WCC-Empa Report 23/1

# System and performance audit of Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide at the Global GAW Station Izaña, Spain, June 2023

Submitted to the World Meteorological Organization by

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GLOBAL ATMOSPHERE WATCH

Empa Materials Science and Technology

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WCC-Empa Report 23/1

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# CONTENTS

# 1 Executive Summary

The 8th WCC-Empa[1] system and performance audit at the Izaña global GAW station (IZO) was conducted from 5 - 9 June 2023 in accordance with the WMO/GAW quality assurance system (WMO, 2017). A list of all WCC-Empa audits and the corresponding audit reports are available from the GAW Empa website. The following people contributed to the audit:

| | |
|---|---|
| Dr Christoph Zellweger | Empa Dübendorf, WCC-Empa |
| Dr Emilio Cuevas | Izaña, station manager, GAW country contact (retired end of August 2023) |
| Mr Carlos Torres | Izaña, station scientist (reactive gases) (station manager since September 2023) |
| Mr Ramón Ramos | Izaña, station operator |
| Mr Pedro Pablo Rivas-Soriano | Izaña, station scientist (greenhouse gases) |

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

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

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

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

# 2 Site Description and Operation

## 2.1 Station management

The Izaña (IZO) Atmospheric Observatory is operated by the Izaña Atmospheric Research Centre (IARC), which is part of Spanish Meteorological Agency (AEMET). The station is visited by scientists and technical staff on weekdays. The headquarters of IARC is located in St. Cruz de Tenerife, about 50 km NE (60 min by car) from the station. A full overview of the organisation is available on the Izaña station website.

## 2.2 Location and access

The IZO station (28.3090°N, 16.4993°W, 2373 m above sea level) is located on the island of Tenerife, Spain, about 300 km west of the African coast. The meteorological observatory is located on a mountain platform, 15 km north-east of the Teide volcano (3718 m above sea level). The local wind field at the site is dominated by north-westerly winds, and the station is located most of the time above the trade wind inversion that persists for most of the year. The ground in the vicinity of Izaña is loosely covered with light volcanic soil. The surrounding vegetation is sparse and consists mainly of broom. Access by road is possible all year round. Further information is available from GAWSIS.

## 2.3 Station facilities

Izaña offers spacious laboratory and office facilities with high-speed internet access. Facilities include offices, a dining room with a kitchen, a library, a conference room, meeting room, and workshops. Accommodation is also available for visiting scientists. All laboratories are temperature controlled. IZO provides an ideal platform for continuous atmospheric research. In addition to the large number of permanent measurements, space is available for campaign-based experiments. More information is available on the Izaña station website.

## 2.4 Measurement Programme

IZO hosts a comprehensive measurement programme covering all focal areas of the GAW programme. An overview of the measured species is available on GAWSIS. The monitoring activities of IZO are well embedded in international programmes and research infrastructures, such as EMEP (European Monitoring and Evaluation Programme), ACTRIS (The Aerosol, Clouds and Trace Gases Research Infrastructure), ICOS (Integrated Carbon Observation System), and the NOAA Cooperative Air Sampling Network. A complete overview of all collaborations is available on the IZO website.

The information available on GAWSIS was reviewed as part of the audit. The information was updated during the audit and is largely up to date. However, some details on instrumentation and station contacts still need to be checked and corrected.

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

## 2.5 Data submission

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

AEMET, submission to the World Data Centre for Reactive Gases (WDCRG):
$O_3$ (1987-2013 and 2014-2022), two data sets.

AEMET, submission to the World Data Centre for Greenhouse Gases (WDCGG):
$CH_4$ (1984-2022), $CO_2$ (1984-2022), $N_2O$ (2007-2016), CO (2008-2022)

NOAA, submission to WDCGG:
$CH_4$ (1991-2022), $CO_2$ (1991-2022), $N_2O$ (1997-2022), CO (1991-2022)

The data presented in this report was accessed on 16 January 2024. All data the scope of the audit except $N_2O$ were submitted with a submission delay of less than one year. The continuation of this timely submission practice is recommended.

> **Recommendation 2 (**, important, 2024)**
> *It is recommended to submit the $N_2O$ data for the period from 2017 onwards as soon as the final quality control has been completed.*

## 2.6 Data review

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

## 2.7 Documentation

Electronic logbooks and handwritten notes are available for all parameters. Instrument manuals are available on site. The information was comprehensive and up to date.

## 2.8 Air inlet system

Two state-of-the-art central inlet systems are available for the measurement of gaseous species. Individual analytical systems are connected to one of these inlets.

| | |
|---|---|
| *Location of air intake:* | Both air intakes are located at the top of the laboratory tower, 5 m above the tower terrace and 30 m above ground. The inlet consists of a stainless steel tube with an inner diameter of 10 cm running from the tower terrace through the central service channel. The part outside the building is heated. A pump flushes the inlet with 2180 l/min. |
| *Inlet protection:* | Protected from rain by an upside-down stainless steel bucket. |

All audited instruments are connected to one of the central inlet systems. The following tubing is used for the connection:

Surface ozone:

| | |
|---|---|
| *Tubing:* | Approximately 2 m ¼ inch PFA tubing, flow approx. 1 l/min. |
| *Inlet filter:* | PTFE, exchanged every three months or earlier in case of pollution events |
| *Residence time:* | Approximately 3 s |

GHG and CO:

| | |
|---|---|
| *Tubing:* | ¼ inch Synflex 1300 tubing. Picarro tubing length: 1.8 m, flow 0.17 l/min, LI-COR: 10 m, 0.2 l/min, LGR: 10 m, 0.2 l/min, Agilent: 7.5 m, 0.1 l/min. |
| *Inlet filter:* | Stainless steel, exchanged every three months or earlier in case of pollution events. |
| *Dryer:* | Cryogenic cooler at -70°C. |
| *Residence time:* | Picarro 8 s, LI-COR 38 s, LGR 38 s, Agilent 57 s. |

The air inlets have not been modified since the last WCC-Empa audit in 2019

# 3 Performance Audit

## 3.1 Surface ozone measurements

Surface ozone measurements at IZO were established in 1987, and continuous time series have been available since then. Several different UV absorption $O_3$ analysers have been used since then.

***Instrumentation.*** In November 2022, two new Thermo Scientific 49i ozone analysers were purchased to replace the old Thermo Scientific 49C analysers, as recommended by the WCC-Empa Audit 2019. Currently, IZO is equipped with three Thermo Scientific 49i series analysers. Until the current audit, the Thermo Scientific 49i (#1153030026) analyser was considered the primary instrument for data submission, with the two Thermo Scientific 49C ozone analysers acting as back-up instruments. The two Thermo Scientific 49C analysers have now been decommissioned and the Thermo Scientific 49i #12218618529 is considered to be the primary instrument.

***Standards***. A Thermo Scientific 49i-PS with ozone standard traceability to a NIST SRP is available at the headquarters of IZO in St. Cruz de Tenerife. A new Thermo Scientific 49i-PS ozone calibrator is also available at IZO.

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

***Intercomparison (performance audit).*** Three IZO Ozone Analysers (OA) were compared to the WCC-Empa Travelling Standard (TS) with traceability to SRP#15. The internal ozone generator of the TS was used to generate a random sequence of ozone levels ranging from 0 to 250 nmol mol$^{-1}$. The result of the comparisons is summarised below in relation to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data were acquired using the WCC-Empa data acquisition system. The data were treated in the same way as ambient air measurements, and no further corrections were applied to the readings of the instruments.

The following equations characterise the bias of the instruments and the remaining uncertainty after compensation of the bias. Uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). As the measurements refer to a conventionally agreed value of the ozone absorption cross section of 1.1476x10$^{-17}$ cm$^2$ (Hearn, 1961), the uncertainties reported below do not include the uncertainty of the ozone absorption cross section.

**Thermo Scientific 49i #1153030026** (BKG +0.0 nmol mol$^{-1}$, COEF 1.003):

Unbiased $O_3$ amount fraction $X_{O3}$ (nmol mol$^{-1}$): $X_{O3}$ = ([OA] - 0.27 nmol mol$^{-1}$) / 1.0107 (1)

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

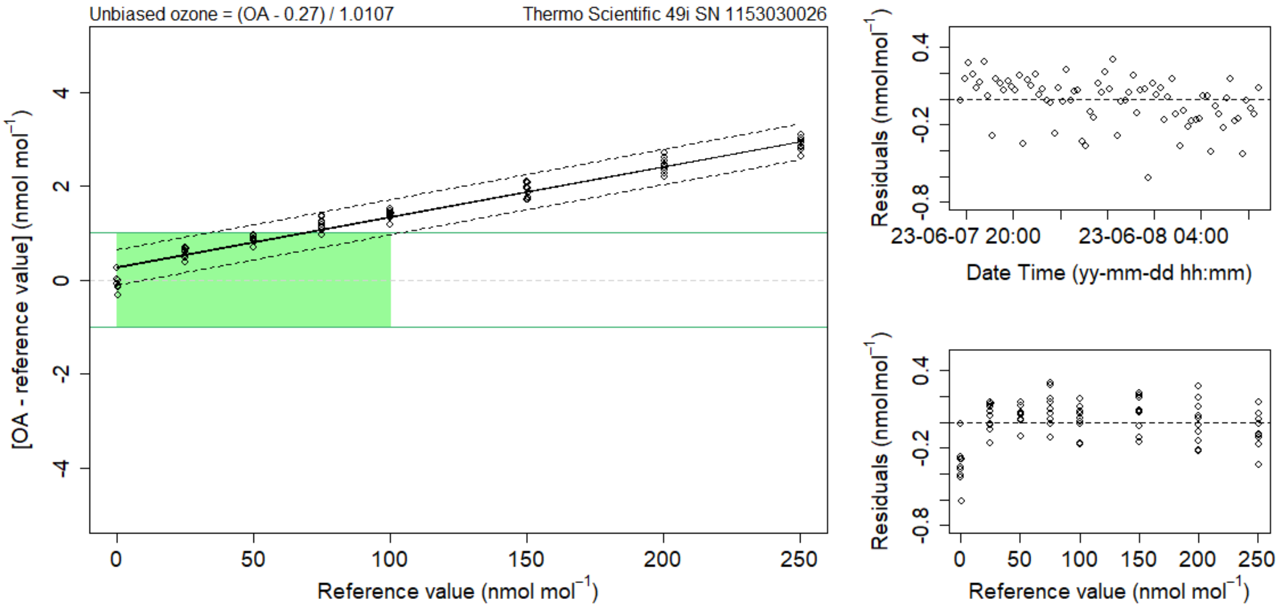


***Figure 1.*** *Left: Bias of the IZO ozone analyser (Thermo Scientific 49i #1153030026, BKG 0.0 nmol mol$^{-1}$, COEF 1.003) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

**Thermo Scientific 49i #12218618528** (BKG +0.0 nmol mol$^{-1}$, COEF 1.010):

Unbiased $O_3$ amount fraction $X_{O3}$ (nmol mol$^{-1}$): $X_{O3}$ = ([OA] - 0.25 nmol mol$^{-1}$) / 1.0175 (3)

Standard uncertainty $u_{O3}$ (nmol mol$^{-1}$): $u_{O3}$ = sqrt (0.29 nmol mol$^{-1}$ + 2.09e-05 * $X_{O3}^2$) (4)

**Thermo Scientific 49i #12218618529** (BKG +0.0 nmol mol$^{-1}$, COEF 1.008):

Unbiased $O_3$ amount fraction $X_{O3}$ (nmol mol$^{-1}$): $X_{O3}$ = ([OA] + 0.56 nmol mol$^{-1}$) / 1.0101 (5)

Standard uncertainty $u_{O3}$ (nmol mol$^{-1}$): $u_{O3}$ = sqrt (0.30 nmol mol$^{-1}$ + 2.09e-05 * $X_{O3}^2$) (6)

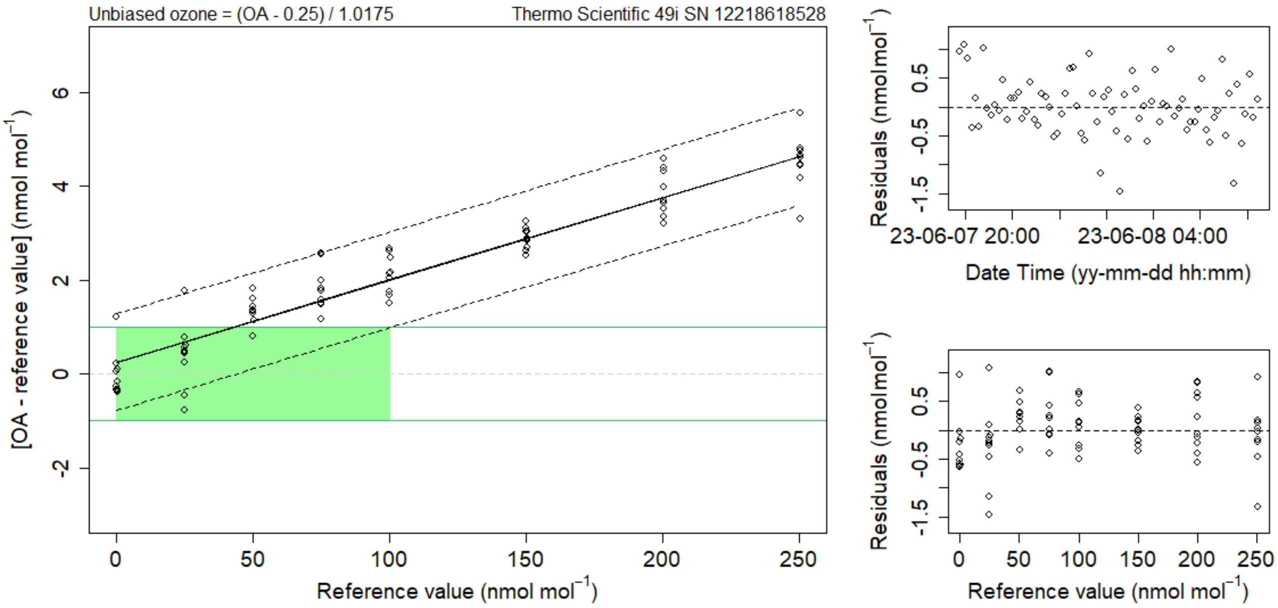


***Figure 2.*** *Left: Bias of the IZO ozone analyser (Thermo Scientific 49i #12218618528, BKG 0.0 nmol mol$^{-1}$, COEF 1.010) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

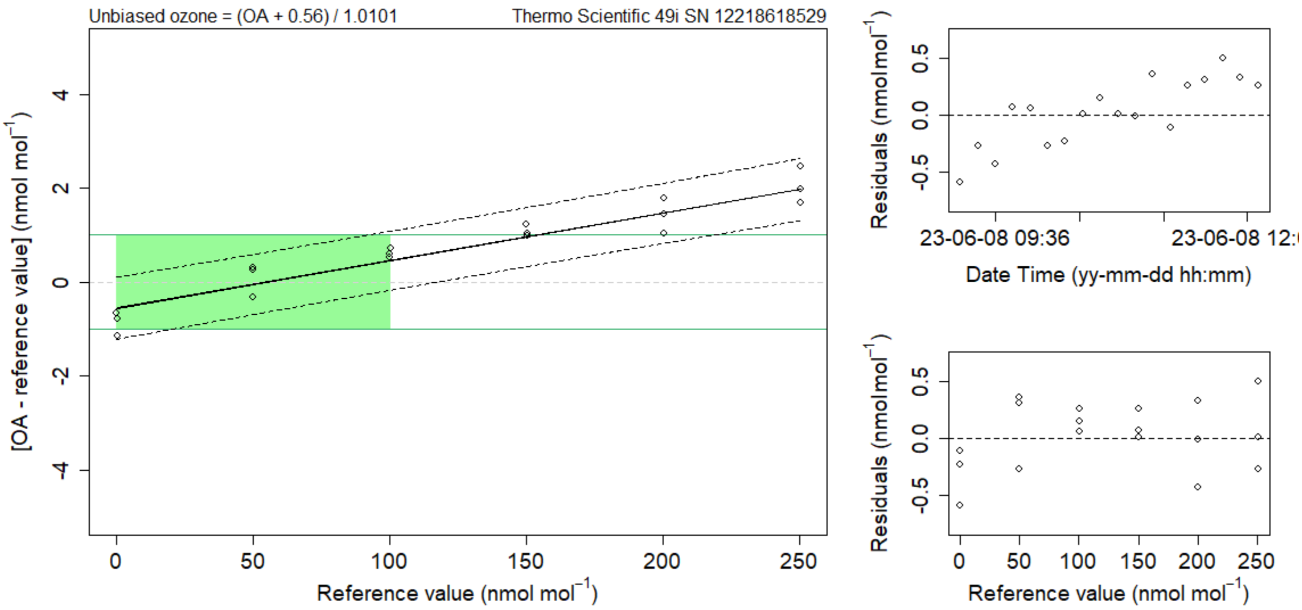


***Figure 3.*** *Left: Bias of the IZO ozone analyser (Thermo Scientific 49i #12218618529, BKG 0.0 nmol mol$^{-1}$, COEF 1.008) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

**Thermo Scientific 49i-PS #CM22277105** (BKG -0.4 nmol mol$^{-1}$, COEF 1.003):

Unbiased $O_3$ amount fraction $X_{O3}$ (nmol mol$^{-1}$): $X_{O3}$ = ([OA] + 0.13 nmol mol$^{-1}$) / 1.0007 (7)

Standard uncertainty $u_{O3}$ (nmol mol$^{-1}$): $u_{O3}$ = sqrt (0.29 nmol mol$^{-1}$ + 2.07e-05 * $X_{O3}^2$) (8)

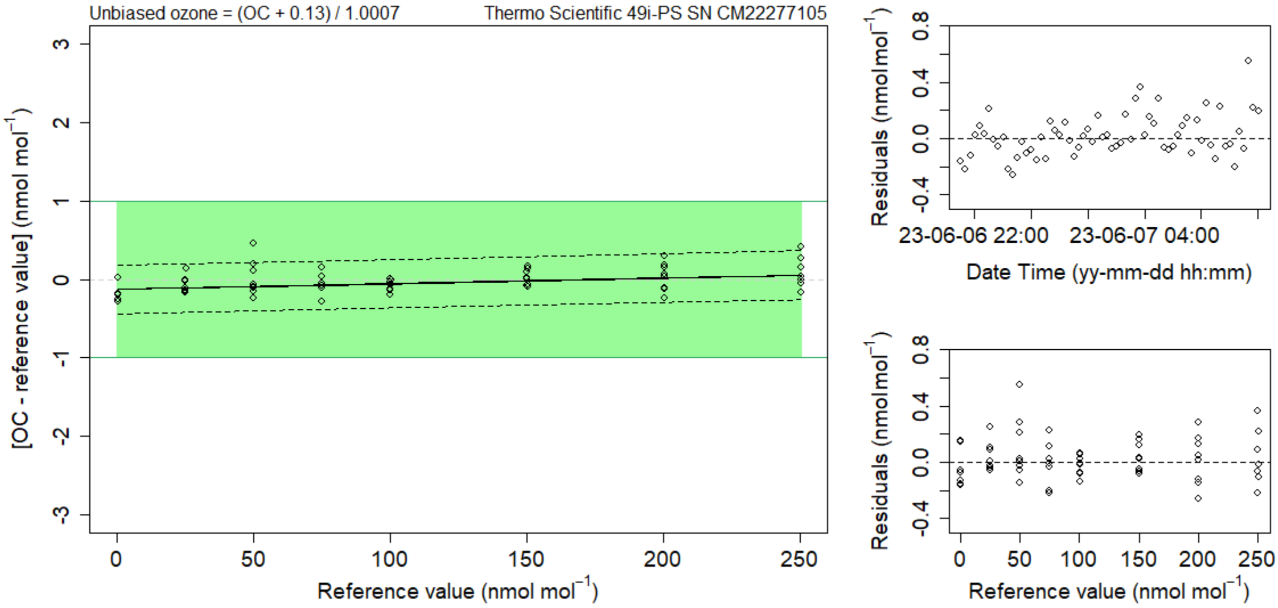


***Figure 4.*** *Left: Bias of the IZO ozone calibrator (Thermo Scientific 49i-PS # CM22277105, BKG -0.4 nmol mol$^{-1}$, COEF 1.003) with respect to the SRP as a function of the amount fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant amount fraction range, while the DQOs are indicated with green lines. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and amount fraction (bottom).*

The results of the comparisons can be summarised as follows:

Thermo Scientific 49i #1153030026: The main IZO ozone analyser read slightly higher than the WCC-Empa reference. About 0.2% of the difference can be explained by the different calibration of the pressure sensor. The instrument is in a good working condition.

Thermo Scientific 49i #12218618528: This instrument is currently used as a backup analyser and was reading slightly higher than the WCC-Empa reference. The instrument showed significantly more noise compared to the other analysers.

**Recommendation 3 (**, important, 2024)**
*Thermo Scientific 49i #12218618528 is not performing well, and the reason needs to be identified. It is recommended that the analyser be returned to the manufacturer for inspection and repair.*

Thermo Scientific 49i #12218618529: Backup instrument, in a good working condition and within the WMO/GAW quality objectives.

Thermo Scientific 49i-PS #CM22277105: The IZO ozone calibrator has been calibrated against the WCC-Empa reference and is well within the WMO/GAW quality objectives. It can be used to check and calibrate the IZO ozone analysers.

In conclusion, the IZO ozone measurements are mostly within the WMO/GAW quality objectives, and the larger number of redundant measurements ensures the long-term quality of the measurements. It is recommended to continue with the current practice, and no immediate action is required.

## 3.2 Carbon Monoxide Measurements

Continuous measurements of CO at IZO started in 1998 using gas chromatography (GC) / mercuric oxide reduction (RGD) detection. Continuous validated time series are available since 2008. Since 2019, measurements have been made using Cavity Ring Down Spectroscopy (CRDS). An Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) analyser is also available.

***Instrumentation.*** The following instrumentation has been audited: Picarro G2401 (near-IR CRDS) and Los Gatos 913-0015 (OA-ICOS). The air is dried with a cryo trap. In addition to the audited instruments, IZO is equipped with a Picarro G2401 and a Los Gatos 913-0015 instrument. These instruments are part of ICOS and were only compared during the ambient air comparison.

***Standards.*** Several NOAA CCL standards are available for the calibration of the CO instruments. An overview of available standards is given in Table 7 in the Appendix.

***Calibration.*** The measurement sequence of the Picarro includes the measurement of two working standards. Each tank is measured for 30 minutes every 10 hours of ambient air. Calibrations using the NOAA tanks are not automated and are performed manually on a monthly basis using 4 standards. The measurement sequence of the LGR includes the measurement of two working standards for 15 minutes every 4 hours. Manual calibrations using the NOAA tanks are performed monthly using 4 standards.

***Data acquisition.*** The Picarro G2401 has an internal data acquisition. The highest resolution (1-2 s resolution) raw data files are daily uploaded to a server and automatically processed. The resulting data are manually checked and flagged once a year. The LGR generates raw data files with a resolution of 4 seconds which are daily uploaded to a server. The processing software is currently in the development phase.

