SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE, CARBON DIOXIDE AND NITROUS OXIDE AT THE

REGIONAL GAW STATION ANMYEON-DO REPULIC OF KOREA JUNE 2022

WCC-Empa Report 22/2

Submitted to the World Meteorological Organization by

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WCC-Empa Report 22/2

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 3rd system and performance audit by WCC-Empa[1] at the regional GAW station Anmyeon-do (AMY) was conducted from 4 to 7 July 2022 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at AMY, as well as 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
Ms Sumin Kim	NIMS, station manager, scientist, measurement leader of reactive gases
Dr Haeyoung Lee	NIMS, scientist, measurement leader of greenhouse gases
Mr Choong Hoon Lee	NIMS, station operator
Mr Hong Woo Choe	NIMS, station operator
Ms Soojeong Lee	NIMS, scientist, central calibration laboratory and WCC for SF_6 operator

This report summarises the assessment of the Anmyeon-do GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide measurements in particular.

The report is distributed to the station manager and measurement leaders of Anmyeon-do GAW station, the national focal point for GAW of the Republic of Korea, 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 Anmyeon-do GAW station (AMY) is operated by the National Institute of Meteorological Sciences (NIMS), which is part of the Korea Meteorological Administration (KMA). The station is visited during weekdays by approximately 5 - 10 scientists, technical and administrational staff. The operation and maintenance of the station is well organized, with clear assignments of responsibilities.

Station Location and Access

AMY (36.5386°N, 126.3300°E, 42 m a.s.l) is located on an island on the west coast of the Korean Peninsula. The station building itself is located on a hill at an elevation of 42 m above sea level, and comprises a 40 m tower. To the west the station is exposed to the open sea, with the Chinese mainland in a distance of 300-400 km, and Seoul is located about 130 km northeast of AMY. East of the station are several small farms producing mainly rice and sweet potatoes. Large parts of the area as well as the immediate surroundings of the station are covered by pine forests. The station is infrequently affected by local pollution, mainly during summer due to recreational activities, and autumn due to burning of crop residues.

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

The location is adequate for the intended purpose. Year-round access to AMY is possible by road.

Station Facilities and Infrastructure

[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.

AMY comprises extensive laboratory space, and office, kitchen and sanitary facilities are available. Internet access is available with sufficient bandwidth. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

AMY, as well as the other Korean GAW stations, is linked to the central calibration laboratory at NIMS.

Measurement Programme

The AMY regional GAW station hosts a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured species is available from GAWSIS.

The information available from GAWSIS was reviewed as part of the audit. Information in GAWSIS has recently been updated (January 2022), and the information was mostly up-to-date. However, some details regarding instrumentation and station contacts needs to be re-visited and corrected.

> **Recommendation 1 (***, 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 December 2022, the following AMY data of the scope of the audit has been submitted to the World Data Centres:

AMY, submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2017-2020)

AMY, submission to World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (1999-2020), CO_2 (1999-2020), CO (2017-2020), N_2O (1999-2020). For N_2O, only daily averages have been submitted.

NOAA, submission to World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (2013-2021), CO_2 (2013-2021), CO (2013-2021), N_2O (2013-2021)

Data shown in this report was accessed on 20 December 2022. All data of the scope of the audit has been submitted with a submission delay of less than two years. Continuation of this timely submission practice is recommended.

> **Recommendation 2 (**, important, ongoing)**
> *Data submission is an obligation of all GAW stations. It is recommended to submit data to the corresponding data centres at least in yearly intervals. One hourly data must be submitted for all parameters.*
> *KMA started submitting hourly data following the WCC-Empa audit in 2017 and hourly data is now available for most parameters.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCRG and WDCGG was reviewed. Time series plots are shown in the Appendix. It was noted that part of the time series contain only filtered data, and the data selection and evaluation procedure is unclear.

Recommendation 3 (*, critical, ongoing)**
All valid data points of a time series, including periods with elevated amount fraction due to pollution episodes, must be submitted to the data centres. If data is filtered, the time series must either be submitted as an additional data set, or it must be clearly indicated by a data flag.

Documentation

All operation and maintenance actions are entered in electronic and hand written log books. The instrument manuals are available at the site, and weekly checklists are available. The reviewed information was mostly up to date. However, the calibration settings of the ozone instrument were frequently changed, and recordings of the changes were only partly available, which complicates post-correction of the ozone data.

Recommendation 4 (*, critical, ongoing)**
The station staff must be aware that documentation of all relevant information is of utmost importance for reliable data and measurements. The current practice is appropriate, but it has to be made sure that the information is archived together with the measurement data.

Air Inlet System

Surface ozone: The inlet location is on top of the laboratory building, about 2 m above the flat roof. The inlet system consist of a ½ inch PTFE tube with a length of about 8 m, which is connected to a glass distribution manifold with an inner diameter of about 2 cm. The inlet line and the manifold are flushed with a flow rate of 25 l/min, and the instruments are connected to the manifold with ¼ inch PFA lines. PFA filter holders / PTFE filter with a diameter of 47 mm are used to protect the instruments from dust. The inlet system is adequate for ozone measurements.

GHG: A common air inlet system for GHG measurements is in place. Air is pumped from the 40 m tower to the laboratory building, and automatically dried to a dew point of -80°C using two cryogenic traps alternating every 24 hours. The stainless steel manifold is pressurized to approx. 2 bar, and instruments are directly connected to this manifold. The inlet is adequate for GHG measurements.

Surface Ozone Measurements

Surface ozone measurements at AMY commenced in 1998; however, data of the early period until the first ozone audit of WCC-Empa is of questionable data quality, and reliable ozone data is available from 2017 onwards.

Recommendation 5 (, important, 2023)**
It should be explored if the data from 1998 to 2017 is of sufficiently high quality to be submitted to WDCRG. If the data can be rescued, submission is highly recommended.

Instrumentation. AMY is currently equipped with two ozone analysers (Thermo Scientific 49i), but only one instrument is used for ozone measurements. The other instrument serves as a backup in case of a failure of the main instrument.

Standards. An ozone standard (Thermo Scientific 49iQ-PS) with traceability to the Korea Research Institute of Standards and Science (KRISS) standard reference photometer is available at AMY. The standard is used twice a year to check the calibration of the analyser. The ozone standard could not be compared during the current audit due to instrument drift and stability issues of the Thermo Scientific 49iQ-PS instrument.

Recommendation 6 (, important, 2023)**
The Thermo Scientific 49iQ-PS instrument must be carefully checked for proper operation. If stability problems persist, repair is required.

Data Acquisition. Data (1-min time resolution) is automatically transmitted in real time using the TEI iPort software. O_3 amount fraction, sample flow and intensity are visualized in real time and all instrument parameters are available with the Thermo iPort software, but this requires manual intervention. The station operator flags events every day. All data reviewed frequently considering the data flags. The analogue signal is also acquired with a data logger (TECH KOREA KTE-1400D).

The current approach for the data acquisition is adequate, but replacement by a system that acquires automatically the digital signals is recommended.

Recommendation 7 (, minor, 2023)**
It should be considered to develop or purchase a data acquisition system that acquires continuously the digital signal of the ozone instrument.

Intercomparison (Performance Audit). The AMY ozone analysers (OA) were 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}. The result of the comparisons is 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.

It was noted that the calibration settings of the two ozone analysers were frequently changed by the external maintenance company. The record of the changes was only partly available, and is summarized in the Table below.

Table 1. *Calibration settings of the AMY ozone analysers.*

Instrument	#1153620133		#0932138786		
Date	BGK	COEF	BGK	COEF	Remarks
2020-12-23	-0.5	1.075	0	1.006	was like this until March 2022 for #0932138786
2020-12-30	-0.6	1.085			
2021-01-15	-0.5	1.104			
Unknown date	2.0	0.948			
2021-10-27	2.2	1.008			(at KRISS)
2022-01-11	0.5	0.966			
2022-03-04			-0.3	1.011	
2022-05-04	0.7	1			
2022-06-28	-0.7	0.964	-1.8	0.987	change made by external contractor (maintenance)

Two comparison were made for both ozone analysers; the first run was made with unadjusted calibration and pressure sensor settings, and the second run was made with adjusted calibration factors and pressure sensor.

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 1.1476×10^{-17} cm^2 (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Main analyser:

Thermo Scientific 49i #1153620133 (initial settings, BKG -0.7 nmol mol^{-1}, COEF 0.964):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -1.10 nmol mol^{-1}) / 0.9750 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.13e-05 * X_{O3}^2) (1b)

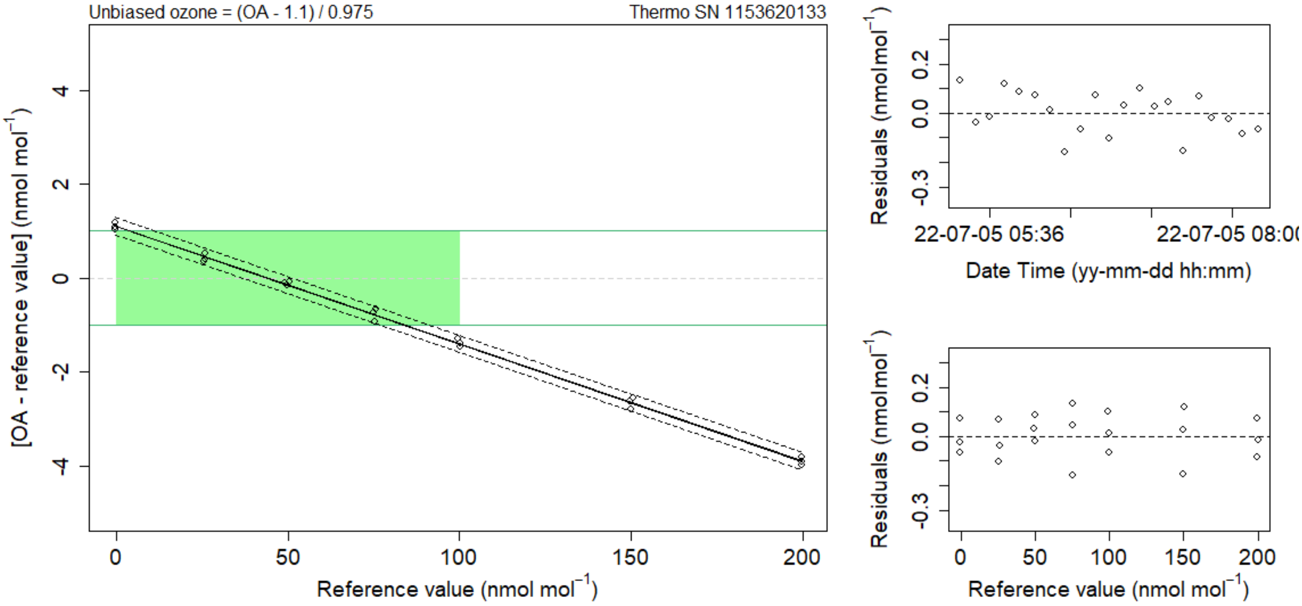

Figure 1. *Left: Bias of the main AMY ozone analyser (Thermo Scientific 49i #1153620133, BKG -0.7 nmol* mol^{-1}*, COEF 0.964) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the 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).*

Thermo Scientific 49i #1153620133 (final settings, BKG 0.2 nmol mol^{-1}, COEF 0.999):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -0.05 nmol mol^{-1}) / 1.0024 (1c)

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

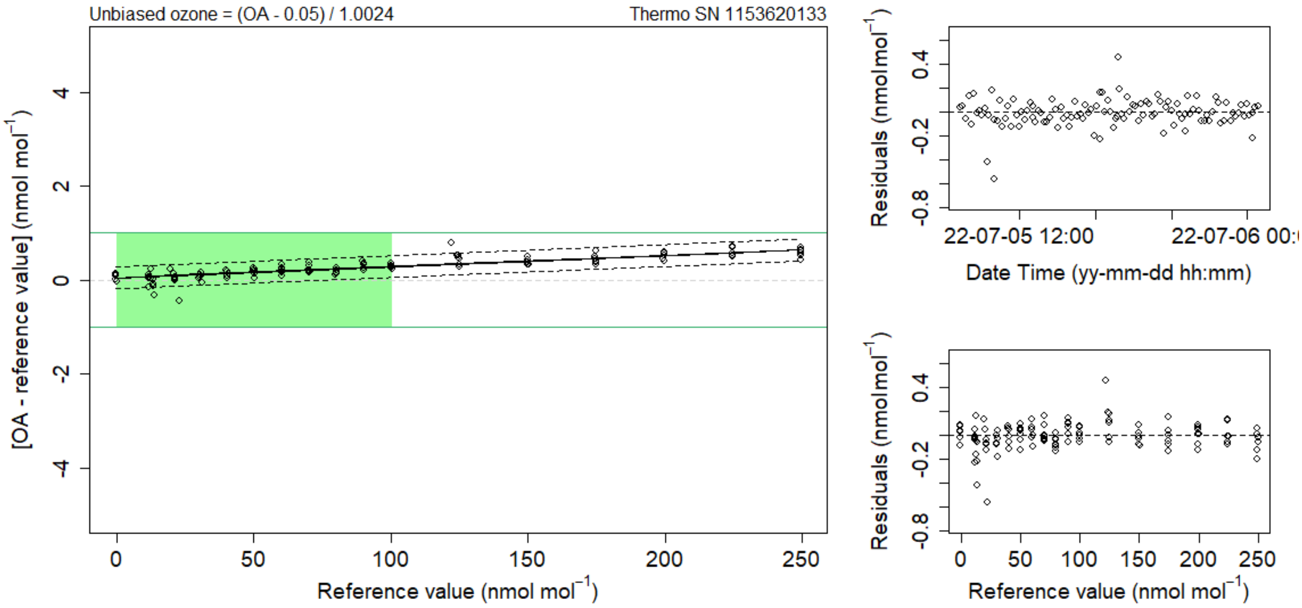

Figure 2. *Same as above, after adjustment of the calibration settings (BKG 0.2 nmol mol^{-1}, COEF 0.999).*

Backup analyser:

Thermo Scientific 49i #0932138786 (initial settings, BKG -1.8 nmol mol^{-1}, COEF 0.987):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -2.07 nmol mol^{-1}) / 0.9813 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.30 + 2.18e-05 * X_{O3}^2) (1b)

