Research Infrastructure Quality Assurance

GAW Report No. 251
WCC-Empa Report No. 19/2

System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide at the Global GAW Station Izaña, Spain

May 2019

WEATHER CLIMATE WATER

WORLD METEOROLOGICAL ORGANIZATION

GLOBAL ATMOSPHERE WATCH

Empa
Materials Science and Technology

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System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide at the Global GAW Station Izaña, Spain

May 2019

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Acknowledgements

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GAW Report No. 251
WCC-Empa Report 19/2
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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 7th system and performance audit by WCC-Empa[1] at the global GAW station Izaña, which is run by the State Meteorological Agency of Spain (AEMET), was conducted from 15 to 21 May 2019 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at the Izaña GAW station, as well as the corresponding audit reports, is available from the WCC-Empa webpage (www.empa.ch/gaw).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr Emilio Cuevas	Izaña, station manager, GAW country contact
Mr Ramón Ramos	Izaña, station operator
Mr Carlos Torres	Izaña, station scientist
Mr Enrique Reyes Sánchez	Izaña, station scientist
Mr Pedro Pablo Rivas-Soriano	Izaña, station scientist

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

The report is distributed to the IZO station manager, the national focal point in Spain for GAW, and the World Meteorological Organization in Geneva. The report will be posted on the internet (www.empa.ch/web/s503/wcc-empa).

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

Station Management and Operation

The Izaña (IZO) Atmospheric Observatory is operated by the Izaña Atmospheric Research Centre (IARC), which is part of AEMET, and has the status of a WMO GAW 'global' station. IARC operates besides IZO also the regional GAW station St. Cruz (SCO) and two other observatories. IZO is also part of the National Oceanic and Atmospheric Administration (NOAA) flask sampling programme, the Network for the Detection of Atmospheric Composition Change (NDACC), the Total Carbon Column Observing Network (TCCON), the Collaborative Carbon Column Observing Network (COCCON), the NASA Micropluse Lidar (MPL) Network, and the AErosol RObotic NETwork (AERONET). An overview of collaborations with other networks can be found on the station website (http://izana.aemet.es) and in Cuevas et al. (2019). IZO is visited during weekdays by scientists and technical staff. The headquarters of IARC is located in St. Cruz de Tenerife, which is located approx. 50 km NE (60 mins by car) from the station.

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[1] *WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.*

Station Location and Access

The Izaña station is located on the Island of Tenerife, Spain, roughly 300 km west of the African coast. The meteorological observatory is situated on a mountain platform (2373 m a.s.l.), 15 km north-east of the volcano Teide (3718 m a.s.l.). The station is normally above the temperature inversion layer, which generally is well established over the island, and therefore mostly free of local anthropogenic influences. The location is adequate for the intended purpose. Year-round access to IZO is possible by car.

Further information is available from GAWSIS (https://gawsis.meteoswiss.ch) and the station website (http://izana.aemet.es).

Station Facilities

The facilities at the site consist of a large building, which comprises spacious laboratories, a workshop, kitchen, library, meeting rooms, and offices for visiting scientists and technicians, and a residence area with seven double rooms with attached bathrooms. A complete overview of the facilities can be found on the station webpage. The IZO research station is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Measurement Programme

The IZO station features a comprehensive measurement programme that covers all focal areas of the GAW programme. Some of the time series date back to 1984 and are among the longest continuous records of the WMO/GAW programme. An overview on measured species is available from GAWSIS and the station website. The information available from GAWSIS was reviewed and partly updated during the audit.

> **Recommendation 1 (**, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. The GAWSIS support should be contacted for updates which are not possible through the web interface (e.g. deletion of station contacts).*

Data Submission

As of February 2020, i.e. the time of the release of the report, the following data of the scope of the audit were available at the World Data Centres:

Submission to the World Data Centre for Greenhouse Gases (WDCGG):
IZO: CO_2 (1984-2018), CH_4 (1984-2018), CO (2008-2016), N_2O (2007-2016), O_3 (1987-2013)
NOAA: CO_2 (1991-2018), CH_4 (1991-2018), CO (2004-2018), N_2O (1997-2018)

Submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (2014-2018)

> **Recommendation 2 (**, important, 2020)**
> *Ozone data submitted to WDCGG is no longer available, since ozone is now hosted by WDCRG. Data (1987 – 2013) needs to be transferred or re-submitted to WDCRG,*

which now is the official data repository for surface ozone data.

Recommendation 3 (, important, ongoing)**
Data submission is an obligation of all GAW stations. It is recommended to submit data to the corresponding data centres at least in yearly intervals. One hourly data must be submitted for all parameters.

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG and WDCRG was reviewed. Data shown in this report was accessed between 30 September 2019 and 26 February 2020. Summary plots findings are presented in the Appendix.

Documentation

Electronic log books and hand written notes are available for all parameters. The instrument manuals are available at the site. The information was comprehensive and up-to-date.

Air Inlet System

Two state-of-the-art central inlet systems are available for the measurement of gaseous species. Both air intakes are located at the top of the laboratory tower. Individual analytical systems are connected to one of these inlets. Details of the inlet system can be found in the previous audit reports.

Surface Ozone Measurements

Surface ozone measurements at IZO were established in 1987, and continuous time series are available since then.

Instrumentation. IZO is currently equipped with three ozone analysers (Thermo Scientific 49C and 49i) and an ozone calibrator (Thermo Scientific 49C-PS). It is foreseen to install one of the TEI 49C instruments at the newly established observatory at the top of the Teide Mountain. The ozone calibrator available at the station was shipped to Empa for calibration in 2017.

Data Acquisition. A custom-made data acquisition system is available for ozone data and other instrument parameters.

Intercomparison (Performance Audit). The IZO analysers and the calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. The result of the comparisons is summarized below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system except for the 49i instrument, for which data from the internal data logger was used due to an issue with the WCC-Empa data acquisition system. The data of the station calibrator was corrected by the equation determined during the comparison at Empa in 2017:

True value = 0.9947 x TEI 49C-PS #56085-306 + 0.23) $nmolmol^{-1}$ (1)

The data of the TEI 49C #72491-371 was corrected by applying a factor of 0.998; this was due to a wrong calibration setting of the span coefficient to 1.021 instead of 1.019 by IZO staff. All other comparison were made without further correction.

The following equations characterize the bias of the instruments:

Thermo Scientific 49C #72491-371 (BKG +0.0 ppb, SPAN 1.021, corrected as described above):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] – 0.40 ppb) / 1.0038 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.52e-05 * X_{O3}^2) (1b)

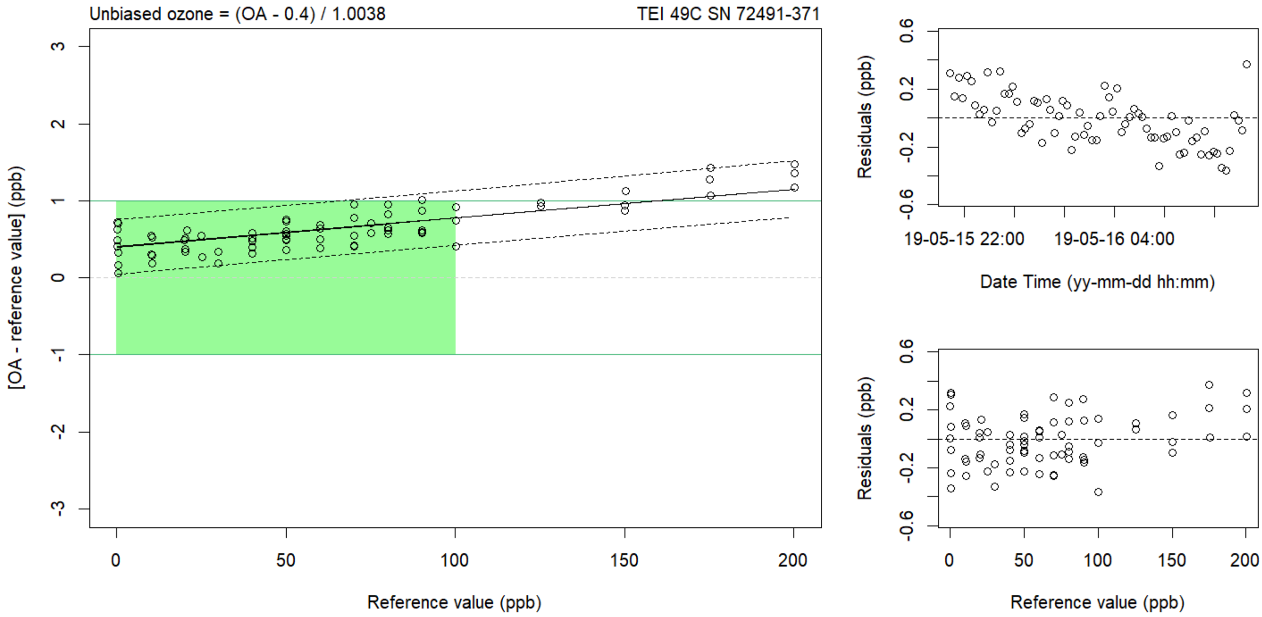

Figure 1. Left: Bias of the IZO ozone analyser (Thermo Scientific 49C #72491-371) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Thermo Scientific 49i #1153030026 (BKG +0.0 ppb, SPAN 1.003):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] – 0.02 ppb) / 1.0045 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.51e-05 * X_{O3}^2) (1d)

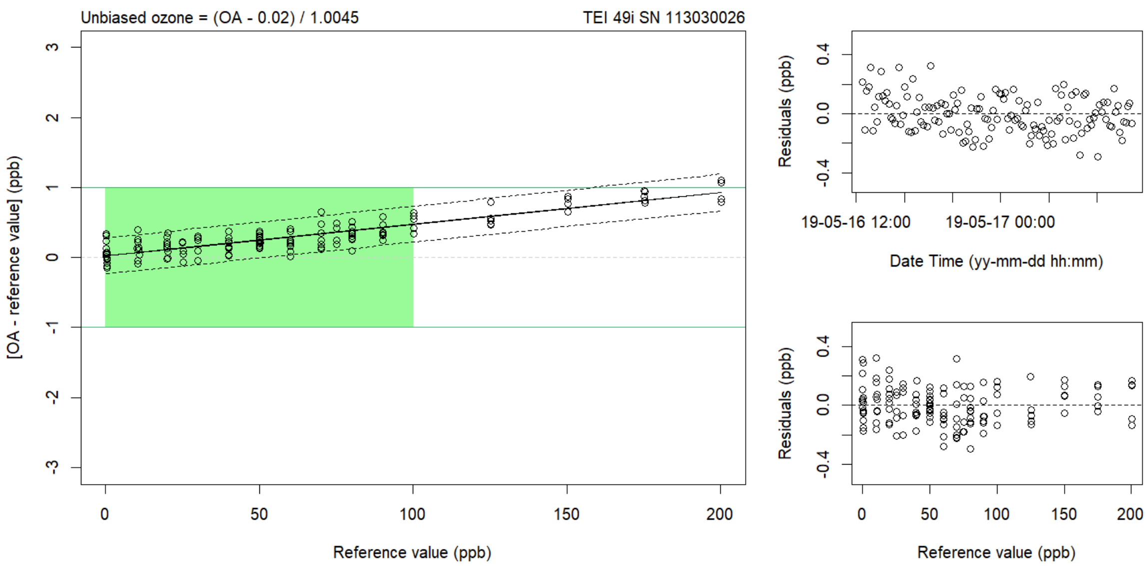

Figure 2. Same as above for the IZO ozone analyser Thermo Scientific 49i #1153030026

Thermo Scientific 49C #62900-337 (BKG +0.0 ppb, SPAN 1.020):

This instrument failed a couple of hours before the audit. The two solenoid valves were replaced other valves from an old decommissioned instrument, and part of the internal tubing was also replaced. Before the comparison the instrument was conditioned at 500 ppb ozone for about 24 hours. After the repair of the instrument, the relationship between the analyser and the WCC-Empa reference was as follows:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.31 ppb) / 1.0006 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.28 ppb^2 + 2.53e-05 * $X_{O3}{}^2$) (1f)

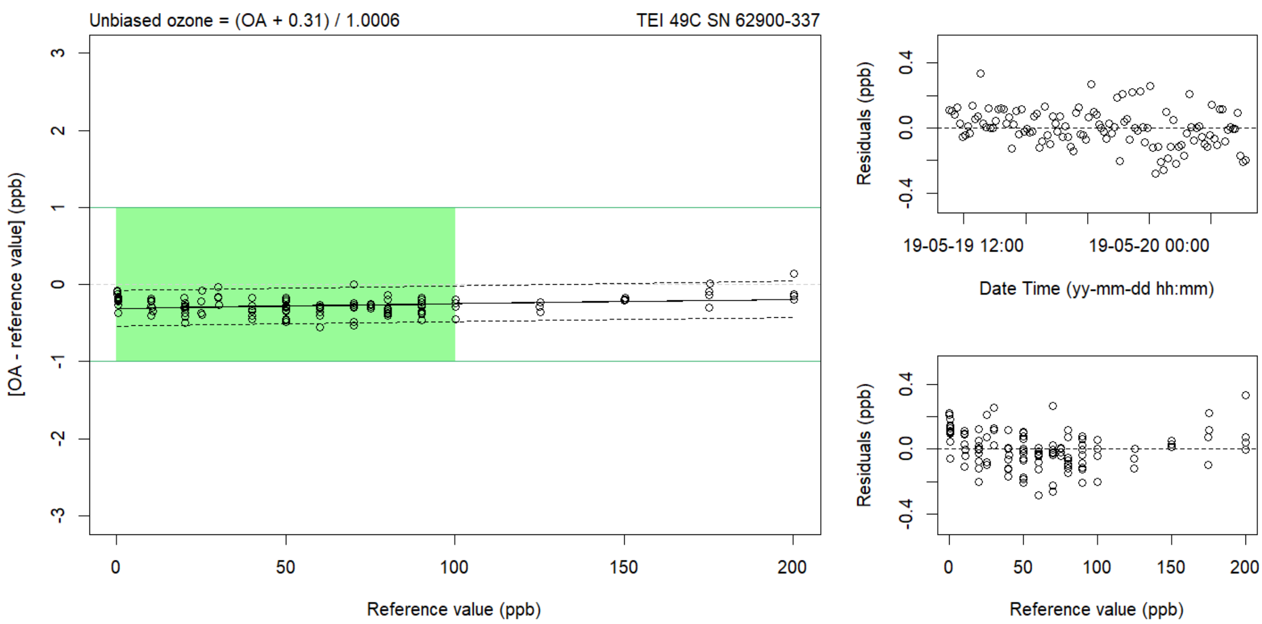

Figure 3. Same as above for the IZO ozone analyser Thermo Scientific 49C #62900-337

Thermo Scientific 49C-PS #56085-306 (BKG -0.6 ppb, SPAN 1.014):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OC] – 0.44 ppb) / 1.0005 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.53e-05 * $X_{O3}{}^2$) (1h)

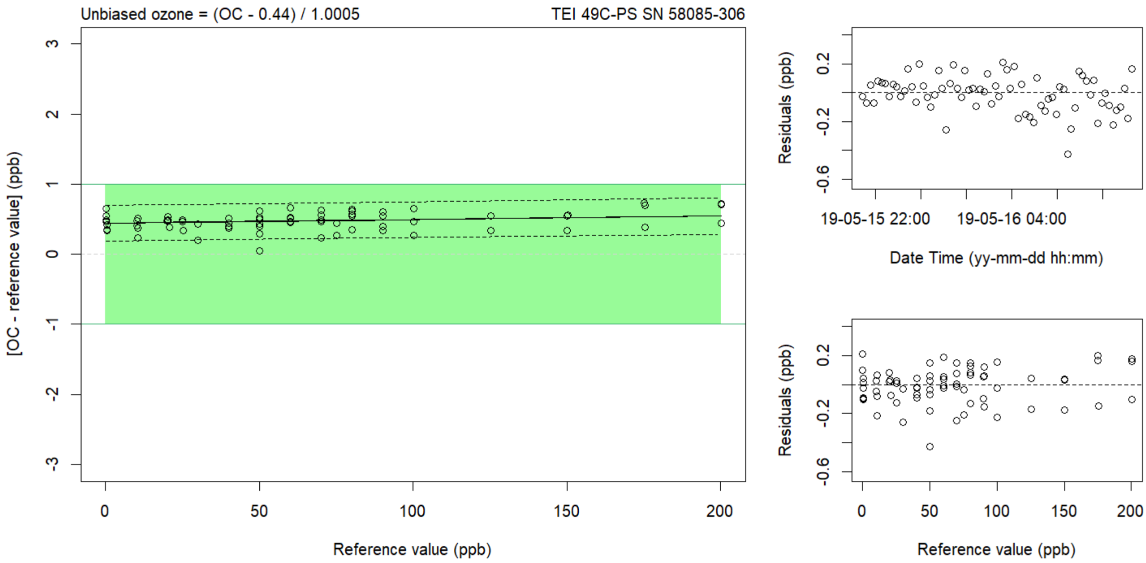

Figure 4. Same as above for the IZO ozone calibrator (Thermo Scientific 49C-PS #56085-306)

The results of the comparisons can be summarized as follows:

Good agreement between the WCC-Empa travelling instrument and the IZO calibrator was found, which confirms the validity of the calibration made at Empa in 2017.

The ozone analysers were all in agreement within 1 ppb at the relevant mole fraction range from 0-100 ppb ozone, which confirms that the calibration made by the IZO staff is appropriate. No further action is required. However, the C-Series instruments are reaching the end of their lifetime.

Recommendation 4 (, important, 2020/21)**
The two Thermo Scientific 49C analysers as well as the calibrator are reaching the end of their expected lifetime. Replacement of these instruments should be made within the next two years.

Recommendation 5 (, important, 2020)**
The Thermo Scientific 49C #62900-337 analyser needed repair just before the current audit. The instrument passed the checks for internal and external leaks after repair, but some of the fittings are worn and the instrument should be serviced.

Carbon Monoxide Measurements

Ongoing measurement of carbon monoxide at Izaña commenced in 1998, and continuous validated data series are available since 2008. These measurements were made by a GC system, and two spectroscopic instruments which also measure CO were installed recently.

Instrumentation. Trace Analytical RGA-3, Los Gatos Research LGR N2OCM-913, Picarro G2401. The RGA-3 instrument was decommissioned after the current audit and could not be assessed due to instrumental problems.

Standards. All instruments have a set of dedicated NOAA standards and working and target standards. A list of standards is given in the Appendix.

