	49	74
CO_2 (Picarro G2401) 2nd comparison	380 - 450	µmol mol^{-1}	✓	49	74

[1] Percentage of stations within the eDQO and DQO

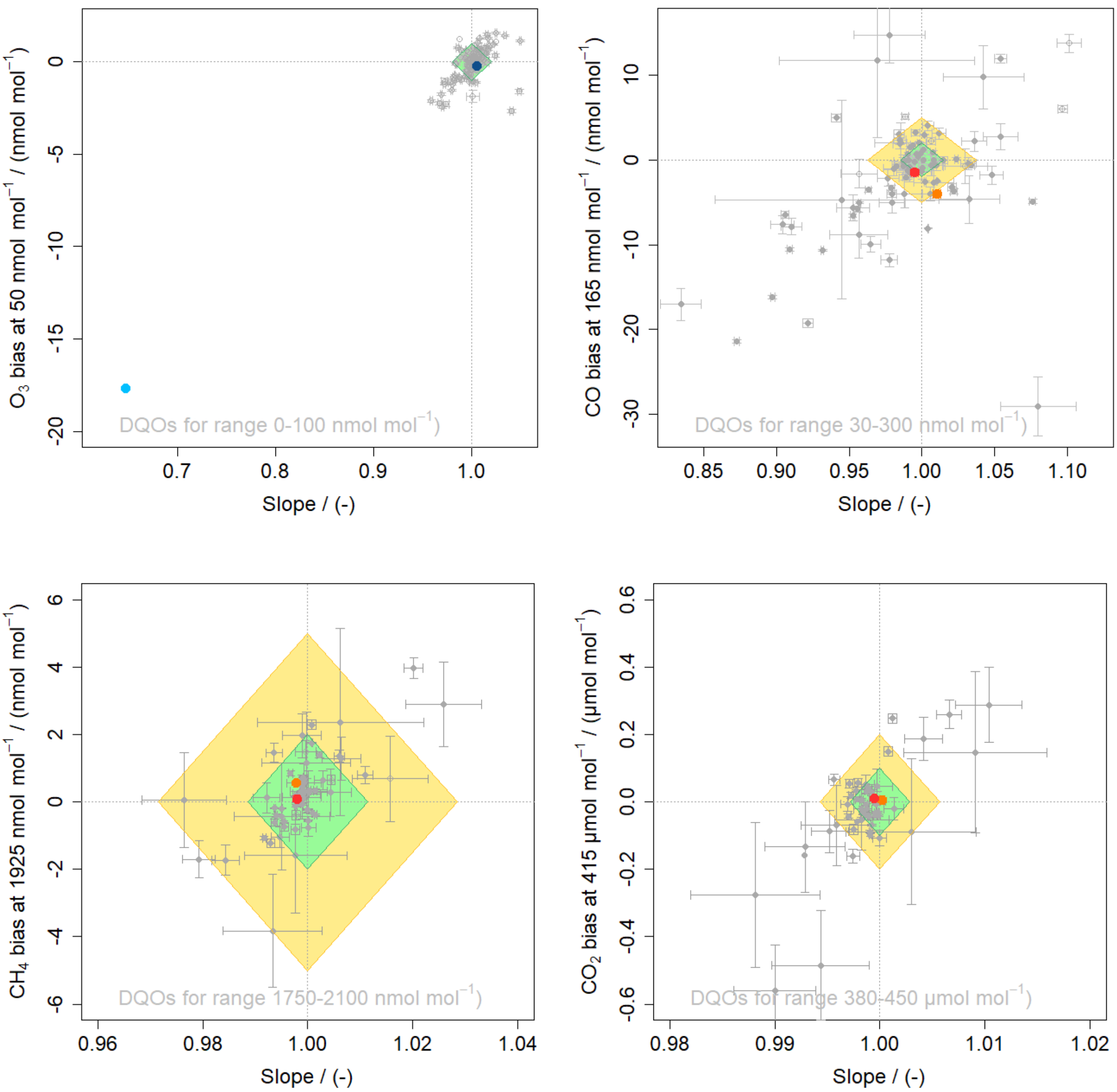

Figure 9. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show PDI results (light blue: Thermo Scientific 49i with broken interface board, dark blue: repaired Thermo Scientific 49i, orange: Picarro G2401, first comparison, red: Picarro G2401, second comparison). Filled symbols refer to a comparison with the same calibration scale at the station and the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow). The ozone comparisons refer to the calibrated / repaired instruments. Initial comparisons were outside the WMO/GAW DQOs.*

CONCLUSIONS

Measurements of greenhouse and reactive gases as well as aerosol parameters were established at the regional GAW station Pha Din in 2014 as part of the CATCOS project. Continuous time series are available since then. These time series are highly valuable, since they cover a region where data availability is extremely sparse. The PDI station comprises sufficient laboratory space, and hosts a small number observations.

The assessed greenhouse gas measurements were of high data quality and met the WMO/GAW network compatibility goal in the relevant mole fraction range. The observed bias of the CO measurements was slightly larger, but within the extended WMO/GAW network compatibility goal after the implementation of a new calibration scheme. An issue with the surface ozone instrument could be fixed during the audit, and traceability to the WMO reference was re-established. However, the past ozone data from 2014 onwards needs to be carefully re-assessed. Historic data should be compared with recent data after the audit to determine potential systematic biases and to identify the beginning of the pressure reading issue.

The continuation of the Pha Din measurement series is highly important for GAW, and continued investments and training of the station staff are needed to ensure high data quality and availability.

Table 4 summarises the results of the performance audit with respect to the WMO/GAW compatibility goals. Please note that Table 4 refers only to the mole fractions relevant to PDI, whereas Table 3 further above covers a wider mole fraction range.

Table 4. *Synthesis of the performance audit results. A tick mark indicates that the compatibility goal (green) or extended compatibility goal (orange) was met on average. Tick marks in parenthesis mean that the goal was only partly reached in the relevant mole fraction range (performance audit only), and ✗ indicates results outside the compatibility goals.*

Comparison type	O_3 (before audit)	O_3 (after audit)	CO Picarro G2401 CFKADS2028 (before audit)	CO Picarro G2401 CFKADS2028 (after audit)	CH_4 Picarro G2401 CFKADS2028	CO_2 Picarro G2401 CFKADS2028
Audit with TS	✗	✓	(✓)	✓	✓	✓

SUMMARY RANKING OF THE PHA DIN GAW STATION

System Audit Aspect	Adequacy[#]	Comment
Measurement programme	(3)	Small programme, adequate for a regional station. No automatic weather station.
Access	(5)	Year round access.
Facilities		
Laboratory and office space	(4)	Adequate, with little space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth.
Air Conditioning	(4)	Available, temperature variations.
Power supply	(4)	Mostly reliable, generator in case of power outages.
General Management and Operation		
Organisation	(3)	Well-coordinated and managed, budget needed to support measurements, infrequent station visits for extended maintenance & repair.
Competence of staff	(2)	More training needed.
Air Inlet System	(4)	Adequate systems.
Instrumentation		
Ozone	(4)	Instruments need service, replacement recommended due to age.
$CO/CH_4/CO_2$ (Picarro G2401)	(5)	State of the art instrumentation.
Standards		
O_3	(0)	Not available.
CO, CO_2, CH_4	(5)	Full traceability to the GAW reference, standards from the CCL.
Data Management		
Data acquisition	(4)	Fully adequate system, data stored only locally, no transfer to server.
Data processing	(3)	Dependent on external partners
Data submission	(4)	All data submitted, usually within one year. Dependent on external partners.

[#]0: inadequate thru 5: adequate.