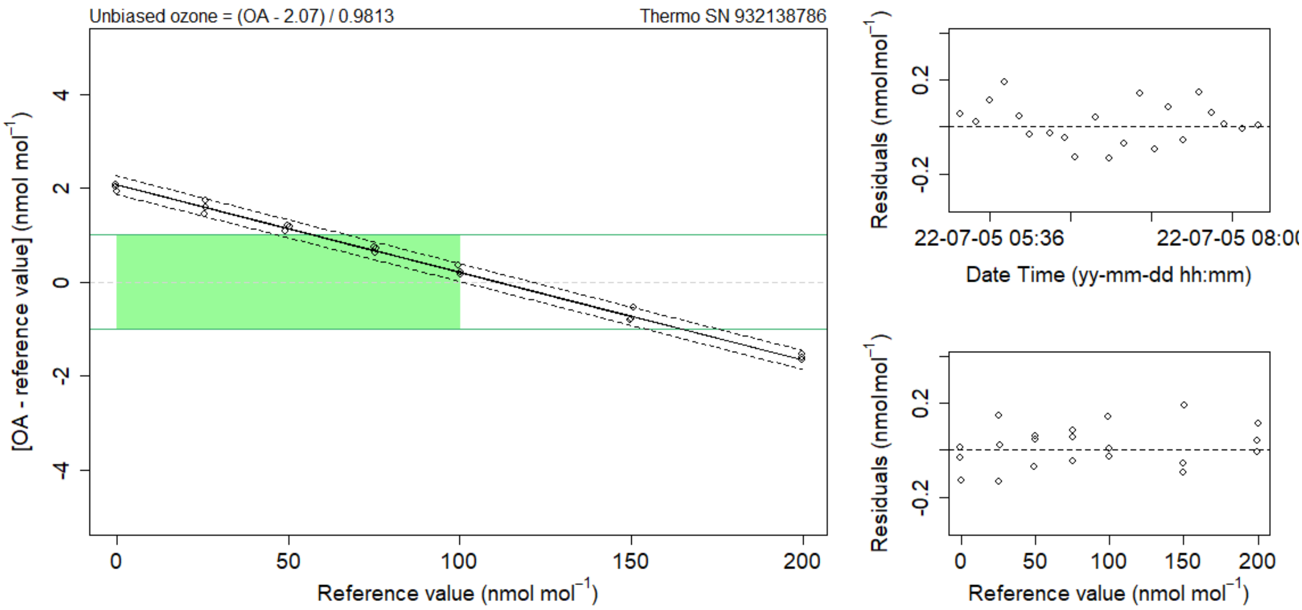

Figure 3. *Left: Bias of the backup AMY ozone analyser (Thermo Scientific 49i #0932138786, BKG -1.8 nmol mol^{-1}, COEF 0.987) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the 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).*

Thermo Scientific 49i #0932138786 (final settings, BKG 0.0 nmol mol^{-1}, COEF 1.006):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] -0.18 nmol mol^{-1}) / 0.9973 (1c)

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

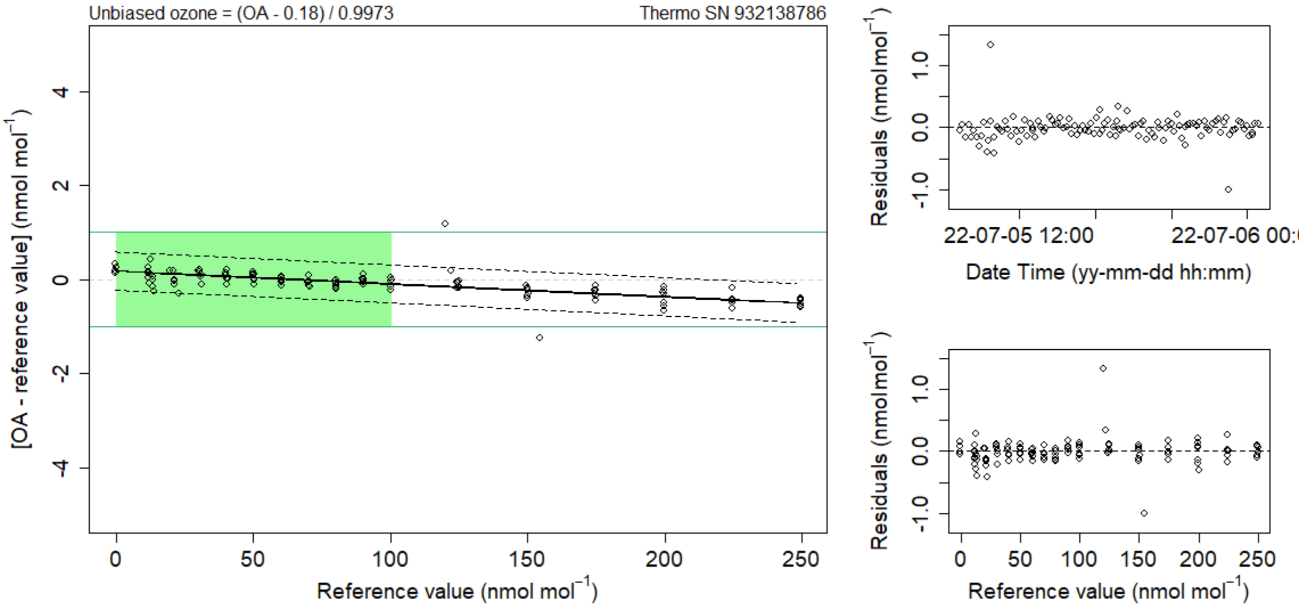

Figure 4. *Same as above, after adjustment of the calibration settings (BKG 0.0 nmol mol^{-1}, COEF 1.006).*

The results of the comparisons can be summarised as follows:

The AMY ozone instruments are in a good working condition, but the calibration settings frequently changed by the external maintenance company since 2020. This is in contradiction to the recommendations made after the WCC-Empa audit in 2017, which recommended not changing the calibration settings of the ozone instruments. The analyser that was in use at AMY in 2017 at the time of the last WCC-Empa audit now serves as a backup instrument. The calibration settings of this instrument were set back to the settings after the audit in 2017 for the final comparison of the current audit, and agreement within the WMO/GAW DQOs were found. This confirms that the calibration remains valid over periods of years in case of a well maintained and fully functional analyser. Therefore, WCC-Empa strongly recommends to keep the current calibration settings of the instruments, and regularly check and record the settings. The maintenance company should be advised accordingly.

Recommendation 8 (*, critical, 2023)**

The current calibration settings as after the second comparison by WCC-Empa should NOT be changed.

Recommendation 9 (*, critical, 2023)**

All data acquired since 2017 need to be recalculated to the calibration settings of 2017 for the Thermo Scientific 49i #0932138786 (BKG 0.0 nmol mol^{-1}, COEF 1.006), and to the final calibration settings of the current audit for the Thermo Scientific 49i #1153620133 (BKG 0.2 nmol mol^{-1}, COEF 0.999).

Recommendation 10 (*, critical, ongoing)**

Calibration settings need to be recorded, especially after inventions by external contractors.

Carbon Monoxide Measurements

Continuous measurements of CO at AMY started in 1998 using non-dispersive infrared (NDIR) technique. Mid-infrared Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) measurements started in 2016, and reliable CO data is available since 2017.

Instrumentation. Los Gatos 23-r EP (OA-ICOS). The air is dried to a dew point of -50°C by a cold trap. In addition, a Thermo 48i-TL is available. This instrument was not audited since only the data of the OA-ICOS analyser will be considered for GAW data submission.

Standards. Several working standards are available at AMY for the calibration of the instruments. The assignments of the WS values are done at the central calibration facility at NIMS, where several laboratory standards from the CCL are available. An overview of available standards at AMY and NIMS is shown in Table 9 in the Appendix.

Calibrations of the instrument with only one working standard are still carried out manually every two weeks. It is recommended to change to an automated calibration scheme, and include more standards to cover a wider amount fraction range.

> **Recommendation 11 (**, important, 2023)**
> *The calibration of the CRDS needs to be automated. At least three different standards should be used to cover the amount fraction range encountered at AMY.*

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equation characterises the instrument bias, and the results are further illustrated in Figure 5 with respect to the WMO GAW DQOs (WMO, 2020):

LGR N_2O/CO-30-EP #15-0213:

Unbiased CO mixing ratio:	X_{CO} (nmol mol^{-1}) = (CO + 3.43 nmol mol^{-1}) / 0.9985	(2a)
Remaining standard uncertainty:	u_{CO} (nmol mol^{-1}) = sqrt (0.7 nmol mol^{-1} + 1.01e-04 * X_{CO}^2)	(2b)

The results of the comparisons can be summarised as follows:

Agreement within the extended WMO/GAW compatibility goals was found for the LGR CO analyser in the relevant amount fraction range. The residuals of the linear regression indicate a non-linearity of the instrument.

> **Recommendation 12 (**, important, 2023)**
> *It is recommended to characterize the linearity of the LGR CO analyser.*
>
> **Recommendation 13 (**, important, 2023)**
> *The calibration strategy should focus on CO standards with higher amount fractions, because CO in air standard gases are usually not stable, and the drift of the standards is independent on the amount fraction.*

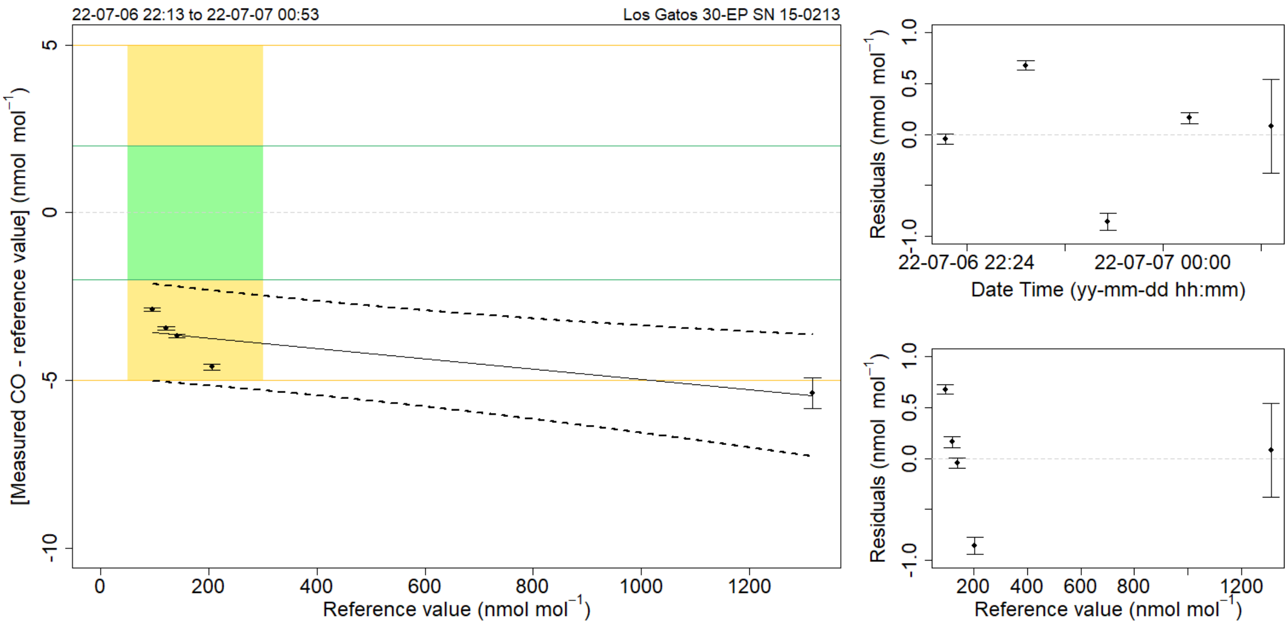

Figure 5. *Left: Bias of the AMY LGR N_2O/CO-30-EP #15-0213 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual 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 AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Methane Measurements

Continuous measurements of CH_4 at AMY started in 1999 using gas chromatography (GC) / flame ionization detection (FID). In 2011, a CRDS CH_4 instrument was installed, and parallel measurements with the GC system were made until 2015. The GC/FID system was decommissioned in 2015.

Instrumentation. Picarro G2301 (near-IR CRDS). The air is dried to a dew point of -50°C by a cold trap.

Standards and calibration. See Carbon Monoxide Measurements.

Calibrations of the instrument with 4 working standards are still carried out manually every two weeks. It is recommended to change to an automated calibration scheme using the Picarro valve sequencer.

> **Recommendation 14 (**, important, 2023)**
> *The calibration of the CRDS needs to be automated, e.g. with the Picarro valve sequencer and a multi position valve.*

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instrument with randomised CH_4 levels from travelling standards. The result of the comparison is summarised and illustrated below.

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

Picarro G2301 #857-CFADS2177):

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 + 3.47 nmol mol^{-1}) / 1.0016 (3a)

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

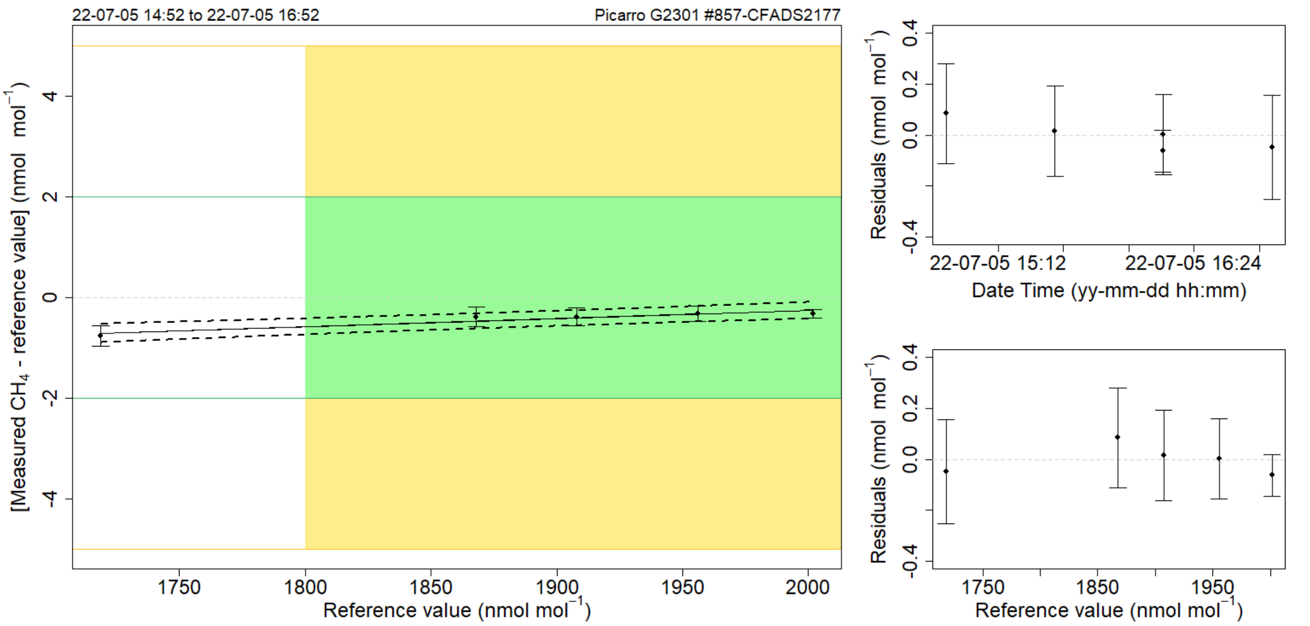

Figure 6. *Left: Bias of the Picarro G2301 #857-CFADS2177 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement 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 AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

Excellent agreement well within the WMO/GAW compatibility goal was found. The good results show that the whole system, including calibration procedures and standards gases, is fully appropriate, and no further action is required.

Carbon Dioxide Measurements

Measurements of carbon dioxide at AMY commenced in 1999, and continuous data series are available since then. Initially, these measurements were made using an NDIR instrument (Siemens Ultramat) for CO_2. In 2011, a Picarro G2301 CRDS instrument was installed, and since the beginning of 2012, data of this instrument is considered for submission to the WMO/GAW data centre.

Instrumentation. Picarro G2301 (near-IR CRDS). The air is dried to a dew point of -50°C by a cold trap.

Standards and calibration. See methane measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instruments with randomised CO_2 levels from travelling standards. The results of the comparisons are summarised and illustrated below.