> **Recommendation 6 (**, important, ongoing)**
> *Cross-checks between different sets of standards are recommended to ensure the internal consistency of the available references gases.*

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterize the instrument bias, and the results are further illustrated in Figures 5 to 7 with respect to the WMO GAW DQOs (WMO, 2014):

Picarro G2401 #2352-CFKADS2196:

The first comparison was made using drift corrections of the CO values of the standard gases based on the measurements of the IZO standards on the RGA-3 system, and the following result was obtained:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 1.94) / 0.9747 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.3 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

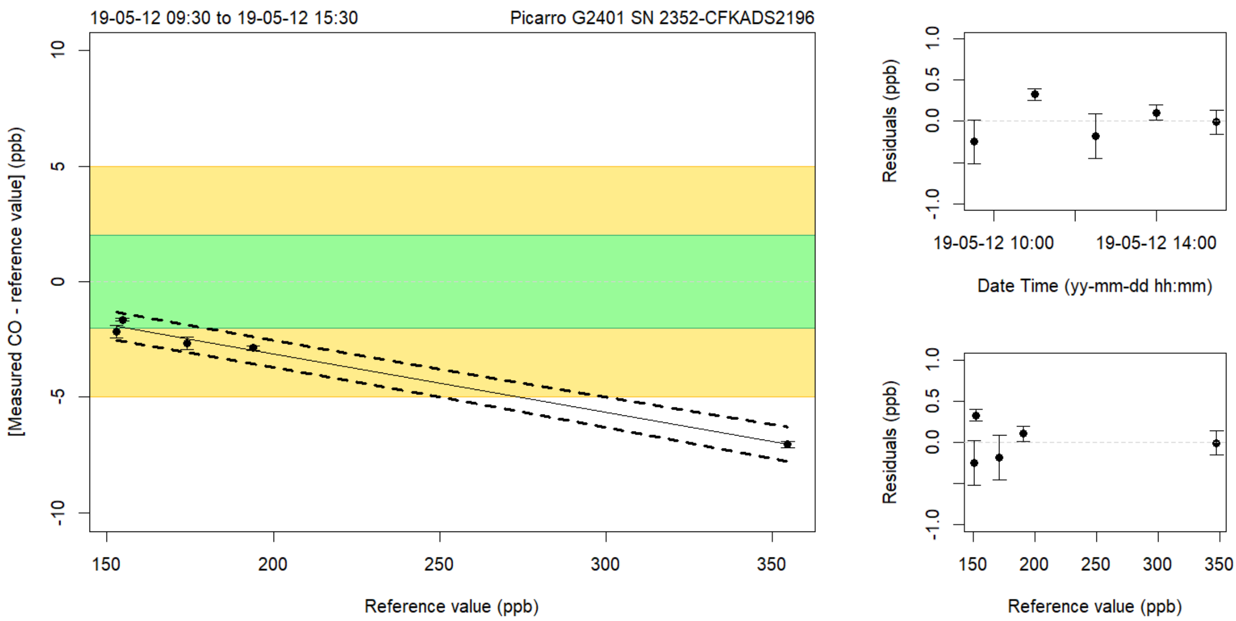

Figure 5. Left: Bias of the IZO Picarro G2401 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement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

Given the fact that standards are drifting, the data was re-processed after the audit using the more recent CO standard gases of the LGR instrument. The following results were obtained after reprocessing:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 2.28) / 0.9904 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.3 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

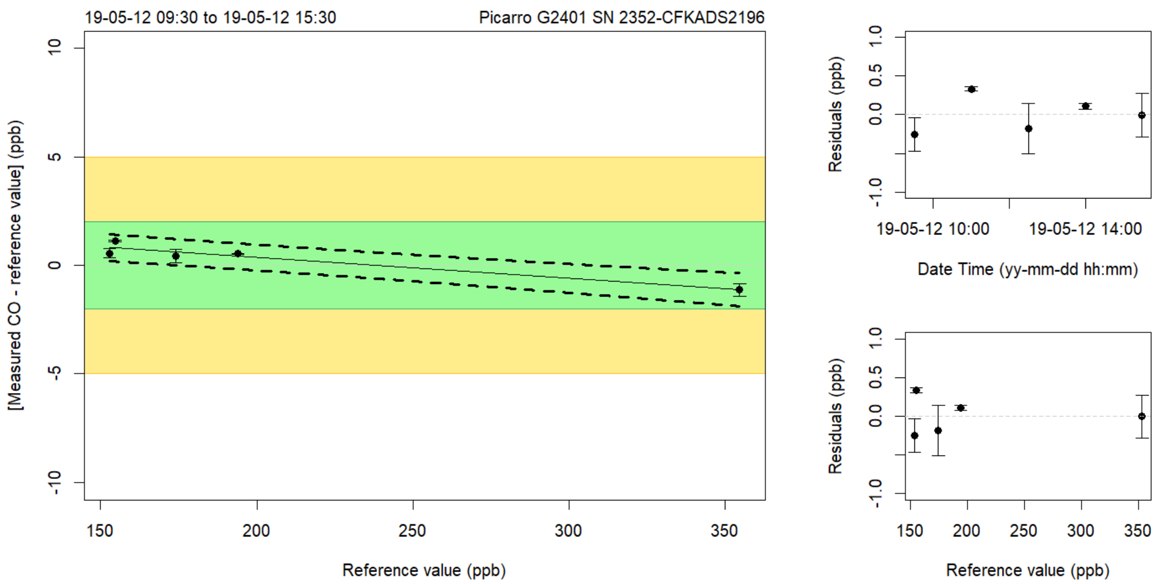

Figure 6. Same as above after reprocessing using the LGR CO standards

LGR N2OCM-913 # US430000170700001433:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 0.30) / 1.0075 (2e)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.3 ppb^2 + 1.01e-04 * X_{CO}^2) (2f)

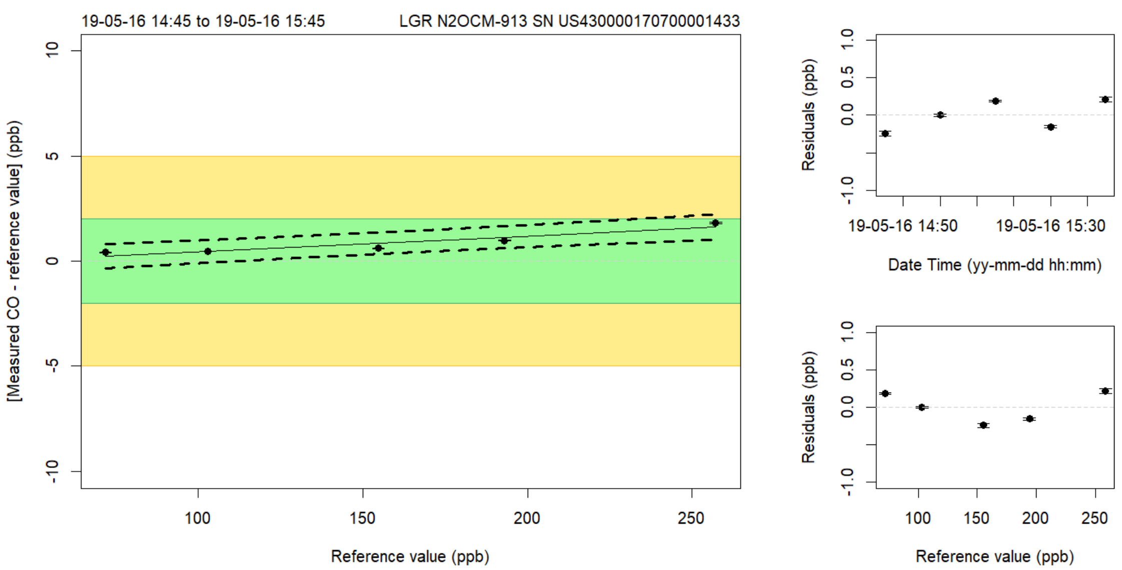

Figure 7. Same as above, for the LGR N2OCM-913 carbon monoxide analyser

The LGR instrument was calibrated using NOAA standards and nitrogen as zero gas. This method gave better results compared to the calibration only based on NOAA standards because it better accounts for potential standard inconsistencies, and covers a wider range.

Recommendation 7 (, important, ongoing)**
Calibrations of the LGR instrument should include a CO free gas to correct for a zero offset.

Recommendation 8 (, important, ongoing)**
Drift of CO standards is a serious issue, and it is important to minimise bias due to drift. It is recommended to use standards with high CO amount fractions (500 ppb or higher), and have them frequently (e.g. yearly) re-calibrated at the CCL. Alternatively, purchasing CO standards in e.g. yearly intervals could also be considered.

RGA-3 #070188-009: The instrument was tested during the current audit, but the results were only partly useable due to instrumental problems. The instrument is now decommissioned, and it was decided to exclude the results of the RGA-3 comparison from the current audit due to the non-conclusive findings and the fact that the instrument is no longer in use.

The results of the CO comparisons can be summarized as follows:

Picarro G2401: The comparison results were initially exceeding the WMO/GAW extended network compatibility goals of 5 ppb. After the audit, the standards of the Picarro instrument were re-calibrated using the standards of the LGR instrument, which significantly improved the comparison results due to the more recent values of the LGR standards.

The results of the LGR instrument fully complied with the WMO/GAW network compatibility goals of 2 ppb. This instrument is currently the most accurate for the measurements of CO and should be considered as the primary method.

WCC-Empa supports the decommissioning of the RGA-3 instrument. No additional valuable information can be obtained using this instrument compared to the other methods.

The results observed during the ambient air comparison with the WCC-Empa travelling instrument confirmed the improvement of the recalibration of the Picarro standards. Good agreement was observed between the IZO and the WCC-Empa Picarro instrument, which is shown further below.

Methane Measurements

Continuous measurements of CH_4 at IZO started in 1994 using a GC/FID (Varian 3800) instrument, and continuous data series are available since then. In 2017, a Cavity Ring-Down Spectrometer (Picarro G2401) was installed, and the Picarro instrument will become the primary instrument for methane measurements, while the GC/FID measurements will be continued for QA/QC reasons and as a backup.

***Instrumentation*.** GC/FID Varian 3800, Picarro G2401.

Standards. All instruments have a set of dedicated NOAA standards and working and target standards. A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instruments with randomised CH_4 levels from travelling standards. The results of the comparison is summarized and illustrated below.

The following equation characterizes the instrument bias. The results are further illustrated in Figures 8 and 9 with respect to the relevant mole fraction range and the WMO/GAW network compatibility goals and extended network compatibility goals (WMO, 2018).

Picarro G2401 #2352-CFKADS2196:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 4.27 ppb) / 0.99777 (3a)

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

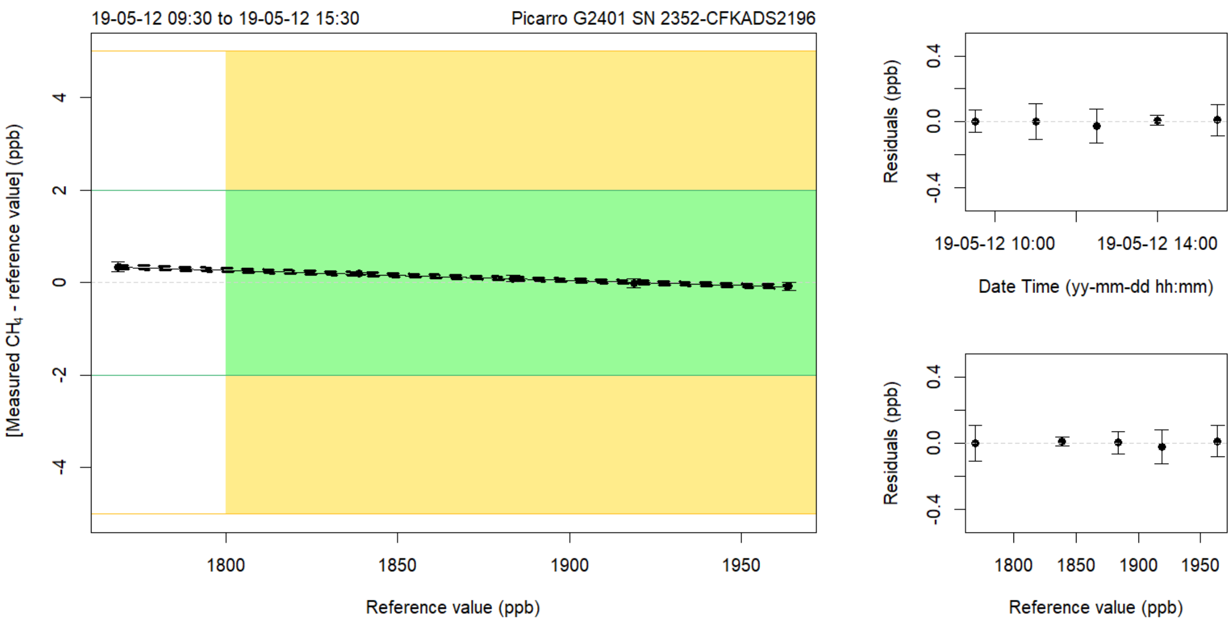

Figure 8. Left: Bias of the Picarro G2401 methane instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

GC/FID Varian 3800 #3405:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 + 20.20 ppb) / 1.01090 (3c)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.4 ppb^2 + 1.30e-07 * $X_{CH4}{}^2$) (3d)

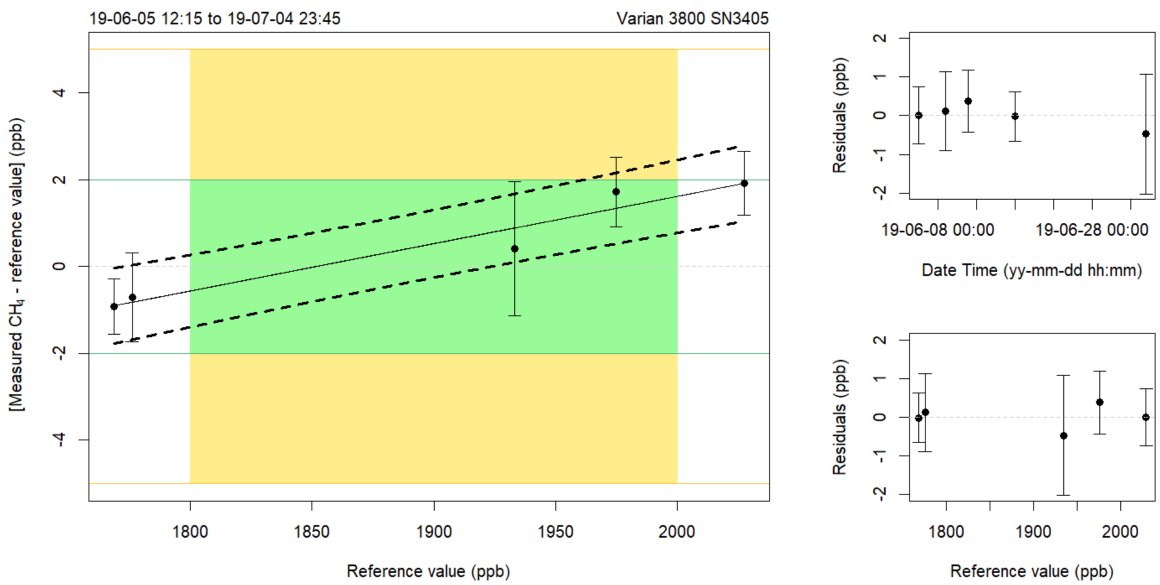

Figure 9. Same as above for the Varian 3800 GC

The results of the comparisons can be summarized as follows:

Excellent agreement within the WMO/GAW compatibility goal was found for the Picarro G2401, which confirms that the implemented calibration scheme is appropriate.

The GC/FID instrument also agreed within the WMO GAW network compatibility goals, but the associated uncertainties are significantly larger. The comparison clearly showed that Cavity Ring-Down Spectroscopy (CRDS) is superior compared to the GC/FID technique.

Recommendation 9 (*, minor, ongoing)
The Picarro G2401 CRDS analyser is giving more reliable CH_4 values compared to the GC system. Available resources should focus on the CRDS technique, and data of this instrument should be considered for data submission.

Perfect agreement, with no significant bias, was also observed during the ambient air comparison between the IZO and the WCC-Empa Picarro instrument, which confirms the results of the performance audit based on travelling standards.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at IZO started in 1994 using NDIR technique (LI-COR 7000), and continuous data series are available since then. In 2017, a Cavity Ring-Down Spectrometer (Picarro G2401) was installed, and this instrument will become the primary instrument for CO_2 measurements, while the LI-COR measurements will be continued for QA/QC reasons and as a backup.

Instrumentation. LI-COR 7000, Picarro G2401.

Standards. All instruments have a set of dedicated NOAA standards and working and target standards. A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instruments with randomised CO_2 levels from travelling standards. The result of the comparison is summarized and illustrated below.

The following equations characterizes the instrument bias. The results are further illustrated in Figure 10 and 11 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2401 #2352-CFKADS2196:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 1.19 ppm) / 0.99702 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.002 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4b)

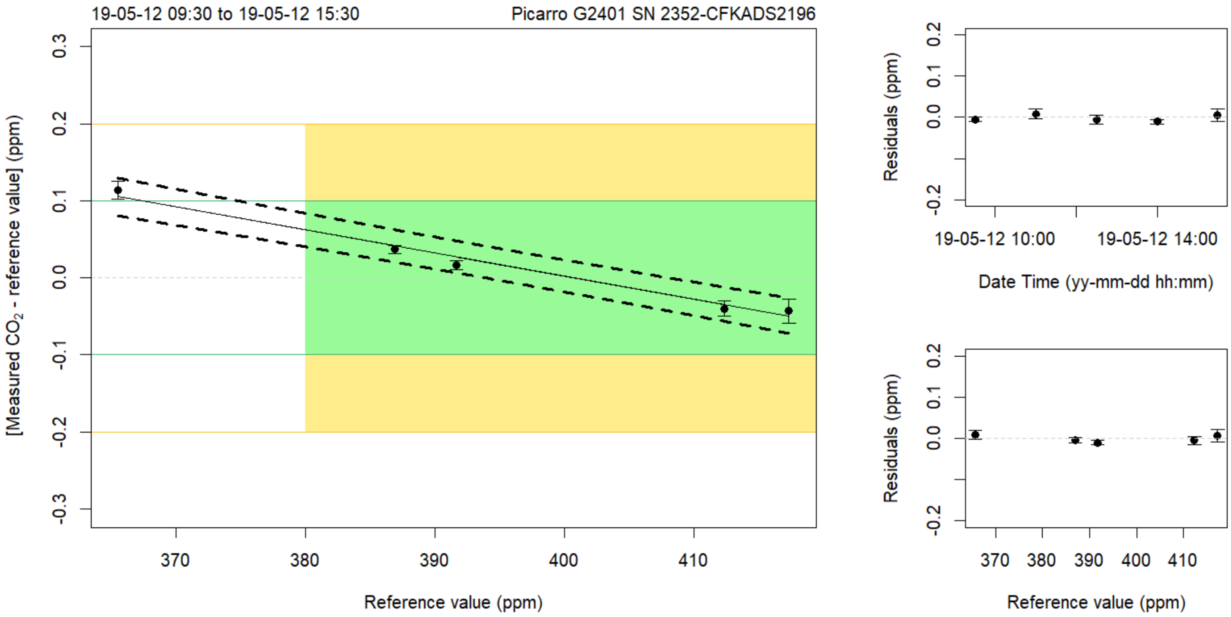

Figure 10. Left: Bias of the Picarro G2401 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

LI-COR 7000 #IRG4-0524:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.67 ppm) / 0.99825 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.021 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4d)

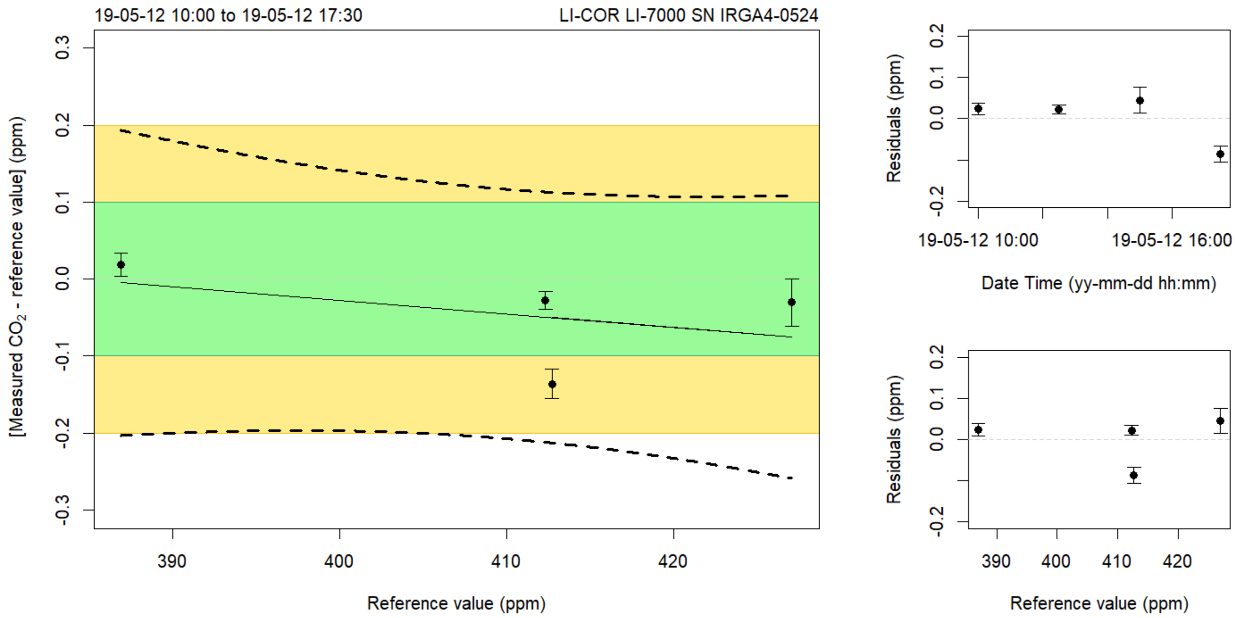

Figure 11. Same as above for the LI-COR 7000 analyser

The result of the comparison can be summarized as follows:

The IZO instruments showed agreement within the WMO/GAW compatibility goals in the relevant mole fraction range, and no further action is required. However, a mole fraction dependency was found, with is most likely associated with the uncertainty of the WMO-X2007 calibration scale.

The good results were also confirmed during the ambient air comparisons with the WCC-Empa travelling instrument, which are shown further below.

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. In 2018, an Integrated Cavity Output meter (Los Gatos Research LGR N2OCM-913) was installed, and this instrument will become the primary instrument for N_2O measurements, while the GC/ECD system will be continued for QA/QC reasons and as a backup.

Instrumentation. GC/ECD Varian 3800, Los Gatos Research LGR N2OCM-913.