Dübendorf, July 2023

Dr C. Zellweger
WCC-Empa

Dr M. Steinbacher
QA/SAC Switzerland

Dr B. Buchmann
Head of Department

APPENDIX

Data Review

The following figures show summary plots of PDI data accessed on 25 November 2022 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

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

Surface ozone:

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

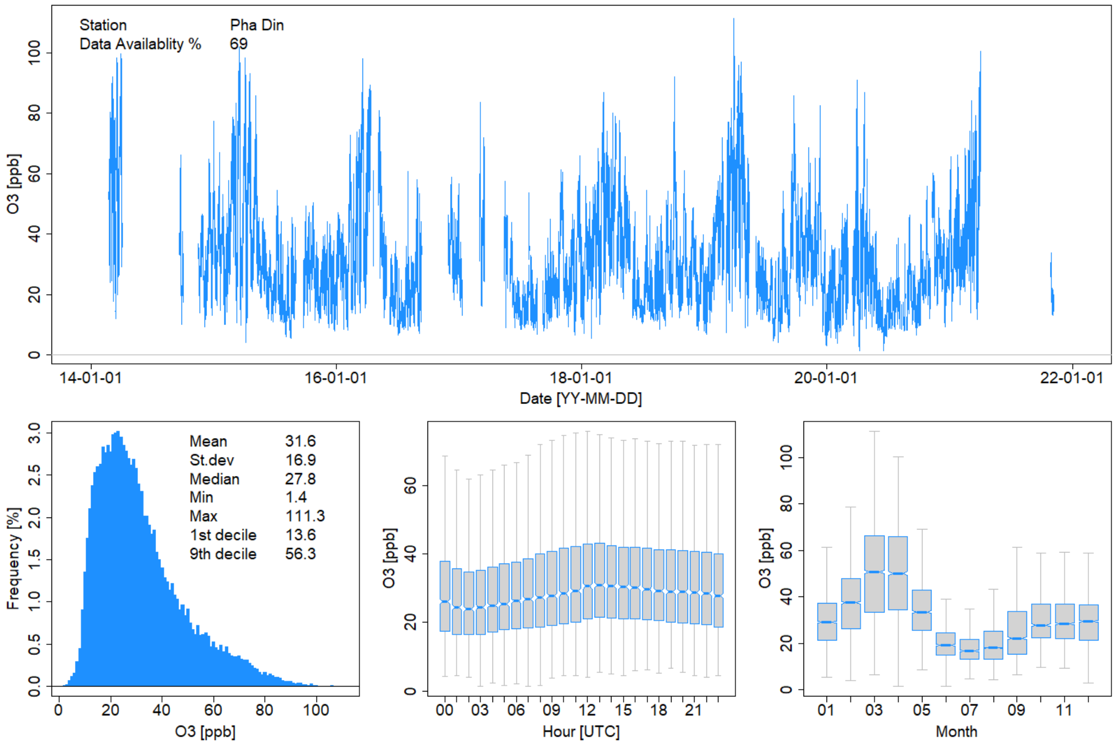

Figure 10. *O_3 data for the period from 2014 to 2021 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data look sound with respect to mole fraction, trend, seasonal and diurnal variation.
- However, an issue with the pressure sensor reading was found during the current audit. Data needs to be re-visited to identify the period when the pressure sensor issue started. Reassessment of the data should be pursued when several months of new data with a correct pressure reading are gathered.

Carbon monoxide:

The CO data submitted by VNMHA is shown below.

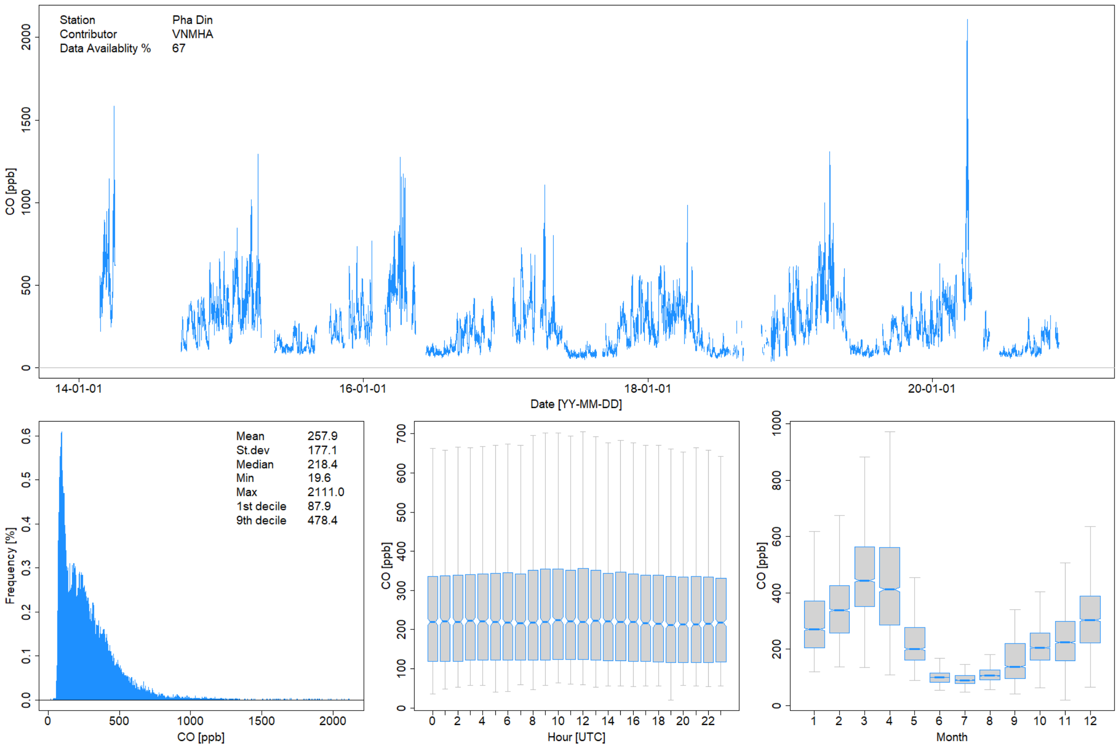

Figure 11. *Pha Din in-situ CO data (2014-2020) submitted by VNMHA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The VNMHA data set looks sound with respect to amount fraction, trend, seasonal and diurnal variation.

Methane:

The CH_4 data submitted by VNMHA is shown below.