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

Picarro G2301 #857-CFADS2177:

Unbiased CO_2 mixing ratio:	X_{CO2} (µmol mol^{-1}) = (CO_2 + 0.39 µmol mol^{-1}) / 1.0008	(4a)
Remaining standard uncertainty:	u_{CO2} (µmol mol^{-1}) = sqrt (0.002 µmol mol^{-1} + 3.28e-8 * X_{CO2}^2)	(4b)

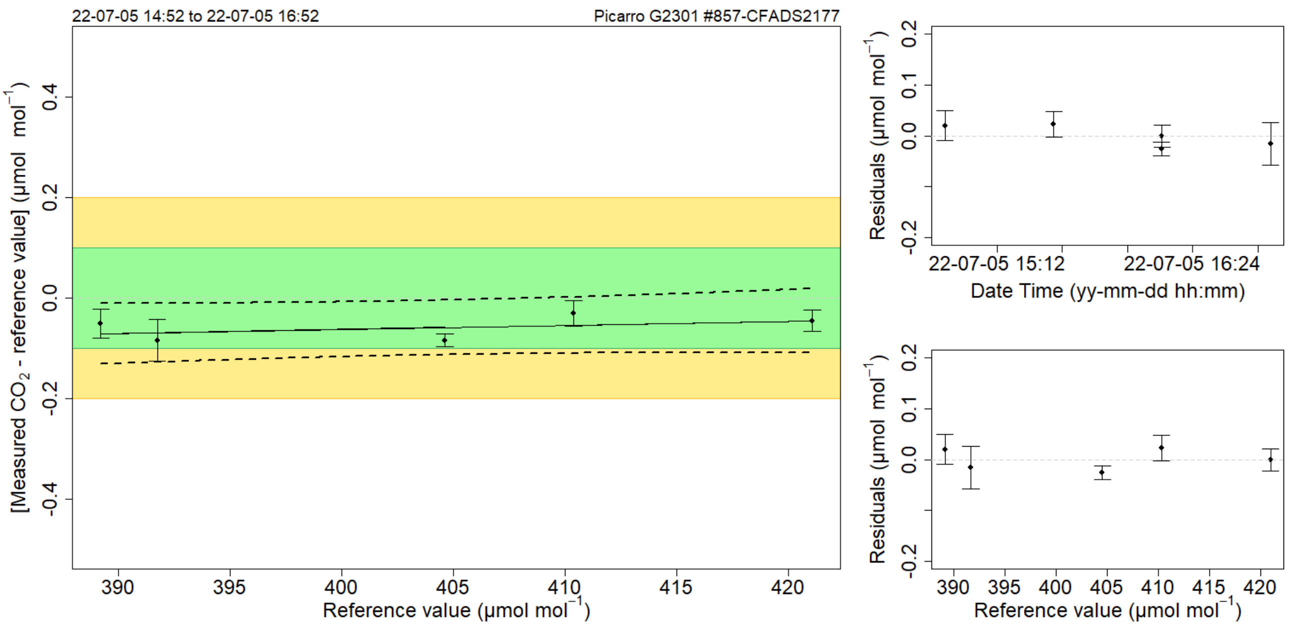

Figure 7. *Left: Bias of the Picarro G2301 #857-CFADS2177 CO_2 instrument with respect to the WMO-X2019 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement 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 AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The result was entirely within the WMO/GAW network compatibility goal, which shows that the measurement system including calibration and data evaluation is fully appropriate. No further action is required.

Nitrous Oxide Measurements

Continuous measurements of N_2O at AMY started in 1999 using GC / electron capture detection (ECD), and time series are available since then. Mid-infrared Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) measurements started in 2016, and data of this instrument is considered for submission to WDCGG since then.

Instrumentation. Los Gatos 23-r EP (OA-ICOS). The air is dried to a dew point of -50°C by a cold trap. In addition, a Thermo 48i-TL is available. In addition, a gas chromatograph (Agilent 7890N) with Electron Capture Detector (GC/ECD) is available. This instrument was not audited because only the data of the OA-ICOS analyser will be considered for GAW data submission.

Standards and calibration. See carbon monoxide measurements.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equation characterises the instrument bias, and the result is further illustrated in Figure 8 with respect to the WMO GAW DQOs (WMO, 2020):

LGR N_2O/CO-30-EP #15-0213:

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O – 1.26) / 0.9957 (5a)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.04 + 1.01e-07 * X_{N2O}^2) (5b)

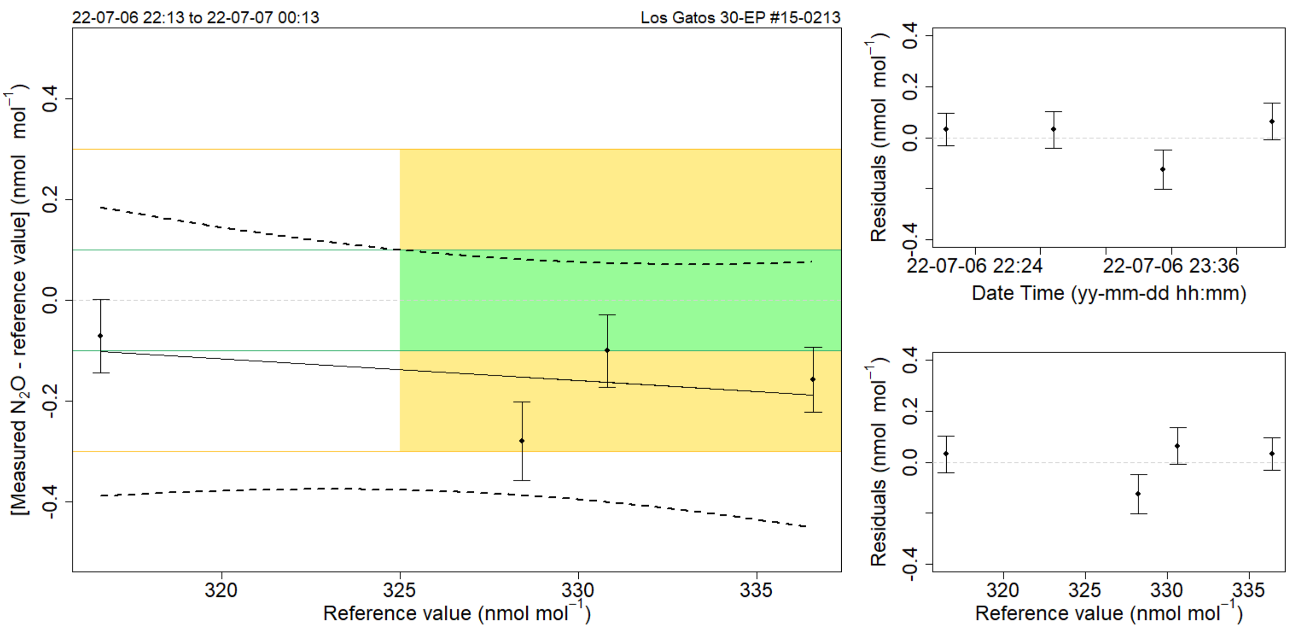

Figure 8. *Left: Bias of the LGR 30-EP #15-0213: nitrous oxide analyser with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement 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 AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

Agreement within the extended WMO/GAW network compatibility goal was found between the AMY analyser and the WCC-Empa reference. Uncertainties for N_2O reference standards are exceeding the WMO/GAW network compatibility goals, and therefore, it is challenging to reach the goal. Therefore, the AMY result can be considered as good, and no further action is required.

AMY PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the AMY 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 N_2O, the mole fraction range covers 10 nmol mol^{-1}and depends on the time of the comparison due to the large annual increase combined with low variability (see Zellweger et al. (2019) for details). For surface ozone the mole fraction range of 0-100 nmol mol^{-1}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, while the results for CO, CH_4, CO_2 and N_2O are shown in Figure 10. 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 AMY audit are shown as coloured dots in Figure 9 and 10, and are also summarised in Table 2. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 2.

The results were within the DQOs for CO_2 and CH_4, and within the extended DQOs for CO and N_2O. The ozone instruments were meeting the DQOs after the adjustment of the calibration settings by WCC-Empa.

Table 2. *AMY 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 and WCC-N_2O audits until September 2020 within these criteria since 1996 (O_3), 2002 (N_2O), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound / Instrument	**Range**	**Unit**	**AMY within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**
O_3 (Thermo 49i #1153620133, initial settings)	0 -100	nmol mol^{-1}	✗	64	NA
O_3 (Thermo 49i #1153620133, final settings)	0 -100	nmol mol^{-1}	✓	64	NA
O_3 (Thermo 49i-0932138786, initial settings)	0 -100	nmol mol^{-1}	✗	64	NA
O_3 (Thermo 49i-0932138786, final settings)	0 -100	nmol mol^{-1}	✓	64	NA
CO (Picarro G2301 857-CFADS2177)	30 - 300	nmol mol^{-1}	✓	17	49
CH_4 (Picarro G2301 857-CFADS2177)	1750 - 2100	nmol mol^{-1}	✓	76	94
CO_2 (Picarro G2301 857-CFADS2177)	380 - 450	µmol mol^{-1}	✓	48	74
N_2O (LGR N_2O/CO-30-EP)	325 - 335	nmol mol^{-1}	✓	4	44

[1] Percentage of stations within the eDQO and DQO

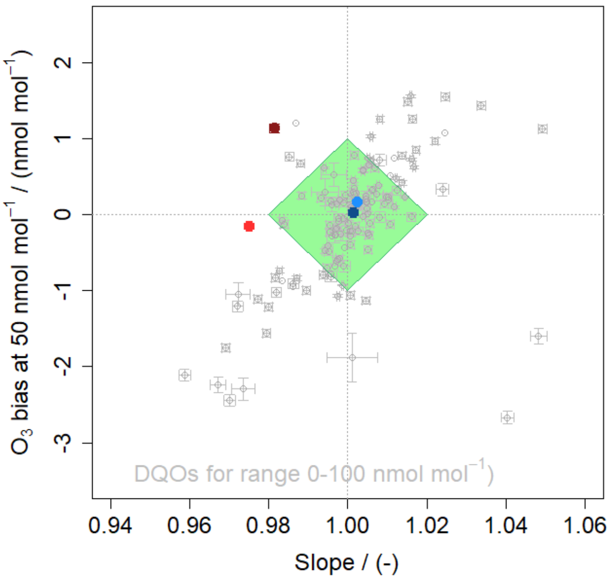

Figure 9. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the results of the AMY Thermo 49i-0932138786 (dark red: unadjusted, dark blue: adjusted settings) and TEI49i-1153620133 (red: unadjusted, light blue: adjusted settings). The uncertainty bars refer to the standard uncertainty, and the green area corresponds to the WMO/GAW DQO for surface ozone.*

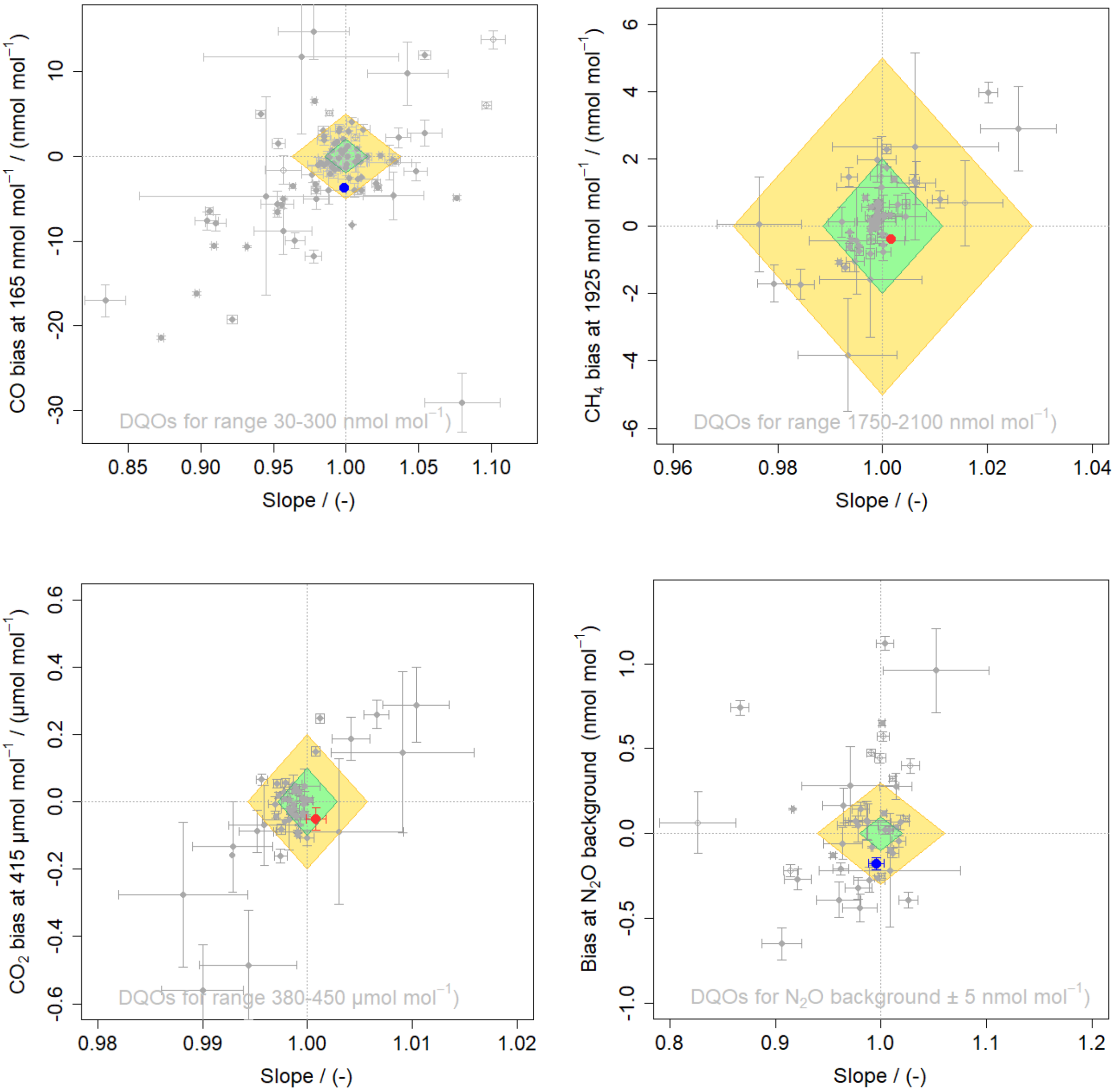

Figure 10. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show AMY results (red: Picarro G2301, blue LGR 30EP). 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).*

CONCLUSIONS

The regional GAW station Anmyeon-do comprises an extensive research infrastructure, and hosts a large number of long-term continuous observations in all WMO/GAW focal areas. The AMY station is well imbedded in the GAW activities of South Korea, and the location of all Korean stations is strategically very important for the GAW programme.

The large number of measured atmospheric constituents at AMY in combination with the high data quality enables state of the art research. Thus, the continuation of the Anmyeon-do measurement series is highly important for GAW.

Most assessed measurements were of high data quality, and met the WMO/GAW network compatibility or extended compatibility goals in the relevant mole fraction range.