Standards. All instruments have a set of dedicated NOAA standards and working and target standards. A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterize the instrument bias, and the results are further illustrated in Figure 12 and 13 with respect to the WMO GAW DQOs (WMO, 2014):

LGR N2OCM-913 # US430000170700001433:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O + 1.14) / 1.00350 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.03 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

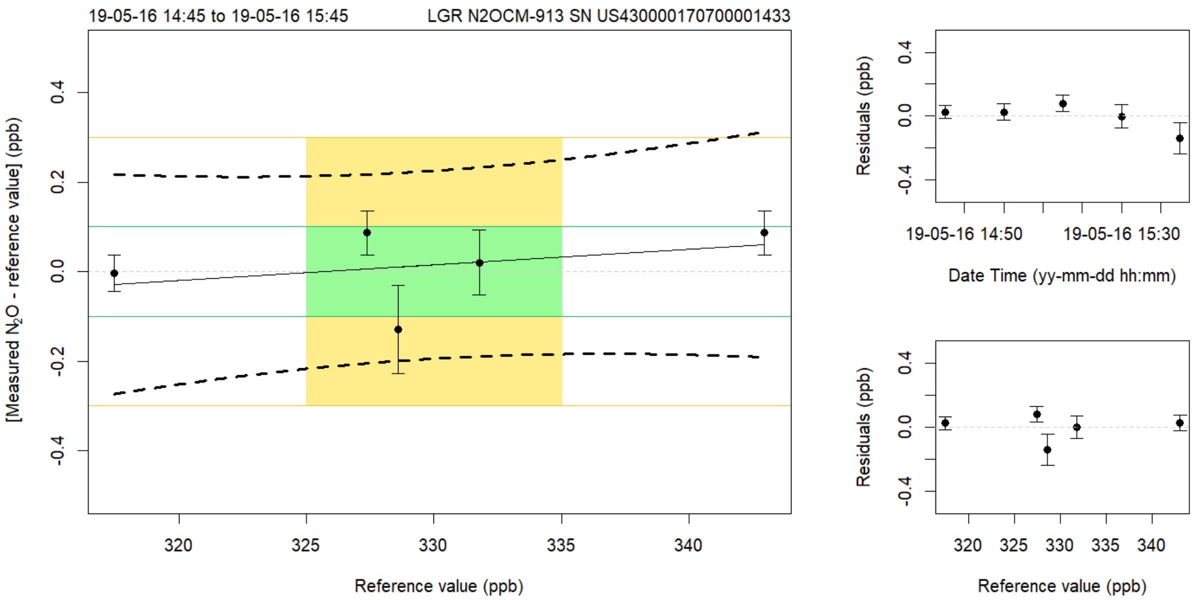

Figure 12. Left: Bias of the LGR N2OCM-913 analyser with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for IZO. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

GC/ECD Varian 3800 #3405:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 12.45) / 0.96179 (5c)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.05 ppb^2 + 1.01e-07 * X_{N2O}^2) (5d)

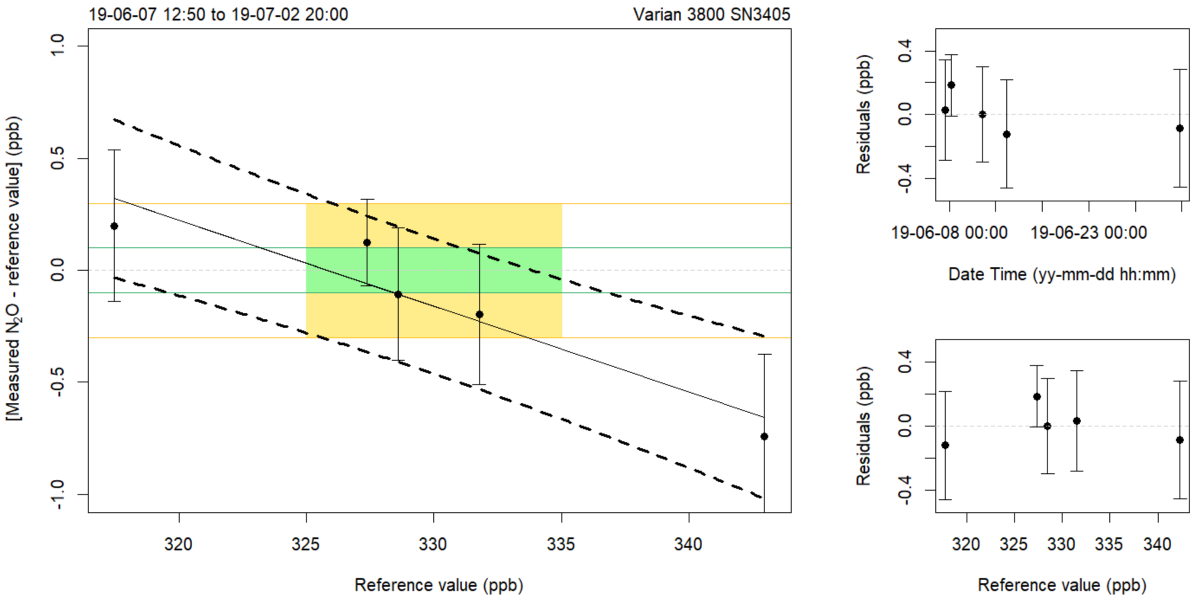

Figure 13. Same as above for the Varian 3800 GC/ECD system

The result of the comparison can be summarized as follows:

On average, the agreement between the LGR and WCC-Empa was within the WMO/GAW network compatibility goal of 0.1 ppb. Such a good agreement over the entire relevant mole fraction range demonstrates that the instrumentation and procedures are fully adequate. A slightly larger deviation was observed for the Varian 3800 GC/ECD system probably due to the non-linear response of the ECD.

Recommendation 10 (, important, ongoing)**
The performance of the Integrated Cavity Output Spectrometer is clearly superior compared to the GC/ECD method. These measurements should now be considered as the primary method, and the GC system should only be used as a backup method and for QA/QC purposes.

Recommendation 11 (*, minor, 2020)
It should be explored if the current GC/ECD system can be optimised with regard to repeatability and reproducibility.

IZO PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the IZO performance audit to other station audits made by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (Zellweger et al., 2016; Zellweger et al., 2019). Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2017 meeting (WMO, 2018) for CO_2, CH_4 and CO and refer to conditions usually found in unpolluted air masses. For N_2O, the mole fraction range covers 10 ppb and depends on the time of the comparison due to the large annual increase combined with low variability. The same method was also applied to surface ozone for which the mole fraction range of 0 -100 ppb was selected because this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 14 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, while the results for CO, CH_4, CO_2 and N_2O are shown in Figure 15. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current IZO audit are shown as coloured dots in Figure 14 and 15, and are also summarized in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

The results were within the DQOs for all ozone instruments as well as for the LGR analyser (CO and N_2O) and the Picarro G2401 (CO and CH_4). The extended WMO/GAW network compatibility goals were reached with the Picarro G2401 (CO_2), the LI-COR 7000 (CO_2) and the Varian 3800 (CH_4), while the goals were not met with the Varian 3800 (N_2O).

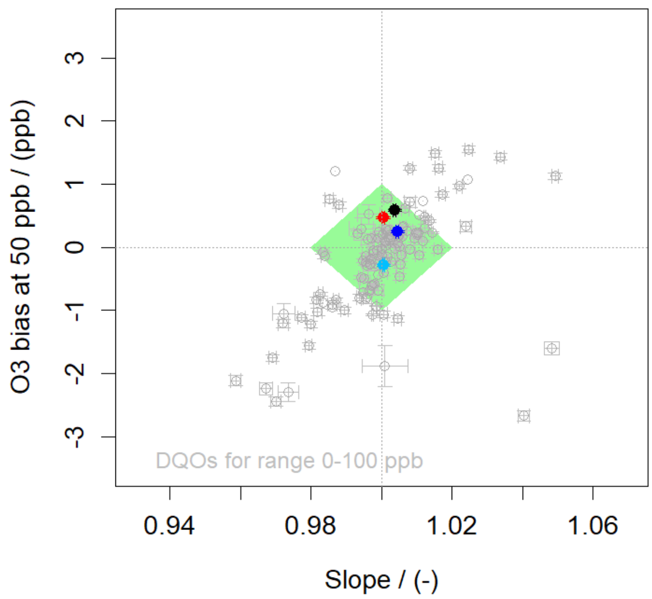

Figure 14. O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show the results of the IZO TEI 49C-PS #56085-306 calibrator (red), the TEI 49C #72491-371 (black), the TEI 49i #1153030026 (blue), and the TEI 49C #62900-337 (light blue) analysers. The green area corresponds to the WMO/GAW DQO for surface ozone.

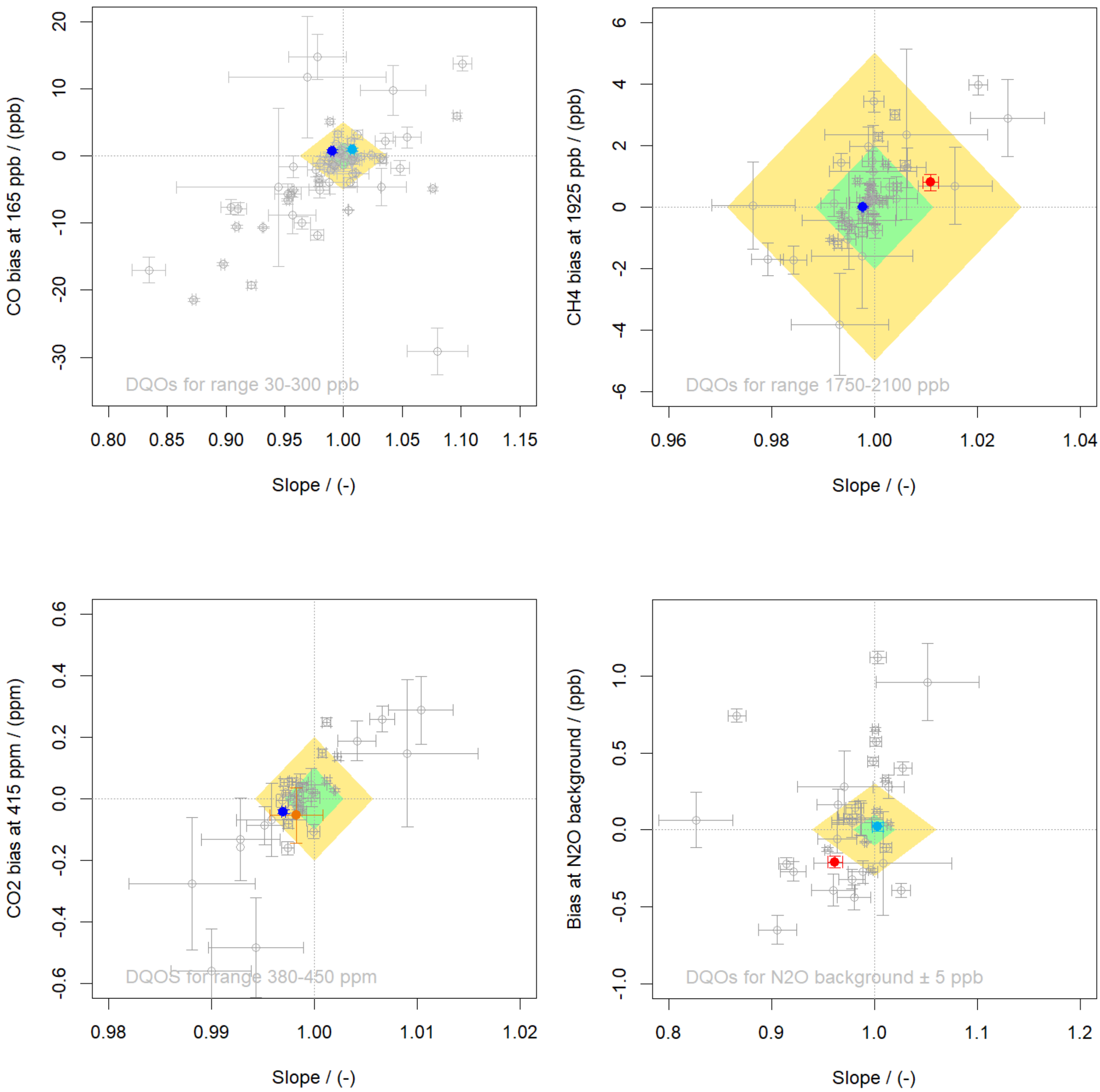

Figure 15. CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show IZO results (blue: Picarro G2410, light blue: LGR N2OCM-913, red: Varian GC, orange: LI-COR LI7000). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).

Table 1. IZO performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5-7th columns show the percentage of all WCC-Empa audits within these criteria since 1996 (O_3), 2005 (CO and CH_4) and 2010 (CO_2).

Compound	Range	Unit	IZO within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]	% of audits outside eDQOs
O_3 (72491-371)	0 -100	p	✓	65	NA	35
O_3 (1153030026)	0 -100	p	✓	65	NA	35
O_3 (62900-337)	0 -100	p	✓	65	NA	35
O_3 (calibrator)	0 -100	p	✓	65	NA	35
CO (Picarro)	30 - 300	p	✓	22	45	55
CO (LGR)	30 - 300	p	✓	22	45	55
CH_4 (GC/FID)	1750 - 2100	p	✓	65	93	7
CH_4 (Picarro)	1750 - 2100	p	✓	65	93	7
CO_2 (LI-COR)	380 - 450	p	✓	36	64	36
CO_2 (Picarro)	380 - 450	p	✓	36	64	36
N_2O (GC/ECD)	326.3-336.3	p	✗	3	34	66
N_2O (LGR)	326.3-336.3	p	✓	3	34	66

[1] *Percentage of stations within the eDQO and DQO*

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). The TI was running from 20 May through 01 July 2019. The TI was connected to a separate independent inlet line sampling from the same location as the IZO analyser, and also sampled from the same inlet system as the station analyser in regular intervals. The TI was sampling air using the following sequence: 1400 min ambient air from the independent inlet, 300 min ambient air from the IZO inlet, followed by measurements three standard gases for 30 min. The air was dried by a Nafion dryer (Model PD-50T-12MPS) in reflux mode using the Picarro pump for the vacuum of the purge air flow. To account for the remaining effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the TI data. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below.

Carbon Monoxide

Figure 16 shows the comparison of hourly CO between the WCC-Empa TS and the IZO Picarro G2401 and the LGR analyser. The corresponding deviation histograms are shown in Figure 17. The agreement was within the WMO/GAW compatibility goal for both the Picarro G2401 and the LGR instrument. This results fully confirm the findings of the performance audit and show that both systems are fully appropriate. No further action is required.

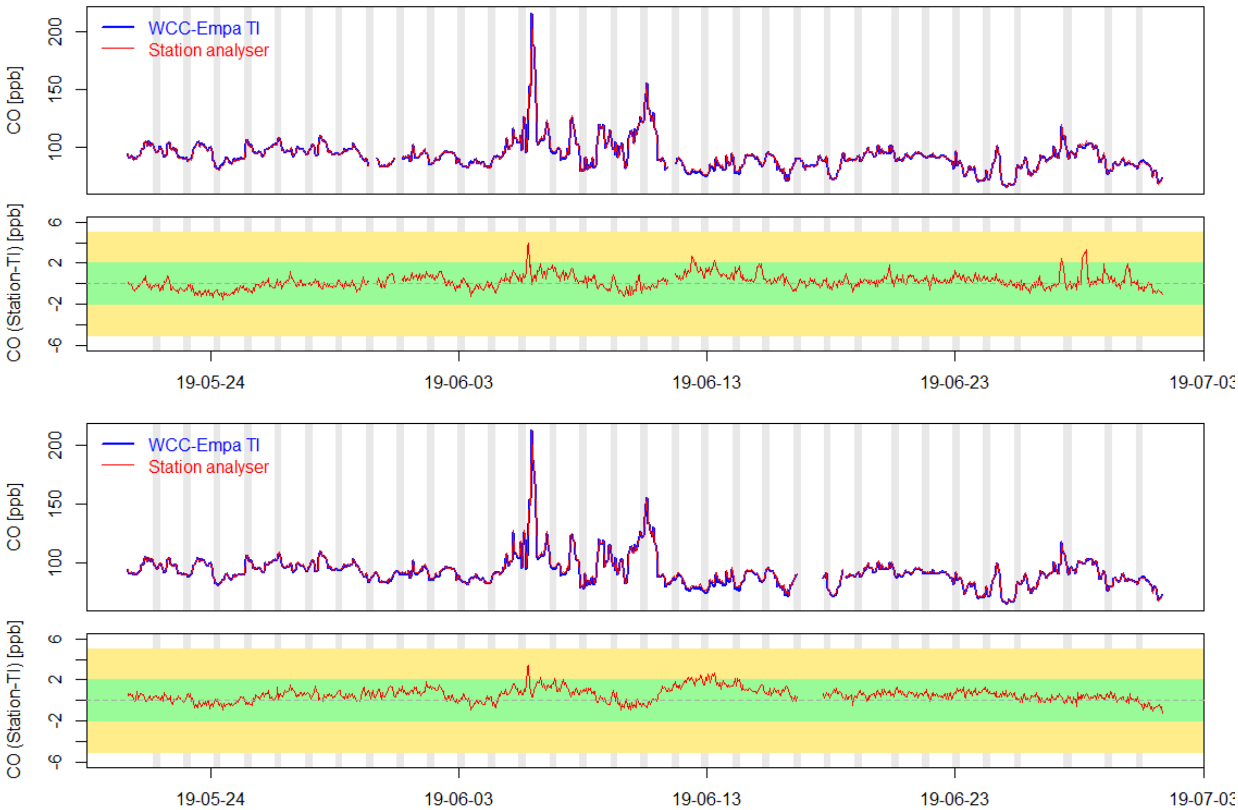

Figure 16. Comparison of the Picarro G2401 analyser (top) and the LGR analyser (bottom) with the WCC-Empa travelling instrument for CO. Time series based on hourly data and the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals. The vertical grey bars indicate periods when the TI was sampling from the same inlet system as the station instrument.

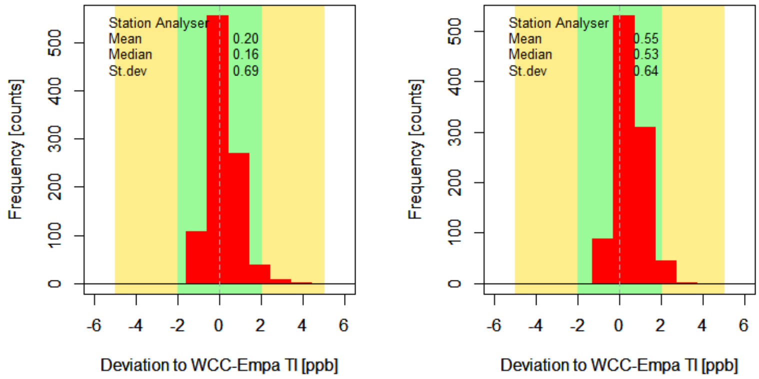

Figure 17. Carbon monoxide deviation histograms for the IZO Picarro G2401 analyser (left) and the LGR analyser (right)

Methane

Figure 18 shows the comparison of hourly CH_4 between the WCC-Empa TS, the IZO Picarro and the IZO Varian 3800 GC/FID system. The corresponding deviation histograms are shown in Figure 19. Excellent agreement was found between the TI and the IZO Picarro G2401, which confirms the results of the performance audit using traveling standards. The temporal variation and the amount fraction was well captured by both instruments, and small variations can be explained by different temporal coverage, response times, and small time differences. The comparison result confirms that the current system is fully adequate.

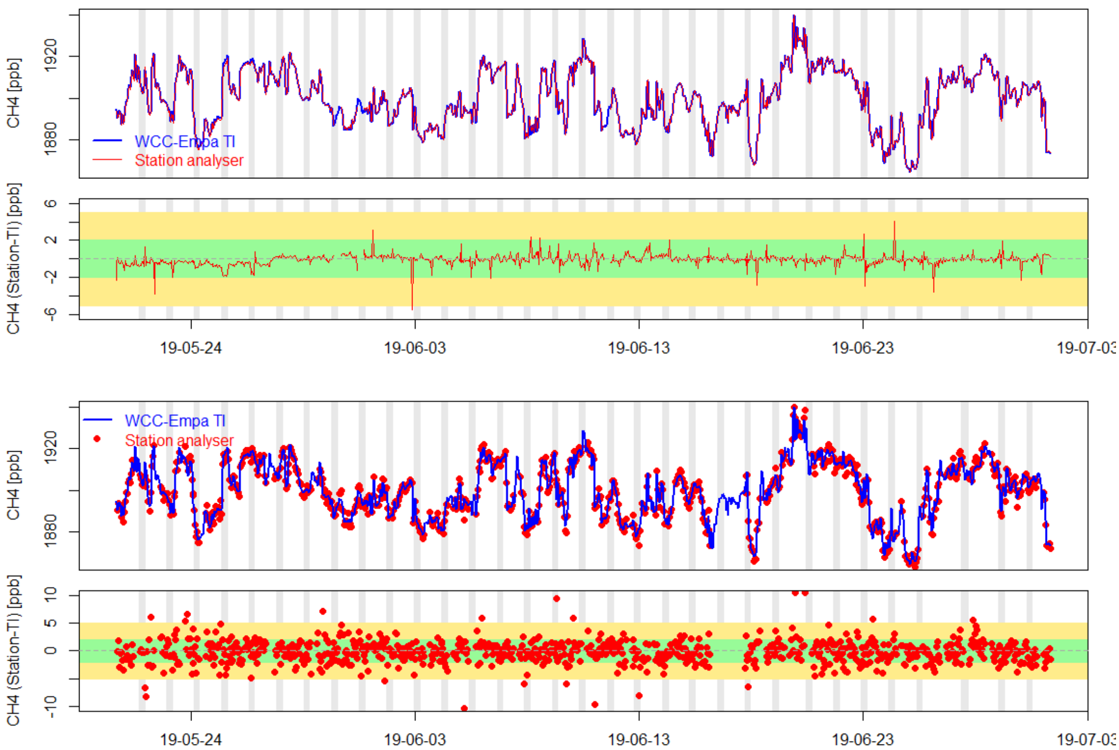

Figure 18. Comparison of the Picarro G2401 analyser (top) and the Varian 3800 GC/FID instrument (bottom) with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data and the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals. The vertical grey bars indicate periods when the TI was sampling from the same inlet system as the station instrument. The vertical grey bars indicate periods when the TI was sampling from the same inlet system as the station instrument.