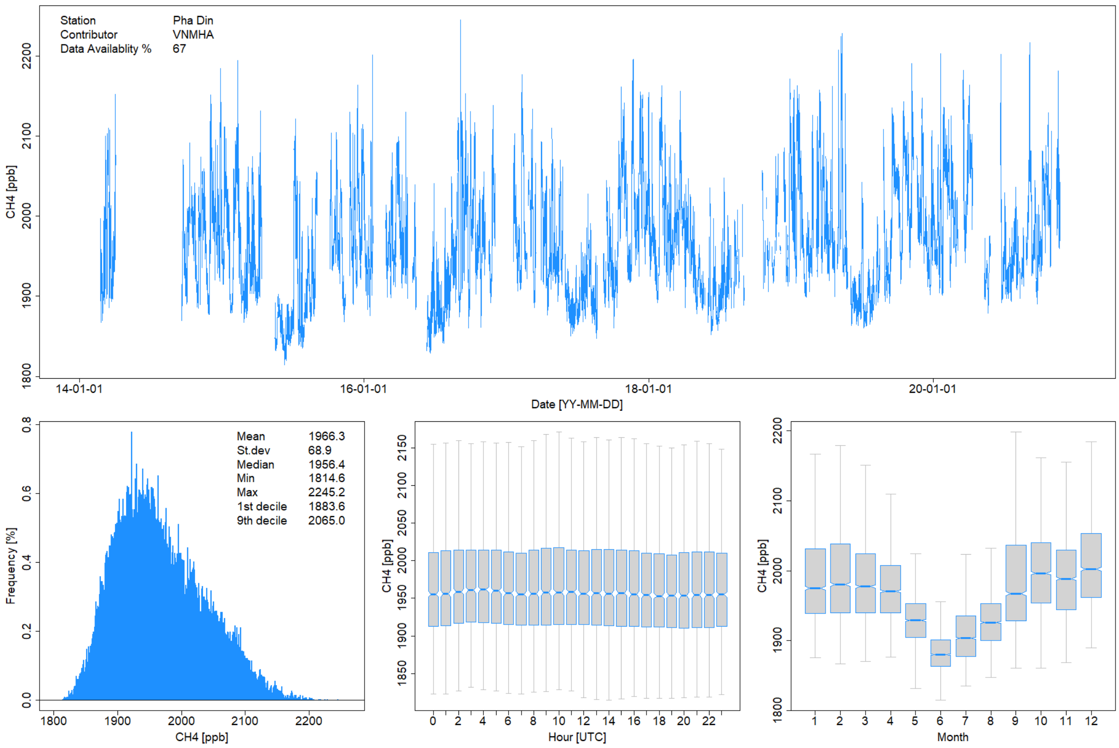

Figure 12. *Pha Din in-situ CH_4 data (2014-2020) submitted by VNMHA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The VNMHA data set looks sound with respect to amount fraction, trend, seasonal and diurnal variation.

Carbon dioxide:

The CO_2 data submitted by VNMHA is shown below.

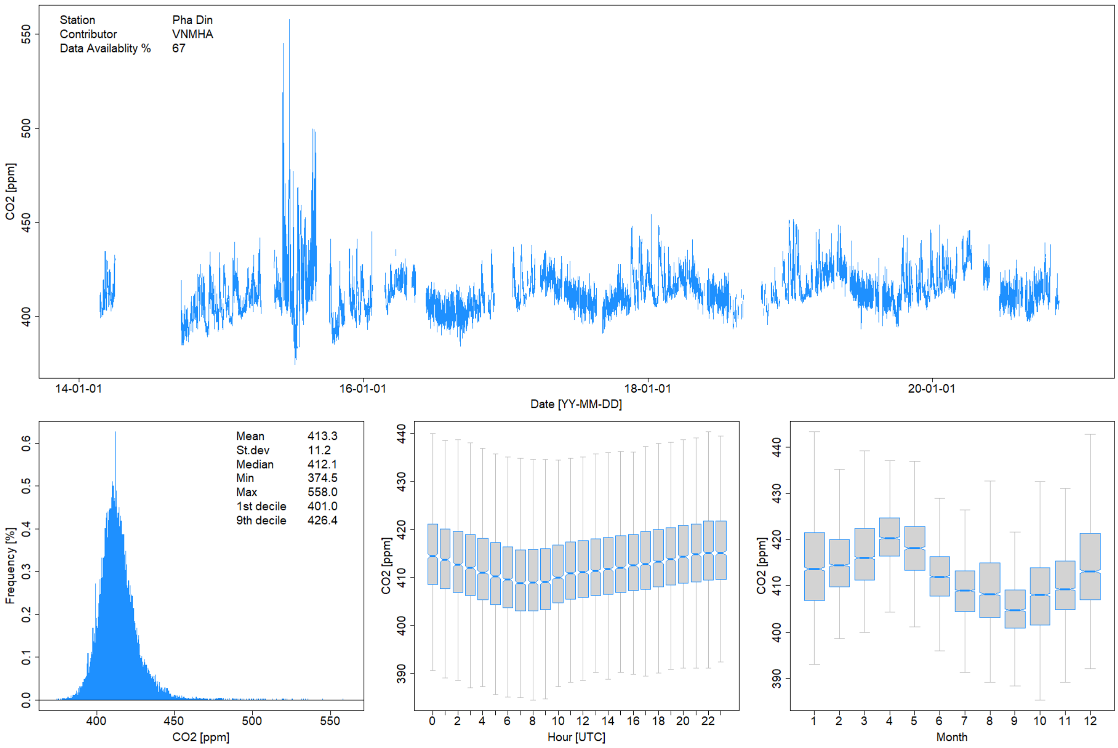

Figure 13. *Pha Din in-situ CO_2 data (2014-2020) submitted by VNMHA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The VNMHA data set looks sound with respect to amount fraction, trend, seasonal and diurnal variation, except for a period in 2015.
- The reason for the large variability during a period in 2015 needs to be identified, and the data needs most likely to be flagged as invalid.

Surface Ozone Comparisons

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 5 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa and PDI data acquisition systems.

Table 5. *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 859.4;TS 859.0 (no adjustment was made)
PDI analyser (OA)	
Model, S/N	Thermo Scientific 49i #1205551879
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG 0.0 nmol mol^{-1}, COEF 1.011
Pressure readings (hPa)	Initial: Ambient 859.4; OA 1333.1 (p-sensor not working) Final: Ambient 860.6; OA 860.6 (after interface board exchange)

Results

Each ozone level was measures for approximately ten minutes, and the last ten 40 s averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 5 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment as for ambient air analysis was applied.
The results of the assessment is shown in the following Table (individual measurement points) and further presented in the Executive Summary.

Table 6. *Comparison of the PDI ozone analyser (OA) Thermo Scientific 49i #1205551879 (BKG 0.0 nmol mol^{-1}, COEF 1.011, unrepaired) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-11-24 04:48	249.98	1.17	162.45	0.08	-87.53	-35.01
2022-11-24 05:00	125.06	0.52	81.24	0.16	-43.82	-35.04
2022-11-24 05:11	175.05	0.78	113.34	0.10	-61.71	-35.25
2022-11-24 05:22	200.04	0.91	129.80	0.09	-70.24	-35.11
2022-11-24 05:34	60.27	0.23	39.08	0.07	-21.19	-35.16
2022-11-24 05:45	150.27	0.59	97.19	0.08	-53.08	-35.32
2022-11-24 05:56	10.38	0.37	6.86	0.08	-3.52	-33.91