Table 3 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Please note that Table 3 refers only to the mole fractions relevant to AMY, whereas Table 2 further above covers a wider mole fraction range.

Table 3. *Synthesis of the performance audit results for the TS comparisons. 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 Thermo 49i	CO LGR N_2O/CO-30-EP	CH_4 Picarro G2301	CO_2 Picarro G2301	N_2O LGR N_2O/CO-30-EP
TS	✓*	✓	✓	✓	✓

* After adjustment of the calibration settings

SUMMARY RANKING OF THE ANMYEON-DO GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access
Facilities		
Laboratory and office space	(5)	Fully adequate, with space for additional research campaigns
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate
Power supply	(5)	Reliable and stable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(4)	Skilled staff, further training with respect to surface ozone needed
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2 Picarro G2301	(5)	State of the art instrumentation
CO/N_2O LGR 23-r	(5)	Adequate instrument
Standards		
O_3	(4)	Adequate, stability issues during the audit
CO, CO_2, CH_4, N_2O	(5)	Full traceability to the GAW reference through central calibration facility at NIMS
Data Management		
Data acquisition	(5)	Adequate systems for GHG and CO, automation needed for O_3
Data processing	(4)	Skilled staff and appropriate procedures
Data submission	(3)	Mostly timely submission, GHG data is filtered, only daily values for N_2O

#0: inadequate thru 5: adequate.

Dübendorf, April 2023

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APPENDIX

Data Review

The following figures show summary plots of AMY data accessed on 12 December 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:

The AMY ozone time series submitted to WDCRG is shown in the following figure.

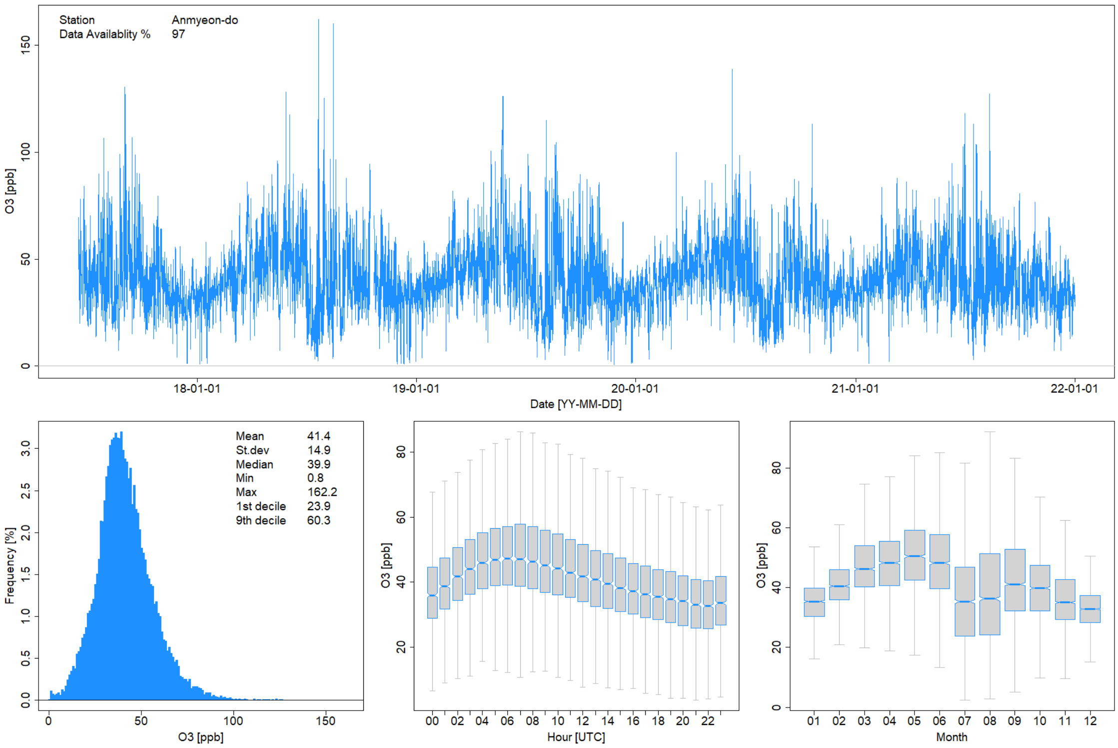

Figure 11. *O_3 data for the period from 2017 to 2021 accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The data sets looks sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Ozone time series start after the calibration of the AMY instrument by WCC-Empa in 2017.

Carbon monoxide:

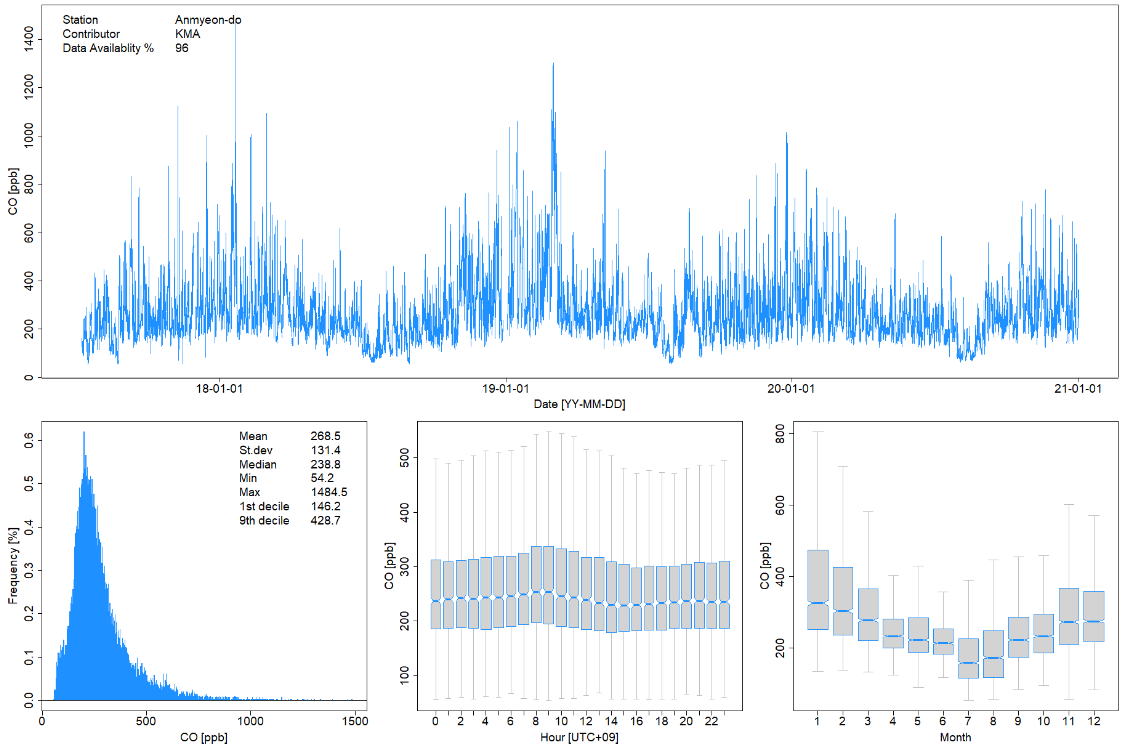

Figure 12. *AMY CO in-situ data (2017-2020) submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

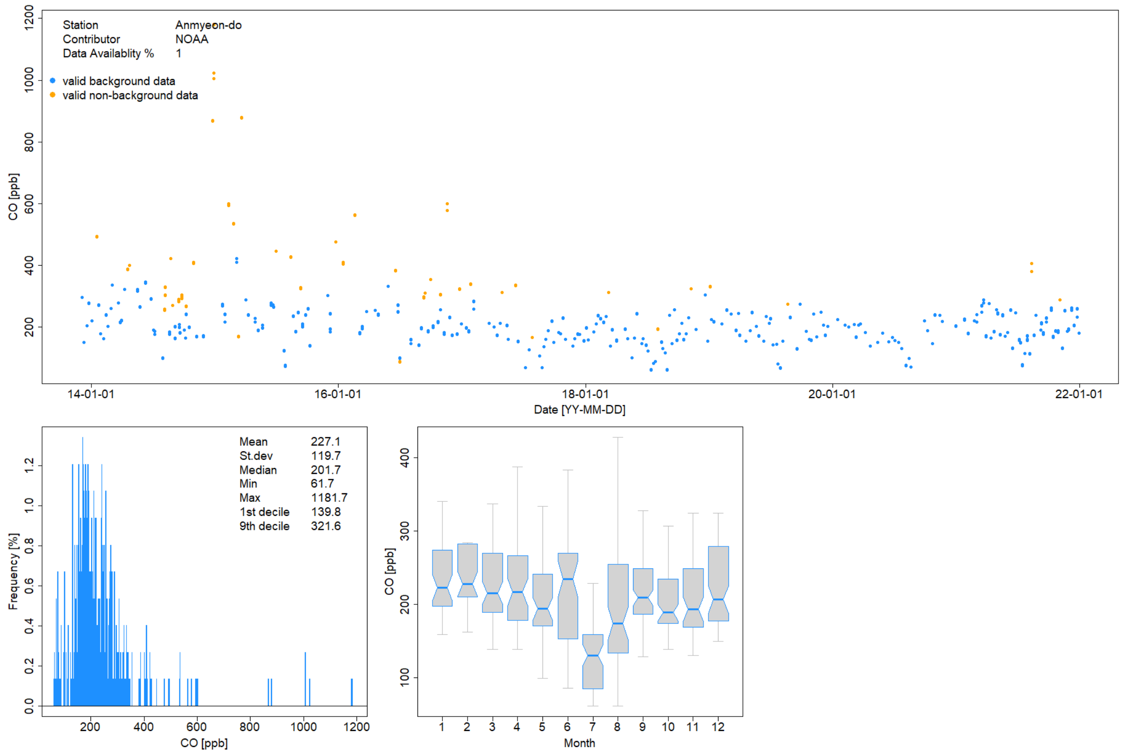

Figure 13. *AMY CO flask data (2013-2021) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, event data. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- Both the AMY in-situ and the NOAA flask CO data set look sound with respect to mole fraction, trend, seasonal and diurnal variation.
- AMY is frequently influenced by polluted air, but lies occasionally also within relatively clean air masses. This makes the station interesting for air pollution modelling.

Methane:

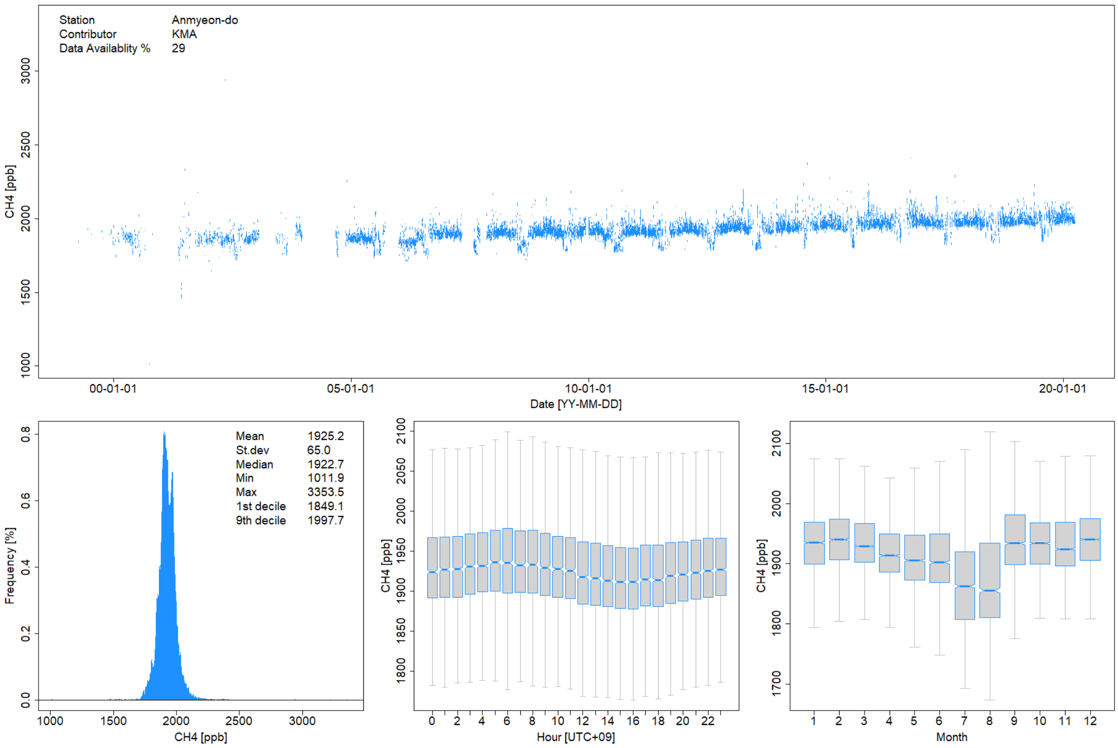

Figure 14. *Anmyeon-do in-situ CH_4 data (2000-2020) submitted by KMA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

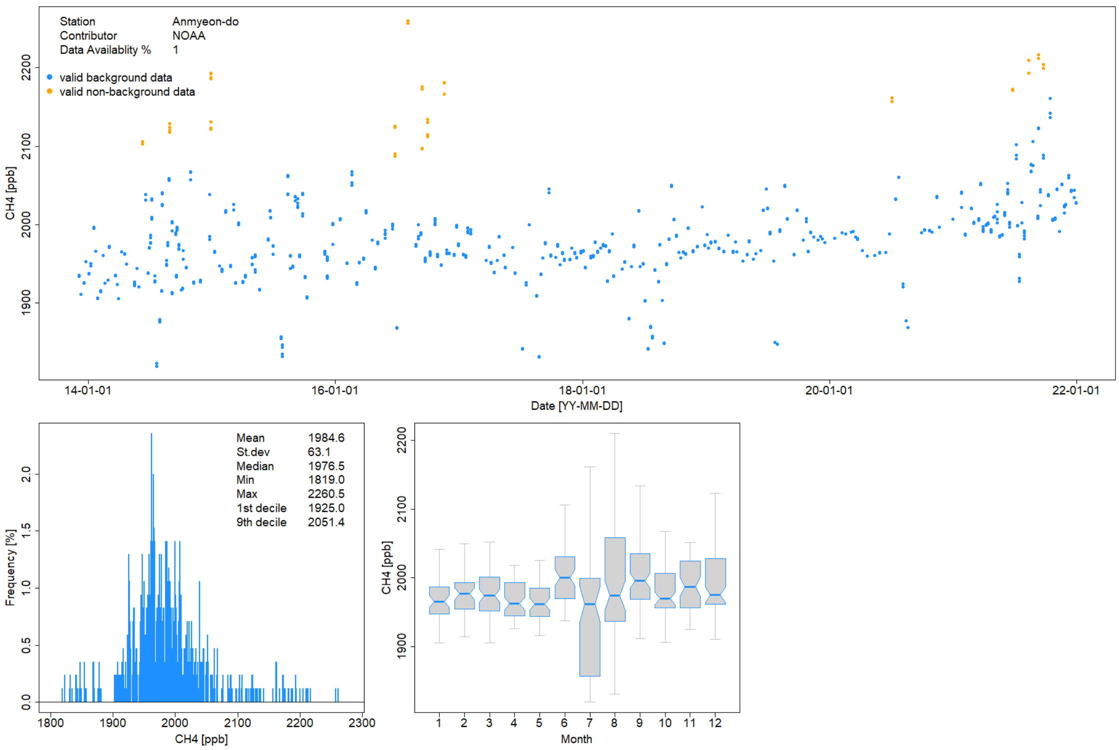

Figure 15. *AMY CH_4 flask data (2013-2021) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, event data. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The AMY in-situ CH_4 data set is only a selection of the entire data set. All pollution episodes were removed. This data does not represent the CH_4 levels at AMY, and all valid data including pollution events must be submitted.
- The lowest values of the AMY in-situ CH_4 data set seem to be too low; on the other hand, a few high values are still in the data set despite the obvious data filtering.
- All AMY in-situ CH_4 data at WDCGG has flag 2 (=valid non-background data). This does not make sense, because most of the valid non-background data has been removed. The data shown is rather representative of background values.
- The AMY in-situ CH_4 data does not show a long-term trend, despite this would be expected for the observation period from 2000 – 2020. This is likely due to the filtering approach, which also seems inappropriate to select background data.
- The NOAA flask data looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