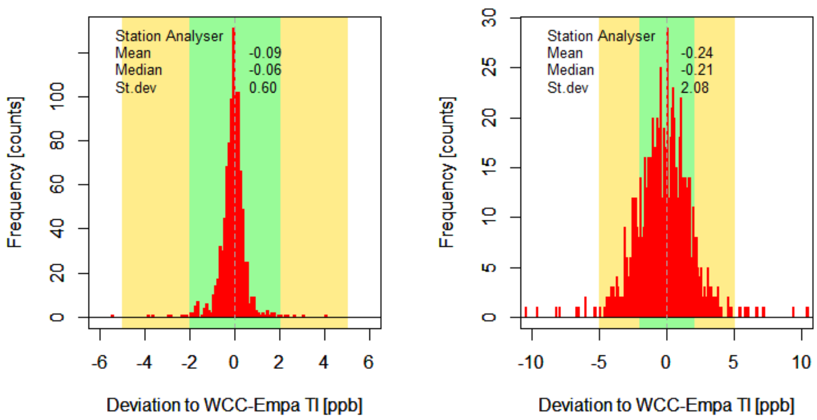

Figure 19. Methane deviation histograms for the IZO Picarro G2401 analyser (left) and the Varian 3800 GC/FID instrument (right).

Carbon Dioxide

Figure 20 shows the comparison of hourly CO_2 between the WCC-Empa TI and the IZO Picarro G2401 and the LI-COR 7000 analyser. Figure 21 shows the corresponding deviation histograms. It can be seen that temporal variability and the amount fraction is well captured by both instruments. Both systems agreed within the WMO/GAW network compatibility goals on average, with slightly larger variations of the LI-COR system. The results confirm that the setup of both CO_2 measurement systems at IZO is fully adequate, and no further action is required.

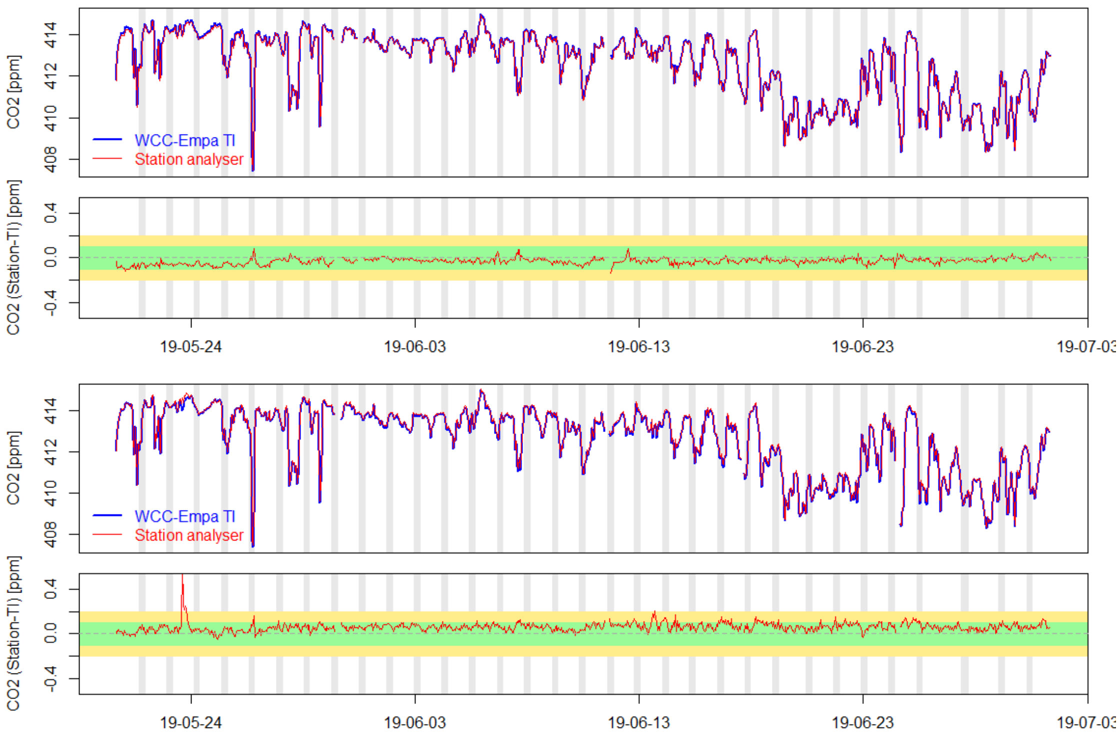

Figure 20. Comparison of the Picarro G2401 (top) and the LI-COR 7000 (bottom) with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data with concurrent availability of the one minute data and the difference between the station instrument and the TI are shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals. The vertical grey bars indicate periods when the TI was sampling from the same inlet system as the station instrument.

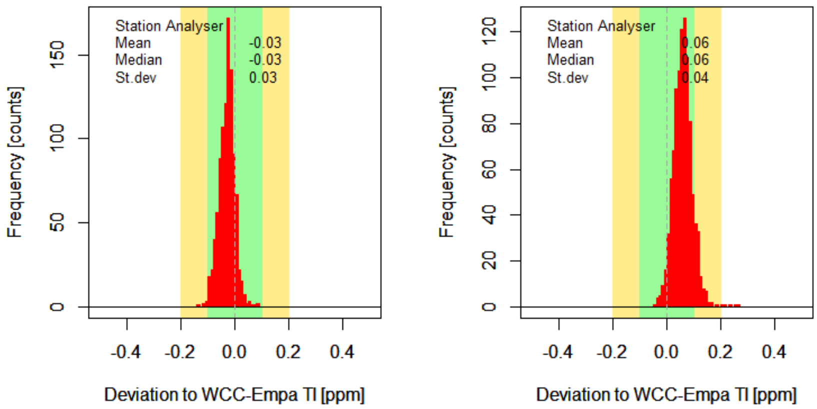

Figure 21. Carbon dioxide deviation histograms for the IZO Picarro G2401 analyser (left) and the LI-COR 7000 analyser (right).

CONCLUSIONS

The global GAW station Izaña provides extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects, which makes it a very significant contribution to the GAW programme. Some of the data series date back the early 80s and are among the longest continuous time series worldwide. Many parameters are independently measured by different analytical techniques, which allows internal comparison and strengthens the quality of the measurements.

The continuation of the Izaña measurement series is highly important for GAW. The large number of measured atmospheric constituents enables research projects and services.
Most assessed measurements were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant amount fraction range. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW network compatibility goals. Note that Table 2 refers only to the mole fractions relevant to IZO, whereas Table 1 further above covers a wider mole fraction range.

Table 2. Synthesis of the performance audit and ambient air comparison results. A tick mark indicates that the compatibility goal (green) or extended compatibility goal (orange) was met on average. Tick marks in parenthesis mean that the goal was only partly reached in the relevant mole fraction range (performance audit only), and ✗ indicates results outside the compatibility goals.

Comparison type	O_3 Analyser	O_3 Calibrator	CO Picarro	CO LGR	CH_4 CG/FID	CH_4 Picarro	CO_2 Li-COR	CO_2 Picarro	N_2O GC/ECD	N_2O LGR
Audit with TS	✓	✓	✓	✓	✓	✓	✓	✓	(✓)	✓
Ambient air comparison	NA	NA	✓	✓	✓	✓	✓	✓	NA	NA

NA no ambient air comparison was made for ozone and N_2O.

SUMMARY RANKING OF THE IZAÑA GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme covering all focal areas of GAW
Access	(5)	Year round access
Facilities		
Laboratory and office space	(5)	Adequate, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable, backup UPS
General Management and Operation		
Organization	(5)	Well managed, clear responsibilities
Competence of staff	(5)	Highly qualified staff
Air Inlet System	(5)	Fully adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2/CO (Picarro)	(5)	State of the art instrumentation
CO_2 (LI-COR-7000)	(4)	Adequate system
CH_4 (Varian 3800 GC/FID)	(3)	Quasi continuous, higher noise
CO and N_2O (LGR)	(5)	State of the art instrumentation
N_2O (Varian 3800 GC/ECD)	(3)	Quasi continuous, higher noise
Standards		
O_3, CO, CO_2, CH_4, N_2O	(5)	NIST traceable (O_3), NOAA and working standards available
Data Management		
Data acquisition	(5)	Fully adequate system
Data processing	(5)	Adequate procedures
Data submission	(5)	Timely data submission of all parameters

#0: inadequate thru 5: adequate.

Dübendorf, March 2020

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APPENDIX

Data Review

The following figures show summary plots of IZO data accessed on 3 September 2019 from WDCGG and on 26 February 2020 from WDCRG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations. The main findings of the data review are discussed below.

Data submitted to WDCGG by IZO:

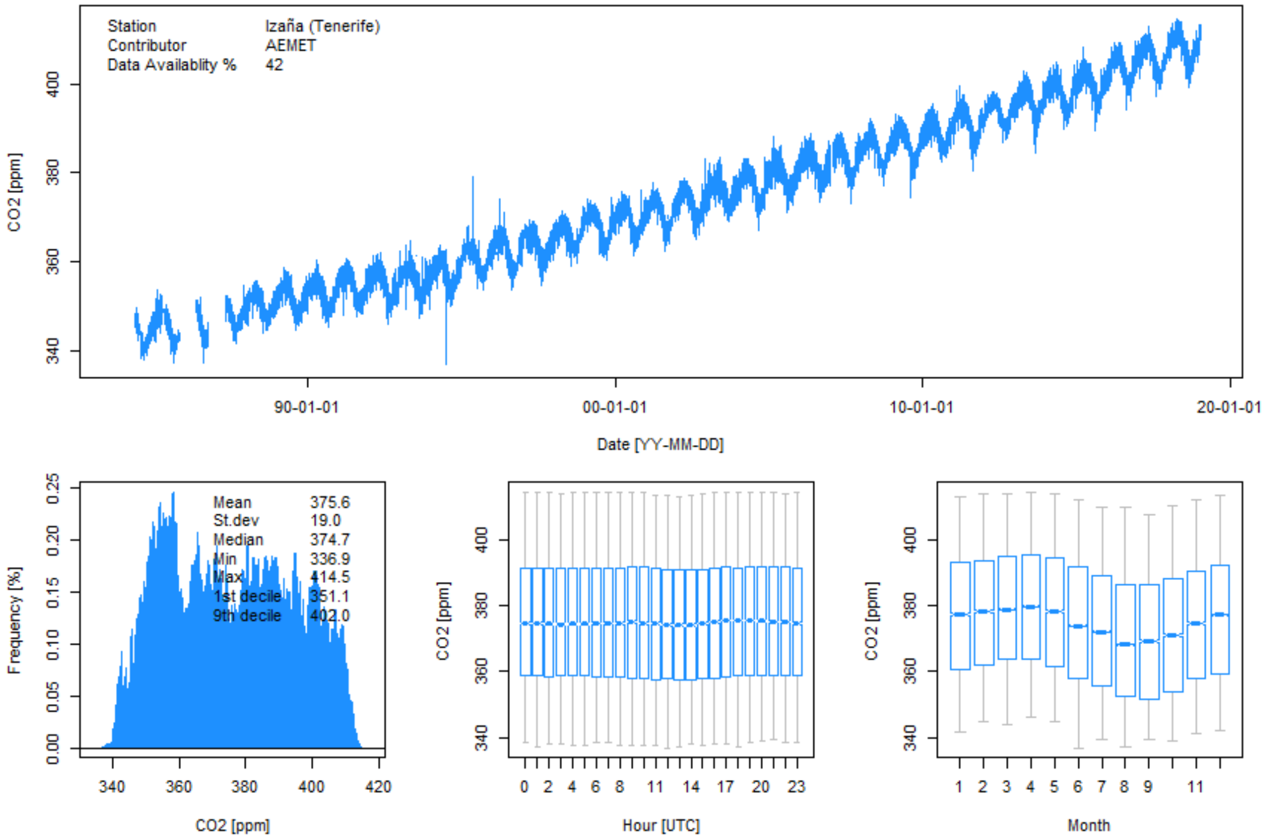

Figure 22. IZO CO_2 data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

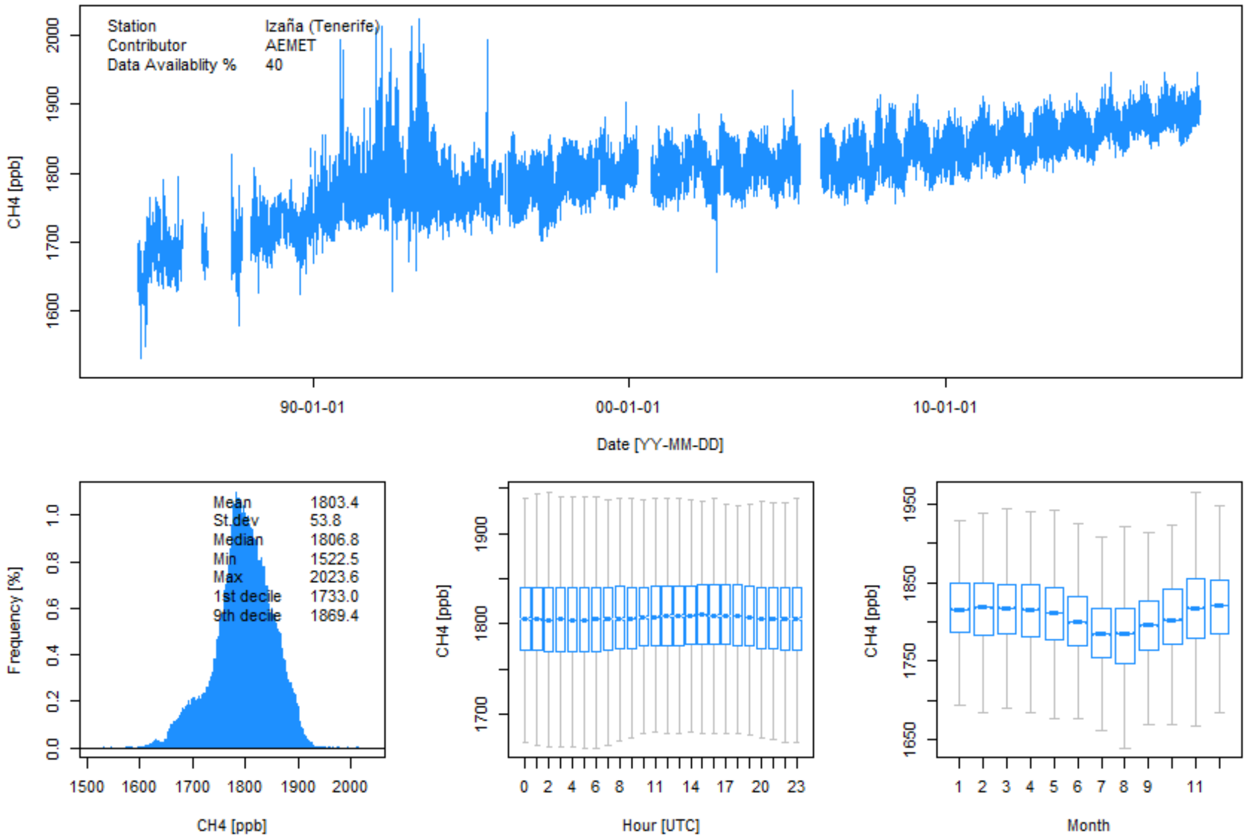

Figure 23. Same as above for CH_4

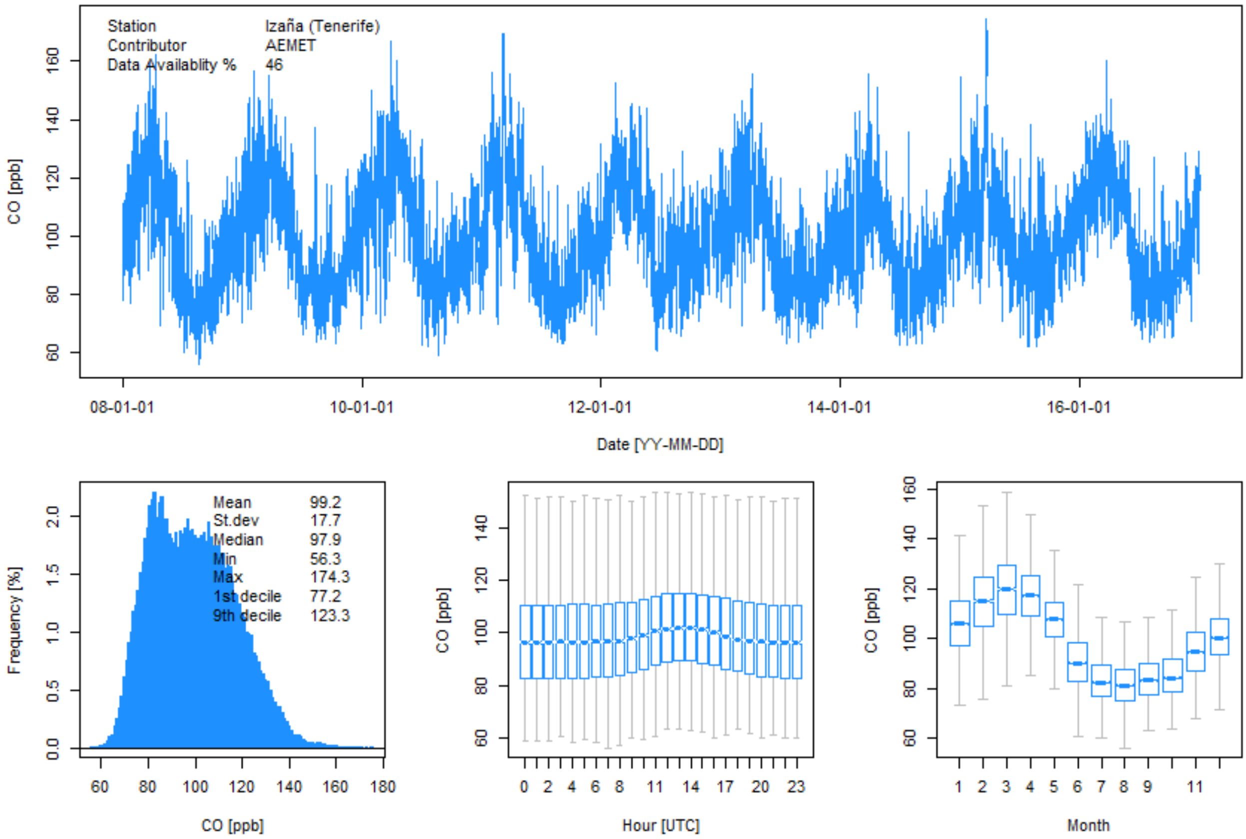

Figure 24. Same as above for CO

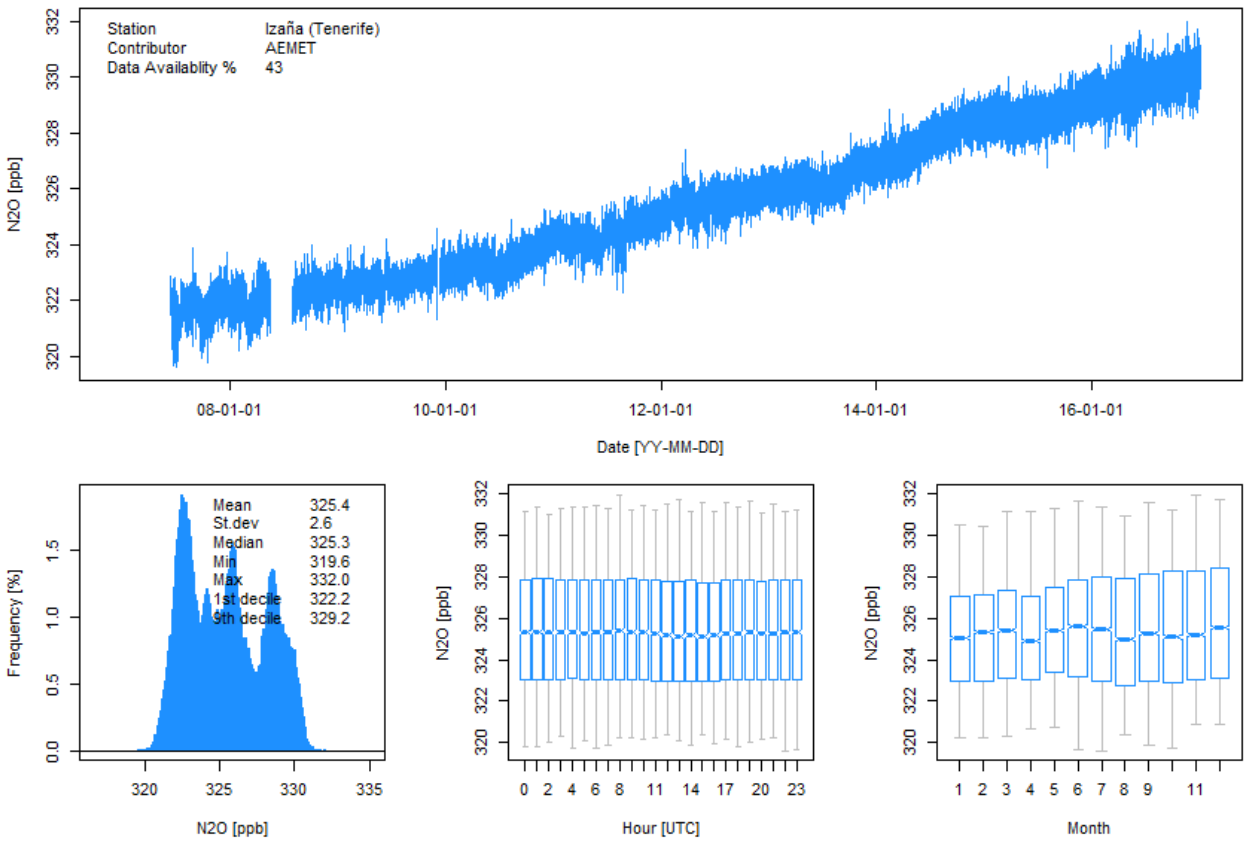

Figure 25. Same as above for N_2O

The data submitted to WDCGG by IZO looks sound. The main findings can be summarized as follows:

Carbon dioxide:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Potentially, a few invalid outliers (in the 90s) have not been identified.