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2022-11-24 06:08	224.75	0.90	145.73	0.13	-79.02	-35.16
2022-11-24 06:19	70.21	0.36	45.67	0.11	-24.54	-34.95
2022-11-24 06:31	0.47	0.13	0.41	0.13	-0.06	NA
2022-11-24 06:42	50.22	0.23	32.66	0.11	-17.56	-34.97
2022-11-24 06:54	80.15	0.40	51.99	0.04	-28.16	-35.13
2022-11-24 07:05	20.28	0.17	13.15	0.09	-7.13	-35.16
2022-11-24 07:16	100.21	0.42	64.87	0.05	-35.34	-35.27
2022-11-24 07:25	90.15	0.42	59.02	0.96	-31.13	-34.53
2022-11-24 07:36	30.20	0.24	19.37	0.07	-10.83	-35.86
2022-11-24 07:45	40.30	0.17	25.58	0.89	-14.72	-36.53
2022-11-24 07:56	200.05	0.94	129.39	0.07	-70.66	-35.32
2022-11-24 08:07	20.61	0.70	13.56	0.16	-7.05	-34.21
2022-11-24 08:08	22.98	NA	13.62	NA	-9.36	-40.73
2022-11-24 08:16	30.25	0.30	19.11	1.07	-11.14	-36.83
2022-11-24 08:27	60.24	0.30	39.11	0.05	-21.13	-35.08
2022-11-24 08:36	50.35	0.23	32.94	1.04	-17.41	-34.58
2022-11-24 08:47	10.44	0.22	6.73	0.21	-3.71	-35.54
2022-11-24 08:58	125.12	0.46	80.79	0.18	-44.33	-35.43
2022-11-24 09:10	225.25	0.98	145.09	0.17	-80.16	-35.59
2022-11-24 09:21	90.19	0.37	58.39	0.10	-31.80	-35.26
2022-11-24 09:36	0.22	0.13	0.14	0.05	-0.08	NA
2022-11-24 09:47	249.90	1.12	161.75	0.08	-88.15	-35.27
2022-11-24 09:59	70.23	0.25	45.38	0.08	-24.85	-35.38
2022-11-24 10:10	150.07	0.70	97.25	0.07	-52.82	-35.20
2022-11-24 10:21	100.23	0.43	64.85	0.04	-35.38	-35.30
2022-11-24 10:33	175.10	0.79	113.23	0.09	-61.87	-35.33
2022-11-24 10:44	40.28	0.22	25.76	0.13	-14.52	-36.05
2022-11-24 10:55	80.18	0.33	51.78	0.07	-28.40	-35.42
2022-11-24 11:07	175.08	0.79	113.46	0.05	-61.62	-35.20
2022-11-24 11:18	60.28	0.23	38.83	0.08	-21.45	-35.58
2022-11-24 11:29	200.04	0.89	129.82	0.06	-70.22	-35.10
2022-11-24 11:41	125.26	0.56	81.14	0.11	-44.12	-35.22
2022-11-24 11:52	40.30	0.26	26.00	0.05	-14.30	-35.48
2022-11-24 12:03	225.04	0.97	145.88	0.09	-79.16	-35.18
2022-11-24 12:15	30.30	0.10	19.54	0.14	-10.76	-35.51
2022-11-24 12:23	20.23	0.06	13.62	0.90	-6.61	-32.67
2022-11-24 12:34	80.13	0.41	51.95	0.15	-28.18	-35.17
2022-11-24 13:51	150.06	0.65	97.32	0.05	-52.74	-35.15
2022-11-24 14:02	40.21	0.21	26.09	0.11	-14.12	-35.12
2022-11-24 14:13	175.09	0.73	113.71	0.03	-61.38	-35.06
2022-11-24 14:24	20.31	0.18	12.95	0.06	-7.36	-36.24
2022-11-24 14:36	90.14	0.42	58.67	0.05	-31.47	-34.91
2022-11-24 14:47	60.24	0.27	38.94	0.13	-21.30	-35.36
2022-11-24 14:58	80.20	0.37	52.02	0.08	-28.18	-35.14
2022-11-24 15:10	125.22	0.50	81.07	0.06	-44.15	-35.26
2022-11-24 15:21	199.89	0.86	129.76	0.05	-70.13	-35.08
2022-11-24 15:32	50.21	0.22	32.35	0.15	-17.86	-35.57
2022-11-24 15:44	99.99	0.42	65.01	0.09	-34.98	-34.98

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-11-24 15:55	224.96	0.99	146.01	0.16	-78.95	-35.10
2022-11-24 16:06	70.17	0.30	45.63	0.14	-24.54	-34.97
2022-11-24 16:18	0.32	0.16	0.07	0.05	-0.25	NA
2022-11-24 16:30	249.93	1.07	162.23	0.07	-87.70	-35.09
2022-11-24 16:41	10.32	0.17	6.47	0.12	-3.85	-37.31
2022-11-24 16:52	30.22	0.19	19.58	0.05	-10.64	-35.21
2022-11-24 17:01	20.22	0.14	13.87	1.21	-6.35	-31.40
2022-11-24 17:12	80.11	0.36	52.22	0.05	-27.89	-34.81
2022-11-24 17:24	100.14	0.51	64.86	0.08	-35.28	-35.23
2022-11-24 17:35	60.26	0.30	38.92	0.08	-21.34	-35.41
2022-11-24 17:47	0.28	0.23	0.32	0.18	0.04	NA
2022-11-24 17:58	150.03	0.58	97.18	0.11	-52.85	-35.23
2022-11-24 18:10	249.99	1.05	161.81	0.09	-88.18	-35.27
2022-11-24 18:21	50.26	0.24	32.59	0.05	-17.67	-35.16
2022-11-24 18:32	90.05	0.38	58.42	0.08	-31.63	-35.12
2022-11-24 18:44	30.17	0.14	19.55	0.12	-10.62	-35.20
2022-11-24 18:52	40.23	0.23	25.29	1.05	-14.94	-37.14
2022-11-24 19:03	125.06	0.51	81.20	0.06	-43.86	-35.07
2022-11-24 19:15	175.02	0.63	113.52	0.06	-61.50	-35.14
2022-11-24 19:26	199.99	0.91	129.47	0.05	-70.52	-35.26
2022-11-24 19:37	10.35	0.24	6.81	0.12	-3.54	-34.20
2022-11-24 19:49	224.95	0.97	145.88	0.09	-79.07	-35.15
2022-11-24 20:00	70.29	0.28	45.37	0.04	-24.92	-35.45
2022-11-24 20:09	80.23	0.37	51.44	1.04	-28.79	-35.88
2022-11-24 20:20	60.25	0.36	38.87	0.04	-21.38	-35.49
2022-11-24 20:31	40.31	0.20	26.04	0.02	-14.27	-35.40
2022-11-24 20:43	20.28	0.14	13.06	0.13	-7.22	-35.60
2022-11-24 20:57	90.13	0.39	59.38	1.40	-30.75	-34.12
2022-11-24 21:08	250.20	1.05	161.95	0.07	-88.25	-35.27
2022-11-24 21:19	70.24	0.30	45.49	0.06	-24.75	-35.24
2022-11-24 21:31	50.25	0.22	32.58	0.05	-17.67	-35.16
2022-11-24 21:42	224.95	1.04	145.65	0.14	-79.30	-35.25
2022-11-24 04:48	249.98	1.17	162.45	0.08	-87.53	-35.01
2022-11-24 05:00	125.06	0.52	81.24	0.16	-43.82	-35.04
2022-11-24 05:11	175.05	0.78	113.34	0.10	-61.71	-35.25
2022-11-24 05:22	200.04	0.91	129.80	0.09	-70.24	-35.11
2022-11-24 05:34	60.27	0.23	39.08	0.07	-21.19	-35.16
2022-11-24 05:45	150.27	0.59	97.19	0.08	-53.08	-35.32
2022-11-24 05:56	10.38	0.37	6.86	0.08	-3.52	-33.91
2022-11-24 06:08	224.75	0.90	145.73	0.13	-79.02	-35.16
2022-11-24 06:19	70.21	0.36	45.67	0.11	-24.54	-34.95
2022-11-24 06:31	0.47	0.13	0.41	0.13	-0.06	NA
2022-11-24 06:42	50.22	0.23	32.66	0.11	-17.56	-34.97
2022-11-24 06:54	80.15	0.40	51.99	0.04	-28.16	-35.13
2022-11-24 07:05	20.28	0.17	13.15	0.09	-7.13	-35.16
2022-11-24 07:16	100.21	0.42	64.87	0.05	-35.34	-35.27
2022-11-24 07:25	90.15	0.42	59.02	0.96	-31.13	-34.53
2022-11-24 07:36	30.20	0.24	19.37	0.07	-10.83	-35.86