Carbon dioxide:

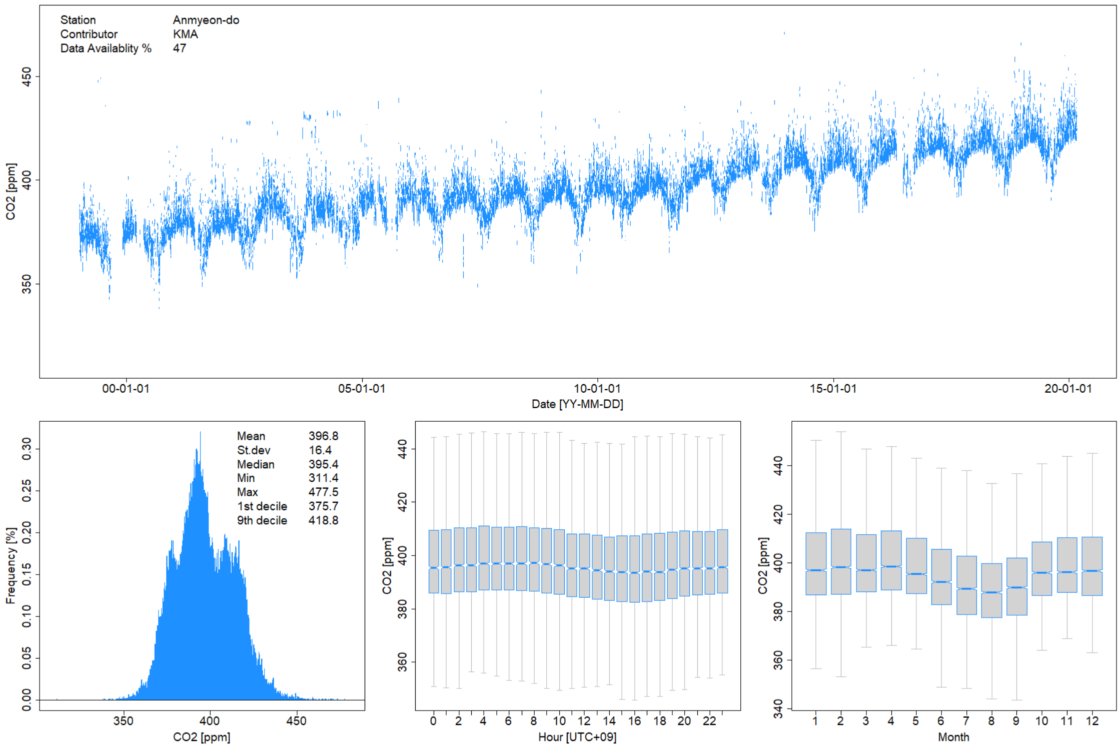

Figure 16. *Anmyeon-do in-situ CO_2 data (1999-2020) submitted by KMA. All valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

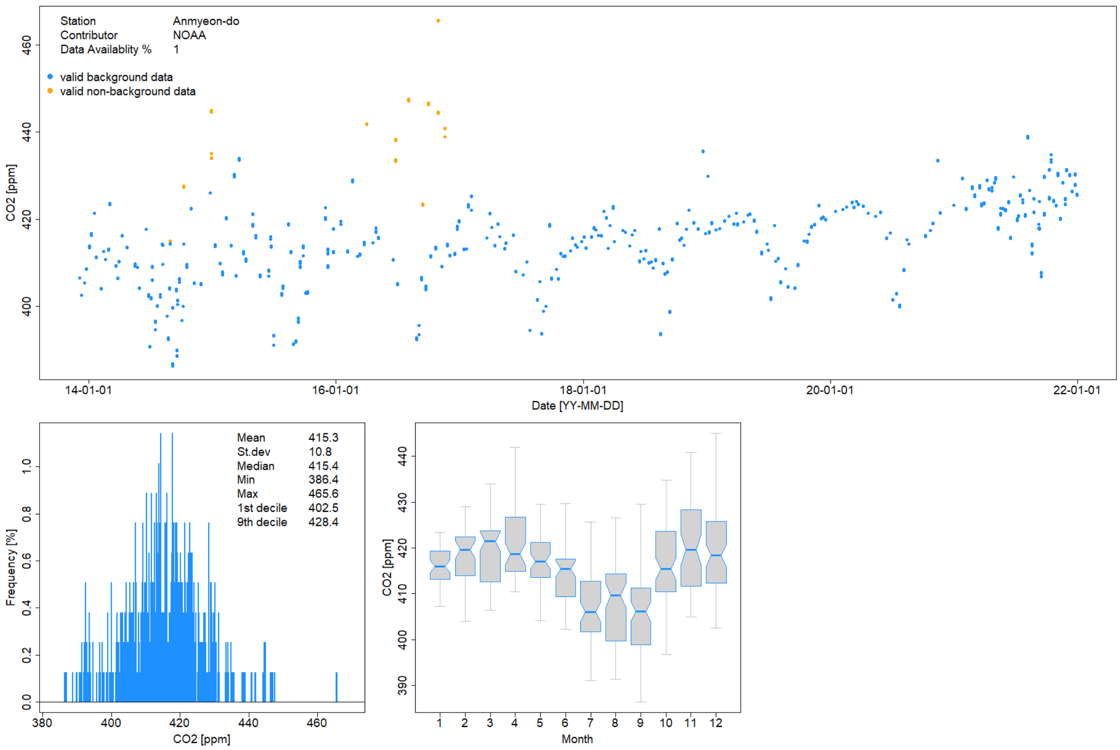

Figure 17. *AMY CO_2 flask data (2013-2021) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, event data. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The AMY in-situ CO_2 data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.
- However, it looks like this data set is also only a selection of the entire data set. Pollution episodes were removed, and the data availability is only 47%.
- The NOAA flask data looks sound with respect to mole fraction, trend, seasonal and diurnal variation, but the variability was significantly larger during the first period of the data set.

Nitrous oxide:

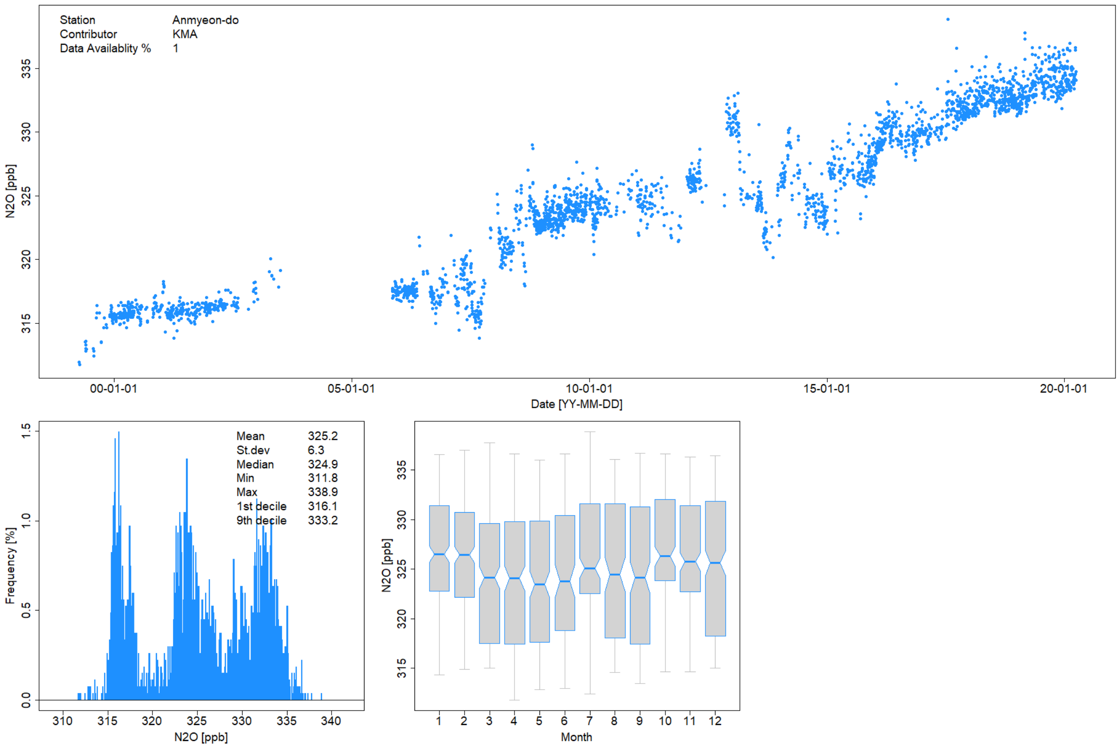

Figure 18. *Anmyeon-do in-situ daily N_2O data (1999-2020) submitted by KMA. All valid data is shown. Top: Time series, daily averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

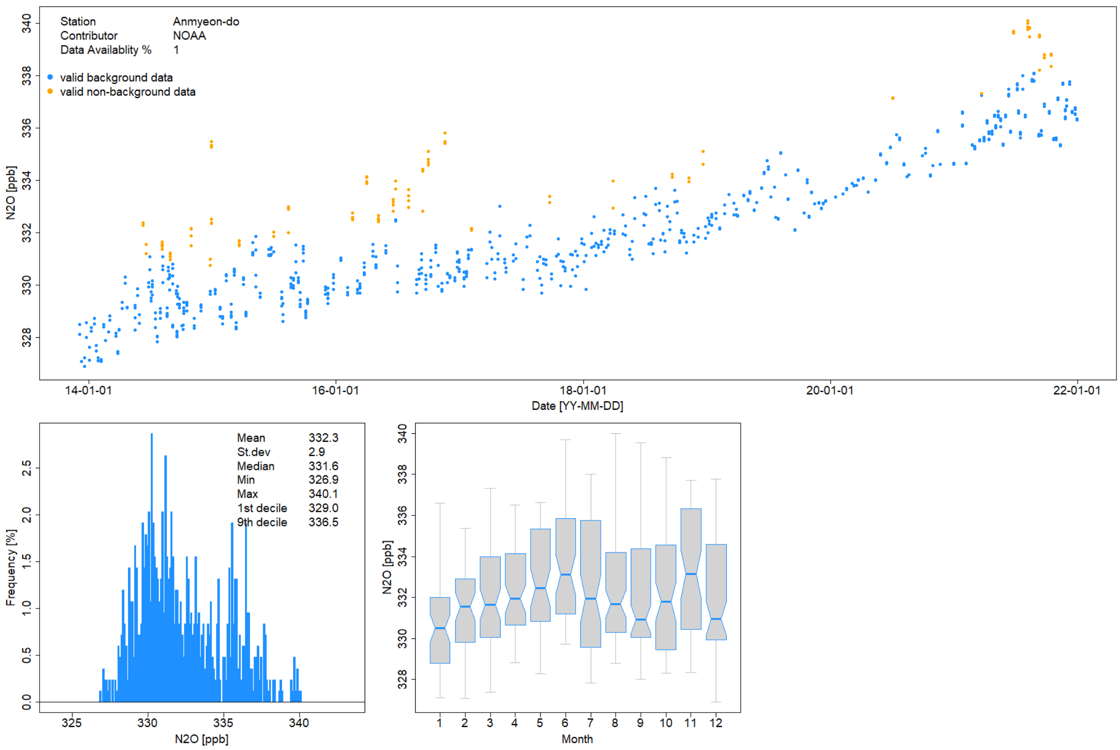

Figure 19. *AMY N_2O flask data (2013-2021) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, event data. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The KMA daily N_2O values look mostly sound. However, some step changes were observed in the periods of 2007/08, and 2013/14. At that time, measurements were made using GC/ECD techniques, and the associated measurement uncertainty is relatively high.
- The NOAA N_2O flask data series looks mostly sound with respect to mole fraction, trend, and seasonal variation.

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 200 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 4 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 AMY data acquisition systems.

Table 4. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49C-PS #54509-300 (WCC-Empa)
Settings	BKG +0.0 COEF 1.007
Pressure readings (hPa)	Ambient 1001.3;TS 1000.5 (adjusted to 1001.3 before the comparison)
AMY analyser (OA) (main instrument)	
Model, S/N	Thermo Scientific 49i #1153620133
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	Initial: BKG -0.7 nmol mol^{-1}, COEF 0.964 (1st comparison) Final: BKG 0.2 nmol mol^{-1}, COEF 0.999 (2nd comparison)
Pressure readings (hPa)	Initial: Ambient 1001.4; OA 991.9 (no adjustment was made) Final: Ambient 1001.3; OA adjusted to 1001.3 (2nd comparison)
AMY analyser (OA) (backup instrument)	
Model, S/N	Thermo Scientific 49i #0932138786
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	Initial: BKG -1.8 nmol mol^{-1}, COEF 0.987 (1st comparison) Final: BKG 0.0 nmol mol^{-1}, COEF 1.006 (2nd comparison)
Pressure readings (hPa)	Initial: Ambient 1001.4; OA 997.4 (no adjustment was made) Final: Ambient 1001.3; OA adjusted to 1001.3 (2nd comparison)

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 4 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 5. *Comparison of the main AMY ozone analyser (OA) Thermo Scientific 49i #1153620133 (initial settings,* BKG -0.7 nmol mol^{-1}, COEF *0.964) 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 (%)**
2022-07-05 05:19	75.61	0.28	74.95	0.14	-0.66	-0.87
2022-07-05 05:28	26.05	0.24	26.46	0.16	0.41	1.57
2022-07-05 05:36	199.82	0.25	195.90	0.18	-3.92	-1.96
2022-07-05 05:45	150.49	0.39	147.94	0.46	-2.55	-1.69
2022-07-05 05:54	50.40	0.18	50.33	0.16	-0.07	-0.14
2022-07-05 06:03	-0.19	0.08	0.99	0.09	1.18	NA
2022-07-05 06:12	100.11	0.14	98.71	0.13	-1.40	-1.40
2022-07-05 06:21	75.23	0.42	74.29	0.15	-0.94	-1.25
2022-07-05 06:30	-0.16	0.07	0.88	0.07	1.04	NA
2022-07-05 06:39	199.64	0.29	195.81	0.22	-3.83	-1.92
2022-07-05 06:47	25.57	0.20	25.93	0.21	0.36	1.41
2022-07-05 06:56	49.29	0.57	49.19	0.47	-0.10	-0.20
2022-07-05 07:05	99.47	0.64	98.18	0.59	-1.29	-1.30
2022-07-05 07:14	149.67	0.13	147.05	0.24	-2.62	-1.75
2022-07-05 07:22	75.12	0.12	74.38	0.16	-0.74	-0.99
2022-07-05 07:31	149.79	0.25	146.99	0.25	-2.80	-1.87
2022-07-05 07:40	25.88	0.30	26.40	0.21	0.52	2.01
2022-07-05 07:48	49.76	0.43	49.59	0.31	-0.17	-0.34
2022-07-05 07:58	-0.20	0.08	0.88	0.21	1.08	NA
2022-07-05 08:06	199.78	0.27	195.79	0.17	-3.99	-2.00
2022-07-05 08:15	100.07	0.24	98.60	0.22	-1.47	-1.47