Methane:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- The data quality significantly improved after 1995. A further improvement is expected for the CRDS data which will be submitted in future.

Carbon monoxide:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.

Nitrous oxide:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Further improvement is expected with the new OA-ICOS instrumentation.

Flask data submitted to WDCGG by NOAA:

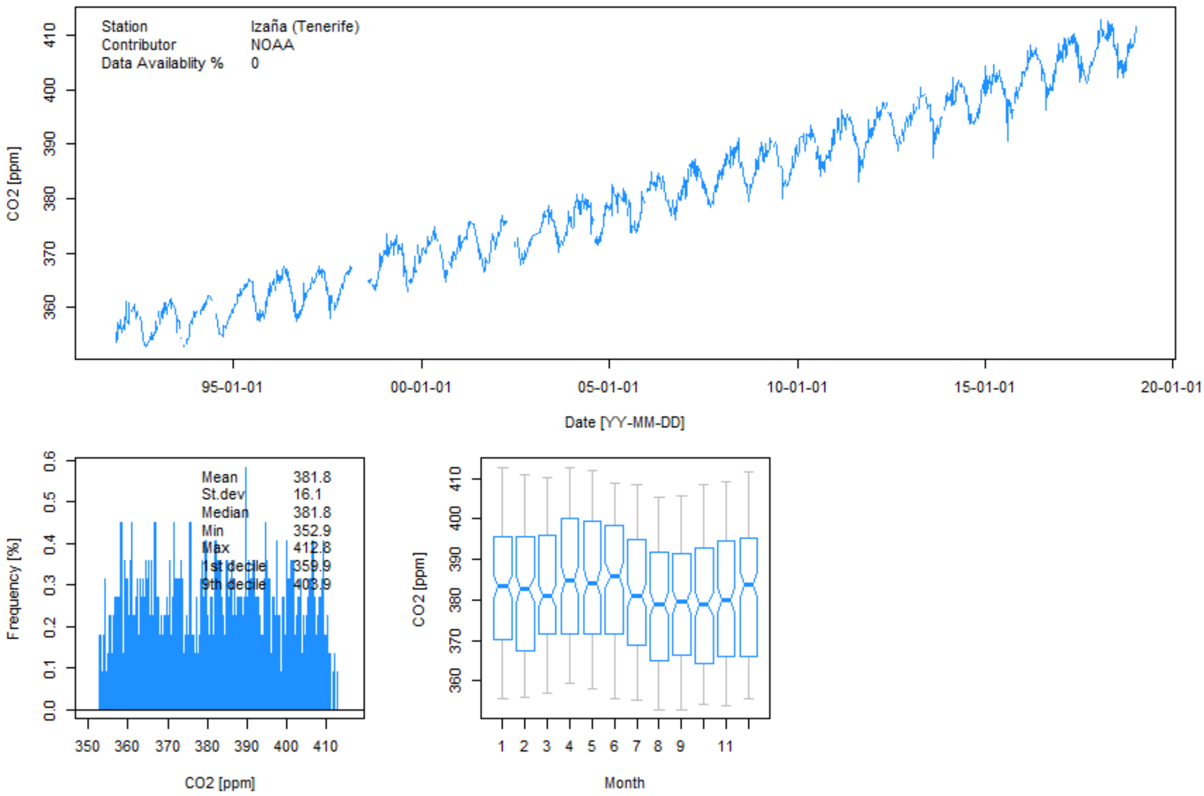

Figure 26. NOAA CO_2 flask data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Right: seasonal variation; the horizontal blue lines denotes to the median, and the blue boxes show the inter-quartile range.

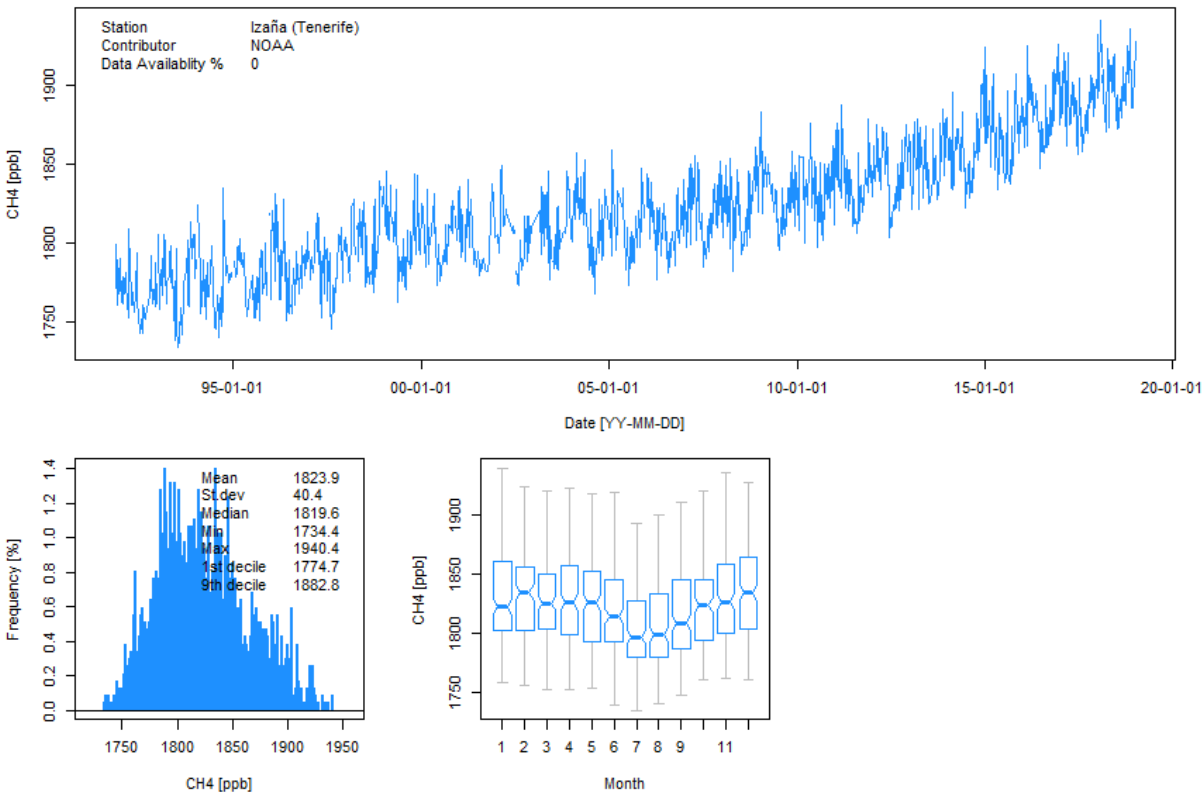

Figure 27. Same as above for CH_4

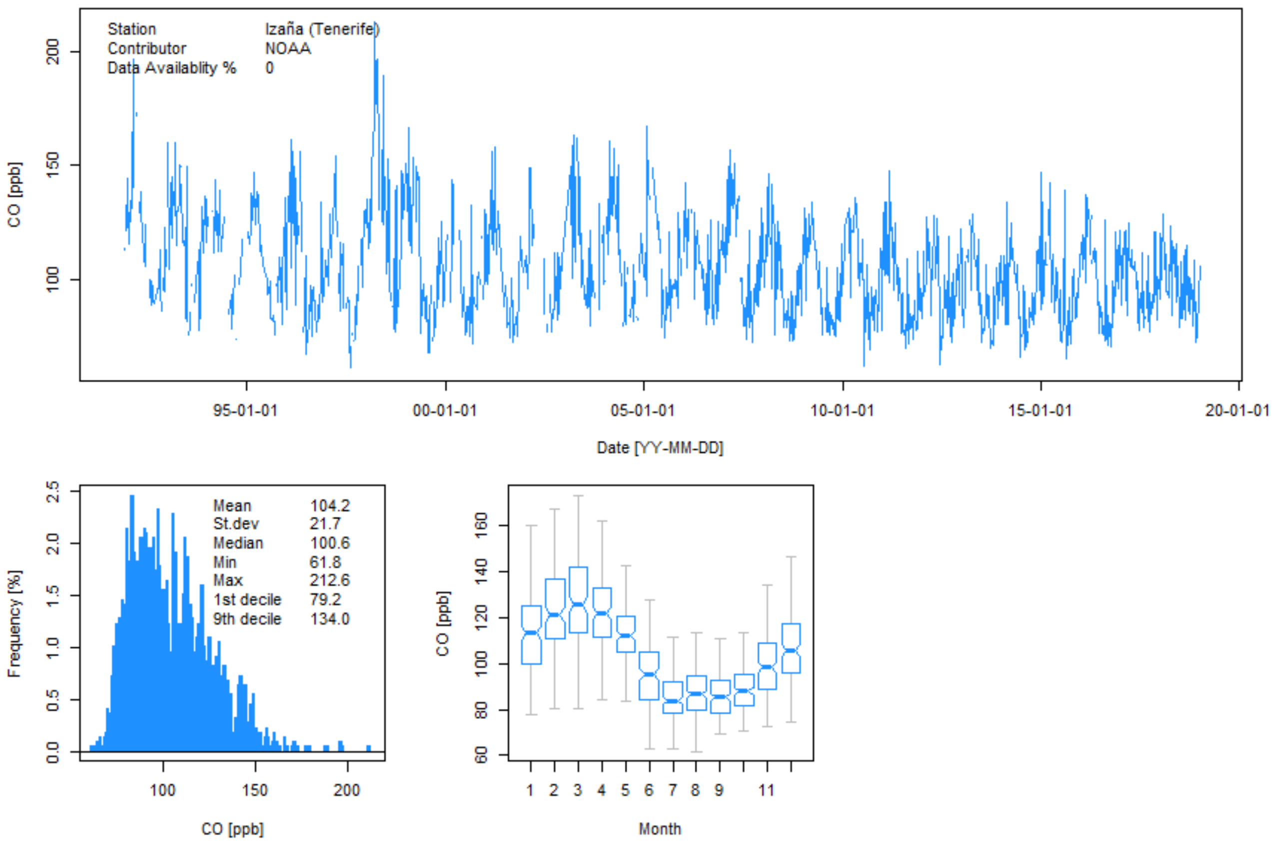

Figure 28. Same as above for CO

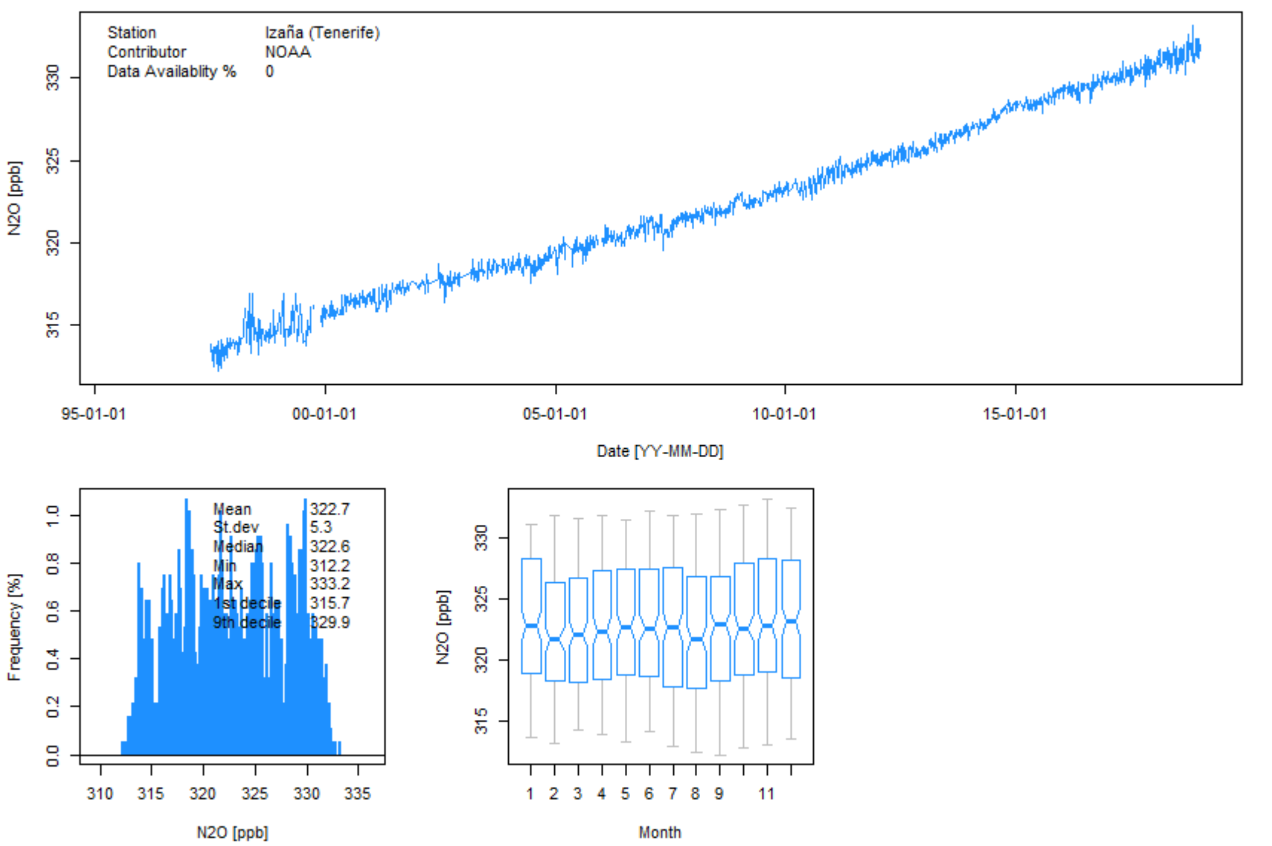

Figure 29. Same as above for N_2O

NOAA flask data:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.

Data submitted to WDCRG by IZO:

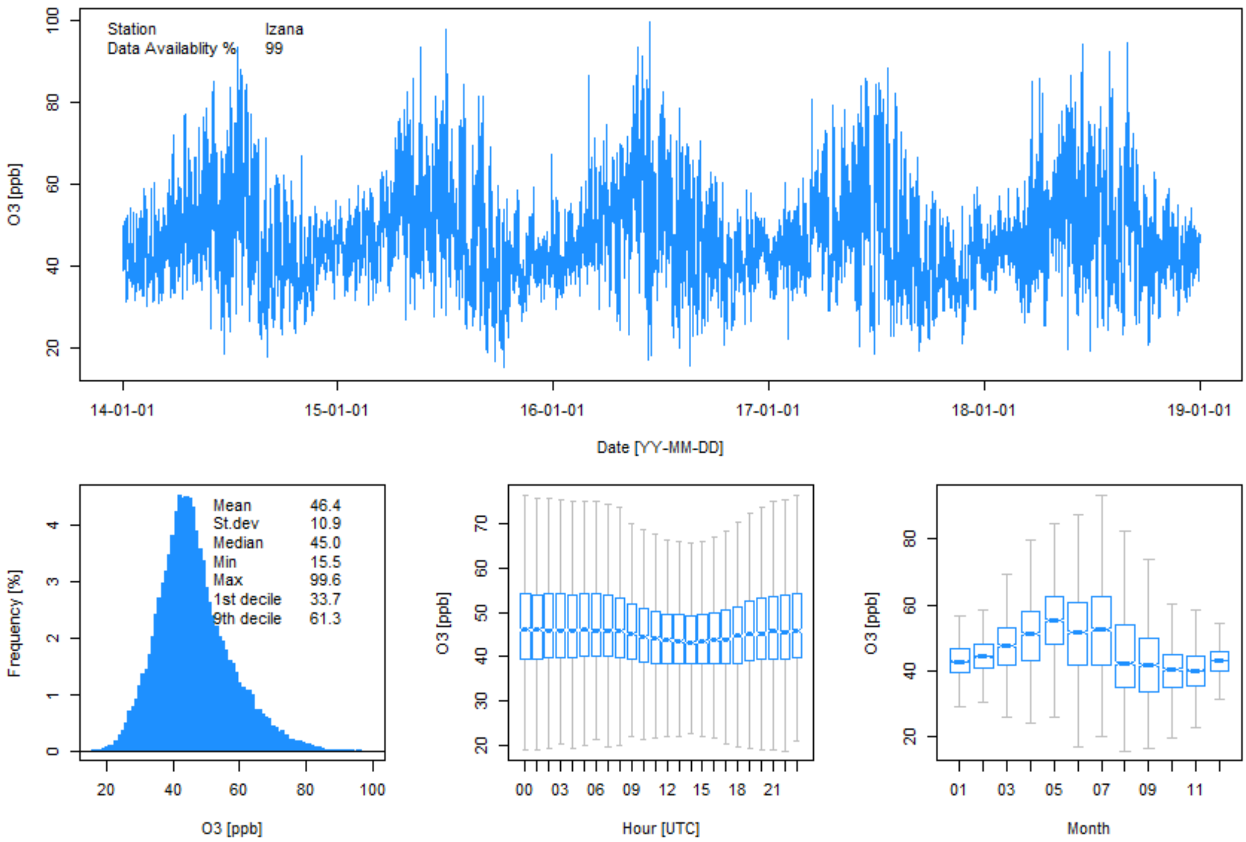

Figure 30. IZO O_3 data accessed from WDCRG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

The ozone data submitted to WDCGG is no longer available and is transferred to WDCRG. Currently, this data cannot be downloaded (see recommendation in the executive summary).

The O_3 data accessed from WDCRG looks sound with respect to amount fraction, seasonal and diurnal cycle.

Surface Ozone Comparisons

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

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa acquisition system.

Table 3. Experimental details of the ozone comparison

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG -0.3, COEF 0.991
Pressure readings (hPa)	Ambient 768.1; TS 767.0, (no adjustment was made)
IZO Station analyser (OA)	
Model, S/N	Thermo Scientific 49C #72491-371
Principle	UV absorption
Range	0-1 ppm
Settings	BKG +0.0 ppb, COEF 1.021
Pressure readings (hPa)	Ambient 768.0; OA 766.7 (no adjustment was made)
IZO Station analyser (OA)	
Model, S/N	Thermo Scientific 49i #1153030026
Principle	UV absorption
Range	0-1 ppm
Settings	BKG +0.0 ppb, COEF 1.003
Pressure readings (hPa)	Ambient 768.4; OA 767.3 (no adjustment was made)
IZO Station analyser (OA)	
Model, S/N	Thermo Scientific 49C #62900-337
Principle	UV absorption
Range	0-1 ppm
Settings	BKG +0.0 ppb, COEF 1.020
Pressure readings (hPa)	Ambient 769.0; OA 767.3 (no adjustment was made)
IZO Station calibrator (OC)	
Model, S/N	Thermo Scientific 49C-PS #56085-306
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.5 ppb, COEF 1.023
Pressure readings (hPa)	Ambient 768.0; OC 761.9 (unadjusted), 766.7 (after adjustment)

Results

Each ozone level was applied for 10 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary.