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-11-24 07:45	40.30	0.17	25.58	0.89	-14.72	-36.53
2022-11-24 07:56	200.05	0.94	129.39	0.07	-70.66	-35.32
2022-11-24 08:07	20.61	0.70	13.56	0.16	-7.05	-34.21
2022-11-24 08:08	22.98	NA	13.62	NA	-9.36	-40.73
2022-11-24 08:16	30.25	0.30	19.11	1.07	-11.14	-36.83
2022-11-24 08:27	60.24	0.30	39.11	0.05	-21.13	-35.08
2022-11-24 08:36	50.35	0.23	32.94	1.04	-17.41	-34.58
2022-11-24 08:47	10.44	0.22	6.73	0.21	-3.71	-35.54
2022-11-24 08:58	125.12	0.46	80.79	0.18	-44.33	-35.43
2022-11-24 09:10	225.25	0.98	145.09	0.17	-80.16	-35.59
2022-11-24 09:21	90.19	0.37	58.39	0.10	-31.80	-35.26
2022-11-24 09:36	0.22	0.13	0.14	0.05	-0.08	NA
2022-11-24 09:47	249.90	1.12	161.75	0.08	-88.15	-35.27
2022-11-24 09:59	70.23	0.25	45.38	0.08	-24.85	-35.38
2022-11-24 10:10	150.07	0.70	97.25	0.07	-52.82	-35.20
2022-11-24 10:21	100.23	0.43	64.85	0.04	-35.38	-35.30
2022-11-24 10:33	175.10	0.79	113.23	0.09	-61.87	-35.33
2022-11-24 10:44	40.28	0.22	25.76	0.13	-14.52	-36.05
2022-11-24 10:55	80.18	0.33	51.78	0.07	-28.40	-35.42
2022-11-24 11:07	175.08	0.79	113.46	0.05	-61.62	-35.20
2022-11-24 11:18	60.28	0.23	38.83	0.08	-21.45	-35.58
2022-11-24 11:29	200.04	0.89	129.82	0.06	-70.22	-35.10
2022-11-24 11:41	125.26	0.56	81.14	0.11	-44.12	-35.22
2022-11-24 11:52	40.30	0.26	26.00	0.05	-14.30	-35.48
2022-11-24 12:03	225.04	0.97	145.88	0.09	-79.16	-35.18
2022-11-24 12:15	30.30	0.10	19.54	0.14	-10.76	-35.51
2022-11-24 12:23	20.23	0.06	13.62	0.90	-6.61	-32.67
2022-11-24 12:34	80.13	0.41	51.95	0.15	-28.18	-35.17
2022-11-24 13:51	150.06	0.65	97.32	0.05	-52.74	-35.15
2022-11-24 14:02	40.21	0.21	26.09	0.11	-14.12	-35.12
2022-11-24 14:13	175.09	0.73	113.71	0.03	-61.38	-35.06
2022-11-24 14:24	20.31	0.18	12.95	0.06	-7.36	-36.24
2022-11-24 14:36	90.14	0.42	58.67	0.05	-31.47	-34.91
2022-11-24 14:47	60.24	0.27	38.94	0.13	-21.30	-35.36
2022-11-24 14:58	80.20	0.37	52.02	0.08	-28.18	-35.14
2022-11-24 15:10	125.22	0.50	81.07	0.06	-44.15	-35.26
2022-11-24 15:21	199.89	0.86	129.76	0.05	-70.13	-35.08
2022-11-24 15:32	50.21	0.22	32.35	0.15	-17.86	-35.57
2022-11-24 15:44	99.99	0.42	65.01	0.09	-34.98	-34.98
2022-11-24 15:55	224.96	0.99	146.01	0.16	-78.95	-35.10
2022-11-24 16:06	70.17	0.30	45.63	0.14	-24.54	-34.97
2022-11-24 16:18	0.32	0.16	0.07	0.05	-0.25	NA
2022-11-24 16:30	249.93	1.07	162.23	0.07	-87.70	-35.09
2022-11-24 16:41	10.32	0.17	6.47	0.12	-3.85	-37.31
2022-11-24 16:52	30.22	0.19	19.58	0.05	-10.64	-35.21
2022-11-24 17:01	20.22	0.14	13.87	1.21	-6.35	-31.40
2022-11-24 17:12	80.11	0.36	52.22	0.05	-27.89	-34.81
2022-11-24 17:24	100.14	0.51	64.86	0.08	-35.28	-35.23

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2022-11-24 17:35	60.26	0.30	38.92	0.08	-21.34	-35.41
2022-11-24 17:47	0.28	0.23	0.32	0.18	0.04	NA
2022-11-24 17:58	150.03	0.58	97.18	0.11	-52.85	-35.23
2022-11-24 18:10	249.99	1.05	161.81	0.09	-88.18	-35.27
2022-11-24 18:21	50.26	0.24	32.59	0.05	-17.67	-35.16
2022-11-24 18:32	90.05	0.38	58.42	0.08	-31.63	-35.12
2022-11-24 18:44	30.17	0.14	19.55	0.12	-10.62	-35.20
2022-11-24 18:52	40.23	0.23	25.29	1.05	-14.94	-37.14
2022-11-24 19:03	125.06	0.51	81.20	0.06	-43.86	-35.07
2022-11-24 19:15	175.02	0.63	113.52	0.06	-61.50	-35.14
2022-11-24 19:26	199.99	0.91	129.47	0.05	-70.52	-35.26
2022-11-24 19:37	10.35	0.24	6.81	0.12	-3.54	-34.20
2022-11-24 19:49	224.95	0.97	145.88	0.09	-79.07	-35.15
2022-11-24 20:00	70.29	0.28	45.37	0.04	-24.92	-35.45
2022-11-24 20:09	80.23	0.37	51.44	1.04	-28.79	-35.88
2022-11-24 20:20	60.25	0.36	38.87	0.04	-21.38	-35.49
2022-11-24 20:31	40.31	0.20	26.04	0.02	-14.27	-35.40
2022-11-24 20:43	20.28	0.14	13.06	0.13	-7.22	-35.60
2022-11-24 20:57	90.13	0.39	59.38	1.40	-30.75	-34.12
2022-11-24 21:08	250.20	1.05	161.95	0.07	-88.25	-35.27
2022-11-24 21:19	70.24	0.30	45.49	0.06	-24.75	-35.24
2022-11-24 21:31	50.25	0.22	32.58	0.05	-17.67	-35.16
2022-11-24 21:42	224.95	1.04	145.65	0.14	-79.30	-35.25

Table 7. *Comparison of the PDI ozone analyser (OA) Thermo Scientific 49i #1205551879 (BKG 0.0 nmol mol-1, COEF 1.011, repaired) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2022-11-25 08:29	150.12	0.18	150.70	0.29	0.58	0.39
2022-11-25 08:38	100.11	0.08	100.54	0.20	0.43	0.43
2022-11-25 08:46	30.19	0.09	29.94	0.32	-0.25	-0.83
2022-11-25 08:55	20.26	0.14	20.01	0.20	-0.25	-1.23
2022-11-25 09:03	10.43	0.22	9.80	0.18	-0.63	-6.04
2022-11-25 09:18	0.43	0.15	-0.08	0.20	-0.51	NA
2022-11-25 09:27	150.02	0.13	150.39	0.65	0.37	0.25
2022-11-25 09:35	224.91	0.09	225.81	0.45	0.90	0.40
2022-11-25 09:44	20.24	0.18	19.38	0.24	-0.86	-4.25
2022-11-25 11:00	249.96	0.07	250.89	0.27	0.93	0.37
2022-11-25 11:09	100.15	0.15	100.09	0.28	-0.06	-0.06
2022-11-25 11:17	10.46	0.21	10.03	0.46	-0.43	-4.11
2022-11-25 11:26	70.17	0.09	70.28	0.21	0.11	0.16
2022-11-25 11:34	40.21	0.15	39.70	0.31	-0.51	-1.27
2022-11-25 11:43	249.93	0.16	251.20	0.25	1.27	0.51
2022-11-25 11:51	175.06	0.13	175.77	0.19	0.71	0.41
2022-11-25 12:00	225.01	0.10	225.93	0.27	0.92	0.41
2022-11-25 12:08	20.27	0.16	19.92	0.14	-0.35	-1.73
2022-11-25 12:17	50.15	0.13	50.09	0.34	-0.06	-0.12