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

The following equations characterise the instrument bias, and the results are further illustrated in Figures 5 and 6 with respect to the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020):

**Picarro G2401 #2352-CFKADS2196:**

Unbiased CO mixing ratio: $X_{CO}$ (nmol mol$^{-1}$) = (CO – 0.65 nmol mol$^{-1}$) / 0.9984 (9)

Remaining standard uncertainty: $u_{CO}$ (nmol mol$^{-1}$) = sqrt (4.2 nmol mol$^{-1}$ + 1.01e-04 * $X_{CO}{}^2$) (10)

**LGR 913-0015 SN US430000170700001433:**

Unbiased CO mixing ratio: $X_{CO}$ (nmol mol$^{-1}$) = (CO – 0.94 nmol mol$^{-1}$) / 0.9989 (11)

Remaining standard uncertainty: $u_{CO}$ (nmol mol$^{-1}$) = sqrt (5.6 nmol mol$^{-1}$ + 1.01e-04 * $X_{CO}{}^2$) (12)

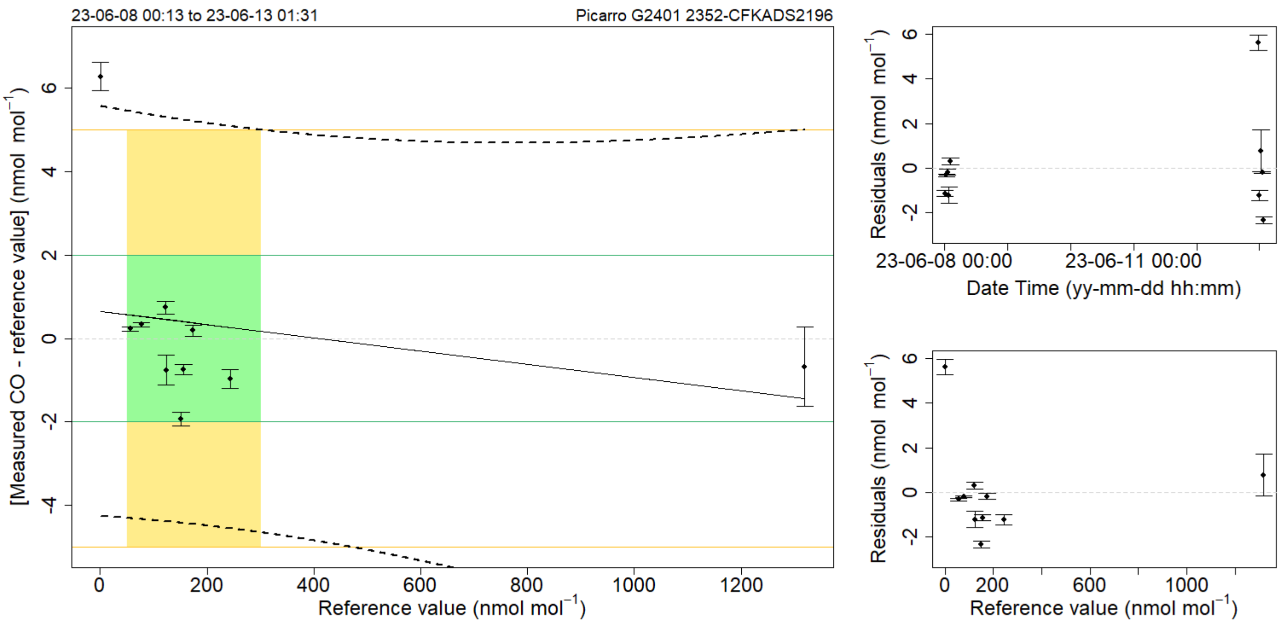


***Figure 5.*** *Left: Bias of the IZO Picarro G2401 #2352-CFKADS2196 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

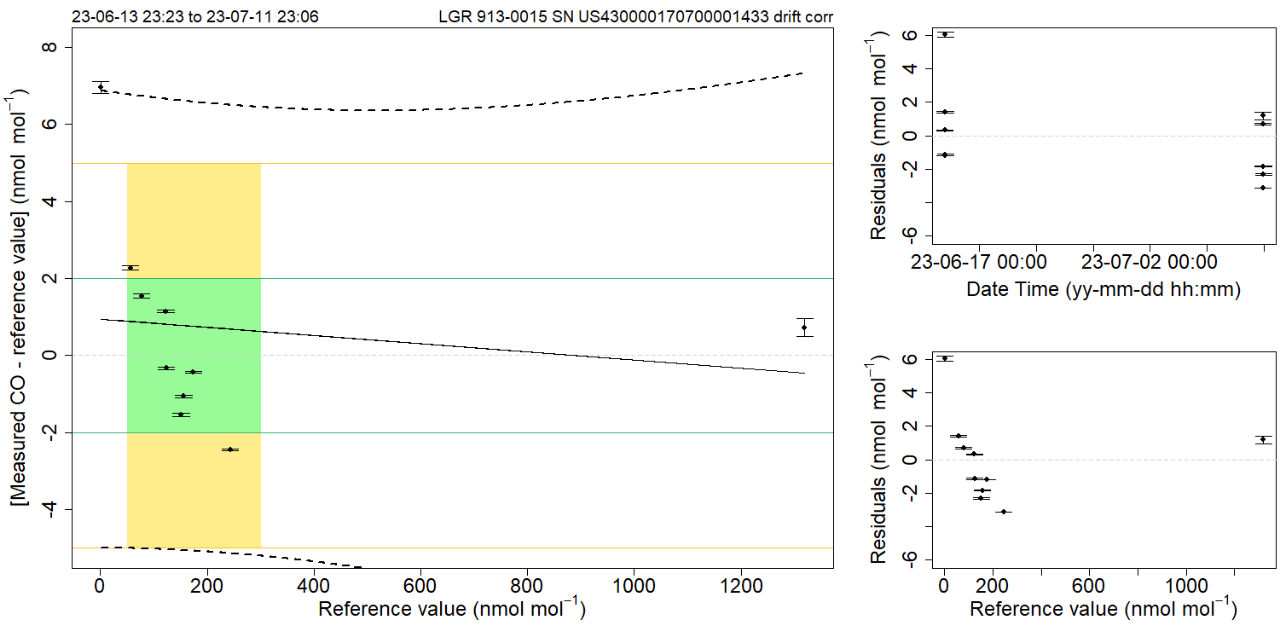


***Figure 6.*** *Left: Bias of the IZO LGR 913-0015 SN US430000170700001433 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

Except for the travelling standard with a very low CO amount fraction, the comparison results were within the WMO/GAW network compatibility goals for the CRDS analyser and within the extended network compatibility goals for the OA-ICOS instrument. Compared to CO audits at other stations, this result is very good, and therefore, no immediate action is required. However, it is recommended to further investigate on the cause of the bias at the zero CO level.

> **Recommendation 4 (*, minor, 2024)**
> *It is recommended to characterise the linearity of the CRDS CO instrument between 0 and 1000 nmol mol$^{-1}$ CO. In particular, the difference observed between zero air and low CO (<100 nmol mol$^{-1}$ in the CRDS measurements needs further attention. High purity nitrogen (grade 6.0) can be used to characterise the instrument response at zero air.*

## 3.3 Methane measurements

Continuous measurements of $CH_4$ at IZO started in 1984 using GC / Flame Ionisation Detection (FID). Since 2019, measurements have been made using Cavity Ring Down Spectroscopy (CRDS).

***Instrumentation, standards and calibration.*** See CO, Picarro G2401.

***Data acquisition.*** See CO.

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

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

**Picarro G2401 #2352-CFKADS2196:**

Unbiased $CH_4$ mixing ratio: $X_{CH4}$ (nmol mol$^{-1}$) = ($CH_4$ – 2.99 nmol mol$^{-1}$) / 0.9985 (13)

Remaining standard uncertainty: $u_{CH4}$ (nmol mol$^{-1}$) = sqrt (0.1 nmol mol$^{-1}$ + 1.30e-07 * $X_{CH4}^2$) (14)

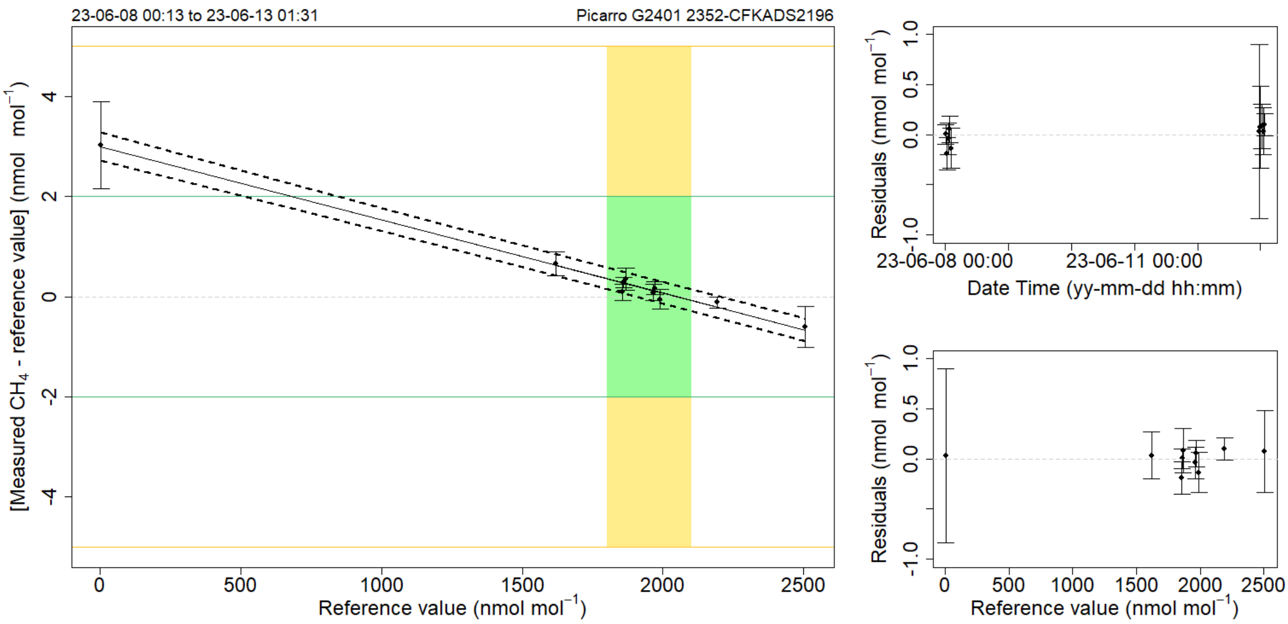


***Figure 7.*** *Left: Bias of the Picarro G2401 #2352-CFKADS2196 instrument with respect to the WMO-X2004A $CH_4$ reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

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

## 3.4 Carbon dioxide measurements

Continuous measurements of $CO_2$ at IZO started in 1984 using NDIR technique. Since 2019, measurements have been made using Cavity Ring Down Spectroscopy (CRDS).

***Instrumentation, standards and calibration.*** See CO, Picarro G2401. In addition, a LI-COR LI-7000 (NDIR) was audited. However, this instrument is no longer considered for data submission.

***Intercomparison (performance audit).*** The comparison consisted of repeated challenges of the IZO instrument with randomised $CO_2$ levels from travelling standards.

The following equations characterise the instrument bias. The result is further illustrated in Figure 8 and 9 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

**Picarro G2401 #2352-CFKADS2196:**

| | | |
|---|---|---|
| Unbiased $CO_2$ mixing ratio: | $X_{CO2}$ (µmol mol$^{-1}$) = ($CO_2$ – 0.55 µmol mol$^{-1}$) / 0.99860 | (15) |
| Remaining standard uncertainty: | $u_{CO2}$ (µmol mol$^{-1}$) = sqrt (0.00 µmol mol$^{-1}$ + 3.28e-8 * $X_{CO2}^2$) | (16) |

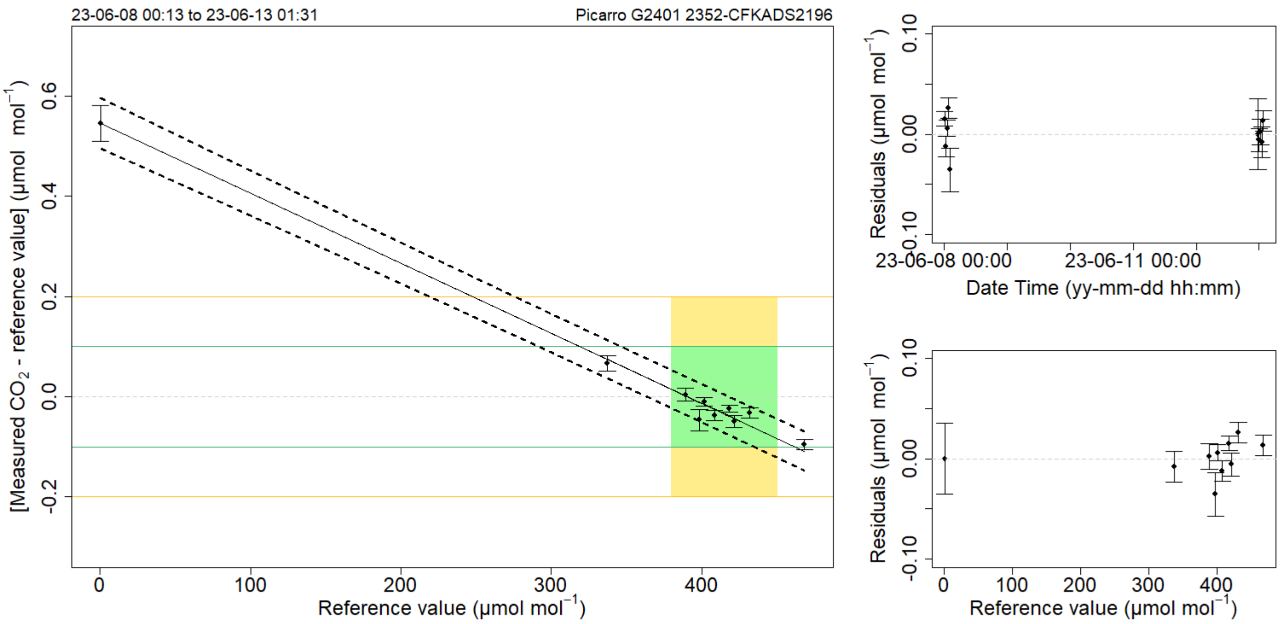


***Figure 8.*** *Left: Bias of the Picarro G2401 #2352-CFKADS2196 $CO_2$ instrument with respect to the WMO-X2007 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

**LI-COR LI-7000 #IRG4-052:**

| | | |
|---|---|---|
| Unbiased $CO_2$ mixing ratio: | $X_{CO2}$ (µmol mol$^{-1}$) = ($CO_2$ – 2.31 µmol mol$^{-1}$) / 0.99451 | (17) |
| Remaining standard uncertainty: | $u_{CO2}$ (µmol mol$^{-1}$) = sqrt (0.31 µmol mol$^{-1}$ + 3.28e-8 * $X_{CO2}^2$) | (18) |

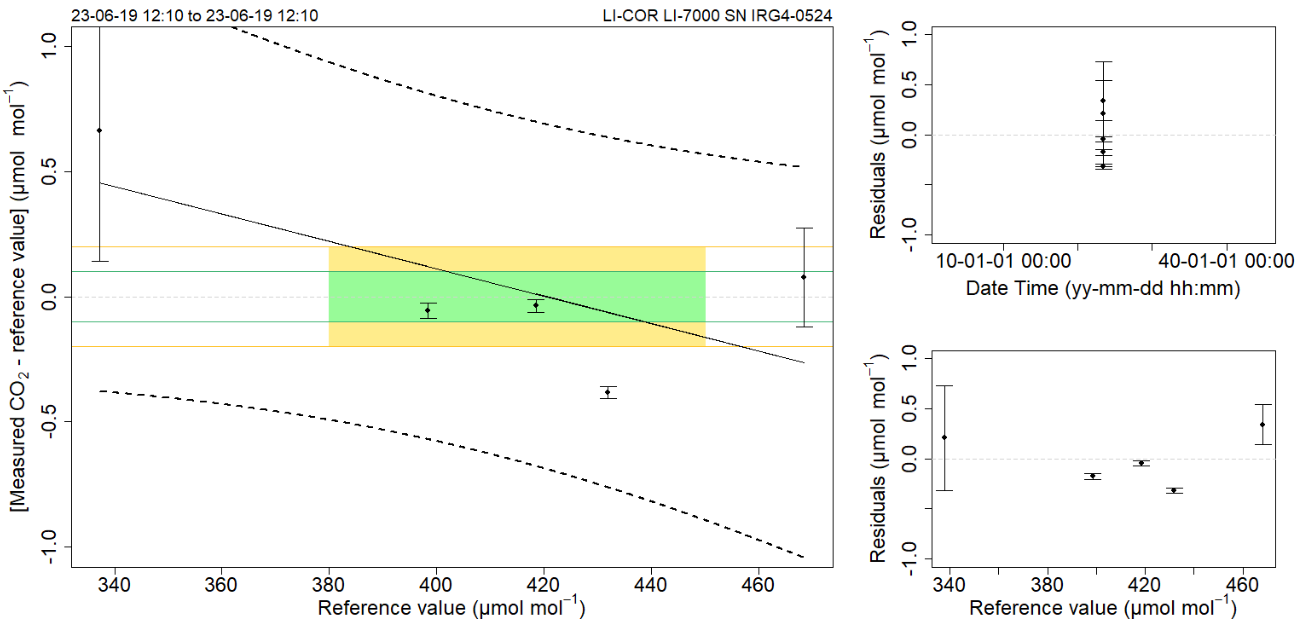


***Figure 9.*** *Left: Bias of the LI-COR LI-7000 #IRG4-052 $CO_2$ instrument with respect to the WMO-X2007 reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

The result was within the WMO/GAW network compatibility goal in the relevant $CO_2$ range. The bias showed small dependence on the amount fraction with an offset of about 0.55 µmol mol$^{-1}$ at zero. This could be due to small inconsistencies in the standards available at IZO. However, due to the good results in the relevant amount fraction range, no further action is required at this time.

## 3.5 Nitrous oxide measurements

Continuous measurements of $N_2O$ at IZO started in 2007 using GC/ECD (Varian 3800) technique, and continuous data series are available since then. Since 2018, measurements have been made with an OA-ICOS analyser. The GC/ECD system is still operational and serves as a backup, but was under repair at the time of the audit.

***Instrumentation, standards and calibration.*** See CO, LGR.

***Intercomparison (performance audit).*** The comparison involved repeated challenges of the IZO instrument with randomly selected $N_2O$ levels from travelling standards.

The following equation characterises the instrument bias. The result is further illustrated in Figure 10 with respect to the relevant amount fraction range and the WMO/GAW compatibility goals and the extended compatibility goals (WMO, 2020).

**LGR 913-0015 SN US430000170700001433:**

Unbiased $N_2O$ mixing ratio: $X_{N2O}$ (nmol mol$^{-1}$) = ($N_2O$ + 0.09 nmol mol$^{-1}$) / 1.0002 (19)

Remaining standard uncertainty: $u_{N2O}$ (nmol mol$^{-1}$) = sqrt (0.0 nmol mol$^{-1}$ + 1.01e-04 * $X_{N2O}^2$) (20)

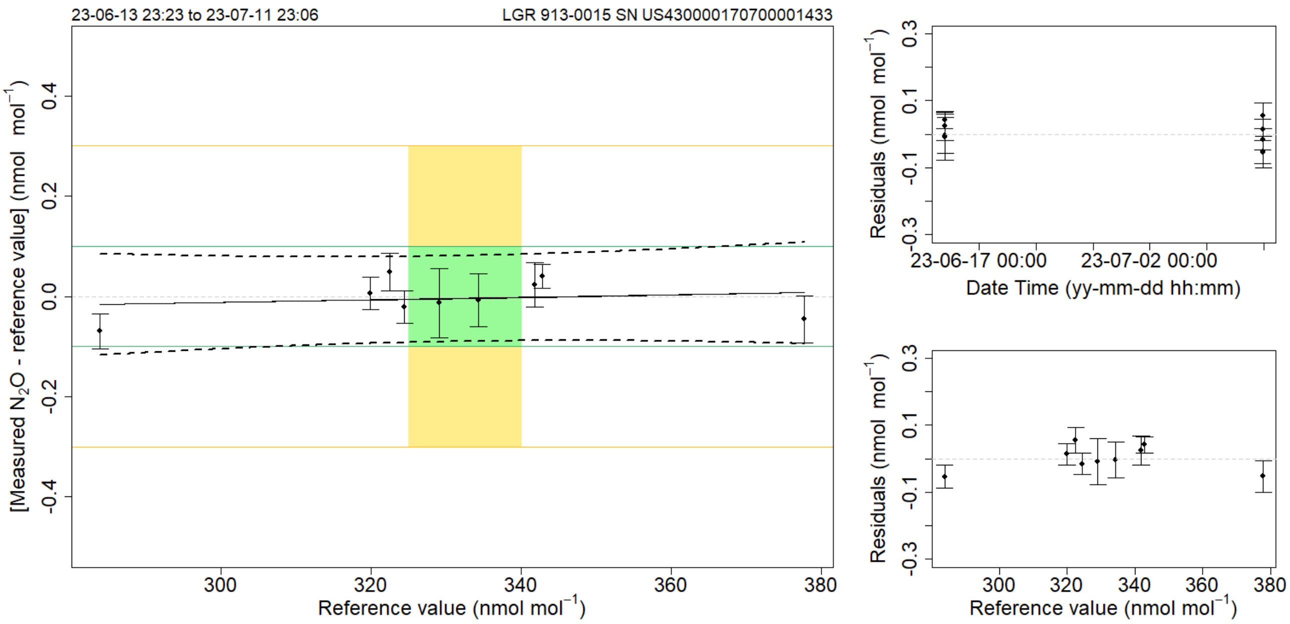


***Figure 10.*** *Left: Bias of the IZO LGR 913-0015 SN US430000170700001433 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of the amount fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of each measurement point. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas correspond to the amount fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and amount fraction dependence).*

The result of the comparison can be summarised as follows:

Excellent agreement well with the WMO/GAW compatibility goal was found in the relevant range of amount fractions. The good results indicate that the whole system, including calibration procedures and standard gases, is fully adequate and no further action is required at this time.

# 4 Comparison of IZO Performance Audit Results with other Stations

This section compares the results of the IZO performance audit with other station audits carried out by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for $CO_2$ and $CH_4$, and Zellweger et al. (2019) for CO, but is also applicable to other compounds. Essentially, the bias in the middle of the relevant amount fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant amount fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for $CO_2$, $CH_4$, and CO and refer to conditions commonly found in unpolluted air masses. For surface ozone the amount fraction range of 0-100 nmol $mol^{-1}$ was chosen as this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations that are acceptable for meeting the WMO/GAW compatibility network goals in a given amount fraction range. Figure 12 shows the bias vs. slope of the WCC-Empa performance audits by for $O_3$, CO, $CH_4$, and $CO_2$. The grey dots show all comparisons made during WCC-Empa audits for the main station analysers, but exclude cases with known instrumental problems. Where an adjustment was made during an audit, only the final comparison is shown. The results of the current IZO audit are shown as coloured dots in Figures 11 and 12.

For surface ozone, the results were within the DQOs for one of the three ozone analysers and the ozone calibrator. The WMO/GAW network compatibility goals were also met for the main instruments for CO, $CH_4$, $CO_2$ and $N_2O$. For the OA-ICOS CO and NDIR $CO_2$ analysers, a slightly larger bias was observed. However, this is less relevant as these instruments are not considered for data submission.