Table 4. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the IZO ozone analyser (OA) Thermo Scientific 49C #72491-371 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2019-05-15 21:29	1	0	0.32	1.20	0.05	0.09	0.88	NA
2019-05-15 21:39	1	50	49.98	50.90	0.03	0.22	0.92	1.8
2019-05-15 21:49	1	90	89.93	91.14	0.08	0.12	1.21	1.3
2019-05-15 21:59	1	20	20.64	21.43	0.93	1.06	0.79	3.8
2019-05-15 22:09	1	70	70.02	71.17	0.09	0.13	1.15	1.6
2019-05-15 22:19	1	80	79.96	81.11	0.13	0.13	1.15	1.4
2019-05-15 22:29	1	10	10.40	11.09	0.42	0.40	0.69	6.6
2019-05-15 22:39	1	40	39.99	40.75	0.10	0.17	0.76	1.9
2019-05-15 22:49	1	60	59.98	60.85	0.09	0.12	0.87	1.5
2019-05-15 22:59	2	0	0.22	1.10	0.08	0.13	0.88	NA
2019-05-15 23:09	2	100	99.97	100.92	0.04	0.21	0.95	1.0
2019-05-15 23:19	2	25	25.00	25.71	0.11	0.16	0.71	2.8
2019-05-15 23:29	2	200	200.03	201.75	0.08	0.21	1.72	0.9
2019-05-15 23:39	2	150	149.99	151.34	0.04	0.21	1.35	0.9
2019-05-15 23:49	2	50	50.00	50.94	0.15	0.30	0.94	1.9
2019-05-15 23:59	2	175	174.97	176.48	0.08	0.38	1.51	0.9
2019-05-16 00:09	2	125	124.99	126.19	0.04	0.23	1.20	1.0
2019-05-16 00:19	2	75	75.04	75.81	0.11	0.15	0.77	1.0
2019-05-16 00:29	3	0	0.35	0.84	0.14	0.11	0.49	NA
2019-05-16 00:39	3	40	40.00	40.69	0.08	0.11	0.69	1.7
2019-05-16 00:49	3	80	80.01	81.03	0.10	0.16	1.02	1.3
2019-05-16 00:59	3	10	10.15	10.86	0.21	0.14	0.71	7.0
2019-05-16 01:09	3	30	29.97	30.48	0.13	0.14	0.51	1.7
2019-05-16 01:19	3	90	90.04	91.11	0.12	0.05	1.07	1.2
2019-05-16 01:29	3	60	59.96	60.83	0.04	0.26	0.87	1.5
2019-05-16 01:39	3	20	20.20	20.75	0.48	0.51	0.55	2.7
2019-05-16 01:49	3	50	50.02	50.81	0.09	0.14	0.79	1.6
2019-05-16 01:59	3	70	70.01	70.98	0.06	0.25	0.97	1.4
2019-05-16 02:09	4	0	0.16	0.81	0.21	0.16	0.65	NA
2019-05-16 02:19	4	50	49.99	50.54	0.03	0.24	0.55	1.1
2019-05-16 02:29	4	90	89.94	90.75	0.11	0.25	0.81	0.9
2019-05-16 02:39	4	20	20.01	20.69	0.08	0.22	0.68	3.4
2019-05-16 02:49	4	70	69.98	70.72	0.07	0.38	0.74	1.1
2019-05-16 02:59	4	80	80.01	80.86	0.07	0.15	0.85	1.1
2019-05-16 03:09	4	10	10.39	10.85	0.20	0.36	0.46	4.4
2019-05-16 03:19	4	40	39.99	40.57	0.07	0.16	0.58	1.5
2019-05-16 03:29	4	60	60.01	60.83	0.04	0.20	0.82	1.4
2019-05-16 03:39	5	0	0.02	0.81	0.06	0.07	0.79	NA
2019-05-16 03:49	5	100	100.02	101.14	0.14	0.28	1.12	1.1
2019-05-16 03:59	5	25	25.00	25.72	0.11	0.15	0.72	2.9
2019-05-16 04:09	5	200	200.01	201.61	0.12	0.22	1.60	0.8
2019-05-16 04:19	5	150	149.95	151.05	0.11	0.21	1.10	0.7
2019-05-16 04:29	5	50	49.97	50.70	0.10	0.13	0.73	1.5
2019-05-16 04:39	5	175	175.06	176.37	0.03	0.26	1.31	0.7
2019-05-16 04:49	5	125	125.03	126.18	0.05	0.15	1.15	0.9

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2019-05-16 04:59	5	75	74.97	75.88	0.07	0.10	0.91	1.2
2019-05-16 05:09	6	0	0.12	0.69	0.12	0.12	0.57	NA
2019-05-16 05:19	6	40	39.96	40.62	0.07	0.17	0.66	1.7
2019-05-16 05:29	6	80	80.03	80.79	0.08	0.21	0.76	0.9
2019-05-16 05:39	6	10	10.10	10.57	0.17	0.10	0.47	4.7
2019-05-16 05:49	6	30	30.00	30.36	0.15	0.15	0.36	1.2
2019-05-16 05:59	6	90	90.00	90.80	0.08	0.20	0.80	0.9
2019-05-16 06:09	6	60	59.97	60.65	0.12	0.30	0.68	1.1
2019-05-16 06:19	6	20	19.96	20.62	0.10	0.12	0.66	3.3
2019-05-16 06:29	6	50	50.02	50.69	0.09	0.16	0.67	1.3
2019-05-16 06:39	6	70	70.01	70.61	0.08	0.15	0.60	0.9
2019-05-16 06:49	7	0	0.34	0.67	0.14	0.15	0.33	NA
2019-05-16 06:59	7	50	49.99	50.75	0.06	0.12	0.76	1.5
2019-05-16 07:09	7	90	90.01	90.79	0.08	0.13	0.78	0.9
2019-05-16 07:19	7	20	20.02	20.53	0.14	0.13	0.51	2.5
2019-05-16 07:29	7	70	70.04	70.65	0.06	0.12	0.61	0.9
2019-05-16 07:39	7	80	80.00	80.81	0.14	0.25	0.81	1.0
2019-05-16 07:49	7	10	10.37	10.72	0.31	0.39	0.35	3.4
2019-05-16 07:59	7	40	39.98	40.48	0.14	0.20	0.50	1.3
2019-05-16 08:09	7	60	60.02	60.59	0.04	0.13	0.57	0.9
2019-05-16 08:19	8	0	0.32	0.55	0.05	0.12	0.23	NA
2019-05-16 08:29	8	100	100.02	100.63	0.07	0.11	0.61	0.6
2019-05-16 08:39	8	25	25.05	25.49	0.15	0.20	0.44	1.8
2019-05-16 08:49	8	200	200.04	201.46	0.08	0.17	1.42	0.7
2019-05-16 08:59	8	150	149.98	151.15	0.02	0.07	1.17	0.8
2019-05-16 09:09	8	50	49.96	50.65	0.05	0.24	0.69	1.4
2019-05-16 09:19	8	175	175.04	176.70	0.08	0.33	1.66	0.9

Table 5. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the IZO ozone analyser (OA) Thermo Scientific 49i #1153030026 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-16 12:35	1	0	0.10	0.50	0.16	0.16	0.40	NA
2019-05-16 12:45	1	50	50.01	50.33	0.18	0.19	0.32	0.6
2019-05-16 12:55	1	90	90.02	90.80	0.06	0.24	0.78	0.9
2019-05-16 13:05	1	20	19.97	20.43	0.13	0.10	0.46	2.3
2019-05-16 13:15	1	70	69.97	70.81	0.13	0.18	0.84	1.2
2019-05-16 13:25	1	80	80.06	80.52	0.06	0.17	0.46	0.6
2019-05-16 13:35	1	10	10.59	10.87	0.71	0.68	0.28	2.6
2019-05-16 13:45	1	40	40.01	40.34	0.05	0.12	0.33	0.8
2019-05-16 13:55	1	60	60.05	60.65	0.03	0.11	0.60	1.0
2019-05-16 14:05	2	0	0.22	0.70	0.07	0.07	0.48	NA
2019-05-16 14:15	2	100	99.95	100.75	0.05	0.16	0.80	0.8
2019-05-16 14:25	2	25	25.01	25.41	0.11	0.16	0.40	1.6

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-16 14:35	2	200	199.97	201.29	0.04	0.12	1.32	0.7
2019-05-16 14:45	2	150	150.02	151.01	0.07	0.15	0.99	0.7
2019-05-16 14:55	2	50	50.04	50.44	0.08	0.23	0.40	0.8
2019-05-16 15:05	2	175	175.05	176.06	0.07	0.12	1.01	0.6
2019-05-16 15:15	2	125	125.02	125.75	0.07	0.25	0.73	0.6
2019-05-16 15:25	2	75	75.02	75.63	0.04	0.09	0.61	0.8
2019-05-16 15:35	3	0	0.14	0.64	0.11	0.16	0.50	NA
2019-05-16 15:45	3	40	39.97	40.28	0.09	0.14	0.31	0.8
2019-05-16 15:55	3	80	79.98	80.54	0.10	0.11	0.56	0.7
2019-05-16 16:05	3	10	10.32	10.74	0.28	0.32	0.42	4.1
2019-05-16 16:15	3	30	29.99	30.44	0.05	0.32	0.45	1.5
2019-05-16 16:25	3	90	89.99	90.50	0.09	0.32	0.51	0.6
2019-05-16 16:35	3	60	60.02	60.37	0.04	0.17	0.35	0.6
2019-05-16 16:45	3	20	20.06	20.59	0.08	0.08	0.53	2.6
2019-05-16 16:55	3	50	49.97	50.29	0.09	0.07	0.32	0.6
2019-05-16 17:05	3	70	70.02	70.56	0.11	0.23	0.54	0.8
2019-05-16 17:15	4	0	0.14	0.43	0.12	0.18	0.29	NA
2019-05-16 17:25	4	50	49.97	50.35	0.10	0.16	0.38	0.8
2019-05-16 17:35	4	90	90.06	90.61	0.04	0.16	0.55	0.6
2019-05-16 17:45	4	20	19.95	20.28	0.15	0.16	0.33	1.7
2019-05-16 17:55	4	70	70.04	70.48	0.09	0.26	0.44	0.6
2019-05-16 18:05	4	80	80.05	80.68	0.08	0.21	0.63	0.8
2019-05-16 18:15	4	10	10.33	10.89	0.45	0.57	0.56	5.4
2019-05-16 18:25	4	40	39.95	40.37	0.14	0.24	0.42	1.1
2019-05-16 18:35	4	60	59.99	60.42	0.11	0.26	0.43	0.7
2019-05-16 18:45	5	0	0.38	0.62	0.10	0.05	0.24	NA
2019-05-16 18:55	5	100	99.94	100.57	0.09	0.18	0.63	0.6
2019-05-16 19:05	5	25	25.00	25.38	0.14	0.24	0.38	1.5
2019-05-16 19:15	5	200	200.03	201.07	0.07	0.16	1.04	0.5
2019-05-16 19:25	5	150	149.99	150.98	0.08	0.27	0.99	0.7
2019-05-16 19:35	5	50	49.92	50.35	0.04	0.15	0.43	0.9
2019-05-16 19:45	5	175	175.03	176.08	0.11	0.34	1.05	0.6
2019-05-16 19:55	5	125	125.03	125.73	0.06	0.24	0.70	0.6
2019-05-16 20:05	5	75	74.99	75.67	0.09	0.26	0.68	0.9
2019-05-16 20:15	6	0	0.16	0.38	0.17	0.10	0.22	NA
2019-05-16 20:25	6	40	39.99	40.45	0.06	0.23	0.46	1.2
2019-05-16 20:35	6	80	79.98	80.44	0.06	0.25	0.46	0.6
2019-05-16 20:45	6	10	10.31	10.70	0.32	0.43	0.39	3.8
2019-05-16 20:55	6	30	30.02	30.15	0.12	0.16	0.13	0.4
2019-05-16 21:05	6	90	90.03	90.47	0.07	0.07	0.44	0.5
2019-05-16 21:15	6	60	60.01	60.42	0.06	0.23	0.41	0.7
2019-05-16 21:25	6	20	20.02	20.18	0.12	0.20	0.16	0.8
2019-05-16 21:35	6	50	49.95	50.43	0.07	0.17	0.48	1.0
2019-05-16 21:45	6	70	70.03	70.33	0.10	0.33	0.30	0.4
2019-05-16 21:55	7	0	0.41	0.42	0.20	0.05	0.01	NA
2019-05-16 22:05	7	50	49.96	50.43	0.07	0.23	0.47	0.9
2019-05-16 22:15	7	90	89.99	90.65	0.07	0.36	0.66	0.7
2019-05-16 22:25	7	20	19.99	20.39	0.12	0.17	0.40	2.0

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-16 22:35	7	70	69.98	70.30	0.08	0.21	0.32	0.5
2019-05-16 22:45	7	80	79.94	80.49	0.04	0.15	0.55	0.7
2019-05-16 22:55	7	10	10.99	11.19	0.98	0.95	0.20	1.8
2019-05-16 23:05	7	40	39.99	40.20	0.08	0.12	0.21	0.5
2019-05-16 23:15	7	60	60.00	60.39	0.10	0.07	0.39	0.6
2019-05-16 23:25	8	0	0.35	0.56	0.09	0.16	0.21	NA
2019-05-16 23:35	8	100	99.97	100.81	0.09	0.35	0.84	0.8
2019-05-16 23:45	8	25	25.03	25.30	0.15	0.21	0.27	1.1
2019-05-16 23:55	8	200	200.05	201.36	0.09	0.20	1.31	0.7
2019-05-17 00:05	8	150	149.99	151.05	0.09	0.10	1.06	0.7
2019-05-17 00:15	8	50	49.98	50.51	0.09	0.17	0.53	1.1
2019-05-17 00:25	8	175	175.00	176.19	0.05	0.46	1.19	0.7
2019-05-17 00:35	8	125	125.07	125.84	0.07	0.18	0.77	0.6
2019-05-17 00:45	8	75	74.97	75.41	0.05	0.14	0.44	0.6
2019-05-17 00:55	9	0	0.18	0.35	0.14	0.10	0.17	NA
2019-05-17 01:05	9	40	40.02	40.57	0.08	0.15	0.55	1.4
2019-05-17 01:15	9	80	79.99	80.53	0.03	0.19	0.54	0.7
2019-05-17 01:25	9	10	10.94	11.15	0.78	0.72	0.21	1.9
2019-05-17 01:35	9	30	29.99	30.41	0.14	0.17	0.42	1.4
2019-05-17 01:45	9	90	89.96	90.51	0.07	0.19	0.55	0.6
2019-05-17 01:55	9	60	60.02	60.41	0.08	0.14	0.39	0.6
2019-05-17 02:05	9	20	20.00	20.31	0.08	0.09	0.31	1.6
2019-05-17 02:15	9	50	50.01	50.51	0.12	0.12	0.50	1.0
2019-05-17 02:25	9	70	70.02	70.35	0.12	0.21	0.33	0.5
2019-05-17 02:35	10	0	0.40	0.43	0.11	0.25	0.03	NA
2019-05-17 02:45	10	50	49.97	50.32	0.05	0.14	0.35	0.7
2019-05-17 02:55	10	90	89.99	90.51	0.08	0.24	0.52	0.6
2019-05-17 03:05	10	20	19.96	20.32	0.11	0.18	0.36	1.8
2019-05-17 03:15	10	70	69.96	70.34	0.06	0.11	0.38	0.5
2019-05-17 03:25	10	80	79.98	80.47	0.10	0.19	0.49	0.6
2019-05-17 03:35	10	10	10.33	10.44	0.41	0.30	0.11	1.1
2019-05-17 03:45	10	40	39.92	40.13	0.02	0.12	0.21	0.5
2019-05-17 03:55	10	60	59.95	60.22	0.12	0.26	0.27	0.5
2019-05-17 04:05	11	0	0.36	0.50	0.20	0.14	0.14	NA
2019-05-17 04:15	11	100	100.00	100.54	0.11	0.14	0.54	0.5
2019-05-17 04:25	11	25	25.02	25.12	0.06	0.26	0.10	0.4
2019-05-17 04:35	11	200	199.98	201.33	0.13	0.42	1.35	0.7
2019-05-17 04:45	11	150	150.00	150.87	0.07	0.12	0.87	0.6
2019-05-17 04:55	11	50	49.97	50.38	0.05	0.20	0.41	0.8
2019-05-17 05:05	11	175	175.05	176.23	0.13	0.17	1.18	0.7
2019-05-17 05:15	11	125	124.95	125.95	0.06	0.06	1.00	0.8
2019-05-17 05:25	11	75	74.95	75.33	0.11	0.20	0.38	0.5
2019-05-17 05:35	12	0	0.20	0.42	0.14	0.21	0.22	NA
2019-05-17 05:45	12	40	39.99	40.32	0.04	0.14	0.33	0.8
2019-05-17 05:55	12	80	79.98	80.69	0.09	0.32	0.71	0.9
2019-05-17 06:05	12	10	10.32	10.39	0.19	0.25	0.07	0.7
2019-05-17 06:15	12	30	30.00	30.48	0.14	0.18	0.48	1.6
2019-05-17 06:25	12	90	89.98	90.53	0.12	0.21	0.55	0.6

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-17 06:35	12	60	59.99	60.19	0.10	0.13	0.20	0.3
2019-05-17 06:45	12	20	19.98	20.13	0.06	0.23	0.15	0.8
2019-05-17 06:55	12	50	49.99	50.55	0.08	0.20	0.56	1.1
2019-05-17 07:05	12	70	70.00	70.67	0.11	0.30	0.67	1.0
2019-05-17 07:15	13	0	0.34	0.42	0.08	0.12	0.08	NA
2019-05-17 07:25	13	50	50.06	50.46	0.07	0.16	0.40	0.8
2019-05-17 07:35	13	90	89.97	90.52	0.04	0.19	0.55	0.6
2019-05-17 07:45	13	20	20.02	20.28	0.19	0.24	0.26	1.3
2019-05-17 07:55	13	70	70.00	70.54	0.12	0.17	0.54	0.8
2019-05-17 08:05	13	80	80.00	80.28	0.08	0.18	0.28	0.4
2019-05-17 08:15	13	10	10.00	10.29	0.09	0.20	0.29	2.9
2019-05-17 08:25	13	40	39.97	40.36	0.09	0.13	0.39	1.0
2019-05-17 08:35	13	60	60.00	60.56	0.06	0.13	0.56	0.9
2019-05-17 08:45	14	0	0.36	0.51	0.13	0.12	0.15	NA
2019-05-17 08:55	14	100	99.95	100.71	0.06	0.33	0.76	0.8
2019-05-17 09:05	14	25	25.02	25.24	0.06	0.11	0.22	0.9
2019-05-17 09:15	14	200	200.05	201.13	0.05	0.20	1.08	0.5
2019-05-17 09:25	14	150	150.01	151.11	0.04	0.17	1.10	0.7
2019-05-17 09:35	14	50	49.99	50.43	0.05	0.12	0.44	0.9
2019-05-17 09:45	14	175	175.00	176.10	0.08	0.18	1.10	0.6
2019-05-17 09:55	14	125	125.02	125.70	0.06	0.21	0.68	0.5
2019-05-17 10:05	14	75	75.03	75.41	0.09	0.20	0.38	0.5
2019-05-17 10:15	15	0	0.28	0.41	0.13	0.06	0.13	NA
2019-05-17 10:25	15	40	39.97	40.29	0.08	0.25	0.32	0.8
2019-05-17 10:35	15	80	80.04	80.67	0.07	0.06	0.63	0.8
2019-05-17 10:45	15	10	10.66	10.97	0.47	0.26	0.31	2.9
2019-05-17 10:55	15	30	29.99	30.25	0.10	0.25	0.26	0.9

Table 6. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the IZO ozone analyser (OA) Thermo Scientific 49C #62900-337 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-19 11:06	1	0	0.23	0.20	0.12	0.14	-0.03	-13.0
2019-05-19 11:16	1	50	50.00	50.01	0.07	0.09	0.01	0.0
2019-05-19 11:26	1	90	89.94	89.96	0.05	0.17	0.02	0.0
2019-05-19 11:36	1	20	19.98	19.98	0.06	0.15	0.00	0.0
2019-05-19 11:46	1	70	69.96	69.91	0.11	0.27	-0.05	-0.1
2019-05-19 11:56	1	80	79.98	79.86	0.09	0.20	-0.12	-0.2
2019-05-19 12:06	1	10	10.53	10.35	0.37	0.27	-0.18	-1.7
2019-05-19 12:16	1	40	39.96	39.87	0.11	0.19	-0.09	-0.2
2019-05-19 12:26	1	60	59.98	59.86	0.10	0.23	-0.12	-0.2
2019-05-19 12:36	2	0	0.31	0.30	0.11	0.20	-0.01	-3.2
2019-05-19 12:46	2	100	99.96	99.97	0.08	0.28	0.01	0.0
2019-05-19 12:56	2	25	24.94	24.89	0.05	0.22	-0.05	-0.2

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-19 13:06	2	200	199.98	200.37	0.05	0.11	0.39	0.2
2019-05-19 13:16	2	150	150.03	150.06	0.06	0.14	0.03	0.0
2019-05-19 13:26	2	50	50.03	49.94	0.03	0.20	-0.09	-0.2
2019-05-19 13:36	2	175	175.02	175.17	0.09	0.10	0.15	0.1
2019-05-19 13:46	2	125	125.07	125.05	0.06	0.26	-0.02	0.0
2019-05-19 13:56	2	75	75.01	74.94	0.08	0.14	-0.07	-0.1
2019-05-19 14:06	3	0	0.35	0.25	0.05	0.10	-0.10	-28.6
2019-05-19 14:16	3	40	39.96	39.97	0.12	0.16	0.01	0.0
2019-05-19 14:26	3	80	79.98	80.03	0.04	0.13	0.05	0.1
2019-05-19 14:36	3	10	10.24	10.21	0.25	0.39	-0.03	-0.3
2019-05-19 14:46	3	30	30.05	29.96	0.12	0.11	-0.09	-0.3
2019-05-19 14:56	3	90	90.02	90.02	0.05	0.11	0.00	0.0
2019-05-19 15:06	3	60	59.96	59.74	0.05	0.09	-0.22	-0.4
2019-05-19 15:16	3	20	20.03	19.92	0.07	0.12	-0.11	-0.5
2019-05-19 15:26	3	50	50.01	50.02	0.06	0.15	0.01	0.0
2019-05-19 15:36	3	70	69.95	69.83	0.06	0.19	-0.12	-0.2
2019-05-19 15:46	4	0	0.33	0.29	0.14	0.16	-0.04	-12.1
2019-05-19 15:56	4	50	49.97	49.85	0.07	0.11	-0.12	-0.2
2019-05-19 16:06	4	90	89.95	89.89	0.12	0.20	-0.06	-0.1
2019-05-19 16:16	4	20	20.01	19.85	0.09	0.18	-0.16	-0.8
2019-05-19 16:26	4	70	69.97	69.88	0.04	0.18	-0.09	-0.1
2019-05-19 16:36	4	80	79.99	79.99	0.07	0.14	0.00	0.0
2019-05-19 16:46	4	10	10.24	10.19	0.40	0.27	-0.05	-0.5
2019-05-19 16:56	4	40	39.97	39.74	0.07	0.19	-0.23	-0.6
2019-05-19 17:06	4	60	60.02	59.85	0.07	0.16	-0.17	-0.3
2019-05-19 17:16	5	0	0.33	0.31	0.13	0.15	-0.02	-6.1
2019-05-19 17:26	5	100	99.94	99.85	0.08	0.10	-0.09	-0.1
2019-05-19 17:36	5	25	25.02	24.80	0.12	0.09	-0.22	-0.9
2019-05-19 17:46	5	200	200.00	200.12	0.05	0.12	0.12	0.1
2019-05-19 17:56	5	150	149.97	150.00	0.03	0.08	0.03	0.0
2019-05-19 18:06	5	50	49.97	49.85	0.08	0.14	-0.12	-0.2
2019-05-19 18:16	5	175	174.97	175.07	0.04	0.22	0.10	0.1
2019-05-19 18:26	5	125	124.93	124.85	0.02	0.26	-0.08	-0.1
2019-05-19 18:36	5	75	75.02	74.96	0.07	0.15	-0.06	-0.1
2019-05-19 18:46	6	0	0.38	0.18	0.17	0.12	-0.20	-52.6
2019-05-19 18:56	6	40	39.92	39.70	0.08	0.12	-0.22	-0.6
2019-05-19 19:06	6	80	80.03	79.81	0.06	0.32	-0.22	-0.3
2019-05-19 19:16	6	10	9.99	9.95	0.14	0.11	-0.04	-0.4
2019-05-19 19:26	6	30	30.00	30.01	0.20	0.21	0.01	0.0
2019-05-19 19:36	6	90	90.01	89.92	0.11	0.17	-0.09	-0.1
2019-05-19 19:46	6	60	60.04	59.91	0.08	0.16	-0.13	-0.2
2019-05-19 19:56	6	20	20.04	19.84	0.09	0.11	-0.20	-1.0
2019-05-19 20:06	6	50	50.06	50.03	0.09	0.13	-0.03	-0.1
2019-05-19 20:16	6	70	70.02	70.21	0.14	0.22	0.19	0.3
2019-05-19 20:26	7	0	0.29	0.25	0.18	0.06	-0.04	-13.8
2019-05-19 20:36	7	50	49.96	49.95	0.09	0.14	-0.01	0.0
2019-05-19 20:46	7	90	90.01	89.97	0.10	0.27	-0.04	0.0
2019-05-19 20:56	7	20	19.97	19.84	0.11	0.11	-0.13	-0.7