Table 6. *Comparison of the main AMY ozone analyser (OA) Thermo Scientific 49i #1153620133 (final settings, BKG 0.2 nmol mol^{-1}, COEF 0.999)* 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 (%)**
2022-07-05 08:55	30.86	0.24	31.02	0.16	0.16	0.52
2022-07-05 09:03	50.00	0.31	50.21	0.35	0.21	0.42
2022-07-05 09:12	40.34	0.05	40.43	0.13	0.09	0.22
2022-07-05 09:21	60.18	0.12	60.50	0.09	0.32	0.53
2022-07-05 09:29	80.11	0.16	80.24	0.18	0.13	0.16
2022-07-05 09:38	174.68	0.20	175.29	0.14	0.61	0.35
2022-07-05 09:47	149.87	0.17	150.26	0.12	0.39	0.26
2022-07-05 09:55	199.72	0.25	200.25	0.11	0.53	0.27
2022-07-05 10:04	70.45	0.19	70.63	0.18	0.18	0.26
2022-07-05 10:13	-0.16	0.09	-0.09	0.10	0.07	NA
2022-07-05 10:22	13.91	0.86	13.57	0.87	-0.34	-2.44
2022-07-05 10:25	11.94	0.37	11.99	0.40	0.05	0.42
2022-07-05 10:34	124.59	0.27	125.11	0.22	0.52	0.42
2022-07-05 10:42	22.86	NA	22.40	NA	-0.46	-2.01
2022-07-05 10:43	21.42	0.49	21.45	0.43	0.03	0.14
2022-07-05 10:51	224.35	0.31	224.85	0.25	0.50	0.22
2022-07-05 11:00	89.99	0.20	90.34	0.24	0.35	0.39
2022-07-05 11:08	249.37	0.27	249.89	0.17	0.52	0.21

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 (%)
2022-07-05 11:17	100.28	0.13	100.50	0.12	0.22	0.22
2022-07-05 11:26	60.14	0.18	60.38	0.18	0.24	0.40
2022-07-05 11:34	50.21	0.14	50.25	0.10	0.04	0.08
2022-07-05 11:43	90.02	0.16	90.38	0.17	0.36	0.40
2022-07-05 11:52	99.99	0.14	100.24	0.23	0.25	0.25
2022-07-05 12:00	21.24	0.50	21.22	0.48	-0.02	-0.09
2022-07-05 12:09	69.97	0.15	70.18	0.12	0.21	0.30
2022-07-05 12:18	30.41	0.25	30.46	0.15	0.05	0.16
2022-07-05 12:26	199.47	0.25	200.00	0.21	0.53	0.27
2022-07-05 12:35	40.10	0.22	40.32	0.20	0.22	0.55
2022-07-05 12:44	11.67	0.53	11.79	0.37	0.12	1.03
2022-07-05 12:44	12.69	NA	12.72	NA	0.03	0.24
2022-07-05 12:52	80.03	0.22	80.19	0.18	0.16	0.20
2022-07-05 13:01	249.35	0.30	250.00	0.19	0.65	0.26
2022-07-05 13:10	224.57	0.27	225.13	0.18	0.56	0.25
2022-07-05 13:18	150.17	0.13	150.49	0.15	0.32	0.21
2022-07-05 13:28	-0.08	0.11	-0.12	0.14	-0.04	NA
2022-07-05 13:37	174.77	0.33	175.18	0.24	0.41	0.23
2022-07-05 13:45	124.83	0.20	125.28	0.17	0.45	0.36
2022-07-05 13:54	80.15	0.17	80.40	0.25	0.25	0.31
2022-07-05 14:03	174.57	0.29	174.90	0.18	0.33	0.19
2022-07-05 14:12	-0.22	0.09	-0.13	0.13	0.09	NA
2022-07-05 14:21	124.86	0.27	125.15	0.22	0.29	0.23
2022-07-05 14:30	30.70	0.37	30.79	0.44	0.09	0.29
2022-07-05 14:38	199.49	0.25	199.88	0.24	0.39	0.20
2022-07-05 14:47	70.13	0.13	70.31	0.17	0.18	0.26
2022-07-05 14:56	149.74	0.24	150.23	0.15	0.49	0.33
2022-07-05 15:04	21.40	0.59	21.46	0.49	0.06	0.28
2022-07-05 15:13	60.09	0.10	60.26	0.10	0.17	0.28
2022-07-05 15:22	89.95	0.14	90.16	0.16	0.21	0.23
2022-07-05 15:30	50.12	0.13	50.34	0.16	0.22	0.44
2022-07-05 15:39	224.52	0.38	225.08	0.23	0.56	0.25
2022-07-05 15:48	100.04	0.10	100.35	0.18	0.31	0.31
2022-07-05 15:56	249.34	0.38	249.78	0.22	0.44	0.18
2022-07-05 16:05	40.38	0.16	40.57	0.11	0.19	0.47
2022-07-05 16:14	11.88	0.48	11.72	0.43	-0.16	-1.35
2022-07-05 16:14	12.65	NA	12.88	NA	0.23	1.82
2022-07-05 16:22	70.14	0.19	70.51	0.15	0.37	0.53
2022-07-05 16:31	30.43	0.20	30.55	0.21	0.12	0.39
2022-07-05 16:40	49.82	0.26	50.08	0.22	0.26	0.52
2022-07-05 16:48	99.92	0.17	100.20	0.16	0.28	0.28
2022-07-05 16:57	79.93	0.11	80.03	0.18	0.10	0.13
2022-07-05 17:06	13.42	0.60	13.44	0.62	0.02	0.15
2022-07-05 17:09	11.78	0.38	11.82	0.24	0.04	0.34
2022-07-05 17:14	121.91	NA	122.70	NA	0.79	0.65
2022-07-05 17:15	124.17	0.66	124.70	0.53	0.53	0.43
2022-07-05 17:24	-0.13	0.09	-0.11	0.12	0.02	NA
2022-07-05 17:32	249.45	0.37	250.03	0.27	0.58	0.23

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 (%)
2022-07-05 17:41	224.56	0.21	225.26	0.19	0.70	0.31
2022-07-05 17:50	60.32	0.12	60.51	0.10	0.19	0.31
2022-07-05 17:58	40.07	0.20	40.27	0.29	0.20	0.50
2022-07-05 18:07	20.73	0.28	20.87	0.30	0.14	0.68
2022-07-05 18:16	174.58	0.28	174.96	0.16	0.38	0.22
2022-07-05 18:24	89.93	0.17	90.25	0.31	0.32	0.36
2022-07-05 18:33	149.62	0.15	150.00	0.15	0.38	0.25
2022-07-05 18:42	199.68	0.26	200.28	0.29	0.60	0.30
2022-07-05 18:51	100.13	0.09	100.48	0.18	0.35	0.35
2022-07-05 18:59	80.09	0.06	80.29	0.21	0.20	0.25
2022-07-05 19:08	60.18	0.10	60.35	0.09	0.17	0.28
2022-07-05 19:17	89.87	0.39	90.27	0.15	0.40	0.45
2022-07-05 19:26	-0.23	0.09	-0.10	0.08	0.13	NA
2022-07-05 19:35	31.01	0.58	30.95	0.50	-0.06	-0.19
2022-07-05 19:43	174.46	0.27	174.96	0.20	0.50	0.29
2022-07-05 19:52	70.02	0.10	70.32	0.22	0.30	0.43
2022-07-05 20:01	50.17	0.14	50.34	0.19	0.17	0.34
2022-07-05 20:09	40.15	0.09	40.18	0.10	0.03	0.07
2022-07-05 20:18	199.45	0.19	200.03	0.11	0.58	0.29
2022-07-05 20:27	124.78	0.20	125.11	0.22	0.33	0.26
2022-07-05 20:35	224.55	0.37	225.07	0.23	0.52	0.23
2022-07-05 20:44	13.31	0.59	13.23	0.54	-0.08	-0.60
2022-07-05 20:46	11.91	0.39	11.97	0.34	0.06	0.50
2022-07-05 20:53	19.61	0.32	19.83	0.22	0.22	1.12
2022-07-05 21:01	249.42	0.18	250.04	0.19	0.62	0.25
2022-07-05 21:10	149.72	0.16	150.14	0.18	0.42	0.28
2022-07-05 21:19	224.49	0.28	225.20	0.12	0.71	0.32
2022-07-05 21:28	90.26	0.15	90.53	0.23	0.27	0.30
2022-07-05 21:36	21.40	0.61	21.42	0.52	0.02	0.09
2022-07-05 21:45	29.87	0.15	29.91	0.17	0.04	0.13
2022-07-05 21:54	11.65	0.53	11.70	0.59	0.05	0.43
2022-07-05 22:02	80.00	0.14	80.17	0.20	0.17	0.21
2022-07-05 22:11	174.52	0.20	174.98	0.17	0.46	0.26
2022-07-05 22:20	124.74	0.21	125.21	0.27	0.47	0.38
2022-07-05 22:28	100.05	0.12	100.41	0.14	0.36	0.36
2022-07-05 22:37	60.40	0.21	60.49	0.26	0.09	0.15
2022-07-05 22:46	199.39	0.27	199.83	0.26	0.44	0.22
2022-07-05 22:55	-0.23	0.09	-0.11	0.12	0.12	NA
2022-07-05 23:07	149.74	0.17	150.07	0.24	0.33	0.22
2022-07-05 23:15	40.59	0.22	40.73	0.32	0.14	0.34
2022-07-05 23:24	50.10	0.09	50.23	0.10	0.13	0.26
2022-07-05 23:33	70.05	0.14	70.25	0.17	0.20	0.29
2022-07-05 23:41	249.28	0.25	249.98	0.18	0.70	0.28
2022-07-05 23:50	70.14	0.12	70.32	0.16	0.18	0.26
2022-07-05 23:59	60.11	0.10	60.37	0.13	0.26	0.43
2022-07-06 00:07	80.04	0.20	80.25	0.28	0.21	0.26
2022-07-06 00:16	13.40	0.68	13.26	0.53	-0.14	-1.04
2022-07-06 00:18	11.88	0.44	11.94	0.52	0.06	0.51

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 (%)
2022-07-06 00:25	49.74	0.27	49.94	0.32	0.20	0.40
2022-07-06 00:33	199.51	0.24	200.07	0.19	0.56	0.28

Table 7. *Comparison of the backup AMY ozone analyser (OA) Thermo Scientific 49i #0932138786 (initial settings*, BKG -1.8 nmol mol^{-1}, COEF *0.987) 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 (%)
2022-07-05 05:19	75.61	0.28	76.32	0.21	0.71	0.94
2022-07-05 05:28	26.05	0.24	27.65	0.21	1.60	6.14
2022-07-05 05:36	199.82	0.25	198.27	0.35	-1.55	-0.78
2022-07-05 05:45	150.49	0.39	149.94	0.42	-0.55	-0.37
2022-07-05 05:54	50.40	0.18	51.58	0.23	1.18	2.34
2022-07-05 06:00	-0.16	0.15	1.88	0.12	2.04	NA
2022-07-05 06:12	100.11	0.14	100.28	0.17	0.17	0.17
2022-07-05 06:21	75.23	0.42	75.85	0.19	0.62	0.82
2022-07-05 06:27	0.00	0.63	1.94	0.18	1.94	NA
2022-07-05 06:39	199.64	0.29	198.02	0.21	-1.62	-0.81
2022-07-05 06:47	25.57	0.20	27.03	0.23	1.46	5.71
2022-07-05 06:56	49.29	0.57	50.37	0.60	1.08	2.19
2022-07-05 07:05	99.47	0.64	99.83	0.59	0.36	0.36
2022-07-05 07:14	149.67	0.13	148.85	0.18	-0.82	-0.55
2022-07-05 07:22	75.12	0.12	75.86	0.21	0.74	0.99
2022-07-05 07:31	149.79	0.25	149.01	0.15	-0.78	-0.52
2022-07-05 07:40	25.88	0.30	27.60	0.15	1.72	6.65
2022-07-05 07:48	49.76	0.43	50.96	0.37	1.20	2.41
2022-07-05 07:55	-0.19	0.07	1.89	0.22	2.08	NA
2022-07-05 08:06	199.78	0.27	198.11	0.34	-1.67	-0.84
2022-07-05 08:15	100.07	0.24	100.28	0.11	0.21	0.21

Table 8. *Comparison of the backup AMY ozone analyser (OA) Thermo Scientific 49i #0932138786 (final settings, BKG 0.0 nmol mol^{-1}, COEF 1.0006)* 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 (%)
2022-07-05 08:55	30.86	0.24	30.92	0.26	0.06	0.19
2022-07-05 09:03	50.00	0.31	50.09	0.37	0.09	0.18
2022-07-05 09:12	40.34	0.05	40.25	0.16	-0.09	-0.22
2022-07-05 09:21	60.18	0.12	60.24	0.12	0.06	0.10
2022-07-05 09:29	80.11	0.16	79.90	0.28	-0.21	-0.26
2022-07-05 09:38	174.68	0.20	174.33	0.26	-0.35	-0.20
2022-07-05 09:47	149.87	0.17	149.48	0.28	-0.39	-0.26
2022-07-05 09:55	199.72	0.25	199.05	0.20	-0.67	-0.34
2022-07-05 10:04	70.45	0.19	70.30	0.30	-0.15	-0.21
2022-07-05 10:11	-0.11	0.29	0.15	0.27	0.26	NA
2022-07-05 10:22	13.91	0.86	13.65	0.69	-0.26	-1.87
2022-07-05 10:25	11.94	0.37	11.87	0.42	-0.07	-0.59