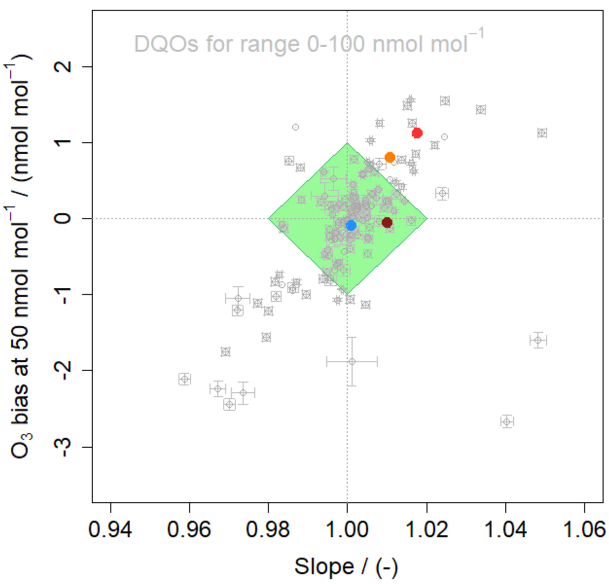


***Figure 11.*** *$O_3$ bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show IZO results (blue: 49iPS #CM22277105, orange: 49i #1153030026, red: 49i #12218618528, dark red: 49i #12218618529). The uncertainty bars refer to the standard uncertainty. The green area corresponds to the WMO/GAW DQOs for ozone. Data of the Thermo 49i #1153030026 (orange) has been used for data submission.*

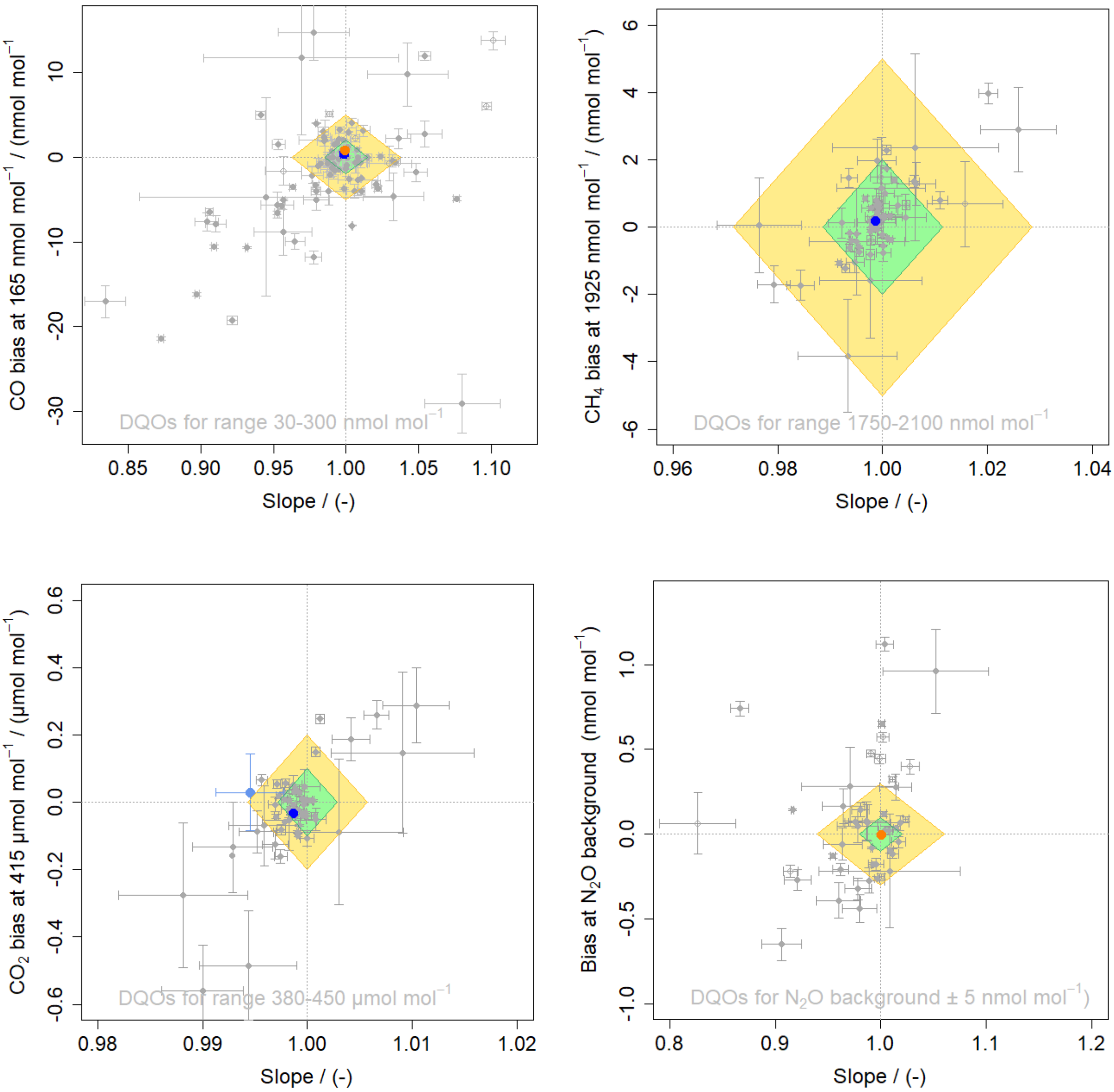


***Figure 12.*** *CO (top left), $CH_4$ (top right), $CO_2$ (bottom left) and $N_2O$ (bottom right) bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits. The grey dots correspond to previous performance audits by WCC-Empa at different stations, while the coloured dots show IZO results (blue: Picarro G2401, light blue: LI-COR LI-7000, orange: LGR 913-0015). Filled symbols refer to a comparison with the same calibration scale at the station and at the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and the extended compatibility goals (yellow).*

# 5 Parallel Measurements of Ambient Air

The audit included parallel measurements of $CO_2$, $CH_4$ and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401 #1497-CFKADS2098). Both the Izaña GAW and ICOS CRDS instruments were compared to the TI between 6 June to 3 July 2023. The TI was connected to an independent inlet line leading to the same inlet location as for the IZO analyser. In addition, the TI occasionally sampled from the IZO central inlet system for a period of 5 hours. The TI sampled air in the following sequence: 2440 min ambient air from the independent inlet, 300 min air from the IZO inlet system followed by 45 min measurement of three standard gases, each for 15 min. The sample air was dried with a Nafion dryer (model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum in the purge air stream. To account for the residual effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the $CO_2$ and $CH_4$ data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The IZO data were processed by the IZO station staff (IZO GAW analyser) and by the ICOS Atmospheric Thematic Centre (ATC) (ICOS analyser).

Figures 13 to 18 show the comparison of hourly CO, $CH_4$, and $CO_2$ measurements between the WCC-Empa TI and the IZO Picarro G2401 analysers operated by AEMET (GAW instrument) and ICOS. Hourly averages were calculated based on 1 minute data with simultaneous data availability from the station analysers and the WCC-Empa TI.

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

## 5.1 Carbon Monoxide

IZO measurements from both AEMET and ICOS were about 2 nmol mol$^{-1}$ lower compared to WCC-Empa, which is a slightly larger deviation than observed in the TS comparison. The ICOS analyser showed a more pronounced amount fraction dependence of the bias compared to the GAW analyser. The temporal variation was well captured by all instruments. The results were mostly within the extended WMO/GAW compatibility goals.

## 5.2 Methane

Excellent agreement within the WMO/GAW network compatibility goals was found between the TI and both the IZO GAW and IZO ICOS instruments. This confirms the results of the travelling standard comparisons made with the IZO GAW instrument. The temporal variation was well captured by all instruments and the deviation between the different instruments was very small.

## 5.3 Carbon dioxide

On average, the agreement between the WCC-Empa TI and the IZO GAW and ICOS instruments was well within the WMO/GAW compatibility goals. The temporal variability was well captured by all instruments, and no significant dependence of the bias on the amount fraction was observed. However, the GAW Picarro often measured higher than the WCC-Empa TI. In contrast, the IZO ICOS analyser often showed lower readings compared to WCC-Empa during the periods when the TI was sampling air from the IZO station inlet. This was most likely due to a leak in the IZO inlet system. These findings were already communicated to IZO during the measurement campaign, and a potential leak has been fixed on 29 June 2023, which resulted in better agreement between the IZO and the WCC-Empa measurements. The diurnal variation of the bias is further illustrated in Figure 19. No diurnal variation of the bias was found for the ICOS analyser; but the IZO analyser often showed higher values during working hours. Consequently, the following recommendation is made:

**Recommendation 5 (***, critical, ongoing)**
*The IZO inlet system must be regularly checked for small leaks. For this purpose, it is also recommended to compare the values of the IZO $CO_2$ analyser with the ICOS data on a regular basis.*

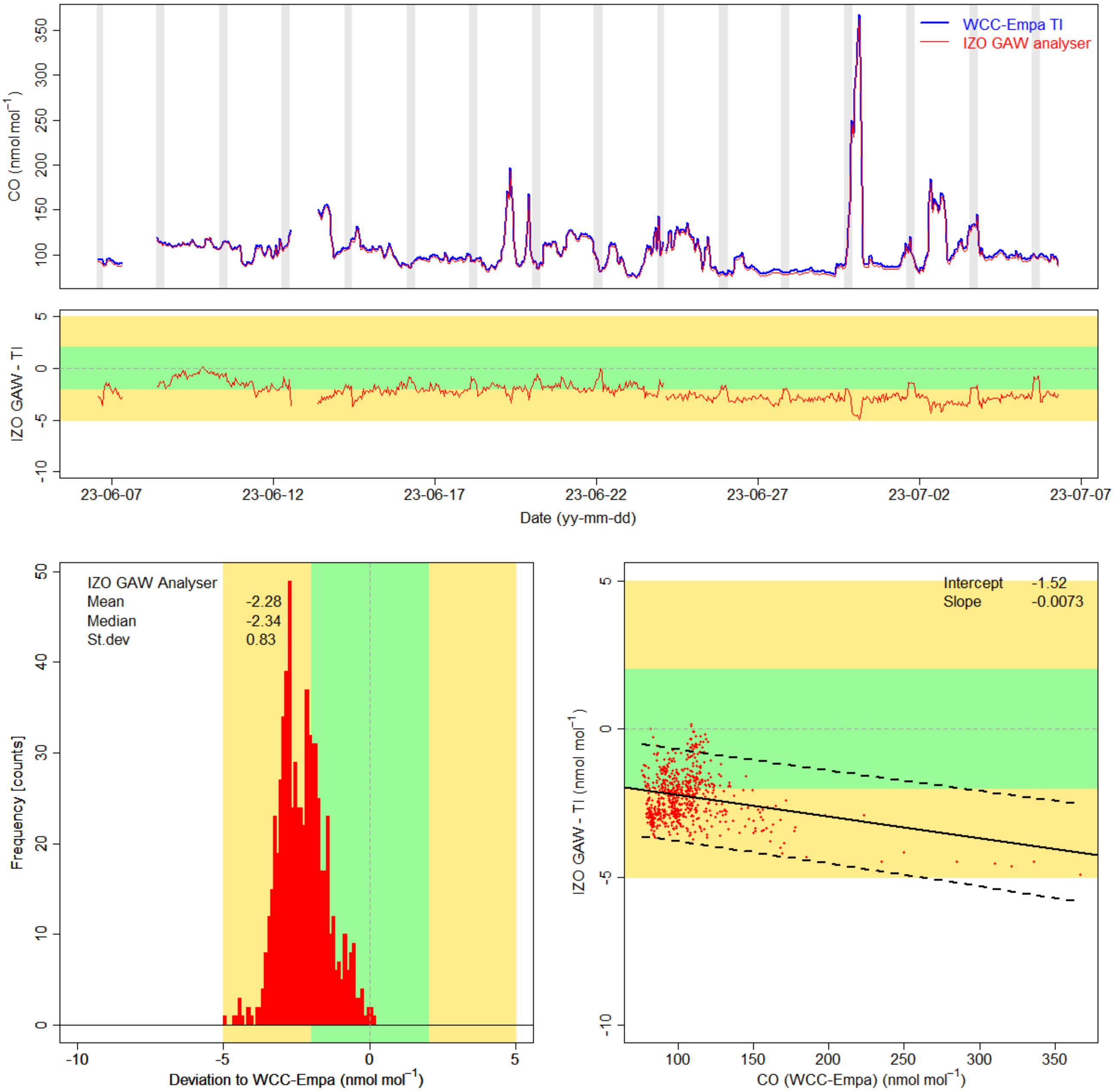


***Figure 13.*** *Top: Comparison of the Picarro G2401#2352-CFKADS2196 (IZO GAW instrument) with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G2401#2352-CFKADS2196 analyser compared to the WCC-Empa TI. Bottom right: IZO instrument bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

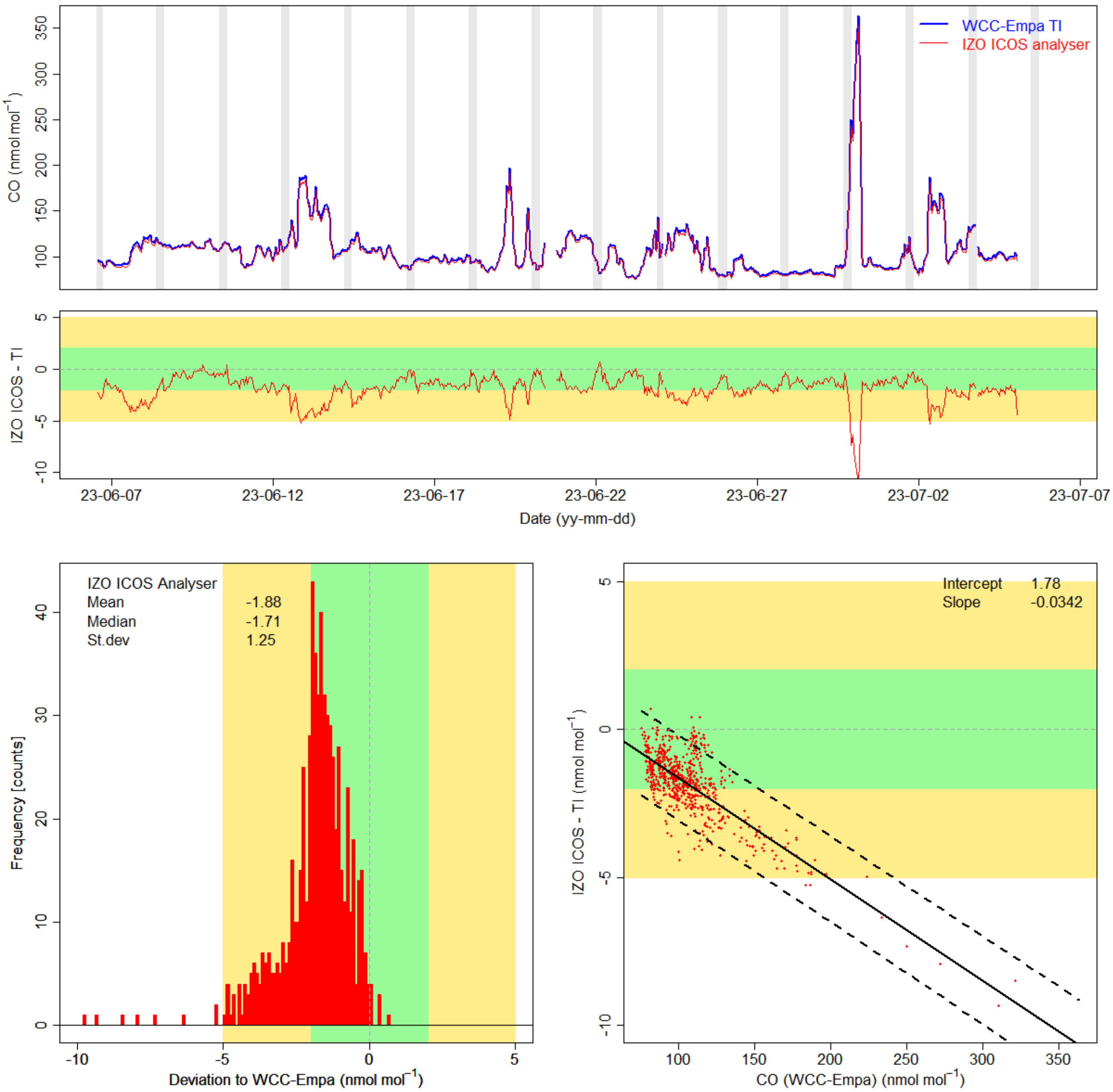


***Figure 14.*** *Top: Comparison of the Picarro G2401#3781-CFKADS2389 (ICOS instrument) with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: CO deviation histograms for the Picarro G2401#2352-CFKADS2196 analyser compared to the WCC-Empa TI. Bottom right: IZO instrument bias as a function of the CO amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

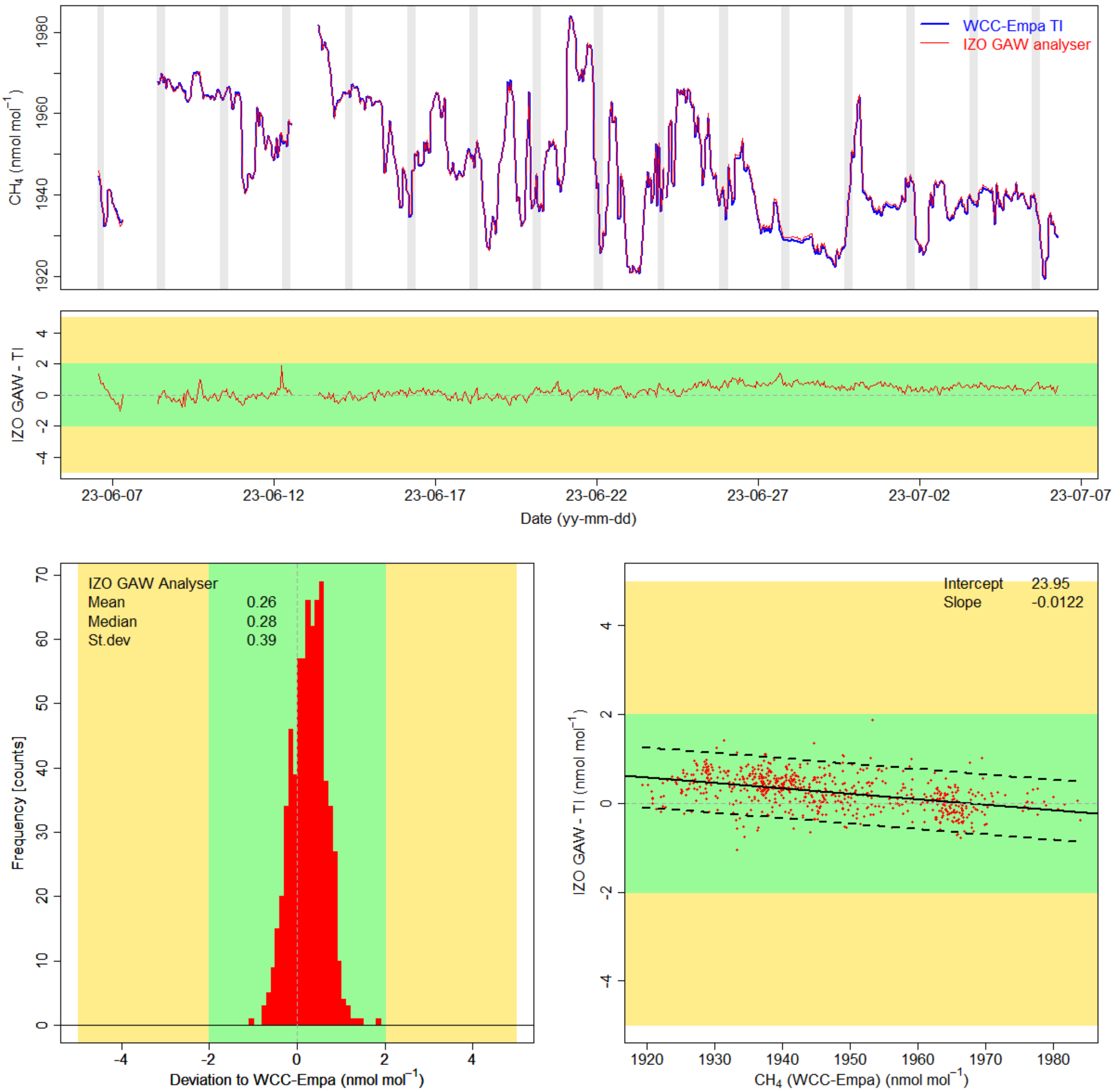


***Figure 15.*** *Top: Comparison of the Picarro G2401#2352-CFKADS2196 (GAW analyser) with the WCC-Empa travelling instrument for $CH_4$. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: $CH_4$ deviation histograms for the Picarro G2401#2352-CFKADS2196 analyser compared to the WCC-Empa TI. Bottom right: IZO instrument bias as a function of the $CH_4$ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

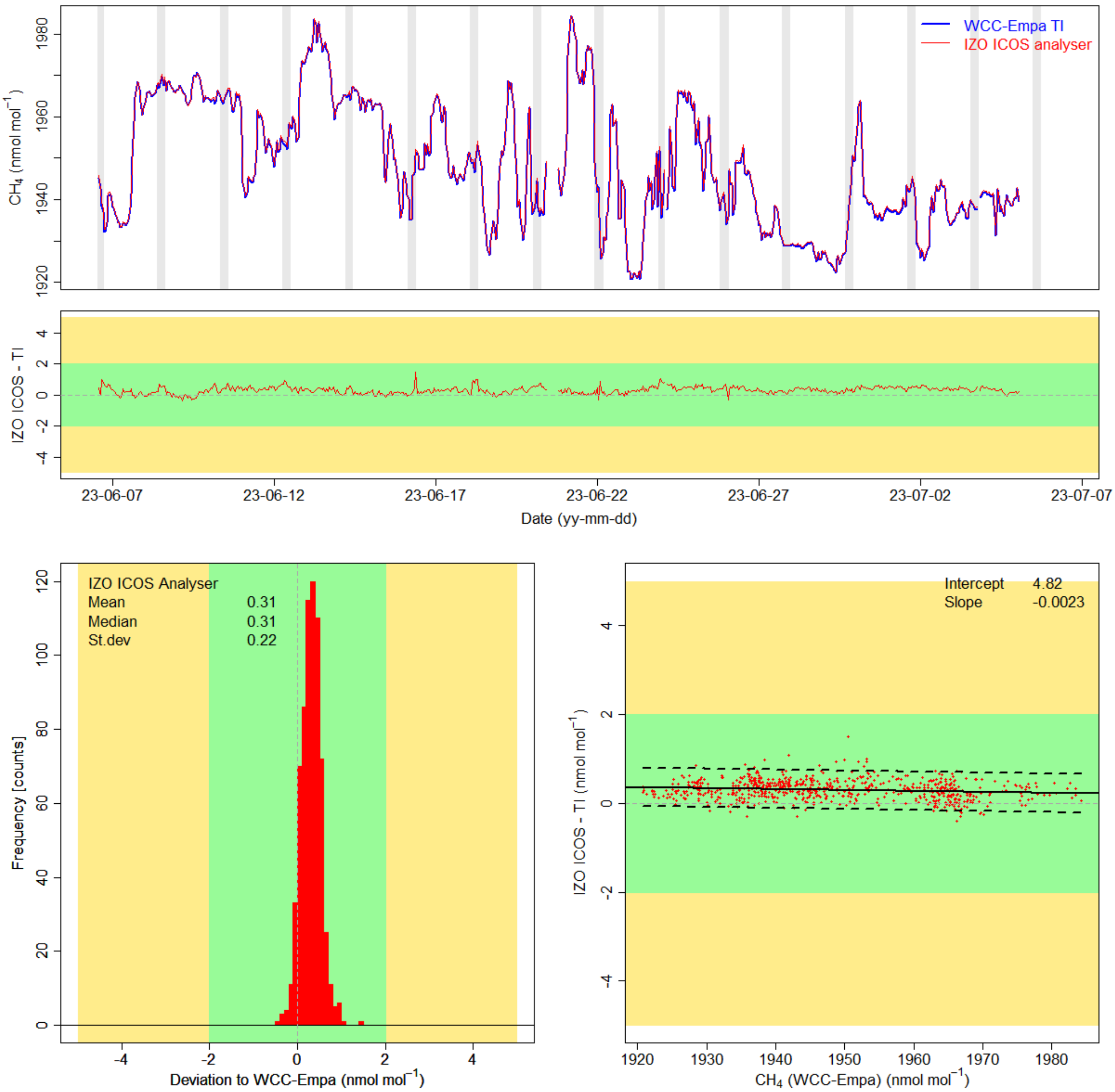


***Figure 16.*** *Top: Comparison of the Picarro G2401#3781-CFKADS2389 (ICOS analyser) with the WCC-Empa travelling instrument for $CH_4$. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: $CH_4$ deviation histograms for the Picarro G2401#2352-CFKADS2196 analyser compared to the WCC-Empa TI. Bottom right: IZO instrument bias as a function of the $CH_4$ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