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2022-11-25 12:25	70.24	0.10	70.10	0.14	-0.14	-0.20
2022-11-25 12:34	30.19	0.17	29.73	0.29	-0.46	-1.52
2022-11-25 12:42	125.10	0.17	125.31	0.23	0.21	0.17
2022-11-25 12:52	0.54	0.10	-0.07	0.14	-0.61	NA
2022-11-25 13:00	40.18	0.16	40.06	0.23	-0.12	-0.30
2022-11-25 13:09	150.02	0.12	150.41	0.16	0.39	0.26
2022-11-25 13:17	10.59	0.44	10.46	0.37	-0.13	-1.23
2022-11-25 13:26	199.98	0.18	200.55	0.18	0.57	0.29
2022-11-25 13:34	60.15	0.12	60.18	0.23	0.03	0.05
2022-11-25 13:43	90.20	0.09	90.56	0.20	0.36	0.40
2022-11-25 13:51	80.22	0.12	80.25	0.25	0.03	0.04
2022-11-25 14:00	100.23	0.14	100.21	0.36	-0.02	-0.02
2022-11-25 14:08	40.20	0.18	40.19	0.14	-0.01	-0.02
2022-11-25 14:17	70.22	0.14	70.13	0.24	-0.09	-0.13
2022-11-25 14:26	0.45	0.10	0.13	0.13	-0.32	NA
2022-11-25 14:35	249.94	0.11	251.02	0.22	1.08	0.43
2022-11-25 14:43	174.99	0.15	175.49	0.27	0.50	0.29
2022-11-25 14:52	150.08	0.19	150.49	0.22	0.41	0.27
2022-11-25 15:00	125.08	0.10	125.32	0.22	0.24	0.19
2022-11-25 15:09	100.16	0.07	100.25	0.18	0.09	0.09
2022-11-25 15:17	20.27	0.15	19.74	0.19	-0.53	-2.61
2022-11-25 15:26	10.47	0.18	10.12	0.25	-0.35	-3.34
2022-11-25 15:34	90.13	0.10	90.17	0.25	0.04	0.04
2022-11-25 15:43	225.01	0.11	225.89	0.16	0.88	0.39
2022-11-25 15:51	50.17	0.18	50.27	0.32	0.10	0.20
2022-11-25 16:00	200.03	0.12	200.66	0.21	0.63	0.31
2022-11-25 16:08	60.22	0.11	60.04	0.22	-0.18	-0.30
2022-11-25 16:17	30.27	0.14	29.96	0.23	-0.31	-1.02
2022-11-25 16:25	80.21	0.13	80.16	0.22	-0.05	-0.06
2022-11-25 16:34	80.18	0.14	80.08	0.24	-0.10	-0.12
2022-11-25 16:42	224.98	0.16	225.69	0.25	0.71	0.32
2022-11-25 16:51	50.19	0.17	49.94	0.30	-0.25	-0.50
2022-11-25 16:59	250.00	0.18	250.91	0.25	0.91	0.36
2022-11-25 17:08	70.25	0.10	70.23	0.22	-0.02	-0.03
2022-11-25 17:16	30.22	0.14	30.01	0.26	-0.21	-0.69
2022-11-25 17:25	100.12	0.12	100.49	0.36	0.37	0.37

Calibration Standards for CO, CH_4, and CO_2

Table 8 shows and overview of available standard gases for the calibration of the CO, CH_4, and CO_2 instruments.

Table 8 *Calibration standards at PDI as of November 2022.*

Cylinder ID	Pressure (psi)	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2(X2019) (µmol mol^{-1})	Usage
CB09677	1010	145.42	1773.84	373.76	NOAA reference standard
CC726879	1350	481.27	2015.99	479.35	NOAA reference standard
120315_CB08982	200				Laboratory standard
190612_CC703042	1990	123.98	1929.96	421.37	Laboratory standard
190612_CC703115	1950	53.43	1955.42	397.71	Laboratory standard
200213_CB08973	2000	370.32	2192.44	459.86	Laboratory standard
200213_CB09148	1990	177.22	1867.5	378.78	Laboratory standard
201210_CC726929	1800	3970.60	2036.03	388.69	Laboratory standard, high CO
220815_CC749999	1990	0.58	0.16	0.05	Nitrogen 6.0, zero calibration for CO

Carbon Monoxide Comparisons

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

Table 9 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the PDI data acquisition system. The standards used for the calibration of the PDI instruments are shown in Table 9.

Table 9. Experimental details of PDI CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Tables 18 and 19.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #1145-CFKADS2028
Principle	CRDS
Drying system	None during the first comparison. Permapure Nafion dryer PD-50T-12MPS operated in reflux mode with the Picarro pump for the vacuum during the second comparison.
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports of the calibration unit.

Results

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

Table 10. *CO aggregates of the first comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1145-CFKADS2028 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-11-25 07:47:00)	200213_CB08973	370.3	0.5	368.3	2.5	9	-2.0	-0.5
(22-11-25 08:07:00)	190612_CC703042	124.0	0.8	118.8	2.3	9	-5.1	-4.2
(22-11-25 08:27:00)	200213_CB09148	177.2	0.6	173.9	3.1	9	-3.4	-1.9
(22-11-25 08:47:00)	190612_CC703115	53.4	0.4	48.5	2.4	9	-5.0	-9.3

Table 11. *CO aggregates of the second comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1145-CFKADS2028 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-11-26 15:32:00)	200213_CB08973	370.3	0.5	368.0	3.3	6	-2.3	-0.6
(22-11-26 15:52:00)	190612_CC703042	124.0	0.8	123.0	3.2	6	-1.0	-0.8
(22-11-26 16:12:00)	200213_CB09148	177.2	0.6	175.0	2.1	6	-2.2	-1.2
(22-11-26 16:32:00)	190612_CC703115	53.4	0.4	52.7	2.7	6	-0.8	-1.4

Methane Comparisons

Procedure: same as for CO, see above.

Results

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

Table 12. *CH_4 aggregates of the first comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1145-CFKADS2028 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-11-25 07:47:00)	200213_CB08973	2192.44	0.02	2192.41	0.13	9	-0.03	0.00
(22-11-25 08:07:00)	190612_CC703042	1929.96	0.04	1930.48	0.20	9	0.52	0.03
(22-11-25 08:27:00)	200213_CB09148	1867.50	0.06	1868.27	0.17	9	0.77	0.04
(22-11-25 08:47:00)	190612_CC703115	1955.42	0.05	1955.82	0.24	9	0.40	0.02

Table 13. *CH_4 aggregates of the second comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1145-CFKADS2028 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-11-26 16:12:00)	200213_CB08973	2192.44	0.02	2191.99	0.09	4	-0.45	-0.02
(22-11-26 16:32:00)	190612_CC703042	1929.96	0.04	1929.91	0.13	4	-0.05	0.00
(22-11-26 16:52:00)	200213_CB09148	1867.50	0.06	1867.82	0.10	4	0.32	0.02
(22-11-26 17:12:00)	190612_CC703115	1955.42	0.05	1955.43	0.19	4	0.01	0.00

Carbon Dioxide Comparisons

Procedure: same as for CO, see above.