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 (%)
2022-07-05 10:30	119.81	2.12	121.00	1.70	1.19	0.99
2022-07-05 10:31	124.32	0.68	124.25	0.62	-0.07	-0.06
2022-07-05 10:42	22.86	NA	22.55	NA	-0.31	-1.36
2022-07-05 10:43	21.42	0.49	21.39	0.51	-0.03	-0.14
2022-07-05 10:51	224.35	0.31	223.91	0.32	-0.44	-0.20
2022-07-05 11:00	89.99	0.20	89.89	0.38	-0.10	-0.11
2022-07-05 11:08	249.37	0.27	248.80	0.17	-0.57	-0.23
2022-07-05 11:17	100.28	0.13	100.27	0.23	-0.01	-0.01
2022-07-05 11:26	60.14	0.18	60.12	0.21	-0.02	-0.03
2022-07-05 11:34	50.21	0.14	50.11	0.14	-0.10	-0.20
2022-07-05 11:43	90.02	0.16	90.13	0.30	0.11	0.12
2022-07-05 11:52	99.99	0.14	99.83	0.14	-0.16	-0.16
2022-07-05 12:00	21.24	0.50	21.12	0.54	-0.12	-0.56
2022-07-05 12:09	69.97	0.15	69.90	0.19	-0.07	-0.10
2022-07-05 12:18	30.41	0.25	30.63	0.16	0.22	0.72
2022-07-05 12:26	199.47	0.25	198.97	0.22	-0.50	-0.25
2022-07-05 12:35	40.10	0.22	40.24	0.22	0.14	0.35
2022-07-05 12:44	11.67	0.53	11.80	0.59	0.13	1.11
2022-07-05 12:44	12.69	NA	12.79	NA	0.10	0.79
2022-07-05 12:52	80.03	0.22	79.83	0.28	-0.20	-0.25
2022-07-05 13:01	249.35	0.30	248.95	0.32	-0.40	-0.16
2022-07-05 13:10	224.57	0.27	224.13	0.17	-0.44	-0.20
2022-07-05 13:18	150.17	0.13	149.87	0.13	-0.30	-0.20
2022-07-05 13:25	-0.09	0.09	0.07	0.22	0.16	NA
2022-07-05 13:37	174.77	0.33	174.64	0.25	-0.13	-0.07
2022-07-05 13:45	124.83	0.20	124.79	0.24	-0.04	-0.03
2022-07-05 13:54	80.15	0.17	80.15	0.18	0.00	0.00
2022-07-05 14:03	174.57	0.29	174.34	0.28	-0.23	-0.13
2022-07-05 14:10	-0.22	0.09	0.11	0.11	0.33	NA
2022-07-05 14:21	124.86	0.27	124.69	0.28	-0.17	-0.14
2022-07-05 14:30	30.70	0.37	30.81	0.25	0.11	0.36
2022-07-05 14:38	199.49	0.25	199.26	0.15	-0.23	-0.12
2022-07-05 14:47	70.13	0.13	70.01	0.18	-0.12	-0.17
2022-07-05 14:56	149.74	0.24	149.53	0.18	-0.21	-0.14
2022-07-05 15:04	21.40	0.59	21.39	0.50	-0.01	-0.05
2022-07-05 15:13	60.09	0.10	60.04	0.27	-0.05	-0.08
2022-07-05 15:22	89.95	0.14	89.90	0.12	-0.05	-0.06
2022-07-05 15:30	50.12	0.13	50.10	0.23	-0.02	-0.04
2022-07-05 15:39	224.52	0.38	224.02	0.22	-0.50	-0.22
2022-07-05 15:48	100.04	0.10	100.01	0.17	-0.03	-0.03
2022-07-05 15:56	249.34	0.38	248.74	0.30	-0.60	-0.24
2022-07-05 16:05	40.38	0.16	40.59	0.22	0.21	0.52
2022-07-05 16:14	11.88	0.48	11.91	0.52	0.03	0.25
2022-07-05 16:14	12.65	NA	13.08	NA	0.43	3.40
2022-07-05 16:22	70.14	0.19	70.07	0.18	-0.07	-0.10
2022-07-05 16:31	30.43	0.20	30.60	0.32	0.17	0.56
2022-07-05 16:40	49.82	0.26	49.97	0.24	0.15	0.30
2022-07-05 16:48	99.92	0.17	99.69	0.19	-0.23	-0.23

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 (%)
2022-07-05 16:57	79.93	0.11	79.89	0.17	-0.04	-0.05
2022-07-05 17:06	13.42	0.60	13.41	0.69	-0.01	-0.07
2022-07-05 17:09	11.78	0.38	12.03	0.28	0.25	2.12
2022-07-05 17:14	121.91	NA	122.10	NA	0.19	0.16
2022-07-05 17:15	124.17	0.66	123.99	0.67	-0.18	-0.14
2022-07-05 17:22	-0.16	0.12	-0.03	0.23	0.13	NA
2022-07-05 17:32	249.45	0.37	248.94	0.34	-0.51	-0.20
2022-07-05 17:41	224.56	0.21	224.38	0.29	-0.18	-0.08
2022-07-05 17:50	60.32	0.12	60.31	0.19	-0.01	-0.02
2022-07-05 17:58	40.07	0.20	40.16	0.19	0.09	0.22
2022-07-05 18:07	20.73	0.28	20.91	0.36	0.18	0.87
2022-07-05 18:16	174.58	0.28	174.14	0.28	-0.44	-0.25
2022-07-05 18:24	89.93	0.17	89.93	0.25	0.00	0.00
2022-07-05 18:33	149.62	0.15	149.49	0.14	-0.13	-0.09
2022-07-05 18:42	199.68	0.26	199.12	0.29	-0.56	-0.28
2022-07-05 18:51	100.13	0.09	99.98	0.18	-0.15	-0.15
2022-07-05 18:59	80.09	0.06	79.95	0.22	-0.14	-0.17
2022-07-05 19:08	60.18	0.10	60.04	0.09	-0.14	-0.23
2022-07-05 19:17	89.87	0.39	89.88	0.17	0.01	0.01
2022-07-05 19:23	-0.21	0.12	-0.04	0.20	0.17	NA
2022-07-05 19:35	31.01	0.58	30.90	0.68	-0.11	-0.35
2022-07-05 19:43	174.46	0.27	174.15	0.16	-0.31	-0.18
2022-07-05 19:52	70.02	0.10	70.11	0.14	0.09	0.13
2022-07-05 20:01	50.17	0.14	50.28	0.13	0.11	0.22
2022-07-05 20:09	40.15	0.09	40.15	0.29	0.00	0.00
2022-07-05 20:18	199.45	0.19	199.29	0.22	-0.16	-0.08
2022-07-05 20:27	124.78	0.20	124.64	0.36	-0.14	-0.11
2022-07-05 20:35	224.55	0.37	223.94	0.19	-0.61	-0.27
2022-07-05 20:44	13.31	0.59	13.17	0.66	-0.14	-1.05
2022-07-05 20:46	11.91	0.39	12.05	0.29	0.14	1.18
2022-07-05 20:53	19.61	0.32	19.78	0.28	0.17	0.87
2022-07-05 21:01	249.42	0.18	248.98	0.21	-0.44	-0.18
2022-07-05 21:10	149.72	0.16	149.55	0.28	-0.17	-0.11
2022-07-05 21:19	224.49	0.28	224.07	0.17	-0.42	-0.19
2022-07-05 21:28	90.26	0.15	90.28	0.18	0.02	0.02
2022-07-05 21:36	21.40	0.61	21.38	0.58	-0.02	-0.09
2022-07-05 21:45	29.87	0.15	30.06	0.25	0.19	0.64
2022-07-05 21:54	11.65	0.53	11.79	0.50	0.14	1.20
2022-07-05 22:02	80.00	0.14	79.92	0.26	-0.08	-0.10
2022-07-05 22:11	174.52	0.20	174.28	0.19	-0.24	-0.14
2022-07-05 22:20	124.74	0.21	124.69	0.19	-0.05	-0.04
2022-07-05 22:28	100.05	0.12	100.09	0.20	0.04	0.04
2022-07-05 22:37	60.40	0.21	60.33	0.39	-0.07	-0.12
2022-07-05 22:46	199.39	0.27	199.10	0.18	-0.29	-0.15
2022-07-05 22:53	-0.25	0.09	0.08	0.18	0.33	NA
2022-07-05 23:03	154.60	2.05	153.35	1.06	-1.25	-0.81
2022-07-05 23:04	150.01	0.60	149.66	0.51	-0.35	-0.23
2022-07-05 23:15	40.59	0.22	40.62	0.36	0.03	0.07

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 (%)
2022-07-05 23:24	50.10	0.09	50.12	0.21	0.02	0.04
2022-07-05 23:33	70.05	0.14	70.13	0.22	0.08	0.11
2022-07-05 23:41	249.28	0.25	248.87	0.19	-0.41	-0.16
2022-07-05 23:50	70.14	0.12	70.10	0.20	-0.04	-0.06
2022-07-05 23:59	60.11	0.10	60.16	0.14	0.05	0.08
2022-07-06 00:07	80.04	0.20	79.86	0.14	-0.18	-0.22
2022-07-06 00:16	13.40	0.68	13.46	0.66	0.06	0.45
2022-07-06 00:18	11.88	0.44	11.90	0.45	0.02	0.17
2022-07-06 00:25	49.74	0.27	49.85	0.33	0.11	0.22
2022-07-06 00:33	199.51	0.24	199.21	0.24	-0.30	-0.15

Calibration Standards for CO, CH_4, CO_2 and N_2O

Table 9 shows an overview of available working standards for the calibration of the CO, CH_4, CO_2 and N_2O at AMY. The reference standards from the CCL that were used for the assignments of the values at the central calibration facility at NIMS are also listed.

Table 9 *Calibration standards at AMY and NIMS as of June 2022.*

Cylinder ID	N_2O (X2006A) (nmol mol^{-1})	CO (X2014A) (nmol mol^{-1})	CH_4 (X2004A) (nmol mol^{-1})	CO_2 (X2019) (µmol mol^{-1})	Usage
CA06497	NA	NA	1888.19	389.41	NIMS Laboratory Standard (NOAA)
CA06366	NA	NA	2005.52	420.47	NIMS Laboratory Standard (NOAA)
CC702840	NA	NA	2237.98	457.37	NIMS Laboratory Standard (NOAA)
CB10980	NA	NA	2440.36	493.75	NIMS Laboratory Standard (NOAA)
CC703122	326.28	92.65	NA	NA	NIMS Laboratory Standard (NOAA)
CC703073	329.74	245.93	NA	NA	NIMS Laboratory Standard (NOAA)
CC702758	334.66	341.61	NA	NA	NIMS Laboratory Standard (NOAA)
CB10990	351.09	NA	NA	NA	NIMS Laboratory Standard (NOAA)
D600663	NA	NA	1889.61	370.51	AMY Working Standard for CRDS
D600654	NA	NA	1946.26	400.5	AMY Working Standard for CRDS
D282767	NA	NA	2085.63	437.49	AMY Working Standard for CRDS
D758235	NA	NA	2205.62	472.14	AMY Working Standard for CRDS
D603603	336.83	NA	NA	NA	AMY Working Standard for GC
D496989	335.54	142.84	NA	NA	AMY Working Standard for OA-ICOS

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 10 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 AMY data acquisition system.

Table 10. Experimental details of the AMY comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Tables 18 and 19.	
Station Analyser (CO, N_2O)	
Model, S/N	LGR 30-EP #15-0213
Principle	OA-ICOS
Drying system	*Cryogenic trap (-50°C)*

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 11. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2301 #857-CFADS2177 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 (%)
(22-07-06 22:52:45)	171123_FA02789	95.5	0.4	92.6	0.1	4	-2.9	-3.0
(22-07-07 00:13:00)	210415_FB03384	121.3	0.4	117.9	0.1	4	-3.5	-2.9
(22-07-06 22:13:15)	171204_FA02769	141.2	0.2	137.5	0.1	4	-3.7	-2.6
(22-07-06 23:33:00)	140514_FB03910	206.2	0.7	201.6	0.1	4	-4.6	-2.2
(22-07-07 00:53:00)	150601_FA02493	1317.1	0.2	1311.7	0.5	4	-5.4	-0.4

Methane 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 10 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 AMY data acquisition system.

Table 12. Experimental details of the AMY comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Tables 18 and 19.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2301 #857-CFADS2177
Principle	Near-IR CRDS
Drying system	*Cryogenic trap (-50°C)*

Results

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

Table 13. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2301 #857-CFADS2177 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 (%)
(22-07-05 16:12:30)	140514_FB03910	2001.87	0.01	2001.55	0.08	4	-0.32	-0.02
(22-07-05 14:52:48)	150601_FA02493	1868.06	0.02	1867.67	0.20	5	-0.39	-0.02
(22-07-05 16:52:36)	171123_FA02789	1718.75	0.01	1717.99	0.20	5	-0.76	-0.04
(22-07-05 16:12:36)	171204_FA02769	1956.05	0.03	1955.72	0.16	5	-0.33	-0.02
(22-07-05 15:32:48)	210415_FB03384	1907.90	0.03	1907.51	0.18	5	-0.39	-0.02

Carbon Dioxide Comparisons

Procedure: same as for CH_4, 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 computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2301 #857-CFADS2177 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 (%)
(22-07-05 16:12:30)	140514_FB03910	404.62	0.02	404.54	0.01	4	-0.08	-0.02
(22-07-05 14:52:48)	150601_FA02493	389.22	0.03	389.17	0.03	5	-0.05	-0.01
(22-07-05 16:52:36)	171123_FA02789	391.76	0.03	391.67	0.04	5	-0.09	-0.02
(22-07-05 16:12:36)	171204_FA02769	421.06	0.04	421.01	0.02	5	-0.05	-0.01

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 (%)
(22-07-05 15:32:48)	210415_FB03384	410.38	0.02	410.35	0.03	5	-0.03	-0.01

Nitrous Oxide Comparisons

Procedure: same as for CO, see above.