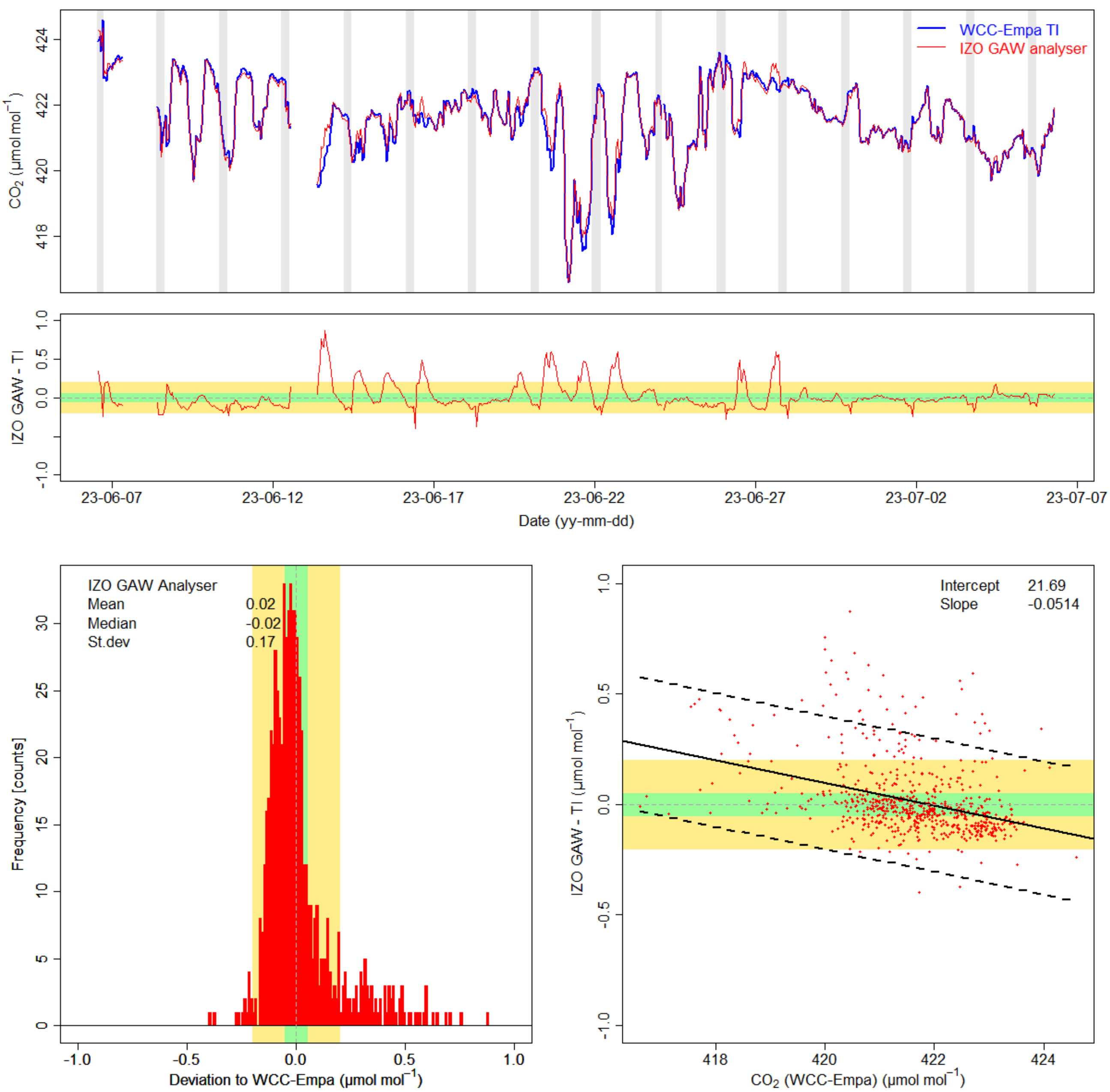


***Figure 17.*** *Top: Comparison of the Picarro G2401#2352-CFKADS2196 (GAW analyser) with the WCC-Empa travelling instrument for $CO_2$. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: $CO_2$ deviation histograms for the Picarro G2401#2352-CFKADS2196 analyser compared to the WCC-Empa TI. Bottom right: IZO instrument bias as a function of the $CH_4$ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

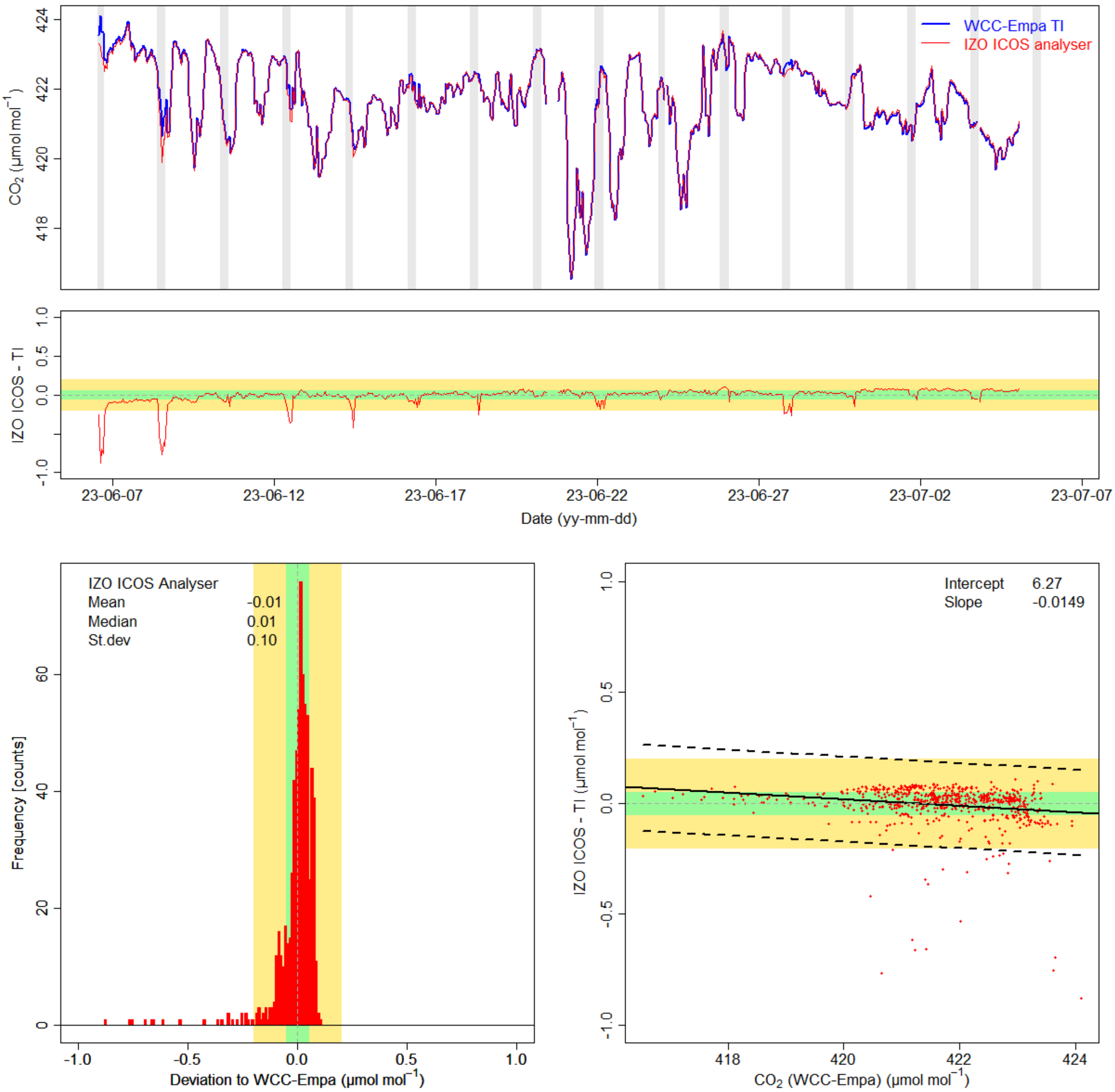


***Figure 18.*** *Top: Comparison of the Picarro G2401#3781-CFKADS2196 (ICOS analyser) with the WCC-Empa travelling instrument for $CO_2$. Time series based on hourly data and the difference between the station instrument and the TI are shown. Bottom left: $CO_2$ deviation histograms for the Picarro G2401#2352-CFKADS2196 analyser compared to the WCC-Empa TI. Bottom right: IZO instrument bias as a function of the $CH_4$ amount fraction. The coloured areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

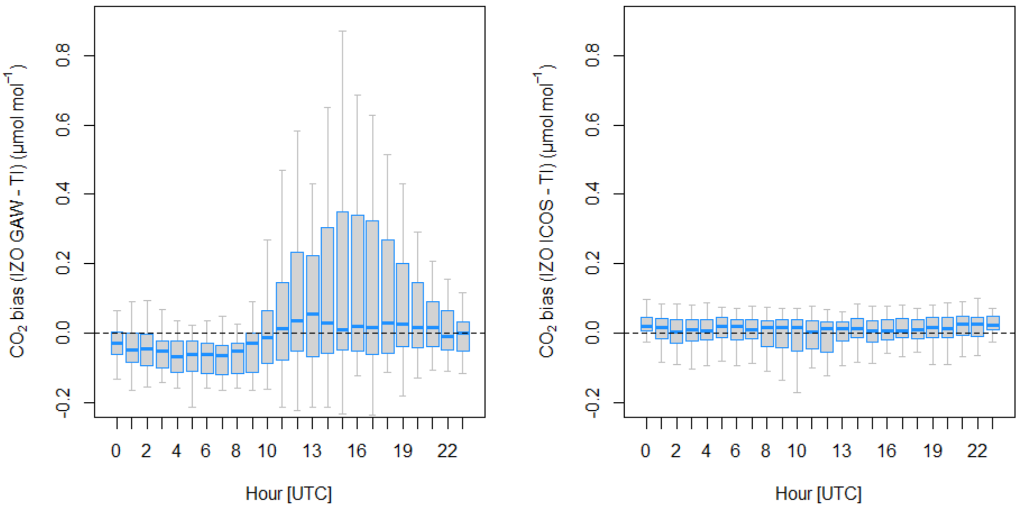


***Figure 19.*** *Left: Boxplot of the diurnal $CO_2$ bias of the IZO analyser compared to the WCC-Empa TI. Right: Same as left for the ICOS analyser.*

# 6 Conclusions

The Izaña Global GAW Station provides a comprehensive research infrastructure that facilitates numerous ongoing observations across in all WMO/GAW focal areas and supports various research projects. The GAW activities at IZO are well embedded in the national and international research landscape, making it a very important contributor to the WMO/GAW programme. Therefore, the continuation of the Izaña measurement series is essential for GAW. With its comprehensive monitoring of atmospheric constituents and exceptional data quality, the station enables cutting-edge research.

Most of the measurements evaluated were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant range of amount fractions. The parallel measurements performed as part of the audit indicated a small potential leak in the Izaña inlet system, which requires further attention. Otherwise, only minor recommendations were made due to the good results of the comparisons and the well-established and fully appropriate operating procedures.

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

***Table 1.*** *Summary of the performance audit and parallel measurement results at Izaña. A tick mark in the table indicates that the compatibility goal (green) or the extended compatibility goal (orange) has been met on average, and ✗ indicates results exceeding the compatibility goals.*

| Compound / Instrument | Range | Unit | IZO within DQO/eDQO |
|---|---|---|---|
| $O_3$ (Thermo 49i #1153030026) | 0 -100 | nmol mol$^{-1}$ | ✗ |
| $O_3$ (Thermo 49i #12218618528) | 0 -100 | nmol mol$^{-1}$ | ✗ |
| $O_3$ (Thermo 49i #12218618529) | 0 -100 | nmol mol$^{-1}$ | ✓ |
| $O_3$ (Thermo 49i-PS #CM22277105) | 0 -100 | nmol mol$^{-1}$ | ✓ |
| CO (Picarro G2401 #2352-CFKADS2196) | 30 - 300 | nmol mol$^{-1}$ | ✓ |
| CO (Picarro G2401 #2352-CFKADS2196), parallel measurements | NA | nmol mol$^{-1}$ | ✓ (orange) |
| CO (Picarro G2401 #3781-CFKADS2389), parallel measurements | NA | nmol mol$^{-1}$ | ✓ |
| CO (LGR 913-0015 SN US430000170700001433) | 30 - 300 | nmol mol$^{-1}$ | ✓ |
| $CH_4$ (Picarro G2401 #2352-CFKADS2196) | 1750 - 2100 | nmol mol$^{-1}$ | ✓ |
| $CH_4$ (Picarro G2401 #2352-CFKADS2196), parallel measurements | NA | nmol mol$^{-1}$ | ✓ |
| $CH_4$ (Picarro G2401 #3781-CFKADS2389), parallel measurements | NA | nmol mol$^{-1}$ | ✓ |
| $CO_2$ (Picarro G2401 #2352-CFKADS2196) | 380 - 450 | µmol mol$^{-1}$ | ✓ |
| $CO_2$ (Picarro G2401 #2352-CFKADS2196), parallel measurements | NA | µmol mol$^{-1}$ | ✓ |
| $CO_2$ (Picarro G2401 #3781-CFKADS2389), parallel measurements | NA | µmol mol$^{-1}$ | ✓ |
| $CO_2$ (LI-COR LI-7000 #IRG4-052) | 380 - 450 | µmol mol$^{-1}$ | ✗ |
| $N_2O$ (LGR 913-0015 SN US430000170700001433) | 325 - 340 | nmol mol$^{-1}$ | ✓ |

# 7 Summary Ranking of the Izaña GAW Station

| System Audit Aspect | Adequacy# | Comment |
|---|---|---|
| Measurement programme | (5) | Comprehensive programme |
| Access | (5) | Year round access |
| Facilities | | |
| Laboratory and office space | (5) | Fully adequate, with space for additional research campaigns |
| Internet access | (5) | High-speed connection |
| Air Conditioning | (5) | Air conditioned, temperature fluctuations of a few degrees (<2°C) |
| Power supply | (5) | Reliable and stable |
| General Management and Operation | | |
| Organisation | (5) | Well-coordinated and managed |
| Competence of staff | (5) | Highly skilled staff |
| Air Inlet System | (4) | Adequate, but small potential leak in the inlet system |
| Instrumentation | | |
| Ozone | (5) | Adequate instrumentation |
| $CH_4$/$CO_2$/CO Picarro G2401 | (5) | State of the art instrumentation |
| $N_2O$/CO LGR 913 | (5) | State of the art instrumentation |
| Standards | | |
| $O_3$ | (5) | Transfer standards with SRP traceability on site |
| CO, $CO_2$, $CH_4$ | (5) | Full traceability to the WMO/GAW reference (NOAA and ICOS FCL) |
| Data Management | | |
| Data acquisition | (5) | Fully adequate systems |
| Data processing | (5) | Skilled staff, appropriate procedures |
| Data submission WDCRG | (5) | Ozone data is available |
| Data submission WDCGG | (4) | Most data is timely submitted, recent $N_2O$ data missing |

#0: inadequate thru 5: adequate.

# Appendix

## A1. List of recommendations

The recommendations made in this report are summarised below, with an indication of their priority, significance and proposed completion date.

| # | Recommendation | Priority | Significance | Date |
|---|---|---|---|---|
| 1 | It is recommended to update GAWSIS annually or when major changes occur. Some of the reviewed information needs to be updated. GAWSIS support should be contacted for updates that are not possible via the web interface (e.g. deletion of station contacts). | Medium | Important | Ongoing |
| 2 | It is recommended to submit the N2O data for the period from 2017 onwards as soon as the final quality control has been completed. | Medium | Important | 2024 |
| 3 | Thermo Scientific 49i #12218618528 is not performing well, and the reason needs to be identified. It is recommended that the analyser be returned to the manufacturer for inspection and repair. | Medium | Important | 2024 |
| 4 | It is recommended to characterise the linearity of the CO instrument between 0 and 1000 nmol mol-1 CO. In particular, the difference observed between zero air and low CO (<100 nmol mol-1 in the CRDS measurements needs further attention. High purity nitrogen (grade 6.0) can be used to characterise the instrument response at zero air. | Low | Minor | 2024 |
| 5 | The IZO inlet system must be regularly checked for small leaks. For this purpose, it is also recommended to compare the values of the AEMET $CO_2$ analyser with the ICOS data on a regular basis. | High | Critical | Ongoing |

## A2. Data review

The following figures show summary plots of IZO data obtained from WDCRG and WDCGG on 16 January 2024. The plots show time series of hourly data, frequency distribution and diurnal and seasonal variations.

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

**Surface ozone:**

The two available data sets for the periods from 1987 to 2013 and 2014 to 2022 are shown below.

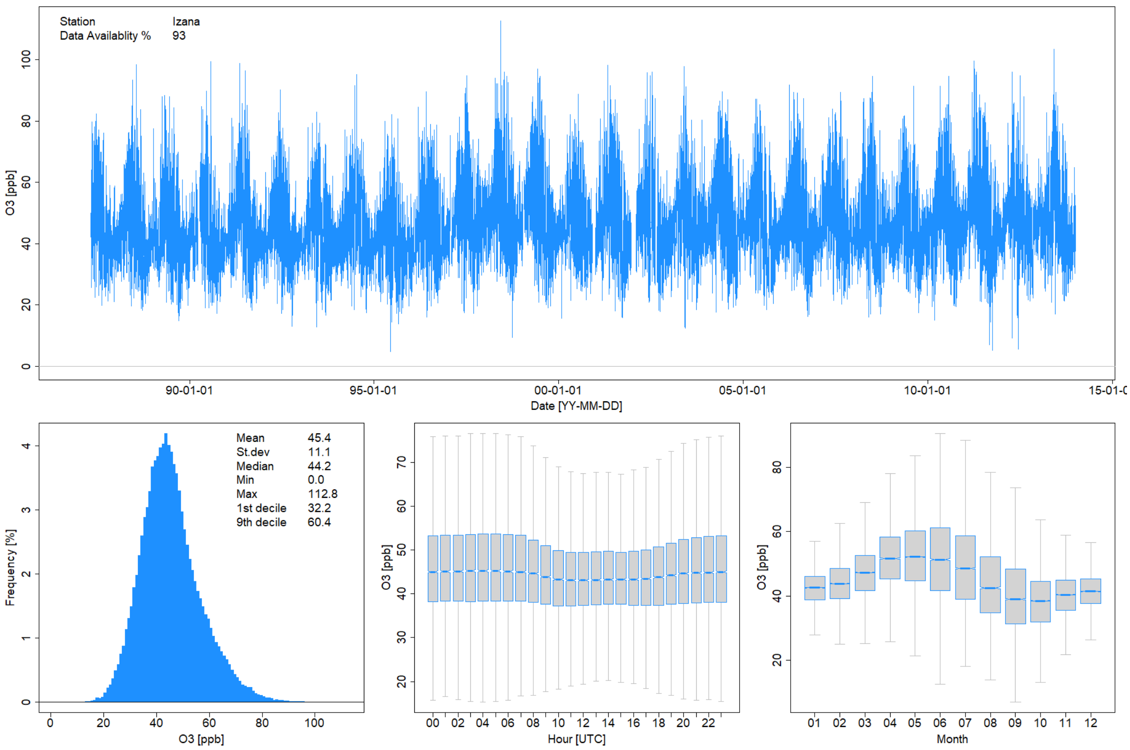


***Figure 20.*** *WDCRG $O_3$ data for the period from 1987 to 2013. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

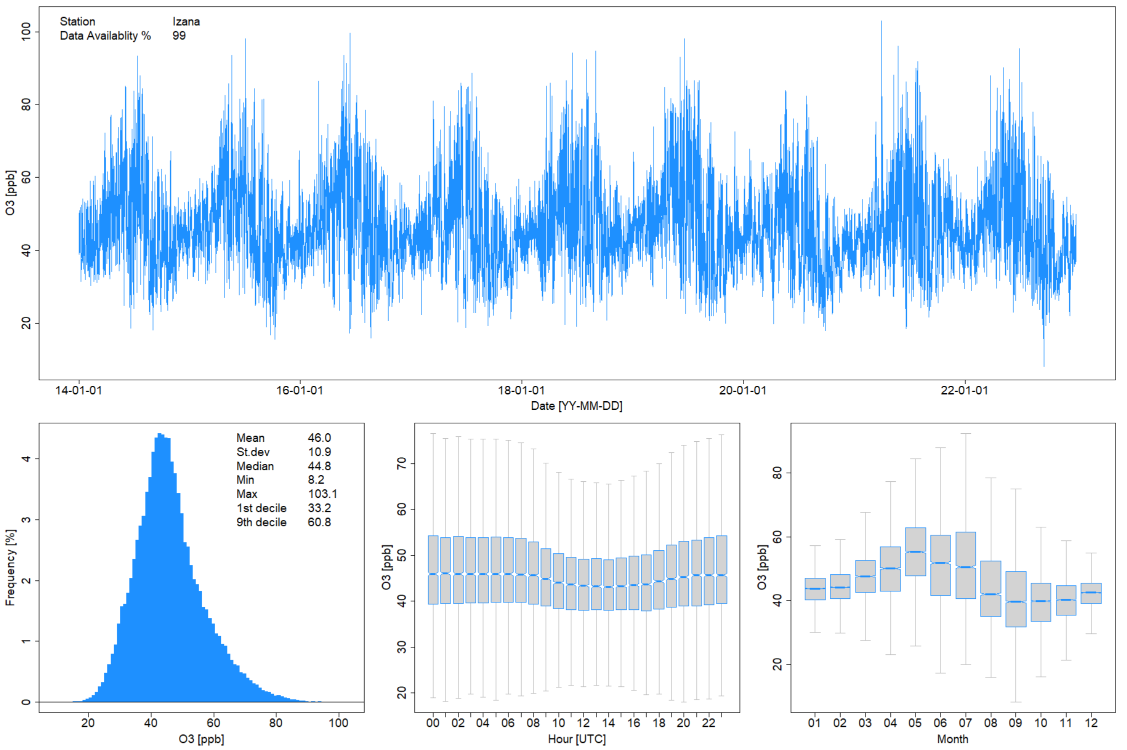


***Figure 21.*** *WDCRG $O_3$ data for the period from 2014 to 2022. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

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

**Carbon monoxide:**

The CO data submitted by AEMET and NOAA is shown in the figures below.