Results

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

Table 14. *CO_2 aggregates of the first comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1145-CFKADS2028 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 (%)
(22-11-25 07:47:00)	200213_CB08973	459.86	0.01	459.88	0.03	9	0.02	0.00
(22-11-25 08:07:00)	190612_CC703042	421.37	0.02	421.37	0.03	9	0.00	0.00
(22-11-25 08:27:00)	200213_CB09148	378.78	0.02	378.79	0.02	9	0.01	0.00
(22-11-25 08:47:00)	190612_CC703115	397.71	0.01	397.70	0.01	9	-0.01	0.00

Table 15. *CO_2 aggregates of the second comparison (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #1145-CFKADS2028 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 (%)
(22-11-26 16:12:00)	200213_CB08973	459.86	0.01	459.85	0.04	4	-0.01	0.00
(22-11-26 16:32:00)	190612_CC703042	421.37	0.02	421.37	0.03	4	0.00	0.00
(22-11-26 16:52:00)	200213_CB09148	378.78	0.02	378.82	0.02	4	0.04	0.01
(22-11-26 17:12:00)	190612_CC703115	397.71	0.01	397.72	0.03	4	0.01	0.00

WCC-Empa Traveling Standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the Standard Reference Photometer before and after the audit. The comparison after the audit was made after the replacement of the faulty interface board. The following instruments were used:

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

The results of the TS calibration before the audit are given in Table 16. The TS passed the assessment criteria defined for maximum acceptable bias before the audit (Klausen et al., 2003) (cf. Figure 14). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (nmol mol}^{-1}\text{)} = \text{([TS] + 0.29 nmol mol}^{-1}\text{) / 1.0013} \quad (6a)$$

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

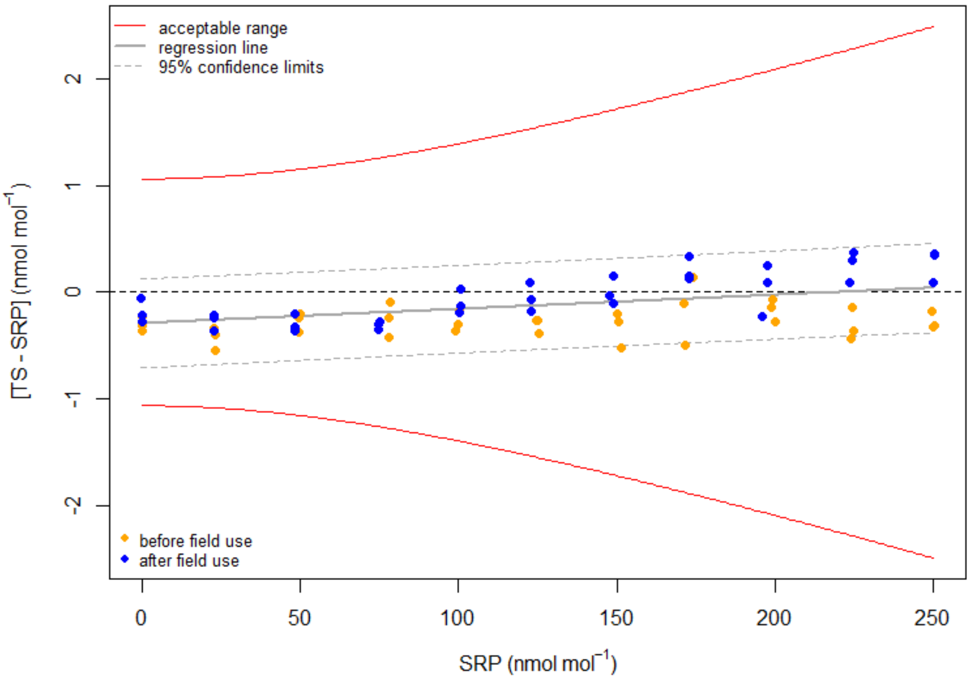

Figure 14. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before use of the TS at the field site.*

Table 16. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-07-13	1	250	250.08	0.31	249.77	0.14
2022-07-13	1	80	77.84	0.35	77.43	0.22
2022-07-13	1	100	100.12	0.34	99.95	0.15
2022-07-13	1	125	124.99	0.35	124.73	0.13
2022-07-13	1	225	224.30	0.31	224.16	0.16
2022-07-13	1	150	150.31	0.28	150.11	0.26
2022-07-13	1	0	0.20	0.34	-0.16	0.09
2022-07-13	1	200	198.65	0.28	198.51	0.14
2022-07-13	1	25	22.91	0.19	22.58	0.16
2022-07-13	1	170	171.41	0.40	170.92	0.29
2022-07-13	1	50	49.74	0.46	49.51	0.16
2022-07-13	2	175	174.18	0.29	174.33	0.13
2022-07-13	2	150	150.50	0.23	150.22	0.13
2022-07-13	2	25	23.15	0.14	22.74	0.19
2022-07-13	2	100	99.19	0.34	98.84	0.10
2022-07-13	2	225	224.05	0.30	223.62	0.08
2022-07-13	2	200	199.91	0.19	199.63	0.08
2022-07-13	2	80	77.83	0.42	77.59	0.20
2022-07-13	2	125	125.23	0.30	124.85	0.16
2022-07-13	2	250	249.86	0.29	249.54	0.26
2022-07-13	2	50	49.62	0.28	49.25	0.30
2022-07-13	2	0	-0.05	0.15	-0.28	0.12
2022-07-13	3	80	78.23	0.27	78.14	0.17
2022-07-13	3	100	99.68	0.17	99.38	0.18
2022-07-13	3	50	49.89	0.27	49.69	0.21
2022-07-13	3	170	171.12	0.42	171.02	0.37
2022-07-13	3	250	249.46	0.26	249.29	0.12
2022-07-13	3	200	199.27	0.28	199.20	0.13
2022-07-13	3	0	0.02	0.29	-0.29	0.20
2022-07-13	3	150	151.37	0.40	150.85	0.51
2022-07-13	3	225	224.57	0.26	224.21	0.17
2022-07-13	3	25	23.17	0.31	22.63	0.24
2022-07-13	3	125	124.49	0.26	124.23	0.14
2023-03-22	4	75	75.18	0.36	74.91	0.08
2023-03-22	4	250	250.02	0.50	250.11	0.27
2023-03-22	4	225	224.23	0.14	224.53	0.09
2023-03-22	4	25	22.73	0.37	22.37	0.11
2023-03-22	4	150	147.84	0.29	147.81	0.10
2023-03-22	4	100	100.69	0.40	100.57	0.11
2023-03-22	4	125	122.94	0.34	122.76	0.15
2023-03-22	4	175	172.98	0.35	173.11	0.19
2023-03-22	4	0	0.01	0.31	-0.27	0.13
2023-03-22	4	195	195.79	0.19	195.56	0.18
2023-03-22	4	50	48.35	0.27	48.03	0.19
2023-03-22	5	175	172.76	0.34	172.91	0.19

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2023-03-22	5	0	-0.01	0.15	-0.22	0.11
2023-03-22	5	100	100.72	0.63	100.75	0.27
2023-03-22	5	125	122.70	0.21	122.79	0.10
2023-03-22	5	250	250.31	0.43	250.65	0.17
2023-03-22	5	75	74.75	0.16	74.46	0.26
2023-03-22	5	200	197.67	0.20	197.77	0.18
2023-03-22	5	225	224.57	0.34	224.94	0.15
2023-03-22	5	25	22.70	0.47	22.47	0.20
2023-03-22	5	50	48.50	0.34	48.29	0.13
2023-03-22	5	150	148.81	0.45	148.70	0.07
2023-03-22	6	100	100.42	0.27	100.23	0.15
2023-03-22	6	175	172.80	0.22	173.13	0.07
2023-03-22	6	150	149.05	0.26	149.21	0.16
2023-03-22	6	25	22.66	0.29	22.45	0.15
2023-03-22	6	225	223.58	0.21	223.68	0.18
2023-03-22	6	75	74.79	0.28	74.45	0.22
2023-03-22	6	0	-0.14	0.16	-0.19	0.08
2023-03-22	6	250	250.13	0.17	250.49	0.21
2023-03-22	6	50	48.37	0.27	48.01	0.24
2023-03-22	6	125	122.83	0.31	122.77	0.18
2023-03-22	6	200	197.63	0.26	197.89	0.20

#the level is only indicative.

Greenhouse gases and carbon monoxide

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

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

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

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy).
CO, CO_2 and CH_4: Picarro G2401 (Cavity Ring-Down 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 17 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including standard deviations of the WCC-Empa TS are listed in Table 18 and 19, and Figures 15 and 16 show the analysis of the TS over time.