Results

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

Table 15. *N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR 913-0015 instrument (AL)) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(22-07-06 22:52:45)	171123_FA02789	316.61	0.05	316.54	0.07	4	-0.07	-0.02
(22-07-07 00:13:00)	210415_FB03384	330.81	0.03	330.71	0.07	4	-0.10	-0.03
(22-07-06 22:13:15)	171204_FA02769	336.58	0.02	336.42	0.06	4	-0.16	-0.05
(22-07-06 23:33:00)	140514_FB03910	328.41	0.01	328.13	0.08	4	-0.28	-0.09

WCC-Empa Traveling Standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the Standard Reference Photometer before and after the audit. The following instruments were used:

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

WCC-Empa TS: Thermo Scientific 49C-PS #54509-300, BKG -0.3, COEF 1.009

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 16. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 20). 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)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] + 0.12\ \text{nmol mol}^{-1}) / 1.0017 \tag{6a}$$

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

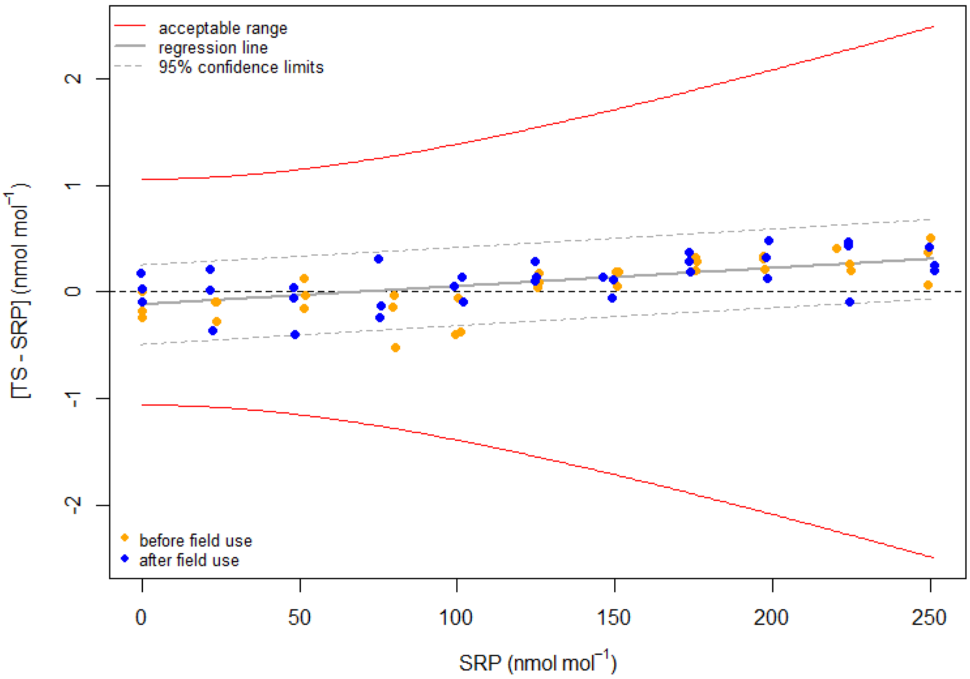

Figure 20. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 16. Mean values computed 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})
2022-05-20	1	25	23.69	0.50	23.42	0.11
2022-05-20	1	50	51.44	0.48	51.57	0.18
2022-05-20	1	175	175.50	0.49	175.82	0.18
2022-05-20	1	80	80.14	0.59	79.61	0.17
2022-05-20	1	0	0.03	0.52	-0.21	0.11
2022-05-20	1	100	99.33	0.29	98.93	0.11
2022-05-20	1	195	197.21	0.29	197.53	0.24
2022-05-20	1	150	150.99	0.56	151.18	0.19
2022-05-20	1	250	249.57	0.46	249.63	0.33
2022-05-20	1	225	225.01	0.29	225.21	0.26
2022-05-20	1	125	126.02	0.39	126.11	0.18
2022-05-20	2	150	150.29	0.26	150.48	0.25
2022-05-20	2	195	196.97	0.19	197.31	0.31
2022-05-20	2	100	100.31	0.18	100.26	0.16
2022-05-20	2	125	125.82	0.34	125.99	0.19
2022-05-20	2	225	224.56	0.17	224.82	0.27
2022-05-20	2	25	23.22	0.20	23.13	0.16
2022-05-20	2	250	250.04	0.21	250.55	0.40
2022-05-20	2	80	79.53	0.28	79.38	0.33
2022-05-20	2	0	0.09	0.25	-0.09	0.05
2022-05-20	2	50	51.59	0.27	51.56	0.15
2022-05-20	2	175	175.61	0.21	175.81	0.24
2022-05-20	3	80	80.02	0.29	79.99	0.18
2022-05-20	3	125	125.29	0.19	125.34	0.18
2022-05-20	3	25	23.59	0.19	23.50	0.13
2022-05-20	3	200	197.70	0.32	197.91	0.24
2022-05-20	3	50	51.23	0.40	51.08	0.21
2022-05-20	3	175	175.96	0.35	176.25	0.25
2022-05-20	3	220	220.27	0.24	220.68	0.30
2022-05-20	3	150	150.92	0.31	150.97	0.21
2022-05-20	3	250	249.44	0.25	249.81	0.38
2022-05-20	3	100	100.94	0.25	100.57	0.20
2022-05-20	3	0	-0.13	0.24	-0.12	0.14
2022-09-16	4	25	22.36	0.34	21.99	0.07
2022-09-16	4	150	146.30	0.35	146.44	0.21
2022-09-16	4	225	224.33	0.29	224.24	0.33
2022-09-16	4	175	173.77	0.25	173.96	0.23
2022-09-16	4	75	75.04	0.18	75.36	0.17
2022-09-16	4	50	48.23	0.39	48.18	0.21
2022-09-16	4	200	198.28	0.36	198.41	0.28
2022-09-16	4	250	251.47	0.32	251.71	0.38
2022-09-16	4	0	-0.11	0.22	-0.20	0.06
2022-09-16	4	100	98.85	0.22	98.90	0.13
2022-09-16	4	125	125.21	0.41	125.35	0.20
2022-09-16	5	225	223.99	0.27	224.42	0.39

Date	Run	Level#	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2022-09-16	5	250	251.24	0.46	251.44	0.34
2022-09-16	5	125	124.68	0.26	124.78	0.27
2022-09-16	5	50	48.33	0.33	47.93	0.14
2022-09-16	5	150	148.97	0.24	148.92	0.13
2022-09-16	5	175	173.43	0.20	173.72	0.18
2022-09-16	5	25	21.47	0.24	21.68	0.17
2022-09-16	5	75	75.93	0.31	75.80	0.18
2022-09-16	5	200	198.11	0.37	198.44	0.23
2022-09-16	5	100	101.82	0.27	101.72	0.29
2022-09-16	5	0	-0.29	0.38	-0.12	0.10
2022-09-16	6	175	173.52	0.48	173.89	0.26
2022-09-16	6	25	21.72	0.24	21.74	0.11
2022-09-16	6	250	249.75	0.40	250.18	0.32
2022-09-16	6	150	149.47	0.21	149.59	0.22
2022-09-16	6	225	224.08	0.23	224.55	0.36
2022-09-16	6	200	198.90	0.30	199.39	0.24
2022-09-16	6	0	-0.16	0.18	-0.13	0.10
2022-09-16	6	125	124.85	0.39	125.14	0.43
2022-09-16	6	75	75.48	0.47	75.24	0.10
2022-09-16	6	100	101.57	0.35	101.71	0.14
2022-09-16	6	50	47.89	0.29	47.94	0.11

#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 and N_2O:	LGR 913-0015	(Mid-IR Spectroscopy).
CO, CO_2 and CH_4:	Picarro G2401	(Cavity Ring-Down Spectroscopy).

For CO, only data of the Picarro G2301 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.

For N_2O, data of the LGR 913-0015 was used, because this instrument shows less cross-sensitivity to CO compared to the Aerodyne mini-cw.

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 21 and 22 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 G2301)

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, and (L) LGR.*

TS	**Press. (psi)**	**CH_4 (P) (nmol mol^{-1})**	**sd**	**CO_2(P) (µmol mol^{-1})**	**sd**	**N_2O (A) (nmol mol^{-1})**	**sd**	**N_2O (L) (nmol mol^{-1})**	**sd**
140514_FB03910	1080	2001.87	0.01	404.62	0.02	328.46	0.04	328.41	0.01
150601_FA02493	1510	1868.06	0.02	389.22	0.03	319.99	0.03	319.93	0.03
171123_FA02789	1080	1718.75	0.01	391.76	0.03	316.56	0.07	316.61	0.05
171204_FA02769	1210	1956.05	0.03	421.06	0.04	336.54	0.05	336.58	0.02
210415_FB03384	1600	1907.9	0.03	410.38	0.02	330.83	0.05	330.81	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, and (L) LGR.*

TS	**Press. (psi)**	**CO (P) (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**	**CO (L) (nmol mol^{-1})**	**sd**
140514_FB03910	1080	206.17	0.73	203.77	0.15	202.35	0.12
150601_FA02493	1510	1317.12	0.15	1307.61	1.07	1319.11	1.37
171123_FA02789	1080	95.49	0.35	93.49	0.14	93.02	0.28
171204_FA02769	1210	141.2	0.19	138.91	0.1	137.97	0.21
210415_FB03384	1600	121.31	0.44	119.05	0.12	118.21	0.21

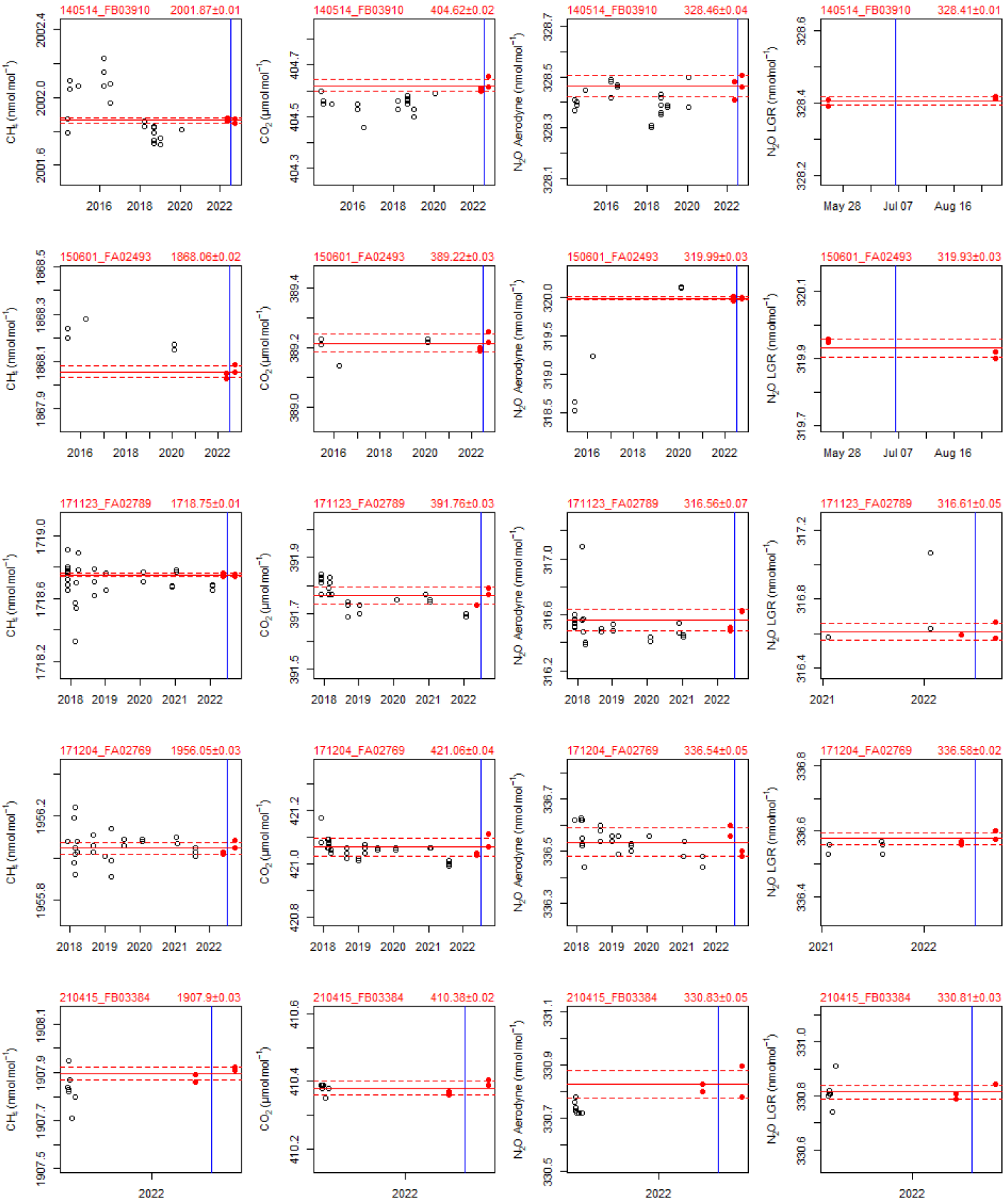

Figure 21. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

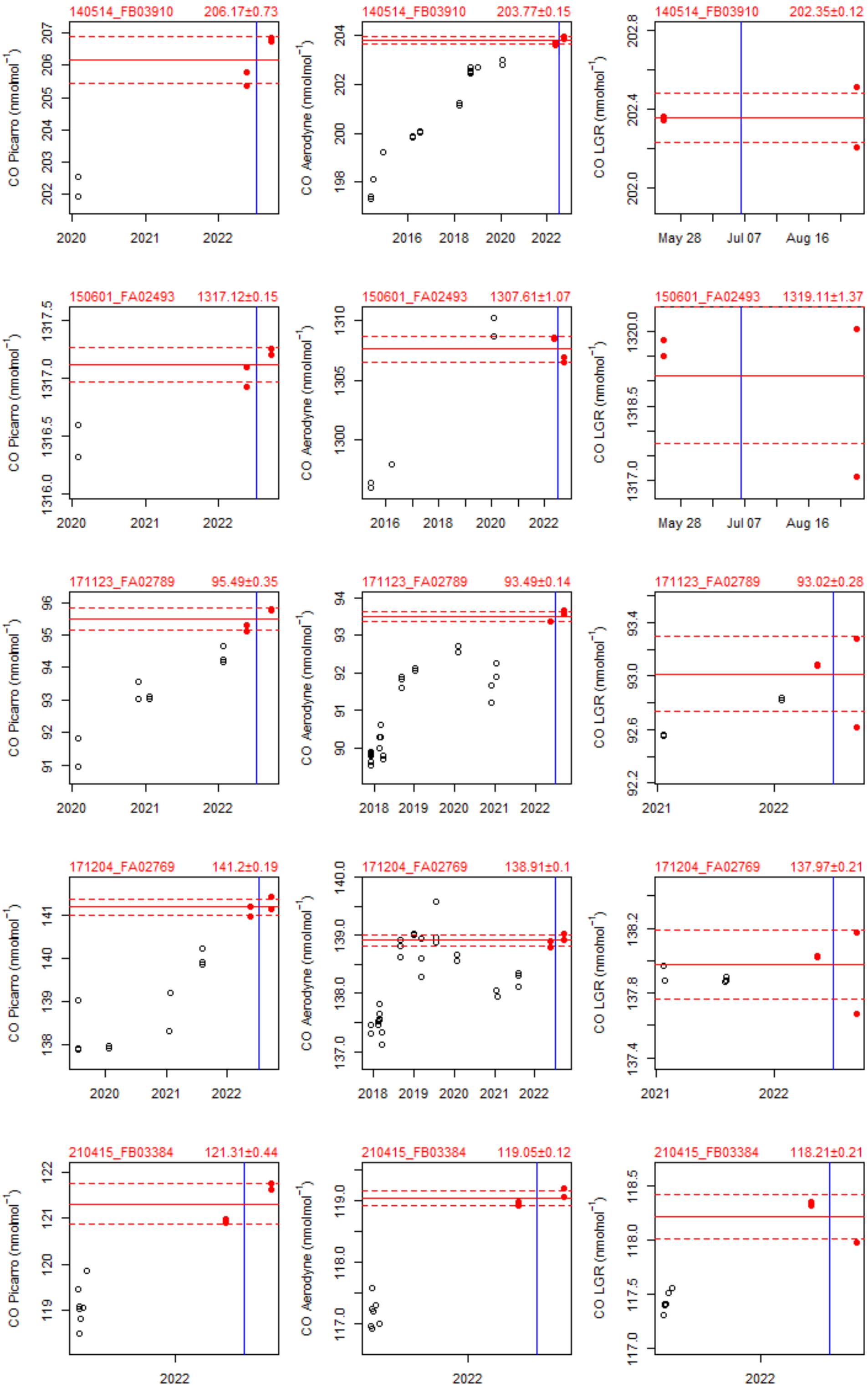

Figure 22. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

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LIST OF ABBREVIATIONS

AMY	Anmyeon-do GAW Station
a.s.l	above sea level
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detection
FID	Flame Ionization Detection
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
IR	infrared
KMA	Korea Meteorological Administration
KRISS	Korea Research Institute of Standards and Science
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NIMS	National Institute of Meteorological Sciences
NOAA	National Oceanic and Atmospheric Administration
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
PFA	Perfluoroalcoxy
PTFE	Polytetrafluoroethylene
QCL	Quantum Cascade Laser
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