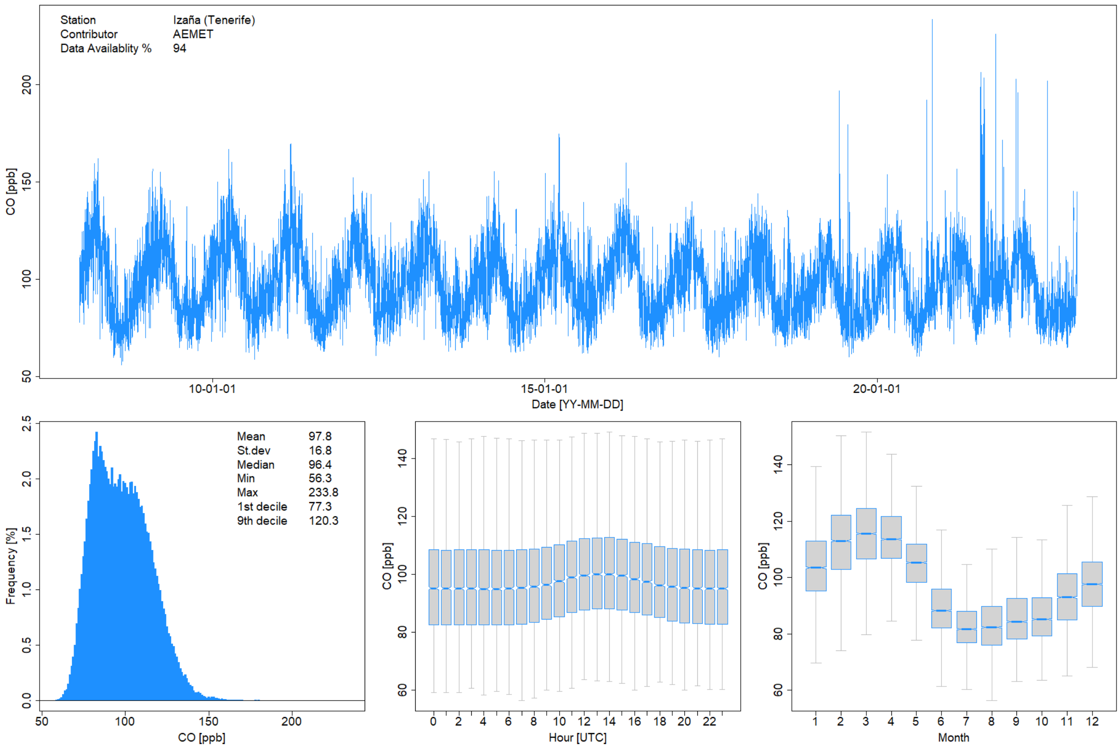


***Figure 22.*** *IZO CO data (2008-2022) submitted to WDCGG by AEMET. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

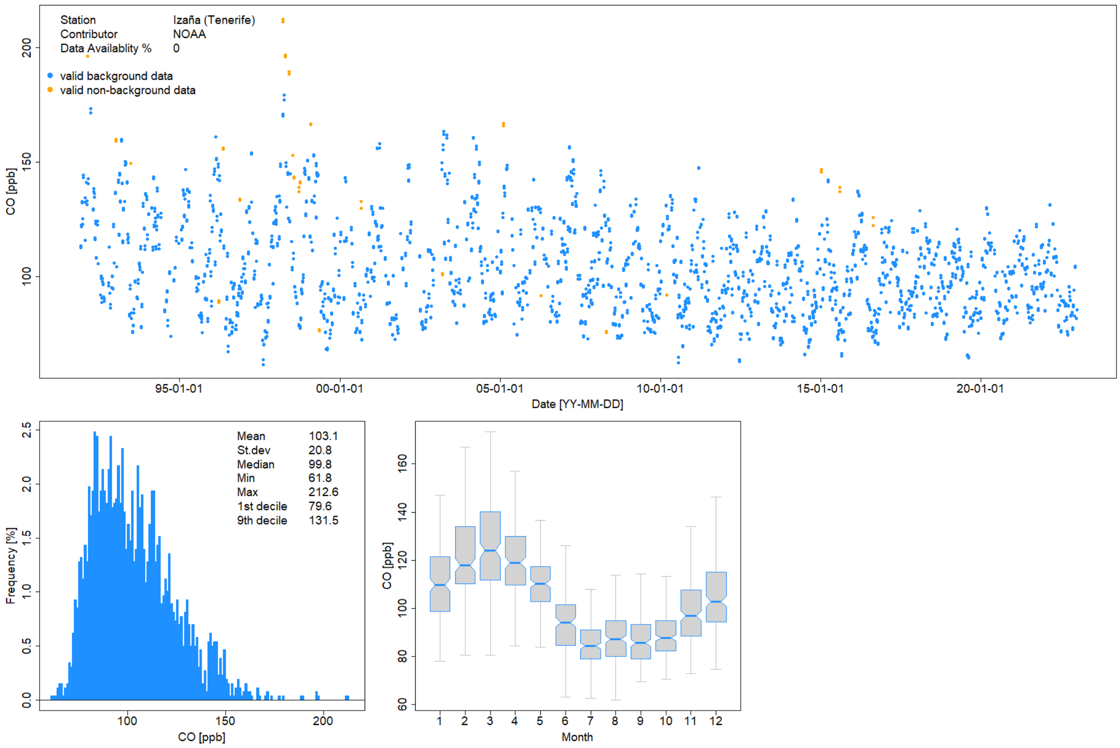


***Figure 23.*** *IZO CO flask data (1991-2021) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- Both the AEMET and the NOAA CO data set looks sound in terms of amount fraction, trend, seasonal and diurnal variation.
- The AEMET CO data series shows significantly more CO values exceeding 150 nmol mol$^{-1}$ in the last three years. Such high values were not present during the earlier years of the AEMET data set. According to the station PI, these spikes are due to the change in instrumentation. The old GC data processing software applied a more demanding filter to data with high variability compared to the Picarro. Therefore, the spikes can be considered as valid data.

**Methane:**

The $CH_4$ data submitted by AEMET and NOAA is shown in the figures below.

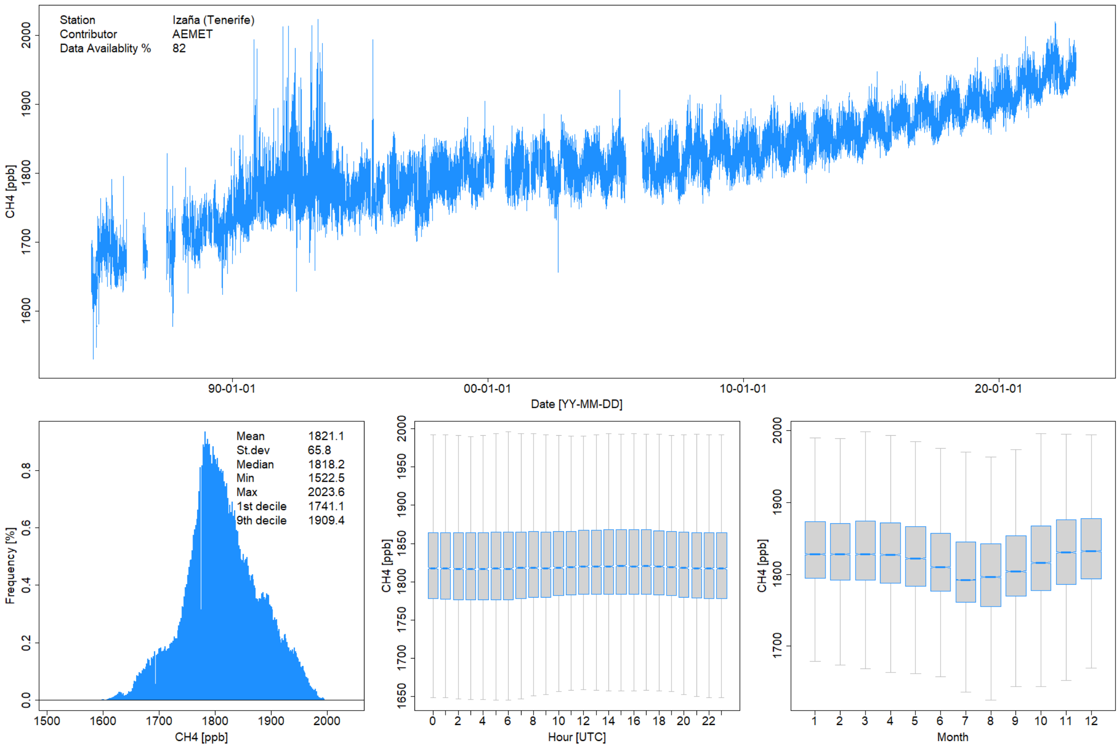


***Figure 24.*** *IZO in-situ $CH_4$ data (1984-2022) provided by AEMET. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

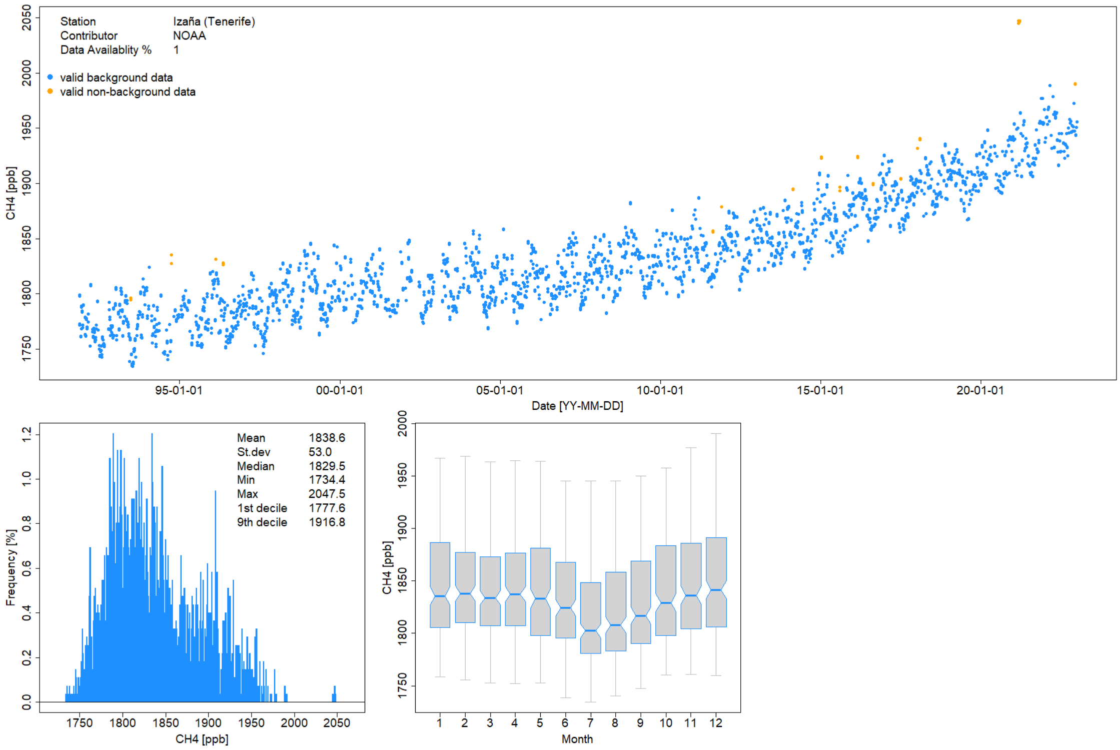


***Figure 25.*** *IZO $CH_4$ flask data (1991-2022) provided by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- Both the AEMET and the NOAA $CH_4$ data set looks sound in terms of amount fraction, trend, seasonal and diurnal variation.
- The variability in the AEMET data significantly decreased with time, most likely due to improved instrumentation. A period with unusual high variability was observed in the early 90s.

## Carbon dioxide:

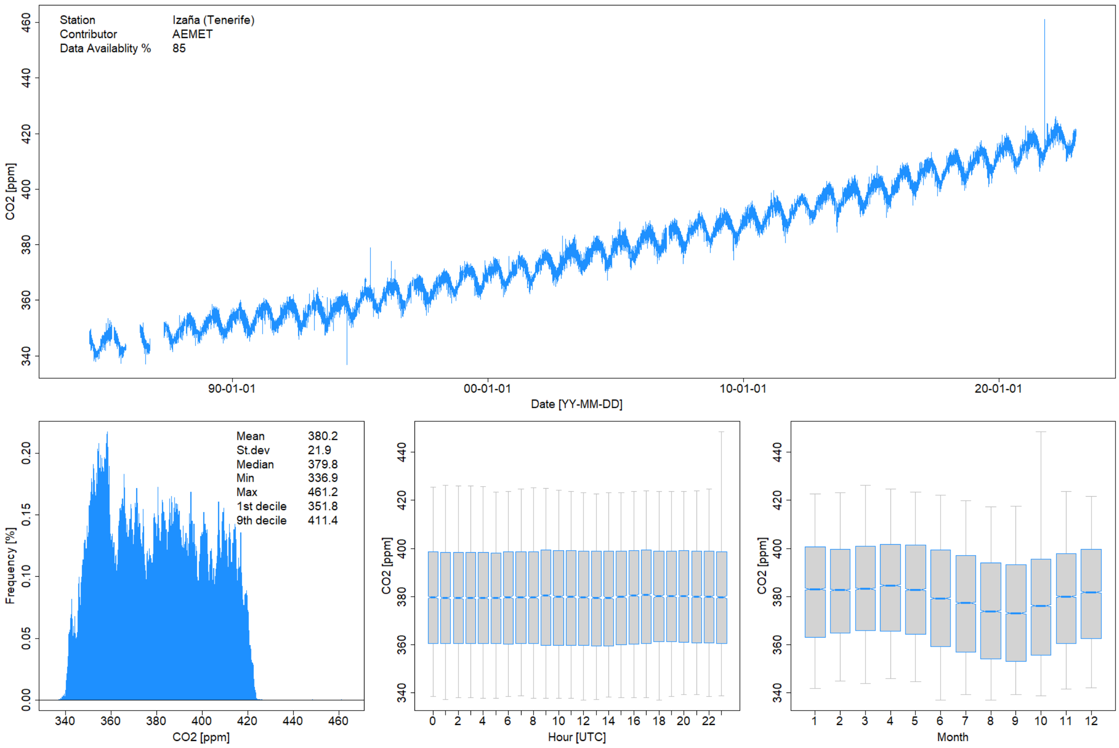


***Figure 26.*** *IZO in-situ $CO_2$ data (1984-2022) submitted by AEMET. All valid data are shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, middle: diurnal variation, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

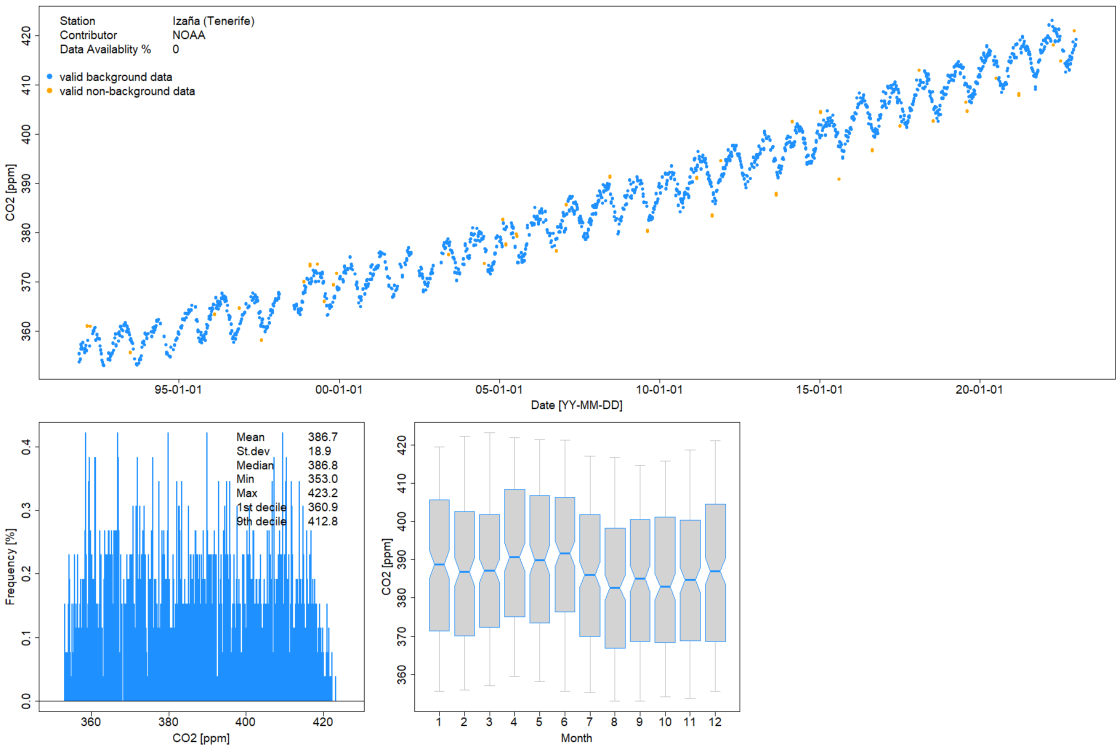


***Figure 27.*** *IZO $CO_2$ flask data (1991-2022) submitted to WDCGG by NOAA. Top: Time series, hourly averages. Bottom: Left: frequency distribution, right: seasonal variation; the horizontal blue line indicates the median, and the blue boxes show the interquartile range.*

- Both the AEMET and the NOAA $CO_2$ data set looks sound in terms of amount fraction, trend, seasonal and diurnal variation.
- The AEMET data contains a few spikes (high and low values). It should be checked if these values need to be flagged as invalid. The spike detected on 12 October 2021 was due to the La Palma volcano eruption and therefore is valid non-background data.

## 7.1 Surface Ozone Comparisons

All procedures were carried out according to the standard operating procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the standard reference photometer at Empa before and after the analyser comparison. The internal ozone generator of the WCC-Empa transfer standard was used to generate a randomised sequence of ozone levels ranging from 0 to 250 nmol mol$^{-1}$. Zero air was generated using a custom built zero air generator (Nafion dryer, Purafil, activated charcoal) for the comparison of the IZO ozone calibrator, and the IZO zero air generator (Teledyne API Model T701H) was used for the comparison of the IZO analysers. The TS was connected to the station analyser using approximately 1.5 m of PFA tubing. Table 2 details the experimental setup for the travelling standard and the station analyser comparisons. The data used for the evaluation were recorded by the WCC-Empa and IZO data acquisition systems.

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

| | |
|---|---|
| **Travelling standard (TS)** | |
| Model, S/N | Thermo Scientific 49i-PS #CM22117100 (WCC-Empa) |
| Settings | BKG +0.0 COEF 1.009 |
| Pressure readings (hPa) | Ambient 764.8; TS 765.8 (no adjustment was made) |
| **Main IZO ozone analyser (OA)** | |
| Model, S/N | Thermo Scientific 49i #1153030026 |
| Principle | UV absorption |
| Settings | BKG 0.0 nmol mol$^{-1}$, COEF 1.003 |
| Pressure readings (hPa) | Ambient 764.5; OA 762.9 (no adjustment was made) |
| **Backup IZO ozone analyser (OA)** | |
| Model, S/N | Thermo Scientific 49i #12218618528 |
| Principle | UV absorption |
| Settings | BKG 0.0 nmol mol$^{-1}$, COEF 1.010 |
| Pressure readings (hPa) | Ambient 764.5; OA 761.3 (no adjustment was made) |
| **Backup IZO ozone analyser (OA)** | |
| Model, S/N | Thermo Scientific 49i #12218618529 |
| Principle | UV absorption |
| Settings | BKG 0.0 nmol mol$^{-1}$, COEF 1.008 |
| Pressure readings (hPa) | Ambient 765.9.5; OA 762.2, adjusted to 765.9 before comparison |
| **IZO ozone calibrator (OC)** | |
| Model, S/N | Thermo Scientific 49i-PS #1153030026 |
| Principle | UV absorption |
| Settings | BKG -0.4 nmol mol$^{-1}$, COEF 1.003 |

| | |
|---|---|
| Pressure readings (hPa) | Ambient 761.8; OC 768.5, adjusted to 761.8 before comparison |

## A3. Results

Each ozone level was measured for ten minutes, and the last five 1 minute averages were aggregated. These aggregates were used to evaluate the comparison. All results are valid for the calibration factors as given in Table 2 above. The travelling standard (TS) readings were compensated for bias with respect to the standard reference photometer (SRP) prior to the evaluation of the ozone analyser values. The same treatment was applied as for the ambient air analysis.
The results of the assessment are shown in the following table (individual measurement points) and are also presented in the Executive Summary.

***Table 3.*** *Comparison of the main IZO ozone analyser (OA) Thermo Scientific 49i #1153030026 (BKG 0.0 nmol mol$^{-1}$, COEF 1.003) with the bias corrected WCC-Empa travelling standard (TS).*

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OA (nmol mol$^{-1}$) | sdOA (nmol mol$^{-1}$) | OA-TS (nmol mol$^{-1}$) | OA-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-07 19:46 | 0.22 | 0.09 | 0.48 | 0.09 | 0.26 | NA |
| 2023-06-07 19:56 | 25.19 | 0.07 | 25.89 | 0.13 | 0.70 | 2.78 |
| 2023-06-07 20:06 | 200.29 | 0.07 | 202.99 | 0.24 | 2.70 | 1.35 |
| 2023-06-07 20:16 | 150.21 | 0.15 | 152.27 | 0.15 | 2.06 | 1.37 |
| 2023-06-07 20:26 | 100.27 | 0.08 | 101.69 | 0.38 | 1.42 | 1.42 |
| 2023-06-07 20:36 | 50.25 | 0.07 | 51.18 | 0.26 | 0.93 | 1.85 |
| 2023-06-07 20:46 | 75.25 | 0.14 | 76.61 | 0.32 | 1.36 | 1.81 |
| 2023-06-07 20:56 | 250.27 | 0.03 | 253.23 | 0.34 | 2.96 | 1.18 |
| 2023-06-07 21:06 | 0.44 | 0.11 | 0.42 | 0.17 | -0.02 | NA |
| 2023-06-07 21:16 | 250.30 | 0.06 | 253.40 | 0.48 | 3.10 | 1.24 |
| 2023-06-07 21:26 | 200.29 | 0.07 | 202.82 | 0.29 | 2.53 | 1.26 |
| 2023-06-07 21:36 | 100.29 | 0.05 | 101.70 | 0.34 | 1.41 | 1.41 |
| 2023-06-07 21:46 | 25.21 | 0.05 | 25.89 | 0.11 | 0.68 | 2.70 |
| 2023-06-07 21:56 | 150.22 | 0.07 | 152.19 | 0.23 | 1.97 | 1.31 |
| 2023-06-07 22:06 | 50.24 | 0.09 | 51.11 | 0.32 | 0.87 | 1.73 |
| 2023-06-07 22:16 | 75.15 | 0.09 | 76.40 | 0.17 | 1.25 | 1.66 |
| 2023-06-07 22:26 | 0.24 | 0.13 | 0.16 | 0.21 | -0.08 | NA |
| 2023-06-07 22:36 | 25.29 | 0.09 | 25.97 | 0.12 | 0.68 | 2.69 |
| 2023-06-07 22:46 | 75.25 | 0.06 | 76.43 | 0.07 | 1.18 | 1.57 |
| 2023-06-07 22:56 | 200.27 | 0.10 | 202.87 | 0.37 | 2.60 | 1.30 |
| 2023-06-07 23:06 | 100.19 | 0.09 | 101.56 | 0.28 | 1.37 | 1.37 |
| 2023-06-07 23:16 | 50.18 | 0.03 | 51.07 | 0.13 | 0.89 | 1.77 |
| 2023-06-07 23:26 | 250.28 | 0.08 | 253.22 | 0.22 | 2.94 | 1.17 |
| 2023-06-07 23:36 | 150.27 | 0.06 | 152.12 | 0.19 | 1.85 | 1.23 |
| 2023-06-07 23:46 | 0.20 | 0.17 | 0.21 | 0.12 | 0.01 | NA |
| 2023-06-07 23:56 | 25.27 | 0.11 | 25.90 | 0.15 | 0.63 | 2.49 |
| 2023-06-08 00:06 | 200.30 | 0.04 | 202.68 | 0.19 | 2.38 | 1.19 |
| 2023-06-08 00:16 | 150.21 | 0.11 | 152.31 | 0.04 | 2.10 | 1.40 |
| 2023-06-08 00:26 | 100.20 | 0.04 | 101.53 | 0.27 | 1.33 | 1.33 |
| 2023-06-08 00:36 | 50.18 | 0.13 | 51.05 | 0.47 | 0.87 | 1.73 |
| 2023-06-08 00:46 | 75.25 | 0.11 | 76.39 | 0.23 | 1.14 | 1.51 |
| 2023-06-08 00:56 | 250.29 | 0.11 | 252.91 | 0.25 | 2.62 | 1.05 |
| 2023-06-08 01:06 | 0.29 | 0.16 | 0.20 | 0.16 | -0.09 | NA |
| 2023-06-08 01:16 | 250.30 | 0.06 | 253.15 | 0.21 | 2.85 | 1.14 |
| 2023-06-08 01:26 | 200.25 | 0.10 | 202.52 | 0.17 | 2.27 | 1.13 |