Table 17. *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 18. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, and N_2O. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne.*

TS	**Press. (psi)**	**CH_4 (P) (nmol mol^{-1})**	**sd**	**CO_2(P) (µmol mol^{-1})**	**sd**	**N_2O (A) (nmol mol^{-1})**	**sd**
190612_CC703042	1990	1929.96	0.04	421.37	0.02	347.34	0.07
190612_CC703115	1950	1955.42	0.05	397.71	0.01	326.21	0.06
200213_CB08973	2000	2192.44	0.02	459.86	0.01	327.52	0.04
200213_CB09148	1990	1867.5	0.06	378.78	0.02	311.41	0.03

Table 19. *Calibration summary of the WCC-Empa travelling standards for CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne.*

TS	**Press. (psi)**	**CO (P) (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**
190612_CC703042	1990	123.98	0.83	122.49	0.19
190612_CC703115	1950	53.43	0.44	52.51	0.58
200213_CB08973	2000	370.32	0.54	369.9	0.11
200213_CB09148	1990	177.22	0.58	176.24	0.19

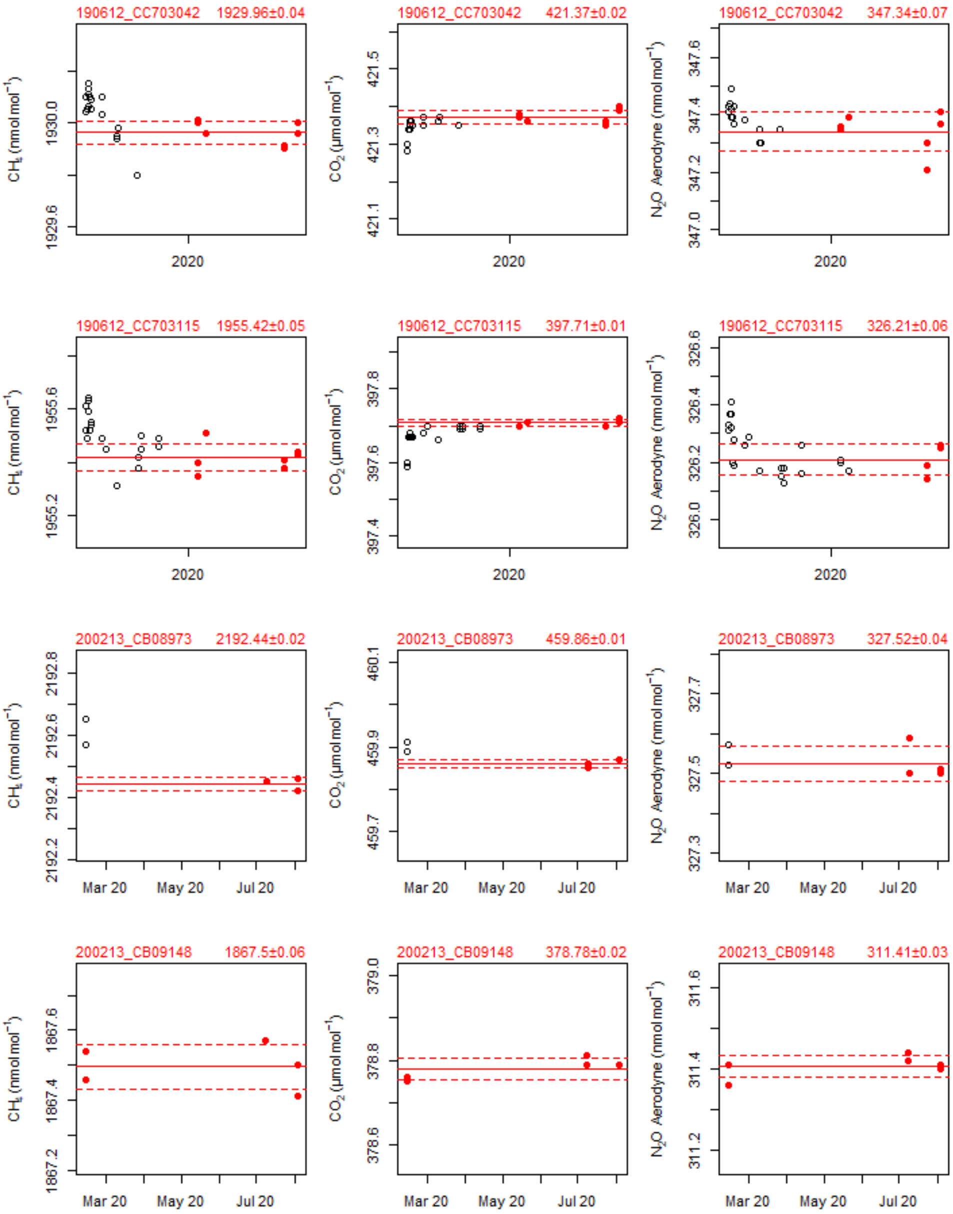

Figure 15. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard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

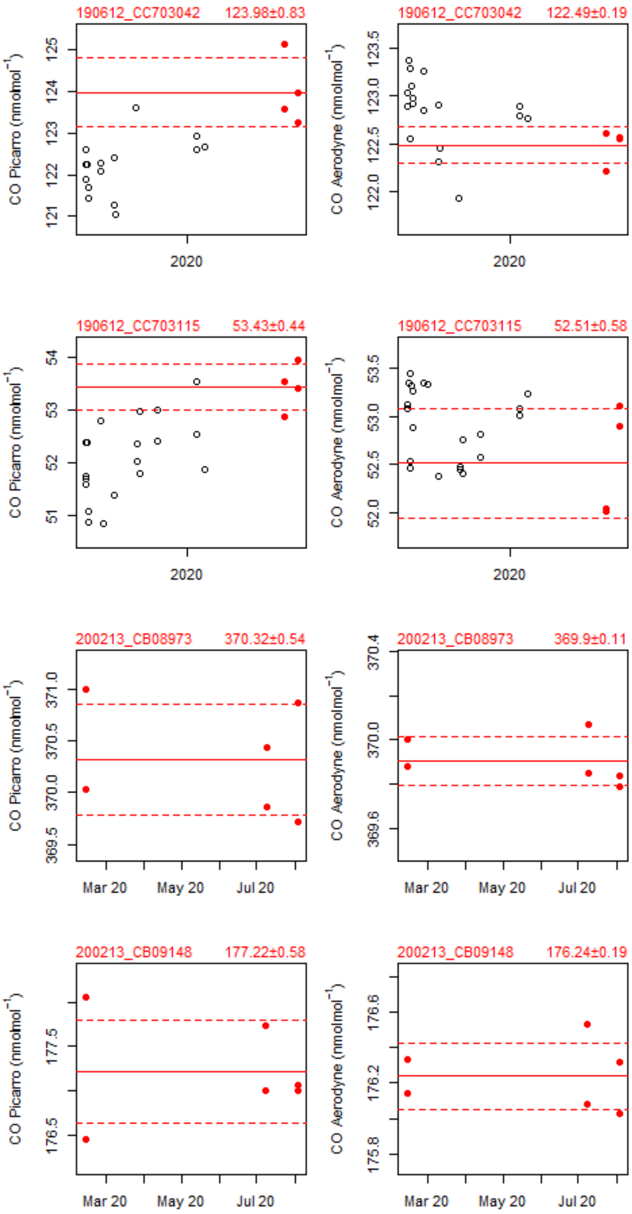

Figure 16. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

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LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
CATCOS	Capacity Building and Twinning for Climate Observing Systems
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
HYMOC	Hydro-Meteorological Observation Center
LS	Laboratory Standard (for calibration)
NA	Not Applicable
NOAA	National Oceanic and Atmospheric Administration
PC	Personal Computer
PDI	Pha Din GAW Station
PI	Principle Investigator
QA/SAC	Quality Assurance / Science Activity Centre
SDC	Swiss Agency for Development and Cooperation
SOP	Standard Operating Procedure
SN	Serial Number
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
VNMHA	Vietnam Hydrological and Meteorological Administration
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 (target gas for quality control)