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-19 21:06	7	70	69.99	69.89	0.08	0.12	-0.10	-0.1
2019-05-19 21:16	7	80	79.98	79.85	0.05	0.12	-0.13	-0.2
2019-05-19 21:26	7	10	10.11	10.00	0.35	0.49	-0.11	-1.1
2019-05-19 21:36	7	40	40.00	39.86	0.09	0.14	-0.14	-0.4
2019-05-19 21:46	7	60	59.98	59.90	0.08	0.14	-0.08	-0.1
2019-05-19 21:56	8	0	0.21	0.25	0.10	0.06	0.04	19.0
2019-05-19 22:06	8	100	99.97	99.72	0.02	0.11	-0.25	-0.3
2019-05-19 22:16	8	25	25.03	25.12	0.06	0.21	0.09	0.4
2019-05-19 22:26	8	200	199.96	200.05	0.08	0.12	0.09	0.0
2019-05-19 22:36	8	150	150.01	150.07	0.07	0.30	0.06	0.0
2019-05-19 22:46	8	50	49.98	49.82	0.07	0.16	-0.16	-0.3
2019-05-19 22:56	8	175	175.03	175.28	0.08	0.14	0.25	0.1
2019-05-19 23:06	8	125	125.00	124.98	0.07	0.24	-0.02	0.0
2019-05-19 23:16	8	75	74.96	74.87	0.07	0.15	-0.09	-0.1
2019-05-19 23:26	9	0	0.19	0.27	0.23	0.06	0.08	42.1
2019-05-19 23:36	9	40	39.95	39.85	0.13	0.23	-0.10	-0.3
2019-05-19 23:46	9	80	79.98	79.83	0.07	0.10	-0.15	-0.2
2019-05-19 23:56	9	10	10.50	10.36	0.37	0.37	-0.14	-1.3
2019-05-20 00:06	9	30	29.95	30.09	0.10	0.31	0.14	0.5
2019-05-20 00:16	9	90	89.96	89.78	0.07	0.20	-0.18	-0.2
2019-05-20 00:26	9	60	60.00	59.63	0.13	0.15	-0.37	-0.6
2019-05-20 00:36	9	20	20.08	19.84	0.12	0.20	-0.24	-1.2
2019-05-20 00:46	9	50	50.02	49.72	0.07	0.25	-0.30	-0.6
2019-05-20 00:56	9	70	70.05	69.71	0.05	0.13	-0.34	-0.5
2019-05-20 01:06	10	0	0.29	0.25	0.09	0.15	-0.04	-13.8
2019-05-20 01:16	10	50	49.93	49.65	0.09	0.26	-0.28	-0.6
2019-05-20 01:26	10	90	89.98	89.81	0.06	0.19	-0.17	-0.2
2019-05-20 01:36	10	20	20.01	19.94	0.09	0.13	-0.07	-0.3
2019-05-20 01:46	10	70	70.03	69.73	0.10	0.17	-0.30	-0.4
2019-05-20 01:56	10	80	80.01	79.82	0.06	0.24	-0.19	-0.2
2019-05-20 02:06	10	10	10.10	9.86	0.16	0.30	-0.24	-2.4
2019-05-20 02:16	10	40	39.91	39.64	0.08	0.14	-0.27	-0.7
2019-05-20 02:26	10	60	59.99	59.87	0.04	0.15	-0.12	-0.2
2019-05-20 02:36	11	0	0.12	0.18	0.09	0.11	0.06	50.0
2019-05-20 02:46	11	100	99.97	99.92	0.04	0.24	-0.05	-0.1
2019-05-20 02:56	11	25	24.96	24.76	0.05	0.10	-0.20	-0.8
2019-05-20 03:06	11	200	199.94	199.99	0.13	0.19	0.05	0.0
2019-05-20 03:16	11	150	149.98	150.00	0.07	0.27	0.02	0.0
2019-05-20 03:26	11	50	49.97	49.82	0.11	0.06	-0.15	-0.3
2019-05-20 03:36	11	175	174.97	174.90	0.10	0.19	-0.07	0.0
2019-05-20 03:46	11	125	124.97	124.83	0.05	0.07	-0.14	-0.1
2019-05-20 03:56	11	75	75.02	74.91	0.08	0.25	-0.11	-0.1
2019-05-20 04:06	12	0	0.29	0.28	0.11	0.08	-0.01	-3.4
2019-05-20 04:16	12	40	39.99	39.82	0.06	0.14	-0.17	-0.4
2019-05-20 04:26	12	80	80.02	79.85	0.04	0.10	-0.17	-0.2
2019-05-20 04:36	12	10	10.03	10.01	0.07	0.14	-0.02	-0.2
2019-05-20 04:46	12	30	29.97	29.97	0.12	0.10	0.00	0.0
2019-05-20 04:56	12	90	89.97	89.83	0.08	0.18	-0.14	-0.2

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-05-20 05:06	12	60	60.03	59.93	0.07	0.10	-0.10	-0.2
2019-05-20 05:16	12	20	20.03	19.90	0.11	0.12	-0.13	-0.6
2019-05-20 05:26	12	50	49.96	49.86	0.14	0.14	-0.10	-0.2
2019-05-20 05:36	12	70	69.97	69.89	0.07	0.34	-0.08	-0.1
2019-05-20 05:46	13	0	0.34	0.29	0.10	0.10	-0.05	-14.7
2019-05-20 05:56	13	50	49.99	49.72	0.07	0.16	-0.27	-0.5
2019-05-20 06:06	13	90	89.94	89.68	0.07	0.24	-0.26	-0.3
2019-05-20 06:16	13	20	20.02	19.69	0.13	0.24	-0.33	-1.6

Table 7. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the IZO ozone calibrator (OC) Thermo Scientific 49C-PS #56085-306 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2019-05-15 00:00	21:29	1	0.00	0.32	0.90	0.05	0.13	0.6
2019-05-15 00:00	21:39	1	50.00	49.98	50.56	0.03	0.15	0.6
2019-05-15 00:00	21:49	1	90.00	89.93	90.67	0.08	0.24	0.7
2019-05-15 00:00	21:59	1	20.00	20.64	21.20	0.93	1.02	0.6
2019-05-15 00:00	22:09	1	70.00	70.02	70.77	0.09	0.17	0.8
2019-05-15 00:00	22:19	1	80.00	79.96	80.71	0.13	0.14	0.8
2019-05-15 00:00	22:29	1	10.00	10.40	11.08	0.42	0.38	0.7
2019-05-15 00:00	22:39	1	40.00	39.99	40.61	0.10	0.13	0.6
2019-05-15 00:00	22:49	1	60.00	59.98	60.69	0.09	0.14	0.7
2019-05-15 00:00	22:59	2	0.00	0.22	0.87	0.08	0.09	0.7
2019-05-15 00:00	23:09	2	100.00	99.97	100.64	0.04	0.22	0.7
2019-05-15 00:00	23:19	2	25.00	25.00	25.64	0.11	0.20	0.6
2019-05-15 00:00	23:29	2	200.00	200.03	200.98	0.08	0.23	1.0
2019-05-15 00:00	23:39	2	150.00	149.99	150.77	0.04	0.13	0.8
2019-05-15 00:00	23:49	2	50.00	50.00	50.58	0.15	0.31	0.6
2019-05-15 00:00	23:59	2	175.00	174.97	175.94	0.08	0.18	1.0
2019-05-16 00:00	00:09	2	125.00	124.99	125.76	0.04	0.28	0.8
2019-05-16 00:00	00:19	2	75.00	75.04	75.68	0.11	0.17	0.6
2019-05-16 00:00	00:29	3	0.00	0.35	0.86	0.14	0.10	0.5
2019-05-16 00:00	00:39	3	40.00	40.00	40.63	0.08	0.05	0.6
2019-05-16 00:00	00:49	3	80.00	80.01	80.84	0.10	0.15	0.8
2019-05-16 00:00	00:59	3	10.00	10.15	10.79	0.21	0.19	0.6
2019-05-16 00:00	01:09	3	30.00	29.97	30.34	0.13	0.28	0.4
2019-05-16 00:00	01:19	3	90.00	90.04	90.79	0.12	0.16	0.8
2019-05-16 00:00	01:29	3	60.00	59.96	60.81	0.04	0.16	0.9
2019-05-16 00:00	01:39	3	20.00	20.20	20.86	0.48	0.38	0.7
2019-05-16 00:00	01:49	3	50.00	50.02	50.64	0.09	0.17	0.6
2019-05-16 00:00	01:59	3	70.00	70.01	70.83	0.06	0.15	0.8
2019-05-16 00:00	02:09	4	0.00	0.16	0.78	0.21	0.05	0.6
2019-05-16 00:00	02:19	4	50.00	49.99	50.67	0.03	0.15	0.7
2019-05-16 00:00	02:29	4	90.00	89.94	90.53	0.11	0.19	0.6

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2019-05-16 00:00 02:39		4	20.00	20.01	20.65	0.08	0.16	0.6
2019-05-16 00:00 02:49		4	70.00	69.98	70.65	0.07	0.12	0.7
2019-05-16 00:00 02:59		4	80.00	80.01	80.82	0.07	0.11	0.8
2019-05-16 00:00 03:09		4	10.00	10.39	10.93	0.20	0.29	0.5
2019-05-16 00:00 03:19		4	40.00	39.99	40.68	0.07	0.04	0.7
2019-05-16 00:00 03:29		4	60.00	60.01	60.64	0.04	0.15	0.6
2019-05-16 00:00 03:39		5	0.00	0.02	0.84	0.06	0.07	0.8
2019-05-16 00:00 03:49		5	100.00	100.02	100.87	0.14	0.18	0.9
2019-05-16 00:00 03:59		5	25.00	25.00	25.66	0.11	0.09	0.7
2019-05-16 00:00 04:09		5	200.00	200.01	200.98	0.12	0.32	1.0
2019-05-16 00:00 04:19		5	150.00	149.95	150.52	0.11	0.34	0.6
2019-05-16 00:00 04:29		5	50.00	49.97	50.68	0.10	0.07	0.7
2019-05-16 00:00 04:39		5	175.00	175.06	175.68	0.03	0.20	0.6
2019-05-16 00:00 04:49		5	125.00	125.03	125.58	0.05	0.08	0.6
2019-05-16 00:00 04:59		5	75.00	74.97	75.44	0.07	0.08	0.5
2019-05-16 00:00 05:09		6	0.00	0.12	0.82	0.12	0.15	0.7
2019-05-16 00:00 05:19		6	40.00	39.96	40.52	0.07	0.23	0.6
2019-05-16 00:00 05:29		6	80.00	80.03	80.58	0.08	0.14	0.6
2019-05-16 00:00 05:39		6	10.00	10.10	10.67	0.17	0.18	0.6
2019-05-16 00:00 05:49		6	30.00	30.00	30.60	0.15	0.14	0.6
2019-05-16 00:00 05:59		6	90.00	90.00	90.54	0.08	0.24	0.5
2019-05-16 00:00 06:09		6	60.00	59.97	60.67	0.12	0.24	0.7
2019-05-16 00:00 06:19		6	20.00	19.96	20.61	0.10	0.12	0.7
2019-05-16 00:00 06:29		6	50.00	50.02	50.24	0.09	0.29	0.2
2019-05-16 00:00 06:39		6	70.00	70.01	70.43	0.08	0.17	0.4
2019-05-16 00:00 06:49		7	0.00	0.34	0.84	0.14	0.13	0.5
2019-05-16 00:00 06:59		7	50.00	49.99	50.79	0.06	0.30	0.8
2019-05-16 00:00 07:09		7	90.00	90.01	90.82	0.08	0.13	0.8
2019-05-16 00:00 07:19		7	20.00	20.02	20.73	0.14	0.21	0.7
2019-05-16 00:00 07:29		7	70.00	70.04	70.70	0.06	0.08	0.7
2019-05-16 00:00 07:39		7	80.00	80.00	80.77	0.14	0.08	0.8
2019-05-16 00:00 07:49		7	10.00	10.37	10.78	0.31	0.37	0.4
2019-05-16 00:00 07:59		7	40.00	39.98	40.55	0.14	0.27	0.6
2019-05-16 00:00 08:09		7	60.00	60.02	60.67	0.04	0.15	0.7
2019-05-16 00:00 08:19		8	0.00	0.32	0.84	0.05	0.07	0.5
2019-05-16 00:00 08:29		8	100.00	100.02	100.49	0.07	0.28	0.5
2019-05-16 00:00 08:39		8	25.00	25.05	25.56	0.15	0.10	0.5
2019-05-16 00:00 08:49		8	200.00	200.04	200.73	0.08	0.17	0.7
2019-05-16 00:00 08:59		8	150.00	149.98	150.76	0.02	0.09	0.8
2019-05-16 00:00 09:09		8	50.00	49.96	50.43	0.05	0.22	0.5
2019-05-16 00:00 09:19		8	175.00	175.04	175.97	0.08	0.15	0.9

Carbon Monoxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix.

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 was recorded by the IZO data acquisition system. The standards used for the calibration of the IZO instruments are shown in Table 9.

Table 8. Experimental details of IZO CO comparison

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 26.	
Station Analyser (Picarro)	
Model, S/N	Picarro G2401 #2352-CFKADS2196
Principle	CRDS
Drying system	Cryo trap
Station Analyser (LGR)	
Model, S/N	LGR N2OCM-913 SN US430000170700001433
Principle	Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)
Drying system	Cryo trap

Table 9. CO Reference standards available at IZO. Calibration scale: CO-WMOX2014A.

Cylinder ID	CO (ppb)	sd (ppb)	Drift (ppb/yr)	Type	Use
CA06968	165.62	0.43	0.39	NOAA	RGA-3
CA06978	222.65	0.65	0.35	NOAA	RGA-3
CA06768	62.98	0.25	0.10	NOAA	RGA-3
CA06946	91.90	0.29	0.75	NOAA	RGA-3
CA06988	120.42	0.17	0.46	NOAA	RGA-3
CB11389	96.54	0.15	0.15	NOAA	Picarro
CB11393	158.22	0.13	0.17	NOAA	Picarro
CB11240	193.45	0.11	1.21	NOAA	Picarro
CB11340	112.55	0.10	0.08	NOAA	Picarro
CA08273	64.71	0.07	NA	NOAA	LGR
CA06479	92.48	0.12	NA	NOAA	LGR
CC499063	126.31	0.03	NA	NOAA	LGR
CC506419	161.16	0.19	NA	NOAA	LGR

Results

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

Table 10. CO aggregates computed from single analysis (mean and standard deviation of 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 (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-05-12 09:30:00)	130819_FB03870	152.8	0.3	150.6	0.3	3	-2.2	-1.4
(19-05-12 11:00:00)	140515_FB03377	154.6	0.5	153.0	0.1	3	-1.6	-1.1
(19-05-12 12:30:00)	160825_FB03382	174.1	0.2	171.4	0.3	3	-2.7	-1.5
(19-05-12 14:00:00)	180318_FA02782	194.0	0.4	191.1	0.1	3	-2.9	-1.5
(19-05-12 15:30:00)	180318_FF61508	354.6	0.1	347.6	0.2	3	-7.0	-2.0

Table 11. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2352-CFKADS2196 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale). The Picarro data was re-processed using the CO standard set of the LGR instrument.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-05-12 09:30:00)	130819_FB03870	152.8	0.3	153.3	0.2	3	0.6	0.4
(19-05-12 11:00:00)	140515_FB03377	154.6	0.5	155.8	0.0	3	1.1	0.7
(19-05-12 12:30:00)	160825_FB03382	174.1	0.2	174.5	0.3	3	0.4	0.3
(19-05-12 14:00:00)	180318_FA02782	194.0	0.4	194.5	0.0	3	0.5	0.3
(19-05-12 15:30:00)	180318_FF61508	354.6	0.1	353.5	0.3	3	-1.1	-0.3

Table 12. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR N2OCM-913 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-05-16 15:00:00)	171204_FA01469	102.8	0.4	103.3	0.0	3	0.5	0.5
(19-05-16 15:15:00)	160922_FB03376	71.7	0.4	72.1	0.0	3	0.4	0.6
(19-05-16 14:45:00)	140515_FB03377	154.6	0.5	155.2	0.0	3	0.6	0.4
(19-05-16 15:30:00)	160825_FB03887	193.0	0.3	194.0	0.0	3	1.0	0.5
(19-05-16 15:45:00)	140514_FB03899	257.2	0.2	259.0	0.0	3	1.8	0.7

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 9, and Table 13 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 13. Experimental details of IZO CH_4 comparison

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 26.	
Station Analyser (CRDS)	
Model, S/N	Picarro G2401 #2352-CFKADS2196
Principle	CRDS
Drying system	Cryo trap
Station Analyser (GC)	
Model, S/N	Varian 3800 #3405
Principle	GC/FID
Connection	WCC-Empa TS were connected to spare sample ports of the instruments

Table 14. CH_4 Reference standards available at IZO. Calibration scale: CH4-WMOX2004A

Cylinder ID	CH_4 (ppb)		Type	Use
CA06932	1825.56	0.14	NOAA	Varian 3800
CA08201	1947.62	0.46	NOAA	Varian 3800
CB11389	1648.73	0.05	NOAA	Picarro
CB11393	1854.82	0.29	NOAA	Picarro
CB11240	1978.30	0.02	NOAA	Picarro
CB11340	1766.20	0.09	NOAA	Picarro

Results

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

Table 15. CH_4 aggregates computed from single analysis (mean and standard deviation of 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 (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-05-12 09:30:00)	130819_FB03870	1883.52	0.10	1883.61	0.07	3	0.09	0.00
(19-05-12 11:00:00)	140515_FB03377	1768.63	0.12	1768.97	0.11	3	0.34	0.02
(19-05-12 12:30:00)	160825_FB03382	1918.65	0.10	1918.63	0.10	3	-0.02	0.00
(19-05-12 14:00:00)	180318_FA02782	1838.76	0.12	1838.95	0.03	3	0.19	0.01
(19-05-12 15:30:00)	180318_FF61508	1963.77	0.08	1963.69	0.10	3	-0.08	0.00

Carbon Dioxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 9, and Table 13 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 16. Experimental details of IZO CO_2 comparison

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 26.	
Station Analyser (CRDS)	
Model, S/N	Picarro G2401 #2352-CFKADS2196
Principle	CRDS
Drying system	Cryo trap
Station Analyser (NDIR)	
Model, S/N	LI-COR LI-7000 SN IRGA4-0524
Principle	NDIR
Connection	WCC-Empa TS were connected to spare sample ports of the instruments

Table 17. CO_2 Reference standards available at IZO. Calibration scale: CO_2-WMOX2007

Cylinder ID	CO_2 (ppm)		Type	Use
CA07969	410.14	0.03	NOAA	LI-COR 7000
CA07421	391.25	0.01	NOAA	LI-COR 7000
CA02839	398.96	0.02	NOAA	LI-COR 7000
IZO0259	418.67	NA	IZO	LI-COR 7000
CB11389	340.33	0.01	NOAA	Picarro
CB11393	405.05	0.00	NOAA	Picarro
CB11240	436.36	0.02	NOAA	Picarro
CB11340	377.00	0.01	NOAA	Picarro

Results

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

Table 18. CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2352-CFKADS2196 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(19-05-12 09:30:00)	130819_FB03870	386.90	0.05	386.94	0.01	3	0.04	0.01
(19-05-12 11:00:00)	140515_FB03377	365.49	0.04	365.60	0.01	3	0.11	0.03
(19-05-12 12:30:00)	160825_FB03382	412.34	0.02	412.30	0.01	3	-0.04	-0.01
(19-05-12 14:00:00)	180318_FA02782	391.65	0.03	391.67	0.01	3	0.02	0.01
(19-05-12 15:30:00)	180318_FF61508	417.32	0.02	417.28	0.02	3	-0.04	-0.01

Table 19. CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LI-COR LI-7000 SN IRGA4-0524 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(19-05-12 10:00:00)	130819_FB03870	386.90	0.05	386.92	0.01	5	0.02	0.01
(19-05-12 12:30:00)	160825_FB03382	412.34	0.02	412.31	0.01	5	-0.03	-0.01
(19-05-12 15:00:00)	160622_FB03911	427.11	0.03	427.08	0.03	5	-0.03	-0.01
(19-05-12 17:30:00)	160926_FB03367	412.73	0.02	412.59	0.02	5	-0.14	-0.03

Nitrous Oxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 9, and Table 13 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 20. Experimental details of IZO N_2O comparison

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 26.	
Station Analyser (LGR)	
Model, S/N	LGR N2OCM-913 SN US430000170700001433
Principle	Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)
Drying system	Cryo trap
Station Analyser (GC)	
Model, S/N	Varian 3800 #3405
Principle	GC/ECD
Connection	WCC-Empa TS were connected to spare sample ports of the instruments

Table 21. N_2O Reference standards available at IZO. Calibration scale: N_2O-WMOX2006A.