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OA (nmol mol$^{-1}$) | sdOA (nmol mol$^{-1}$) | OA-TS (nmol mol$^{-1}$) | OA-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-08 01:36 | 100.19 | 0.08 | 101.65 | 0.08 | 1.46 | 1.46 |
| 2023-06-08 01:46 | 25.17 | 0.09 | 25.75 | 0.20 | 0.58 | 2.30 |
| 2023-06-08 01:56 | 150.25 | 0.13 | 152.34 | 0.25 | 2.09 | 1.39 |
| 2023-06-08 02:06 | 50.24 | 0.09 | 51.12 | 0.35 | 0.88 | 1.75 |
| 2023-06-08 02:16 | 75.22 | 0.08 | 76.60 | 0.23 | 1.38 | 1.83 |
| 2023-06-08 02:26 | 0.37 | 0.30 | 0.37 | 0.16 | 0.00 | NA |
| 2023-06-08 02:36 | 25.27 | 0.06 | 25.79 | 0.13 | 0.52 | 2.06 |
| 2023-06-08 02:46 | 75.18 | 0.07 | 76.24 | 0.32 | 1.06 | 1.41 |
| 2023-06-08 02:56 | 200.25 | 0.10 | 202.71 | 0.18 | 2.46 | 1.23 |
| 2023-06-08 03:06 | 100.24 | 0.03 | 101.76 | 0.13 | 1.52 | 1.52 |
| 2023-06-08 03:16 | 50.26 | 0.07 | 50.96 | 0.33 | 0.70 | 1.39 |
| 2023-06-08 03:26 | 250.30 | 0.11 | 253.32 | 0.22 | 3.02 | 1.21 |
| 2023-06-08 03:36 | 150.25 | 0.10 | 152.20 | 0.26 | 1.95 | 1.30 |
| 2023-06-08 03:46 | 0.50 | 0.14 | 0.17 | 0.13 | -0.33 | NA |
| 2023-06-08 03:56 | 25.26 | 0.10 | 25.92 | 0.13 | 0.66 | 2.61 |
| 2023-06-08 04:06 | 200.25 | 0.08 | 202.70 | 0.31 | 2.45 | 1.22 |
| 2023-06-08 04:16 | 150.22 | 0.07 | 152.18 | 0.37 | 1.96 | 1.30 |
| 2023-06-08 04:26 | 100.15 | 0.09 | 101.33 | 0.26 | 1.18 | 1.18 |
| 2023-06-08 04:36 | 50.28 | 0.05 | 51.10 | 0.14 | 0.82 | 1.63 |
| 2023-06-08 04:46 | 75.24 | 0.06 | 76.48 | 0.08 | 1.24 | 1.65 |
| 2023-06-08 04:56 | 250.28 | 0.04 | 253.11 | 0.10 | 2.83 | 1.13 |
| 2023-06-08 05:06 | 0.16 | 0.10 | 0.06 | 0.15 | -0.10 | NA |
| 2023-06-08 05:16 | 250.30 | 0.10 | 253.15 | 0.20 | 2.85 | 1.14 |
| 2023-06-08 05:26 | 200.28 | 0.05 | 202.48 | 0.13 | 2.20 | 1.10 |
| 2023-06-08 05:36 | 100.24 | 0.06 | 101.41 | 0.22 | 1.17 | 1.17 |
| 2023-06-08 05:46 | 25.23 | 0.13 | 25.61 | 0.24 | 0.38 | 1.51 |
| 2023-06-08 05:56 | 150.27 | 0.06 | 152.00 | 0.24 | 1.73 | 1.15 |
| 2023-06-08 06:06 | 50.23 | 0.14 | 51.06 | 0.26 | 0.83 | 1.65 |
| 2023-06-08 06:16 | 75.20 | 0.11 | 76.30 | 0.23 | 1.10 | 1.46 |
| 2023-06-08 06:26 | 0.38 | 0.19 | 0.24 | 0.17 | -0.14 | NA |
| 2023-06-08 06:36 | 25.22 | 0.15 | 25.70 | 0.14 | 0.48 | 1.90 |
| 2023-06-08 06:46 | 75.19 | 0.04 | 76.15 | 0.11 | 0.96 | 1.28 |
| 2023-06-08 06:56 | 200.29 | 0.09 | 202.48 | 0.23 | 2.19 | 1.09 |
| 2023-06-08 07:06 | 100.24 | 0.06 | 101.59 | 0.33 | 1.35 | 1.35 |
| 2023-06-08 07:16 | 50.17 | 0.09 | 51.13 | 0.17 | 0.96 | 1.91 |
| 2023-06-08 07:26 | 250.31 | 0.04 | 253.09 | 0.14 | 2.78 | 1.11 |
| 2023-06-08 07:36 | 150.22 | 0.10 | 151.94 | 0.25 | 1.72 | 1.14 |
| 2023-06-08 07:46 | 0.38 | 0.14 | 0.22 | 0.20 | -0.16 | NA |
| 2023-06-08 07:56 | 25.20 | 0.11 | 25.73 | 0.17 | 0.53 | 2.10 |
| 2023-06-08 08:06 | 200.27 | 0.08 | 202.62 | 0.27 | 2.35 | 1.17 |
| 2023-06-08 08:16 | 150.25 | 0.08 | 152.01 | 0.17 | 1.76 | 1.17 |
| 2023-06-08 08:26 | 100.25 | 0.15 | 101.68 | 0.22 | 1.43 | 1.43 |

***Table 4.*** *Comparison of the IZO ozone analyser (OA) Thermo Scientific 49i #12218618528 (BKG 0.0 nmol mol$^{-1}$, COEF 1.010) with the bias corrected WCC-Empa travelling standard (TS).*

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OA (nmol mol$^{-1}$) | sdOA (nmol mol$^{-1}$) | OA-TS (nmol mol$^{-1}$) | OA-TS (%) |
|---|---:|---:|---:|---:|---:|---:|
| 2023-06-07 19:46 | 0.22 | 0.09 | 1.43 | 0.77 | 1.21 | NA |
| 2023-06-07 19:56 | 25.19 | 0.07 | 26.96 | 1.12 | 1.77 | 7.03 |
| 2023-06-07 20:06 | 200.28 | 0.06 | 204.87 | 1.54 | 4.59 | 2.29 |
| 2023-06-07 20:16 | 150.21 | 0.15 | 152.72 | 1.53 | 2.51 | 1.67 |
| 2023-06-07 20:26 | 100.27 | 0.08 | 102.42 | 0.31 | 2.15 | 2.14 |
| 2023-06-07 20:36 | 50.25 | 0.07 | 51.04 | 0.86 | 0.79 | 1.57 |
| 2023-06-07 20:46 | 75.25 | 0.14 | 77.83 | 0.82 | 2.58 | 3.43 |
| 2023-06-07 20:56 | 250.27 | 0.03 | 254.87 | 0.33 | 4.60 | 1.84 |
| 2023-06-07 21:06 | 0.44 | 0.11 | 0.54 | 0.51 | 0.10 | NA |
| 2023-06-07 21:16 | 250.30 | 0.06 | 254.96 | 0.52 | 4.66 | 1.86 |
| 2023-06-07 21:26 | 200.29 | 0.07 | 203.99 | 0.85 | 3.70 | 1.85 |
| 2023-06-07 21:36 | 100.29 | 0.05 | 102.77 | 0.72 | 2.48 | 2.47 |
| 2023-06-07 21:46 | 25.21 | 0.05 | 25.68 | 0.61 | 0.47 | 1.86 |
| 2023-06-07 21:56 | 150.22 | 0.07 | 153.25 | 0.73 | 3.03 | 2.02 |
| 2023-06-07 22:06 | 50.24 | 0.09 | 51.52 | 0.47 | 1.28 | 2.55 |
| 2023-06-07 22:16 | 75.15 | 0.09 | 76.96 | 0.35 | 1.81 | 2.41 |
| 2023-06-07 22:26 | 0.24 | 0.13 | 0.28 | 0.18 | 0.04 | NA |
| 2023-06-07 22:36 | 25.29 | 0.09 | 25.89 | 0.30 | 0.60 | 2.37 |
| 2023-06-07 22:46 | 75.25 | 0.06 | 77.25 | 0.11 | 2.00 | 2.66 |
| 2023-06-07 22:56 | 200.27 | 0.10 | 203.79 | 0.20 | 3.52 | 1.76 |
| 2023-06-07 23:06 | 100.19 | 0.09 | 101.87 | 0.46 | 1.68 | 1.68 |
| 2023-06-07 23:16 | 50.18 | 0.03 | 51.53 | 0.59 | 1.35 | 2.69 |
| 2023-06-07 23:26 | 250.28 | 0.08 | 255.09 | 0.71 | 4.81 | 1.92 |
| 2023-06-07 23:36 | 150.27 | 0.06 | 153.15 | 0.63 | 2.88 | 1.92 |
| 2023-06-07 23:46 | 0.20 | 0.17 | -0.07 | 0.37 | -0.27 | NA |
| 2023-06-07 23:56 | 25.27 | 0.11 | 25.51 | 0.40 | 0.24 | 0.95 |
| 2023-06-08 00:06 | 200.30 | 0.04 | 203.93 | 0.36 | 3.63 | 1.81 |
| 2023-06-08 00:16 | 150.21 | 0.11 | 153.33 | 0.64 | 3.12 | 2.08 |
| 2023-06-08 00:26 | 100.20 | 0.04 | 102.87 | 0.37 | 2.67 | 2.66 |
| 2023-06-08 00:36 | 50.18 | 0.13 | 52.00 | 0.87 | 1.82 | 3.63 |
| 2023-06-08 00:46 | 75.25 | 0.11 | 76.83 | 0.32 | 1.58 | 2.10 |
| 2023-06-08 00:56 | 250.29 | 0.11 | 254.47 | 0.38 | 4.18 | 1.67 |
| 2023-06-08 01:06 | 0.29 | 0.16 | -0.05 | 1.07 | -0.34 | NA |
| 2023-06-08 01:16 | 250.30 | 0.06 | 255.84 | 0.74 | 5.54 | 2.21 |
| 2023-06-08 01:26 | 200.25 | 0.10 | 204.23 | 0.90 | 3.98 | 1.99 |
| 2023-06-08 01:36 | 100.19 | 0.08 | 101.93 | 0.94 | 1.74 | 1.74 |
| 2023-06-08 01:46 | 25.17 | 0.09 | 24.71 | 0.35 | -0.46 | -1.83 |
| 2023-06-08 01:56 | 150.25 | 0.13 | 153.29 | 0.69 | 3.04 | 2.02 |
| 2023-06-08 02:06 | 50.24 | 0.09 | 51.66 | 1.68 | 1.42 | 2.83 |
| 2023-06-08 02:16 | 75.22 | 0.08 | 76.70 | 0.42 | 1.48 | 1.97 |
| 2023-06-08 02:26 | 0.37 | 0.30 | 0.21 | 0.51 | -0.16 | NA |
| 2023-06-08 02:36 | 25.27 | 0.06 | 24.49 | 0.43 | -0.78 | -3.09 |
| 2023-06-08 02:46 | 75.18 | 0.07 | 76.95 | 0.57 | 1.77 | 2.35 |
| 2023-06-08 02:56 | 200.25 | 0.10 | 203.45 | 0.93 | 3.20 | 1.60 |
| 2023-06-08 03:06 | 100.24 | 0.03 | 102.86 | 0.56 | 2.62 | 2.61 |
| 2023-06-08 03:16 | 50.26 | 0.07 | 51.70 | 0.15 | 1.44 | 2.87 |
| 2023-06-08 03:26 | 250.30 | 0.11 | 254.73 | 0.35 | 4.43 | 1.77 |
| 2023-06-08 03:36 | 150.25 | 0.10 | 153.14 | 0.54 | 2.89 | 1.92 |

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OA (nmol mol$^{-1}$) | sdOA (nmol mol$^{-1}$) | OA-TS (nmol mol$^{-1}$) | OA-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-08 03:46 | 0.50 | 0.14 | 0.16 | 0.51 | -0.34 | NA |
| 2023-06-08 03:56 | 25.26 | 0.10 | 26.05 | 0.62 | 0.79 | 3.13 |
| 2023-06-08 04:06 | 200.25 | 0.08 | 204.64 | 0.34 | 4.39 | 2.19 |
| 2023-06-08 04:16 | 150.22 | 0.07 | 152.83 | 0.47 | 2.61 | 1.74 |
| 2023-06-08 04:26 | 100.15 | 0.09 | 102.20 | 0.54 | 2.05 | 2.05 |
| 2023-06-08 04:36 | 50.28 | 0.05 | 51.43 | 1.18 | 1.15 | 2.29 |
| 2023-06-08 04:46 | 75.24 | 0.06 | 77.80 | 0.70 | 2.56 | 3.40 |
| 2023-06-08 04:56 | 250.28 | 0.04 | 254.74 | 0.47 | 4.46 | 1.78 |
| 2023-06-08 05:06 | 0.16 | 0.10 | 0.38 | 0.53 | 0.22 | NA |
| 2023-06-08 05:16 | 250.30 | 0.10 | 255.05 | 0.49 | 4.75 | 1.90 |
| 2023-06-08 05:26 | 200.28 | 0.05 | 203.63 | 0.21 | 3.35 | 1.67 |
| 2023-06-08 05:36 | 100.24 | 0.06 | 101.98 | 0.36 | 1.74 | 1.74 |
| 2023-06-08 05:46 | 25.23 | 0.13 | 25.67 | 0.39 | 0.44 | 1.74 |
| 2023-06-08 05:56 | 150.27 | 0.06 | 153.10 | 0.61 | 2.83 | 1.88 |
| 2023-06-08 06:06 | 50.23 | 0.14 | 51.84 | 0.45 | 1.61 | 3.21 |
| 2023-06-08 06:16 | 75.20 | 0.11 | 76.37 | 0.58 | 1.17 | 1.56 |
| 2023-06-08 06:26 | 0.38 | 0.19 | 0.01 | 0.46 | -0.37 | NA |
| 2023-06-08 06:36 | 25.22 | 0.15 | 25.71 | 1.33 | 0.49 | 1.94 |
| 2023-06-08 06:46 | 75.19 | 0.04 | 76.69 | 1.00 | 1.50 | 1.99 |
| 2023-06-08 06:56 | 200.29 | 0.09 | 204.87 | 0.50 | 4.58 | 2.29 |
| 2023-06-08 07:06 | 100.24 | 0.06 | 101.74 | 0.71 | 1.50 | 1.50 |
| 2023-06-08 07:16 | 50.17 | 0.09 | 51.53 | 0.83 | 1.36 | 2.71 |
| 2023-06-08 07:26 | 250.31 | 0.04 | 253.61 | 0.52 | 3.30 | 1.32 |
| 2023-06-08 07:36 | 150.22 | 0.10 | 153.47 | 0.79 | 3.25 | 2.16 |
| 2023-06-08 07:46 | 0.38 | 0.14 | 0.00 | 0.57 | -0.38 | NA |
| 2023-06-08 07:56 | 25.20 | 0.11 | 25.76 | 0.20 | 0.56 | 2.22 |
| 2023-06-08 08:06 | 200.27 | 0.08 | 204.60 | 1.01 | 4.33 | 2.16 |
| 2023-06-08 08:16 | 150.25 | 0.08 | 152.95 | 0.83 | 2.70 | 1.80 |
| 2023-06-08 08:26 | 100.25 | 0.15 | 102.38 | 0.86 | 2.13 | 2.12 |

***Table 5.*** *Comparison of the IZO ozone analyser (OA) Thermo Scientific 49i #12218618529 (BKG 0.0 nmol mol$^{-1}$, COEF 1.008) with the bias corrected WCC-Empa travelling standard (TS).*

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OA (nmol mol$^{-1}$) | sdOA (nmol mol$^{-1}$) | OA-TS (nmol mol$^{-1}$) | OA-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-08 09:16 | 0.35 | 0.22 | -0.80 | 0.17 | -1.15 | NA |
| 2023-06-08 09:26 | 50.17 | 0.09 | 49.85 | 0.26 | -0.32 | -0.64 |
| 2023-06-08 09:36 | 200.28 | 0.05 | 201.31 | 0.11 | 1.03 | 0.51 |
| 2023-06-08 09:46 | 150.30 | 0.09 | 151.33 | 0.21 | 1.03 | 0.69 |
| 2023-06-08 09:56 | 100.17 | 0.07 | 100.69 | 0.12 | 0.52 | 0.52 |
| 2023-06-08 10:06 | 250.30 | 0.07 | 251.99 | 0.15 | 1.69 | 0.68 |
| 2023-06-08 10:16 | 0.44 | 0.12 | -0.35 | 0.38 | -0.79 | NA |
| 2023-06-08 10:26 | 250.26 | 0.08 | 252.23 | 0.28 | 1.97 | 0.79 |
| 2023-06-08 10:36 | 100.18 | 0.04 | 100.78 | 0.13 | 0.60 | 0.60 |
| 2023-06-08 10:46 | 150.24 | 0.10 | 151.21 | 0.24 | 0.97 | 0.65 |
| 2023-06-08 10:56 | 200.32 | 0.08 | 201.77 | 0.33 | 1.45 | 0.72 |
| 2023-06-08 11:06 | 50.18 | 0.06 | 50.48 | 0.24 | 0.30 | 0.60 |
| 2023-06-08 11:16 | 0.29 | 0.09 | -0.39 | 0.15 | -0.68 | NA |

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OA (nmol mol$^{-1}$) | sdOA (nmol mol$^{-1}$) | OA-TS (nmol mol$^{-1}$) | OA-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-08 11:26 | 150.23 | 0.10 | 151.46 | 0.18 | 1.23 | 0.82 |
| 2023-06-08 11:36 | 50.19 | 0.08 | 50.45 | 0.29 | 0.26 | 0.52 |
| 2023-06-08 11:46 | 250.27 | 0.06 | 252.74 | 0.16 | 2.47 | 0.99 |
| 2023-06-08 11:56 | 200.26 | 0.09 | 202.05 | 0.24 | 1.79 | 0.89 |
| 2023-06-08 12:06 | 100.26 | 0.06 | 100.97 | 0.20 | 0.71 | 0.71 |

***Table 6.*** *Comparison of the IZO ozone calibrator (OC) Thermo Scientific 49i-PS # CM22277105 (BKG -0.4 nmol mol$^{-1}$, COEF 1.003) with the bias corrected WCC-Empa travelling standard (TS).*

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OC (nmol mol$^{-1}$) | sdOC (nmol mol$^{-1}$) | OC-TS (nmol mol$^{-1}$) | OC-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-06 21:31 | 0.59 | 0.12 | 0.30 | 0.20 | -0.29 | NA |
| 2023-06-06 21:41 | 250.24 | 0.06 | 250.07 | 0.11 | -0.17 | -0.07 |
| 2023-06-06 21:51 | 200.26 | 0.09 | 200.16 | 0.16 | -0.10 | -0.05 |
| 2023-06-06 22:01 | 100.25 | 0.09 | 100.22 | 0.20 | -0.03 | -0.03 |
| 2023-06-06 22:11 | 25.22 | 0.09 | 25.20 | 0.24 | -0.02 | -0.08 |
| 2023-06-06 22:21 | 150.23 | 0.05 | 150.25 | 0.27 | 0.02 | 0.01 |
| 2023-06-06 22:31 | 50.19 | 0.04 | 50.31 | 0.11 | 0.12 | 0.24 |
| 2023-06-06 22:41 | 75.22 | 0.03 | 75.14 | 0.13 | -0.08 | -0.11 |
| 2023-06-06 22:51 | 0.42 | 0.24 | 0.23 | 0.17 | -0.19 | NA |
| 2023-06-06 23:01 | 25.19 | 0.18 | 25.09 | 0.43 | -0.10 | -0.40 |
| 2023-06-06 23:11 | 75.19 | 0.14 | 74.90 | 0.25 | -0.29 | -0.39 |
| 2023-06-06 23:21 | 200.29 | 0.11 | 200.06 | 0.30 | -0.23 | -0.11 |
| 2023-06-06 23:31 | 100.23 | 0.12 | 100.03 | 0.29 | -0.20 | -0.20 |
| 2023-06-06 23:41 | 50.14 | 0.07 | 50.03 | 0.20 | -0.11 | -0.22 |
| 2023-06-06 23:51 | 250.35 | 0.09 | 250.30 | 0.30 | -0.05 | -0.02 |
| 2023-06-07 00:01 | 150.26 | 0.07 | 150.16 | 0.27 | -0.10 | -0.07 |
| 2023-06-07 00:11 | 0.48 | 0.06 | 0.19 | 0.12 | -0.29 | NA |
| 2023-06-07 00:21 | 25.24 | 0.15 | 25.14 | 0.15 | -0.10 | -0.40 |
| 2023-06-07 00:31 | 200.30 | 0.12 | 200.18 | 0.35 | -0.12 | -0.06 |
| 2023-06-07 00:41 | 150.20 | 0.05 | 150.30 | 0.39 | 0.10 | 0.07 |
| 2023-06-07 00:51 | 100.26 | 0.05 | 100.26 | 0.18 | 0.00 | 0.00 |
| 2023-06-07 01:01 | 50.16 | 0.07 | 50.09 | 0.19 | -0.07 | -0.14 |
| 2023-06-07 01:11 | 75.24 | 0.07 | 75.27 | 0.13 | 0.03 | 0.04 |
| 2023-06-07 01:21 | 250.37 | 0.13 | 250.41 | 0.08 | 0.04 | 0.02 |
| 2023-06-07 01:31 | 0.51 | 0.09 | 0.26 | 0.11 | -0.25 | NA |
| 2023-06-07 01:41 | 250.31 | 0.14 | 250.30 | 0.24 | -0.01 | 0.00 |
| 2023-06-07 01:51 | 200.25 | 0.15 | 200.29 | 0.21 | 0.04 | 0.02 |
| 2023-06-07 02:01 | 100.17 | 0.08 | 100.18 | 0.15 | 0.01 | 0.01 |
| 2023-06-07 02:11 | 25.26 | 0.13 | 25.13 | 0.07 | -0.13 | -0.51 |
| 2023-06-07 02:21 | 150.28 | 0.11 | 150.42 | 0.27 | 0.14 | 0.09 |
| 2023-06-07 02:31 | 50.21 | 0.06 | 50.12 | 0.15 | -0.09 | -0.18 |
| 2023-06-07 02:41 | 75.21 | 0.10 | 75.16 | 0.18 | -0.05 | -0.07 |
| 2023-06-07 02:51 | 0.53 | 0.23 | 0.33 | 0.13 | -0.20 | NA |
| 2023-06-07 03:01 | 25.22 | 0.07 | 25.05 | 0.13 | -0.17 | -0.67 |
| 2023-06-07 03:11 | 75.21 | 0.07 | 75.10 | 0.18 | -0.11 | -0.15 |
| 2023-06-07 03:21 | 200.28 | 0.10 | 200.47 | 0.24 | 0.19 | 0.09 |
| 2023-06-07 03:31 | 100.24 | 0.11 | 100.18 | 0.26 | -0.06 | -0.06 |

| Date – Time | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | OC (nmol mol$^{-1}$) | sdOC (nmol mol$^{-1}$) | OC-TS (nmol mol$^{-1}$) | OC-TS (%) |
|---|---|---|---|---|---|---|
| 2023-06-07 03:41 | 50.24 | 0.07 | 50.44 | 0.34 | 0.20 | 0.40 |
| 2023-06-07 03:51 | 250.27 | 0.07 | 250.69 | 0.20 | 0.42 | 0.17 |
| 2023-06-07 04:01 | 150.23 | 0.11 | 150.23 | 0.16 | 0.00 | 0.00 |
| 2023-06-07 04:11 | 0.40 | 0.18 | 0.42 | 0.20 | 0.02 | 5.00 |
| 2023-06-07 04:21 | 25.27 | 0.06 | 25.27 | 0.15 | 0.00 | 0.00 |
| 2023-06-07 04:31 | 200.28 | 0.08 | 200.58 | 0.26 | 0.30 | 0.15 |
| 2023-06-07 04:41 | 150.22 | 0.09 | 150.14 | 0.14 | -0.08 | -0.05 |
| 2023-06-07 04:51 | 100.22 | 0.09 | 100.09 | 0.31 | -0.13 | -0.13 |
| 2023-06-07 05:01 | 50.27 | 0.13 | 50.12 | 0.19 | -0.15 | -0.30 |
| 2023-06-07 05:11 | 75.22 | 0.07 | 75.17 | 0.13 | -0.05 | -0.07 |
| 2023-06-07 05:21 | 250.30 | 0.12 | 250.45 | 0.35 | 0.15 | 0.06 |
| 2023-06-07 05:31 | 0.45 | 0.22 | 0.47 | 0.15 | 0.02 | NA |
| 2023-06-07 05:41 | 250.33 | 0.06 | 250.28 | 0.18 | -0.05 | -0.02 |
| 2023-06-07 05:51 | 200.25 | 0.04 | 200.40 | 0.33 | 0.15 | 0.07 |
| 2023-06-07 06:01 | 100.27 | 0.09 | 100.20 | 0.24 | -0.07 | -0.07 |
| 2023-06-07 06:11 | 25.29 | 0.13 | 25.43 | 0.18 | 0.14 | 0.55 |
| 2023-06-07 06:21 | 150.26 | 0.07 | 150.20 | 0.22 | -0.06 | -0.04 |
| 2023-06-07 06:31 | 50.26 | 0.08 | 50.02 | 0.20 | -0.24 | -0.48 |
| 2023-06-07 06:41 | 75.19 | 0.04 | 75.34 | 0.31 | 0.15 | 0.20 |
| 2023-06-07 06:51 | 0.47 | 0.19 | 0.28 | 0.11 | -0.19 | NA |
| 2023-06-07 07:01 | 25.25 | 0.06 | 25.10 | 0.06 | -0.15 | -0.59 |
| 2023-06-07 07:11 | 75.20 | 0.09 | 74.92 | 0.27 | -0.28 | -0.37 |
| 2023-06-07 07:21 | 200.29 | 0.08 | 200.36 | 0.39 | 0.07 | 0.03 |
| 2023-06-07 07:31 | 100.22 | 0.02 | 100.09 | 0.21 | -0.13 | -0.13 |
| 2023-06-07 07:41 | 50.20 | 0.22 | 50.66 | 0.53 | 0.46 | 0.92 |
| 2023-06-07 07:51 | 250.32 | 0.12 | 250.60 | 0.15 | 0.28 | 0.11 |
| 2023-06-07 08:01 | 150.26 | 0.05 | 150.43 | 0.26 | 0.17 | 0.11 |

## A4. Calibration Standards for CO, $CH_4$, $CO_2$ and $N_2O$

Table 7 provides an overview the CCL (NOAA) and the ICOS Flask and Calibration Laboratory standard gases available for calibration of the CO, $CH_4$, $CO_2$ and $N_2O$ instruments.

***Table 7*** *IZO calibration standards as of June 2023.*

| Cylinder ID | $N_2O$ (X2006A) (nmol mol$^{-1}$) | CO (X2014A) (nmol mol$^{-1}$) | $CH_4$ (X2004A) (nmol mol$^{-1}$) | $CO_2$ (X2007*) (µmol mol$^{-1}$) | Usage |
|---|---|---|---|---|---|
| CB11240 | NA | 193.45 | 1978.30 | 436.58 | NOAA standard, Picarro G2401 |
| CB11340 | NA | 112.55 | 1766.20 | 377.17 | NOAA standard, Picarro G2401 |
| CB11389 | NA | 96.54 | 1648.73 | 340.40 | NOAA standard, Picarro G2401 |
| CB11393 | NA | 158.22 | 1854.82 | 405.23 | NOAA standard, Picarro G2401 |
| CA08273 | 285.96 | 64.71 | NA | NA | NOAA standard, Los Gatos |
| CA06479 | 315.78 | 92.48 | NA | NA | NOAA standard, Los Gatos |
| CC499063 | 337.89 | 126.31 | NA | NA | NOAA standard, Los Gatos |
| CC506419 | 357.51 | 161.16 | NA | NA | NOAA standard, Los Gatos |
| CB10964 | NA | 485.17 | NA | NA | NOAA standard, Los Gatos |
| CA06996 | 306.01 | NA | NA | NA | NOAA standard, Agilent GC |
| CA06970 | 330.21 | NA | NA | NA | NOAA standard, Agilent GC |
| CA08203 | 321.59 | NA | NA | NA | NOAA standard, Agilent GC |
| CA06964 | 357.01 | NA | NA | NA | NOAA standard, Agilent GC |
| CB10914 | 336.92 | NA | NA | NA | NOAA standard, Agilent GC |
| CA06988 | NA | 127.24 | NA | NA | NOAA standard, CO drift correction |
| CA06978 | NA | 227.41 | NA | NA | NOAA standard, CO drift correction |
| CA06946 | NA | 102.97 | NA | NA | NOAA standard, CO drift correction |
| CA06968 | NA | 171.31 | NA | NA | NOAA standard, CO drift correction |
| CA06768 | NA | 66.13 | NA | NA | NOAA standard, CO drift correction |
| 7996 | 327.337 | 60.38 | 1855.57 | 394.04 | ICOS standard, ICOS instruments |
| 7997 | 335.111 | 100.2 | 1907.61 | 417.433 | ICOS standard, ICOS instruments |
| 7998 | 339.978 | 171.77 | 2008.86 | 435.142 | ICOS standard, ICOS instruments |
| 7999 | 346.924 | 247.28 | 2138.89 | 464.985 | ICOS standard, ICOS instruments |

## A5. Carbon Monoxide Comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before and after the audit. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA are given further below.

Table 8 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation were recorded by the IZO data acquisition system.

***Table 8.*** *Experimental details of the IZO comparison.*

| | |
|---|---|
| *Travelling standard (TS)* | |
| WCC-Empa travelling standards (6 l aluminium cylinders containing a mixture of natural and synthetic air). The assigned values and standard uncertainties are given in Table 17. | |
| *Station analyser (CO, $CH_4$, $CO_2$)* | |
| Model, S/N | Picarro G2401 #2352-CFKADS2196 |
| Principle | Near-IR CRDS |
| Drying system | Cryo trap |
| *Station analyser (CO, $N_2O$)* | |
| Model, S/N | LGR 913-0015 SN US430000170700001433 |
| Principle | OA-ICOS |
| Drying system | Cryo trap |
| *Comparison procedure* | |
| Connection | WCC-Empa TS were connected to spare calibration gas ports. |

### Results

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

***Table 9.*** *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2352-CFKADS2196 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

| Date / Time | TS Cylinder | TS (nmol mol-1) | sdTS (nmol mol-1) | AL (nmol mol-1) | sdAL (nmol mol-1) | N | AL-TS (nmol mol-1) | AL-TS (%) |
|---|---|---|---|---|---|---|---|---|
| (23-06-08 01:43:00) | 220927_FA01469 | 123.7 | 0.8 | 123.0 | 0.4 | 4 | -0.8 | -0.6 |
| (23-06-08 01:13:00) | 150819_FA02464 | 173.9 | 1.4 | 174.1 | 0.1 | 4 | 0.2 | 0.1 |
| (23-06-13 00:01:00) | 160622_FA02474 | 243.5 | 1.0 | 242.6 | 0.2 | 4 | -1.0 | -0.4 |
| (23-06-08 00:13:00) | 171128_FA02476 | 156.0 | 1.0 | 155.3 | 0.1 | 4 | -0.8 | -0.5 |
| (23-06-13 00:31:00) | 150601_FA02493 | 1319.6 | 1.0 | 1318.9 | 1.0 | 4 | -0.7 | -0.1 |
| (23-06-12 23:31:00) | 220124_FA02773 | 0.2 | 0.5 | 6.5 | 0.3 | 4 | 6.3 | NA |
| (23-06-08 00:43:00) | 171122_FA02785 | 56.6 | 1.3 | 56.9 | 0.1 | 4 | 0.2 | 0.4 |
| (23-06-13 01:31:00) | 171124_FA02786 | 151.0 | 0.8 | 149.0 | 0.2 | 4 | -1.9 | -1.3 |
| (23-06-13 01:01:00) | 171122_FA02788 | 77.3 | 0.8 | 77.7 | 0.1 | 4 | 0.3 | 0.4 |
| (23-06-08 02:13:00) | 181128_FF61487 | 122.3 | 1.5 | 123.0 | 0.2 | 4 | 0.7 | 0.6 |

***Table 10.*** *CO aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the LGR 913-0015 SN US430000170700001433 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

| Date / Time | TS Cylinder | TS (nmol mol-1) | sdTS (nmol mol-1) | AL (nmol mol-1) | sdAL (nmol mol-1) | N | AL-TS (nmol mol-1) | AL-TS (%) |
|---|---|---|---|---|---|---|---|---|
| 23-06-14 00:08:43) 2 | 20927_FA01469 | 123.71 0 | 0.8 | 123.37 0 | .04 7 | - | 0.3 | -0.3 |
| (23-06-13 23:53:34) | 150819_FA02464 | 173.9 | 1.4 | 173.5 | 0.0 | 7 | -0.4 | -0.3 |
| (23-07-11 22:36:40) | 160622_FA02474 | 243.5 | 1.0 | 241.1 | 0.0 | 6 | -2.5 | -1.0 |
| (23-07-11 22:51:30) | 171128_FA02476 | 156.0 | 1.0 | 155.0 | 0.0 | 6 | -1.1 | -0.7 |
| (23-07-11 22:06:40) | 150601_FA02493 | 1319.6 | 1.0 | 1320.3 | 0.2 | 6 | 0.7 | 0.1 |
| (23-06-14 00:23:34) | 220124_FA02773 | 0.2 | 0.5 | 7.2 | 0.2 | 7 | 7.0 | NA |
| (23-06-13 23:38:43) | 171122_FA02785 | 56.6 | 1.3 | 58.9 | 0.1 | 7 | 2.3 | 4.0 |
| (23-07-11 23:06:40) | 171124_FA02786 | 151.0 | 0.8 | 149.4 | 0.0 | 6 | -1.5 | -1.0 |
| (23-07-11 22:21:30) | 171122_FA02788 | 77.3 | 0.8 | 78.9 | 0.1 | 6 | 1.6 | 2.0 |
| (23-06-13 23:23:43) | 181128_FF61487 | 122.3 | 1.5 | 123.4 | 0.0 | 7 | 1.1 | 0.9 |

## A6. Methane comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the WCC-Empa travelling standards before and after the audit. Details of the traceability of the travelling standards to the WMO/GAW reference standard at NOAA are given below.

Table 8 shows details of the experimental setup during the comparison of the travelling standard and the station analysers. The data used for the evaluation was recorded by the IZO data acquisition system. The standards used for the calibration of the IZO instruments are listed in Table 7.

**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 11.*** *$CH_4$ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2352-CFKADS2196 instrument (AL) with the WCC-Empa TS (WMO-X2004A $CH_4$ scale).*

| Date / Time | TS Cylinder | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | AL (nmol mol$^{-1}$) | sdAL (nmol mol$^{-1}$) | N | AL-TS (nmol mol$^{-1}$) | AL-TS (%) |
|---|---|---|---|---|---|---|---|---|
| (23-06-08 01:43:00) | 220927_FA01469 | 1971.46 | 0.01 | 1971.63 | 0.13 | 4 | 0.17 | 0.01 |
| (23-06-08 01:13:00) | 150819_FA02464 | 1965.89 | 0.02 | 1965.97 | 0.16 | 4 | 0.08 | 0.00 |
| (23-06-13 00:01:00) | 160622_FA02474 | 2506.82 | 0.07 | 2506.22 | 0.41 | 4 | -0.60 | -0.02 |
| (23-06-08 00:13:00) | 171128_FA02476 | 1860.15 | 0.05 | 1860.43 | 0.10 | 4 | 0.28 | 0.02 |
| (23-06-13 00:31:00) | 150601_FA02493 | 1868.06 | 0.03 | 1868.40 | 0.22 | 4 | 0.34 | 0.02 |
| (23-06-12 23:31:00) | 220124_FA02773 | 3.04 | 0.03 | 6.06 | 0.87 | 4 | 3.02 | NA |
| (23-06-08 00:43:00) | 171122_FA02785 | 1856.35 | 0.03 | 1856.44 | 0.16 | 4 | 0.09 | 0.00 |
| (23-06-13 01:31:00) | 171124_FA02786 | 2193.70 | 0.04 | 2193.59 | 0.11 | 4 | -0.11 | -0.01 |
| (23-06-13 01:01:00) | 171122_FA02788 | 1619.01 | 0.06 | 1619.67 | 0.23 | 4 | 0.66 | 0.04 |
| (23-06-08 02:13:00) | 181128_FF61487 | 1990.61 | 0.04 | 1990.56 | 0.20 | 4 | -0.05 | 0.00 |

## A7. Carbon dioxide comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the WCC-Empa travelling standards 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 8 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation were recorded by the IZO data acquisition system. The standards used to calibrate the IZO instrument are shown in Table 7.

**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.*** *$CO_2$ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the Picarro G2401 #2352-CFKADS2196 instrument (AL) with the WCC-Empa TS (WMO-X2019 $CO_2$ scale).*

| Date / Time | TS Cylinder | TS (µmol mol$^{-1}$) | sdTS (µmol mol$^{-1}$) | AL (µmol mol$^{-1}$) | sdAL (µmol mol$^{-1}$) | N | AL-TS (µmol mol$^{-1}$) | AL-TS (%) |
|---|---|---|---|---|---|---|---|---|
| (23-06-08 01:43:00) | 220927_FA01469 | 431.95 | 0.02 | 431.92 | 0.01 | 4 | -0.03 | -0.01 |
| (23-06-08 01:13:00) | 150819_FA02464 | 401.69 | 0.01 | 401.68 | 0.01 | 4 | -0.01 | 0.00 |
| (23-06-13 00:01:00) | 160622_FA02474 | 421.49 | 0.02 | 421.44 | 0.01 | 4 | -0.05 | -0.01 |
| (23-06-08 00:13:00) | 171128_FA02476 | 418.49 | 0.02 | 418.47 | 0.01 | 4 | -0.02 | 0.00 |
| (23-06-13 00:31:00) | 150601_FA02493 | 389.22 | 0.02 | 389.22 | 0.01 | 4 | 0.00 | 0.00 |
| (23-06-12 23:31:00) | 220124_FA02773 | 0.11 | 0.01 | 0.66 | 0.04 | 4 | 0.54 | NA |
| (23-06-08 00:43:00) | 171122_FA02785 | 408.46 | 0.01 | 408.42 | 0.01 | 4 | -0.04 | -0.01 |
| (23-06-13 01:31:00) | 171124_FA02786 | 468.51 | 0.01 | 468.41 | 0.01 | 4 | -0.10 | -0.02 |
| (23-06-13 01:01:00) | 171122_FA02788 | 337.27 | 0.02 | 337.34 | 0.02 | 4 | 0.07 | 0.02 |
| (23-06-08 02:13:00) | 181128_FF61487 | 398.43 | 0.03 | 398.38 | 0.02 | 4 | -0.05 | -0.01 |

***Table 13.*** *$CO_2$ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the LI-COR LI-7000 #IRG4-052 instrument (AL) with the WCC-Empa TS (WMO-X2019 $CO_2$ scale).*

| Date / Time | TS Cylinder | TS (µmol mol$^{-1}$) | sdTS (µmol mol$^{-1}$) | AL (µmol mol$^{-1}$) | sdAL (µmol mol$^{-1}$) | N | AL-TS (µmol mol$^{-1}$) | AL-TS (%) |
|---|---|---|---|---|---|---|---|---|
| (23-06-19 12:10:00) | 220927_FA01469 | 431.95 | 0.02 | 431.57 | 0.02 | 5 | -0.38 | -0.09 |
| (23-06-19 12:10:00) | 171128_FA02476 | 418.49 | 0.02 | 418.45 | 0.02 | 5 | -0.04 | -0.01 |
| (23-06-19 12:10:00) | 171124_FA02786 | 468.51 | 0.01 | 468.59 | 0.20 | 5 | 0.08 | 0.02 |
| (23-06-19 12:10:00) | 171122_FA02788 | 337.27 | 0.02 | 337.93 | 0.52 | 5 | 0.66 | 0.20 |
| (23-06-19 12:10:00) | 181128_FF61487 | 398.43 | 0.03 | 398.37 | 0.03 | 5 | -0.06 | -0.02 |

## A8. Nitrous oxide comparisons

All procedures were carried out in accordance with the Standard Operating Procedure (WMO, 2007) and included comparisons of the WCC-Empa travelling standards 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 8 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation were recorded by the IZO data acquisition system. The standards used to calibrate the IZO instrument are shown in Table 7.

**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.*** *$N_2O$ aggregates calculated from individual analyses (mean and standard deviation of the mean) for each level during the comparison of the LGR 913-0015 SN US430000170700001433 instrument (AL) with the WCC-Empa TS (WMO-X2006A $N_2O$ scale).*

| Date / Time | TS Cylinder | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) | AL (µmol mol$^{-1}$) | sdAL (nmol mol$^{-1}$) | N | AL-TS (nmol mol$^{-1}$) | AL-TS (%) |
|---|---|---|---|---|---|---|---|---|
| (23-06-13 23:23:43) | 181128_FF61487 | 342.83 | 0.04 | 342.87 | 0.02 | 7 | 0.04 | 0.01 |
| (23-06-13 23:38:43) | 171122_FA02785 | 341.84 | 0.05 | 341.86 | 0.04 | 7 | 0.02 | 0.01 |
| (23-06-13 23:53:34) | 150819_FA02464 | 329.12 | 0.03 | 329.11 | 0.07 | 7 | -0.01 | 0.00 |
| (23-06-14 00:08:43) | 220927_FA01469 | 334.35 | 0.06 | 334.34 | 0.05 | 7 | -0.01 | 0.00 |
| (23-07-11 22:06:40) | 150601_FA02493 | 319.93 | 0.03 | 319.94 | 0.03 | 6 | 0.01 | 0.00 |
| (23-07-11 22:21:30) | 171122_FA02788 | 283.94 | 0.14 | 283.87 | 0.03 | 6 | -0.07 | -0.02 |
| (23-07-11 22:36:40) | 160622_FA02474 | 324.48 | 0.01 | 324.46 | 0.03 | 6 | -0.02 | -0.01 |
| (23-07-11 22:51:30) | 171128_FA02476 | 322.53 | 0.02 | 322.58 | 0.04 | 6 | 0.05 | 0.02 |
| (23-07-11 23:06:40) | 171124_FA02786 | 377.81 | 0.05 | 377.76 | 0.05 | 6 | -0.05 | -0.01 |

## A9. WCC-Empa ozone traveling standard

The WCC-Empa Travelling Standard (TS) was compared with the standard reference photometer before and after the audit. The instruments used were

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

WCC-Empa TS: Thermo Scientific 49i-PS #CM22117100, BKG 0.0, COEF 1.009

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

The results of the TS calibration before and after the audit are shown in Table 15. The TS passed the pre-audit evaluation criteria defined for maximum acceptable bias (Klausen et al., 2003) (see Figure 28). The data were pooled and evaluated by linear regression analysis, taking into account the uncertainties of both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be calculated (equation 6a). The uncertainty of the TS (Equation 6b) was previously estimated (see equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (nmol mol}^{-1}\text{)} = ([TS] + 0.19 \text{ nmol mol}^{-1}) / 0.9997 \quad (21)$$

$$u_{TS} \text{ (nmol mol}^{-1}\text{)} = \text{sqrt}((0.43 \text{ nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (22)$$

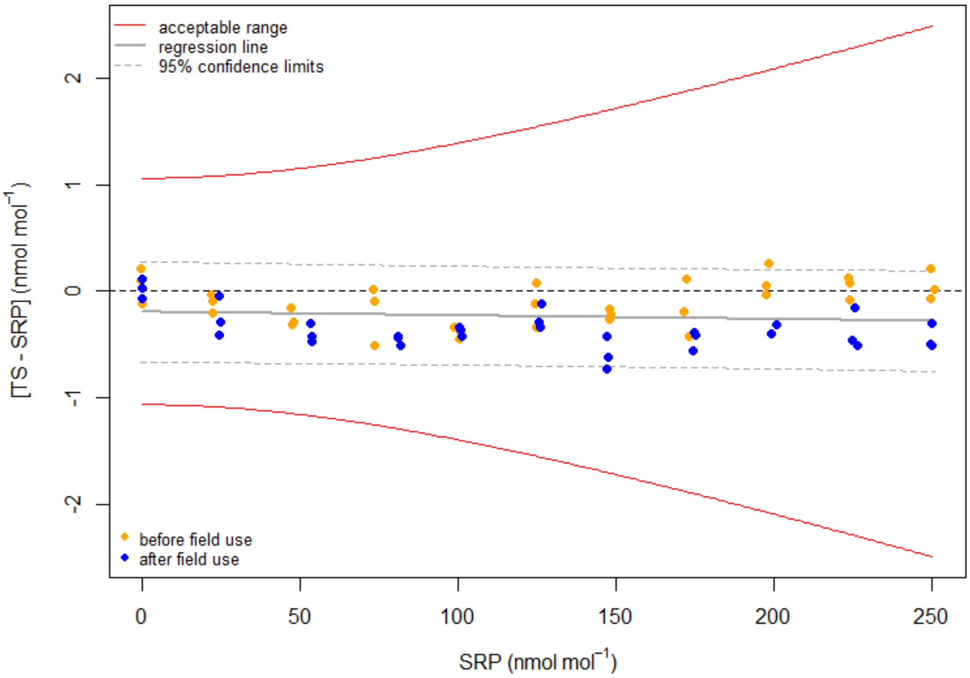


***Figure 28.*** *Deviations between Traveling Standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS in the field.*

***Table 15***. *Mean values calculated over at least five minutes for the comparison of the WCC-Empa Traveling Standard (TS) with the Standard Reference Photometer (SRP).*

| Date | Run | Level# | SRP (nmol mol$^{-1}$) | sdSRP (nmol mol$^{-1}$) | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 2023-03-14 | 1 | 170 | 171.59 | 0.18 | 171.40 | 0.19 |
| 2023-03-14 | 1 | 225 | 223.81 | 0.36 | 223.73 | 0.14 |
| 2023-03-14 | 1 | 20 | 22.22 | 0.45 | 22.02 | 0.21 |
| 2023-03-14 | 1 | 100 | 98.95 | 0.39 | 98.61 | 0.08 |
| 2023-03-14 | 1 | 0 | 0.07 | 0.20 | -0.05 | 0.13 |
| 2023-03-14 | 1 | 50 | 47.83 | 0.23 | 47.54 | 0.18 |
| 2023-03-14 | 1 | 150 | 147.79 | 0.18 | 147.53 | 0.17 |
| 2023-03-14 | 1 | 125 | 124.89 | 0.21 | 124.96 | 0.13 |
| 2023-03-14 | 1 | 250 | 249.42 | 0.26 | 249.36 | 0.18 |
| 2023-03-14 | 1 | 75 | 73.08 | 0.33 | 73.10 | 0.21 |
| 2023-03-14 | 1 | 195 | 197.40 | 0.24 | 197.45 | 0.17 |
| 2023-03-14 | 2 | 45 | 47.38 | 0.41 | 47.07 | 0.25 |
| 2023-03-14 | 2 | 150 | 148.30 | 0.26 | 148.09 | 0.12 |
| 2023-03-14 | 2 | 125 | 124.29 | 0.29 | 124.17 | 0.13 |
| 2023-03-14 | 2 | 195 | 197.40 | 0.11 | 197.37 | 0.25 |
| 2023-03-14 | 2 | 175 | 173.21 | 0.21 | 172.79 | 0.22 |
| 2023-03-14 | 2 | 75 | 73.44 | 0.45 | 72.93 | 0.13 |
| 2023-03-14 | 2 | 20 | 22.33 | 0.28 | 22.24 | 0.18 |
| 2023-03-14 | 2 | 0 | -0.16 | 0.34 | 0.06 | 0.10 |
| 2023-03-14 | 2 | 250 | 249.44 | 0.23 | 249.65 | 0.23 |
| 2023-03-14 | 2 | 100 | 100.71 | 0.19 | 100.32 | 0.24 |
| 2023-03-14 | 2 | 225 | 223.35 | 0.28 | 223.48 | 0.19 |
| 2023-03-14 | 3 | 45 | 47.15 | 0.33 | 47.00 | 0.20 |
| 2023-03-14 | 3 | 170 | 172.10 | 0.18 | 172.21 | 0.17 |
| 2023-03-14 | 3 | 125 | 124.90 | 0.29 | 124.57 | 0.13 |
| 2023-03-14 | 3 | 225 | 223.66 | 0.29 | 223.74 | 0.16 |
| 2023-03-14 | 3 | 200 | 198.34 | 0.34 | 198.60 | 0.43 |
| 2023-03-14 | 3 | 20 | 21.95 | 0.20 | 21.92 | 0.13 |
| 2023-03-14 | 3 | 150 | 147.87 | 0.31 | 147.71 | 0.17 |
| 2023-03-14 | 3 | 100 | 100.45 | 0.21 | 100.00 | 0.12 |
| 2023-03-14 | 3 | 250 | 250.71 | 0.36 | 250.73 | 0.27 |
| 2023-03-14 | 3 | 0 | -0.13 | 0.35 | -0.03 | 0.18 |
| 2023-03-14 | 3 | 75 | 73.44 | 0.38 | 73.36 | 0.24 |
| 2023-07-28 | 4 | 175 | 174.61 | 0.18 | 174.23 | 0.08 |
| 2023-07-28 | 4 | 125 | 125.73 | 0.26 | 125.45 | 0.13 |
| 2023-07-28 | 4 | 200 | 199.13 | 0.20 | 198.74 | 0.26 |
| 2023-07-28 | 4 | 225 | 226.15 | 0.21 | 225.64 | 0.20 |
| 2023-07-28 | 4 | 80 | 81.08 | 0.25 | 80.66 | 0.27 |
| 2023-07-28 | 4 | 100 | 100.32 | 0.25 | 99.98 | 0.19 |
| 2023-07-28 | 4 | 250 | 249.68 | 0.21 | 249.18 | 0.27 |
| 2023-07-28 | 4 | 55 | 53.41 | 0.20 | 53.11 | 0.22 |
| 2023-07-28 | 4 | 25 | 24.82 | 0.45 | 24.52 | 0.18 |
| 2023-07-28 | 4 | 145 | 147.17 | 0.25 | 146.44 | 0.16 |
| 2023-07-28 | 4 | 0 | 0.07 | 0.26 | 0.00 | 0.17 |
| 2023-07-28 | 5 | 200 | 199.15 | 0.31 | 198.75 | 0.14 |

| Date | Run | Level# | SRP (nmol mol$^{-1}$) | sdSRP (nmol mol$^{-1}$) | TS (nmol mol$^{-1}$) | sdTS (nmol mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 2023-07-28 | 5 | 175 | 175.10 | 0.39 | 174.69 | 0.15 |
| 2023-07-28 | 5 | 55 | 53.57 | 0.29 | 53.15 | 0.37 |
| 2023-07-28 | 5 | 250 | 249.74 | 0.30 | 249.44 | 0.32 |
| 2023-07-28 | 5 | 80 | 81.04 | 0.47 | 80.62 | 0.37 |
| 2023-07-28 | 5 | 125 | 126.22 | 0.31 | 125.88 | 0.20 |
| 2023-07-28 | 5 | 145 | 147.23 | 0.19 | 146.81 | 0.18 |
| 2023-07-28 | 5 | 225 | 225.32 | 0.29 | 225.17 | 0.28 |
| 2023-07-28 | 5 | 100 | 101.30 | 0.27 | 100.88 | 0.16 |
| 2023-07-28 | 5 | 25 | 24.60 | 0.35 | 24.55 | 0.19 |
| 2023-07-28 | 5 | 0 | 0.06 | 0.31 | 0.10 | 0.18 |
| 2023-07-28 | 6 | 80 | 81.80 | 0.23 | 81.29 | 0.11 |
| 2023-07-28 | 6 | 125 | 126.27 | 0.29 | 126.16 | 0.53 |
| 2023-07-28 | 6 | 145 | 147.36 | 0.26 | 146.74 | 0.13 |
| 2023-07-28 | 6 | 100 | 100.74 | 0.30 | 100.38 | 0.15 |
| 2023-07-28 | 6 | 175 | 174.48 | 0.29 | 173.92 | 0.21 |
| 2023-07-28 | 6 | 0 | -0.10 | 0.32 | 0.02 | 0.17 |
| 2023-07-28 | 6 | 225 | 224.77 | 0.23 | 224.31 | 0.18 |
| 2023-07-28 | 6 | 25 | 24.53 | 0.27 | 24.12 | 0.11 |
| 2023-07-28 | 6 | 250 | 249.35 | 0.23 | 248.85 | 0.28 |
| 2023-07-28 | 6 | 200 | 200.88 | 0.27 | 200.57 | 0.18 |
| 2023-07-28 | 6 | 55 | 53.58 | 0.71 | 53.11 | 0.30 |

#the level is only indicative.

## A10. WCC-Empa GHG and CO traveling standards

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

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

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

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

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

Table 16 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including the standard deviations of the WCC-Empa TS are given in Table 17, and Figure 29 shows the analysis of the TS over time.

***Table 16.*** *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 17.*** *Calibration summary of the WCC-Empa travelling standards for $CH_4$, $CO_2$, $N_2O$ and CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (L) Los Gatos.*

| TS | Press. (psi) | $CH_4$ (P) (nmol mol$^{-1}$) | sd | $CO_2$ (P) (µmol mol$^{-1}$) | sd | $N_2O$ (L) (nmol mol$^{-1}$) | sd | CO (P) (nmol mol$^{-1}$) | sd |
|---|---|---|---|---|---|---|---|---|---|
| 150601_FA02493 | 1100 | 1868.06 | 0.03 | 389.22 | 0.02 | 319.93 | 0.03 | 1319.58 | 1.02 |
| 150819_FA02464 | 1690 | 1965.89 | 0.02 | 401.69 | 0.01 | 329.12 | 0.03 | 173.9 | 1.44 |
| 160622_FA02474 | 1000 | 2506.82 | 0.07 | 421.49 | 0.02 | 324.48 | 0.01 | 243.53 | 0.99 |
| 171122_FA02785 | 1100 | 1856.35 | 0.03 | 408.46 | 0.01 | 341.84 | 0.05 | 56.63 | 1.29 |
| 171122_FA02788 | 1550 | 1619.01 | 0.06 | 337.27 | 0.02 | 283.94 | 0.14 | 77.32 | 0.78 |
| 171124_FA02786 | 1300 | 2193.7 | 0.04 | 468.51 | 0.01 | 377.81 | 0.05 | 150.97 | 0.76 |
| 171128_FA02476 | 1360 | 1860.15 | 0.05 | 418.49 | 0.02 | 322.53 | 0.02 | 156.01 | 0.95 |
| 181128_FF61487 | 1290 | 1990.61 | 0.04 | 398.43 | 0.03 | 342.83 | 0.04 | 122.28 | 1.54 |
| 220124_FA02773 | 600 | 3.04 | 0.03 | 0.11 | 0.01 | 10.97 | 1.28 | 0.22 | 0.47 |
| 220927_FA01469 | 1820 | 1971.46 | 0.01 | 431.95 | 0.02 | 334.35 | 0.06 | 123.71 | 0.79 |

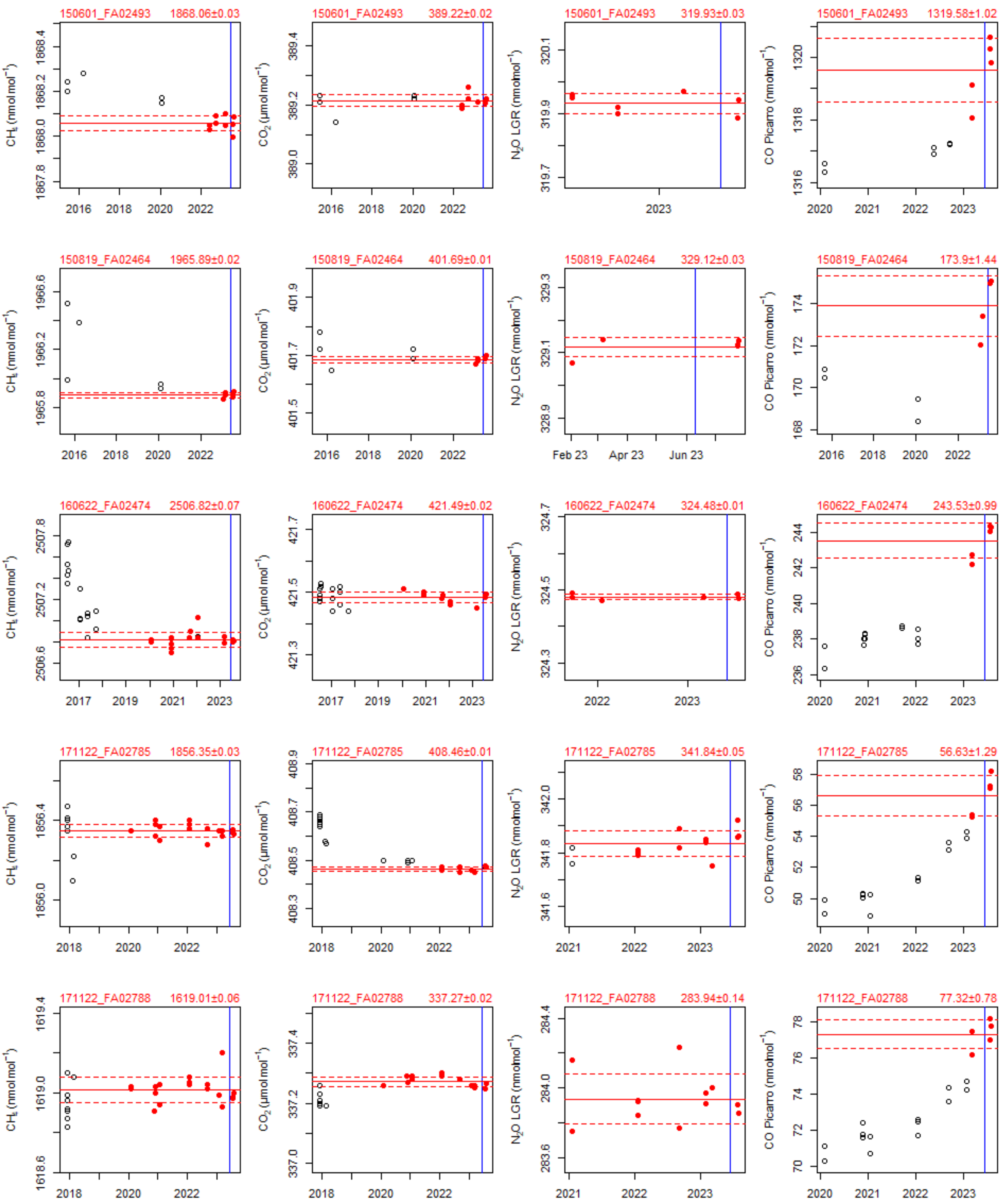


***Figure 29.*** *Results of the WCC-Empa TS calibrations for $CH_4$, $CO_2$, $N_2O$ and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

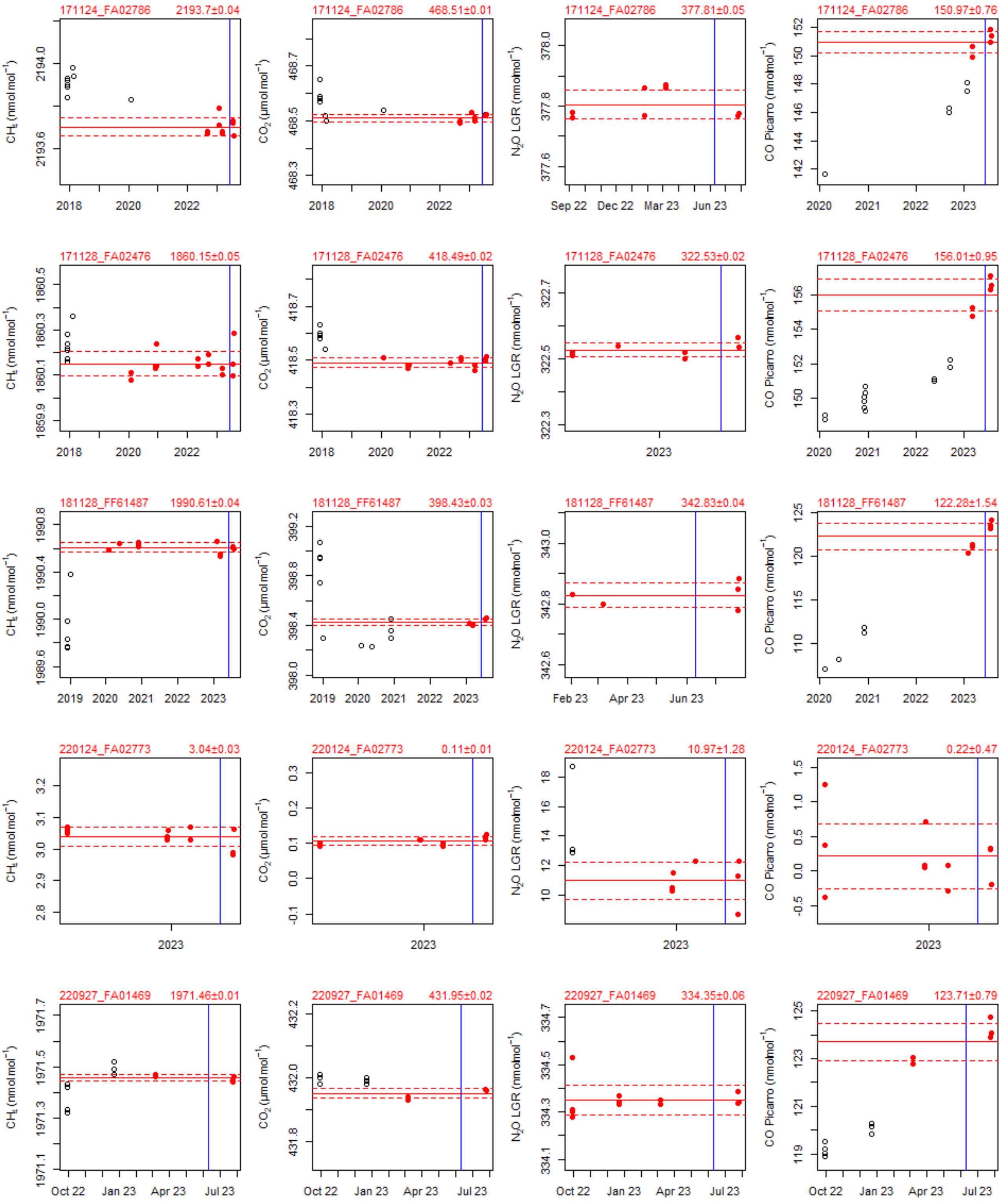


***Figure 30.*** *Results of the WCC-Empa TS calibrations for $CH_4$, $CO_2$, $N_2O$ and CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

## A11. Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For $CH_4$ and $CO_2$, the Picarro G2401 #1497-CFKADS2098 was calibrated every 2740 min using one WCC-Empa TS as a working standard, and two TS as target tanks. Based on the working standard measurements, a loess fit drift correction was applied to the data as shown in the figure below. The maximum drift between two WS measurements was approximately 1.1 nmol $mol^{-1}$ for $CH_4$ and 0.1 µmol $mol^{-1}$ for $CO_2$. All target cylinder measurements were within half of the WMO GAW compatibility goals.

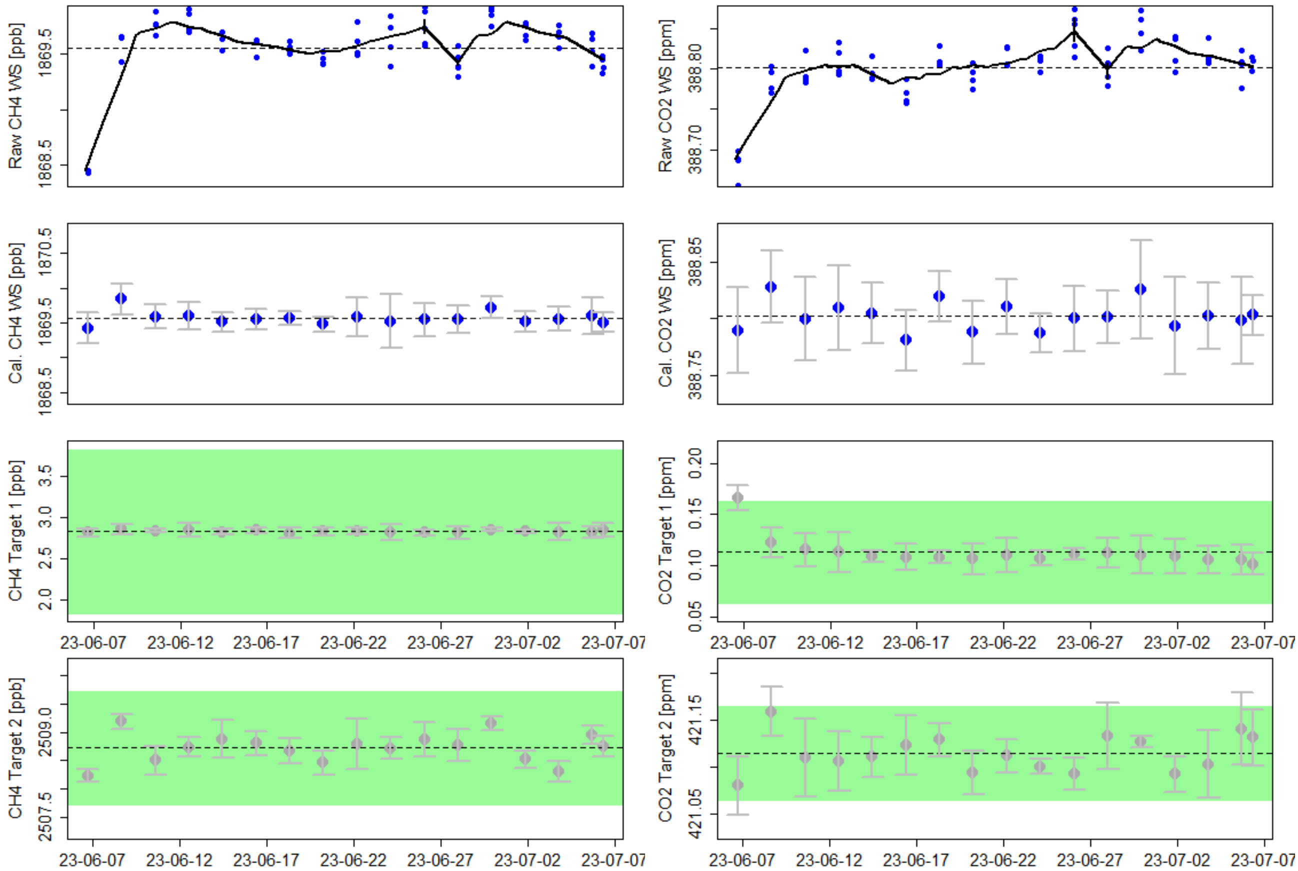


***Figure 31.*** *$CH_4$ (left panel) and $CO_2$ (right panel) calibrations of the WCC-Empa-TI. The top panel shows the raw 1 min values of the working standard and the loess fit (black line) used to account for the drift. The second panel shows the variation of the WS after application of the drift correction. The bottom panel shows the results from the two target cylinders. Individual points in the three lower panels are 5 minute averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 2740 minutes using three WCC-Empa TS as a working standards. Based on the working standard measurements, a loess fit drift correction using was first applied to the data, as shown in the figure below.

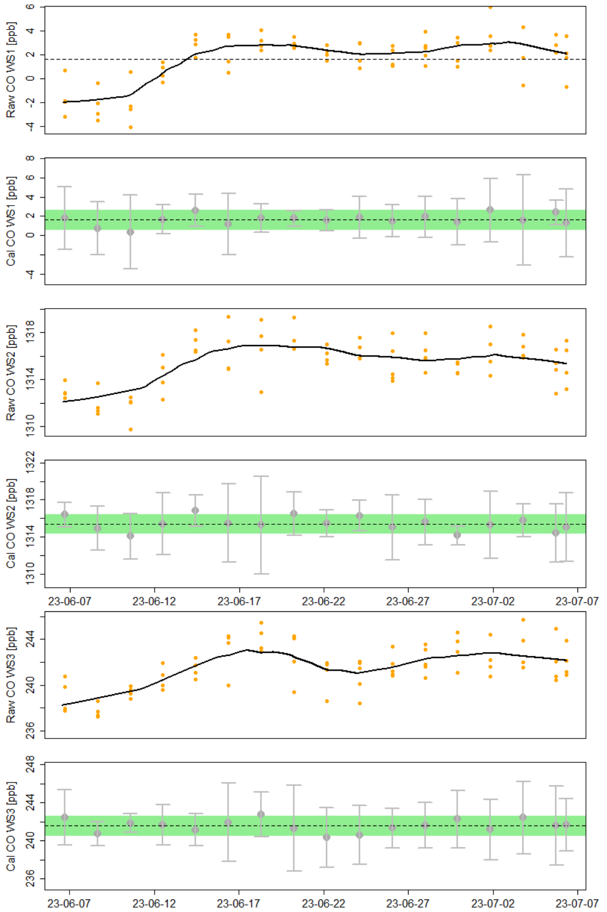

***Figure 32.*** *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show the raw 1 min values of the working standards and the loess fit (black line) used to account for the drift. The other panels show the variation of the WS after application of the drift correction. Individual points in these panels are 5 min averages, and the uncertainty bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

A linear function of the drift-corrected working standard data of then was then used to calculate calibrated CO data, which is shown in the figure below.

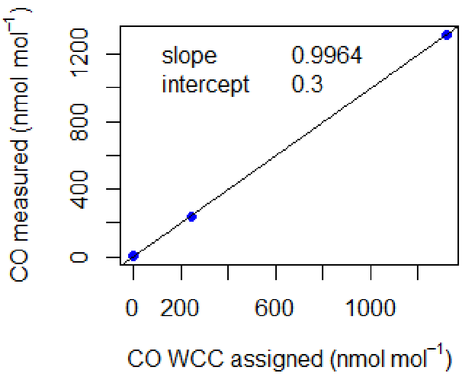


***Figure 33.*** *CO calibration function based on the average values of the drift corrected working standard measurements.*

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# List of abbreviations

| | |
|---|---|
| ACTRIS | Aerosol, Clouds and Trace Gases Research Infrastructure |
| AEMET | Agencia Estatal de Meteorología (State Meteorological Agency) of Spain |
| ATC | Atmosphere Thematic Centre |
| BKG | Background |
| CCL | Central Calibration Laboratory |
| COEF | Coefficient |
| CRDS | Cavity Ring-Down Spectroscopy |
| DQO | Data Quality Objective |
| ECD | Electron Capture Detection |
| eDQO | Extended Data Quality Objective |
| EMEP | European Monitoring and Evaluation Programme |
| FCL | Flask and Calibration Laboratory |
| FID | Flame Ionisation Detection |
| GAW | Global Atmosphere Watch |
| GAWSIS | GAW Station Information System |
| GC | Gas Chromatograph |
| GHG | Greenhouse Gases |
| IARC | Izaña Atmospheric Research Centre |
| ICOS | Integrated Carbon Observation System |
| IR | Infrared |
| IZO | Izaña GAW Station |
| LS | Laboratory Standard |
| NA | Not Applicable |
| NDIR | Non-Dispersive Infrared |
| NOAA | National Oceanic and Atmospheric Administration |
| OA-ICOS | Off-Axis Integrated Cavity Output Spectroscopy |
| 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 |