Cylinder ID	N_2O (ppb)		Type	Use
CB10914	336.92	0.00	NOAA	Varian 3800
CA08203	321.59	0.02	NOAA	Varian 3800
CA06970	330.21	0.01	NOAA	Varian 3800
CA06964	357.01	0.10	NOAA	Varian 3800
CA06996	306.02	0.04	NOAA	Varian 3800
CA08273	285.96	0.00	NOAA	LGR
CA06479	315.78	0.00	NOAA	LGR
CC499063	337.89	0.00	NOAA	LGR
CC506419	357.51	0.00	NOAA	LGR

Results

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

Table 22. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LGR N2OCM-913 instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(19-05-16 15:00:00)	171204_FA01469	342.98	0.10	343.07	0.05	3	0.09	0.03
(19-05-16 15:15:00)	160922_FB03376	327.38	0.04	327.47	0.05	3	0.09	0.03
(19-05-16 14:45:00)	140515_FB03377	317.44	0.04	317.44	0.04	3	0.00	0.00
(19-05-16 15:30:00)	160825_FB03887	331.77	0.07	331.79	0.07	3	0.02	0.01
(19-05-16 15:45:00)	140514_FB03899	328.59	0.06	328.46	0.10	3	-0.13	-0.04

Table 23. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Varian 3800 GC/ECD (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(19-06-08 04:50:00)	160922_FB03376	327.38	0.04	327.50	0.19	3	0.12	0.04
(19-06-07 12:50:00)	160825_FB03887	331.77	0.07	331.57	0.31	3	-0.20	-0.06
(19-06-11 12:50:00)	140514_FB03899	328.59	0.06	328.48	0.30	3	-0.11	-0.03
(19-06-14 04:30:00)	140515_FB03377	317.44	0.04	317.64	0.34	3	0.20	0.06
(19-07-02 20:00:00)	171204_FA01469	342.98	0.10	342.24	0.37	3	-0.74	-0.22

WCC-Empa Traveling Standards

Ozone

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

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

WCC-Empa TS: Thermo Scientific 49i-PS #1171430027, BKG -0.3, COEF 0.991

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 24. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 31). The data were pooled and evaluated by linear regression analysis. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

X_{TS} (ppb) = ([TS] + 0.16 ppb) / 0.9992 (6a)

u_{TS} (ppb) = sqrt ((0.43 ppb)^2 + (0.0034 * X)^2) (6b)

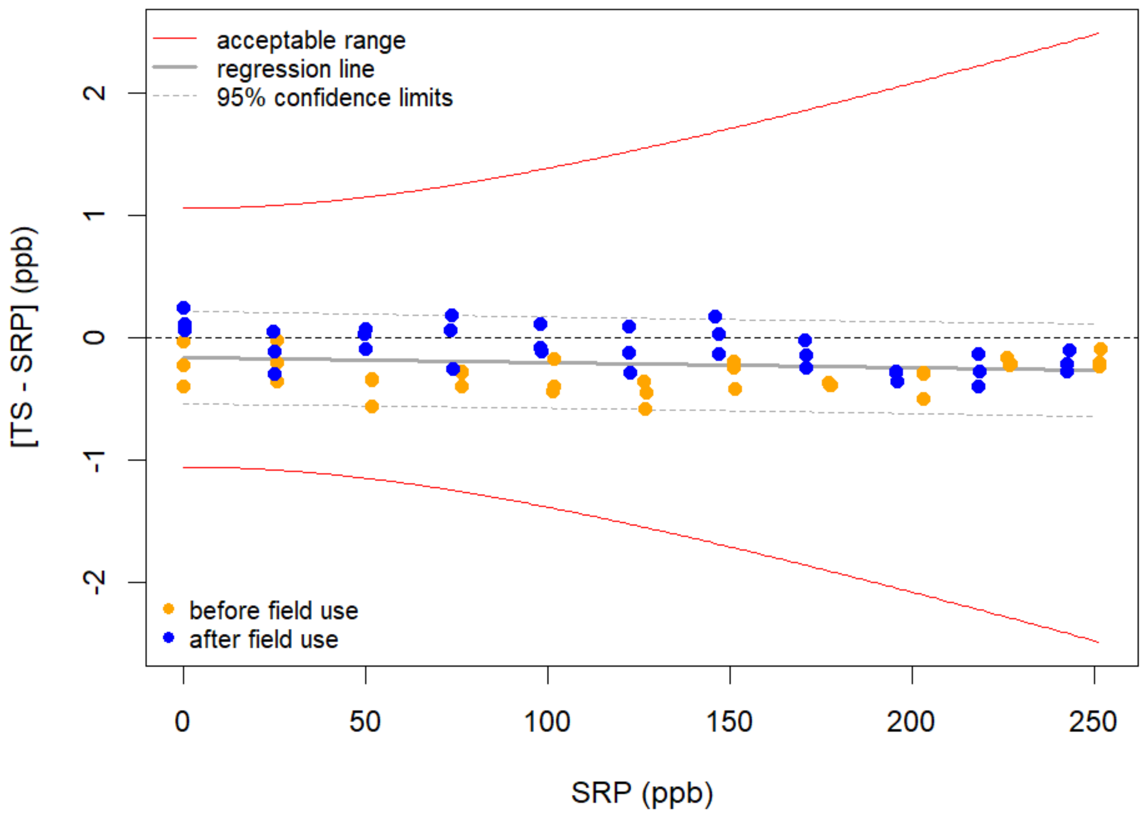

Figure 31. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 24. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2019-03-20	1	125	126.65	0.19	126.06	0.12
2019-03-20	1	50	51.62	0.25	51.06	0.08
2019-03-20	1	205	202.97	0.38	202.47	0.13
2019-03-20	1	25	25.62	0.16	25.42	0.06
2019-03-20	1	150	151.41	0.22	150.99	0.10
2019-03-20	1	100	101.53	0.29	101.12	0.09
2019-03-20	1	175	177.19	0.16	176.80	0.17
2019-03-20	1	0	-0.15	0.24	-0.18	0.08
2019-03-20	1	225	226.86	0.38	226.64	0.43
2019-03-20	1	75	76.18	0.10	75.89	0.12
2019-03-20	1	250	251.24	0.17	251.00	0.19
2019-03-20	2	25	25.77	0.30	25.41	0.11
2019-03-20	2	180	177.53	0.20	177.14	0.20
2019-03-20	2	0	0.10	0.13	-0.29	0.06
2019-03-20	2	225	226.75	0.36	226.53	0.32
2019-03-20	2	75	76.43	0.14	76.16	0.11
2019-03-20	2	125	126.97	0.21	126.51	0.10
2019-03-20	2	150	151.14	0.18	150.90	0.10
2019-03-20	2	50	51.73	0.14	51.39	0.08
2019-03-20	2	205	202.99	0.19	202.70	0.17
2019-03-20	2	100	101.42	0.27	100.98	0.12
2019-03-20	2	250	251.19	0.34	251.00	0.19
2019-03-20	3	175	177.12	0.28	176.75	0.19
2019-03-20	3	50	51.50	0.18	51.16	0.16
2019-03-20	3	25	25.66	0.19	25.65	0.10
2019-03-20	3	100	101.63	0.23	101.45	0.20
2019-03-20	3	205	203.08	0.22	202.79	0.17
2019-03-20	3	75	76.15	0.28	75.75	0.05
2019-03-20	3	150	151.08	0.21	150.89	0.15
2019-03-20	3	225	225.98	0.26	225.82	0.22
2019-03-20	3	125	126.38	0.35	126.03	0.22
2019-03-20	3	0	0.06	0.34	-0.17	0.13
2019-03-20	3	250	251.82	0.49	251.73	0.52
2019-07-24	4	100	98.09	0.30	97.97	0.20
2019-07-24	4	75	73.82	0.18	73.57	0.08
2019-07-24	4	195	195.85	0.23	195.49	0.08
2019-07-24	4	220	218.54	0.27	218.26	0.11
2019-07-24	4	50	49.97	0.21	50.04	0.11
2019-07-24	4	25	24.98	0.08	24.69	0.09
2019-07-24	4	120	122.06	0.12	122.15	0.11
2019-07-24	4	170	170.89	0.41	170.65	0.14
2019-07-24	4	145	145.76	0.22	145.93	0.11
2019-07-24	4	0	0.13	0.20	0.24	0.13
2019-07-24	4	245	242.97	0.44	242.86	0.50
2019-07-24	5	25	24.61	0.21	24.67	0.10
2019-07-24	5	170	170.56	0.19	170.54	0.11
2019-07-24	5	120	122.29	0.27	122.17	0.20
2019-07-24	5	0	0.04	0.27	0.29	0.16
2019-07-24	5	145	147.04	0.31	147.07	0.29
2019-07-24	5	75	73.47	0.16	73.66	0.13
2019-07-24	5	220	218.22	0.16	217.83	0.19

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2019-07-24	5	100	97.93	0.21	97.86	0.15
2019-07-24	5	195	195.66	0.26	195.37	0.08
2019-07-24	5	50	49.68	0.27	49.71	0.12
2019-07-24	5	245	242.56	0.28	242.28	0.16
2019-07-24	6	170	170.90	0.25	170.76	0.08
2019-07-24	6	0	0.15	0.18	0.22	0.17
2019-07-24	6	145	146.95	0.14	146.82	0.21
2019-07-24	6	50	49.91	0.25	49.82	0.22
2019-07-24	6	100	97.81	0.21	97.92	0.11
2019-07-24	6	25	24.79	0.20	24.67	0.16
2019-07-24	6	220	218.06	0.29	217.93	0.11
2019-07-24	6	125	122.51	0.23	122.23	0.12
2019-07-24	6	195	195.45	0.23	195.17	0.10
2019-07-24	6	75	73.08	0.16	73.14	0.14
2019-07-24	6	240	242.49	0.20	242.27	0.19

#the level is only indicative.

Greenhouse Gases and Carbon Monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide and Methane. NOAA/ESRL 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 by way of traveling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-X2014A scale (Novelli et al., 2003)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004A scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

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

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).
CO_2 and CH_4: Picarro G1301 (before the audit); G2401 (after the audit) (Cavity Ring-Down Spectroscopy).

Table 25 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 26, and Figure 32 shows the analysis of the TS over time.

Table 25. NOAA/ESRL laboratory standards at WCC-Empa

Cylinder	CO (ppb)	CH_4 (ppb)	N_2O (ppb)	CO_2 (ppm)
CC339478[#]	463.76	2485.25	357.19	484.39
CB11499[#]	141.03	1933.77	329.15	407.33
CB11485[#]	110.88	1844.78	328.46	394.30
CA02789*	448.67	2097.48	342.18	495.85

[#] used for calibrations of CO_2, CH_4 and N_2O
** used for calibrations of CO*

Table 26. Calibration summary of the WCC-Empa travelling standards

TS	P (psi)	CH_4 (ppb)	sdCH_4 (ppb)	CO_2 (ppm)	sdCO_2 (ppm)	N_2O (ppb)	sdN_2O (ppb)	CO* (ppb)	sdCO* (ppb)	CO[#] (ppb)	sdCO[#] (ppb)
130819_FB03870	1600	1883.52	0.10	386.90	0.05	318.91	0.03	152.76	0.29	152.41	0.48
140514_FB03899	600	1974.67	0.10	404.97	0.02	328.59	0.06	257.17	0.21	257.63	0.53
140515_FB03377	960	1768.63	0.12	365.49	0.04	317.44	0.04	154.62	0.47	154.75	0.44
160622_FB03911	920	2352.59	0.19	427.11	0.03	330.39	0.08	308.07	0.30	307.69	0.40
160825_FB03382	1050	1918.65	0.10	412.34	0.02	318.36	0.11	174.07	0.24	173.79	0.44
160825_FB03887	340	2027.25	0.12	457.68	0.03	331.77	0.07	193.03	0.28	192.69	1.14
160922_FB03376	700	1776.13	0.11	400.07	0.04	327.38	0.04	71.71	0.37	71.25	0.67
160926_FB03367	500	1855.10	0.08	412.73	0.02	339.58	0.13	90.49	0.47	90.65	0.21
171204_FA01469	1000	1933.18	0.11	406.80	0.03	342.98	0.10	102.84	0.37	102.67	0.36
171204_FA02769	1380	1956.05	0.08	420.85	0.01	336.52	0.03	138.88	0.43	138.29	0.64
180318_FA02782	1700	1838.76	0.12	391.65	0.03	312.01	0.07	193.98	0.35	193.65	0.59
180318_FF61508	1680	1963.77	0.08	417.32	0.02	328.26	0.09	354.63	0.14	354.45	0.50

** measured with Aerodyne mini-cw*
[#] measured with Picarro G2401

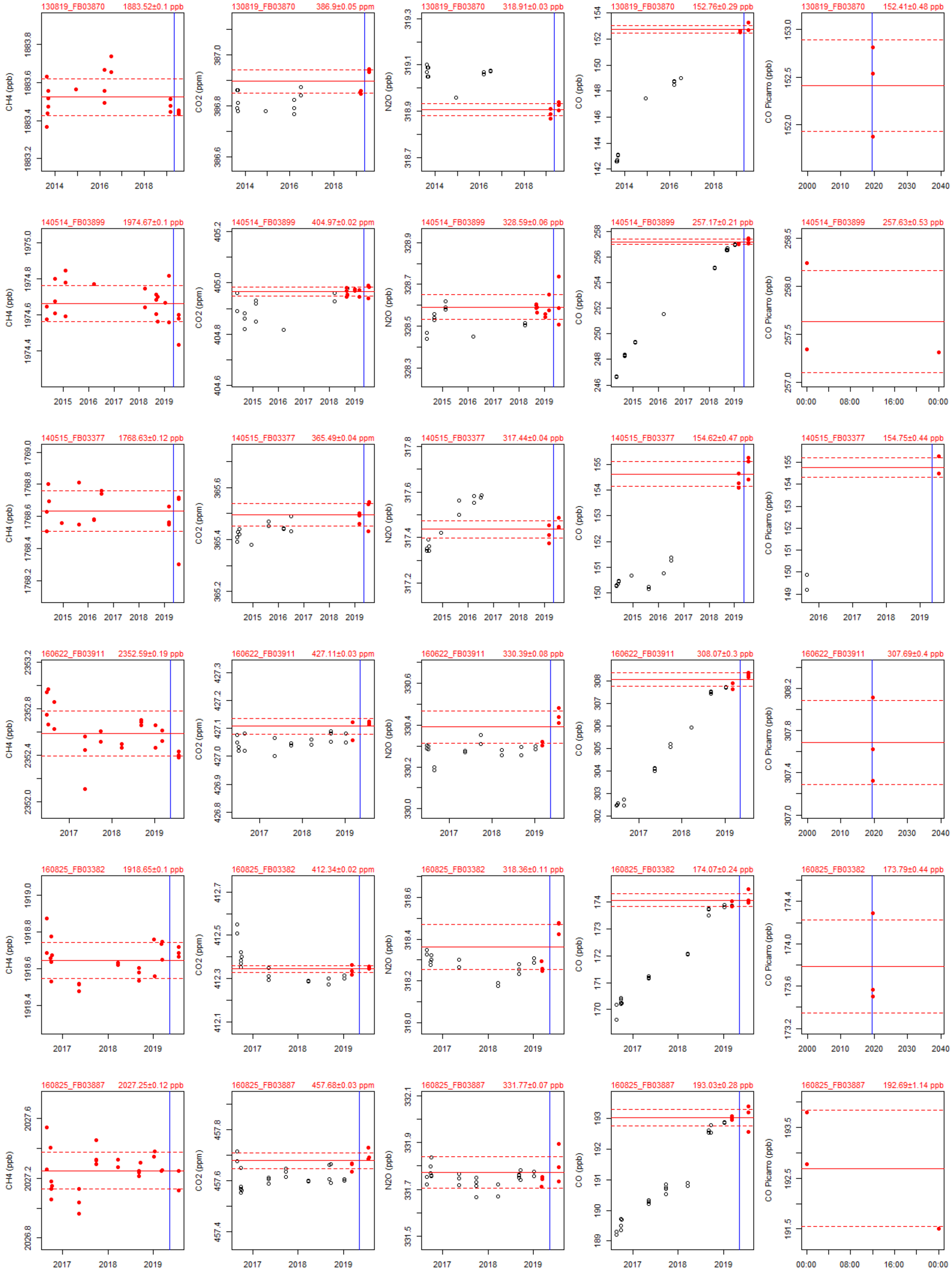

Figure 32. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.

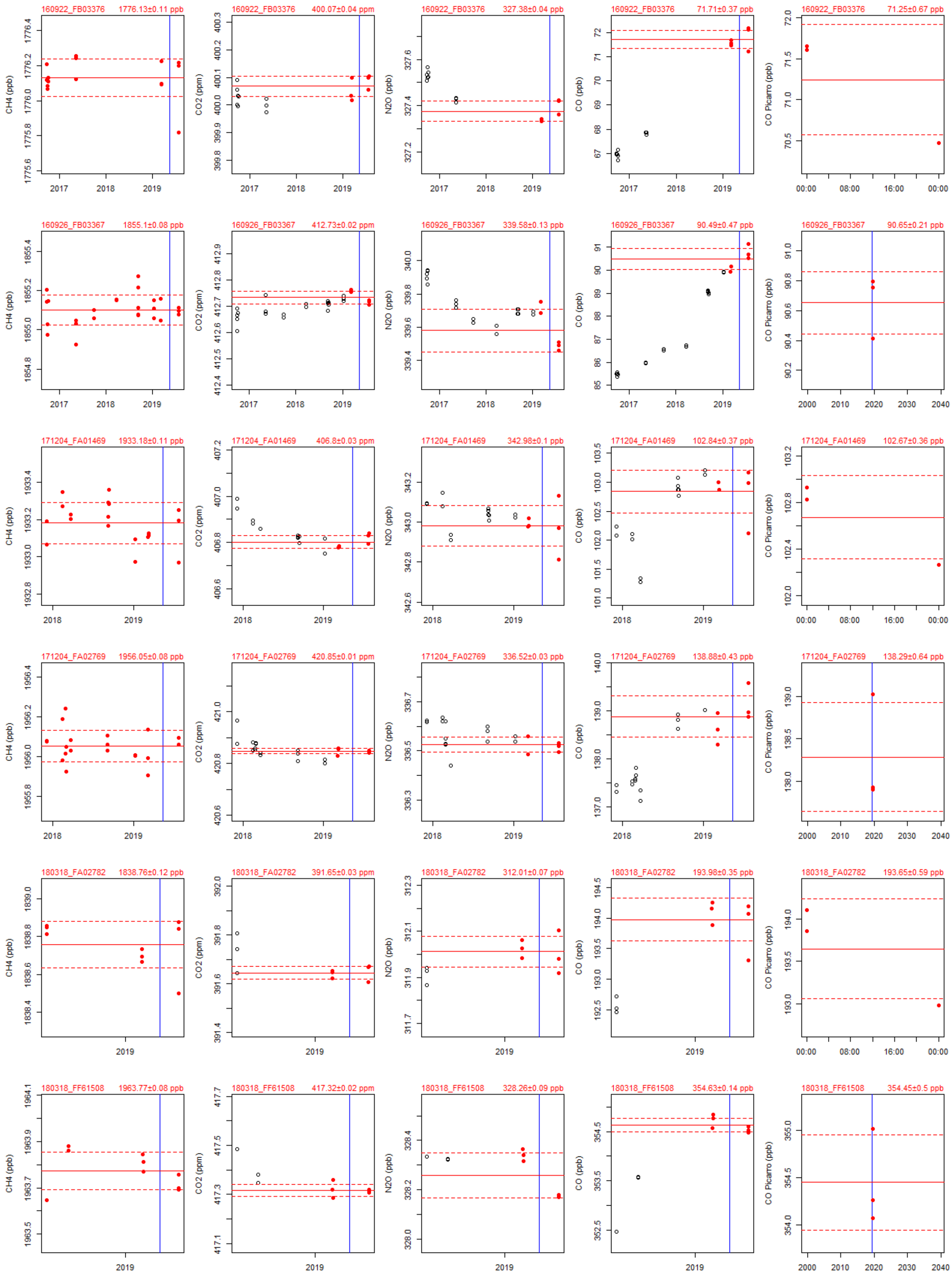

Figure 33. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.

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 SN #1497-CFKADS2098 was calibrated every 1745 min using one WCC-Empa TS as a working standard, and two TS as target tanks. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 0.5 ppb for CH_4 and 0.02 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

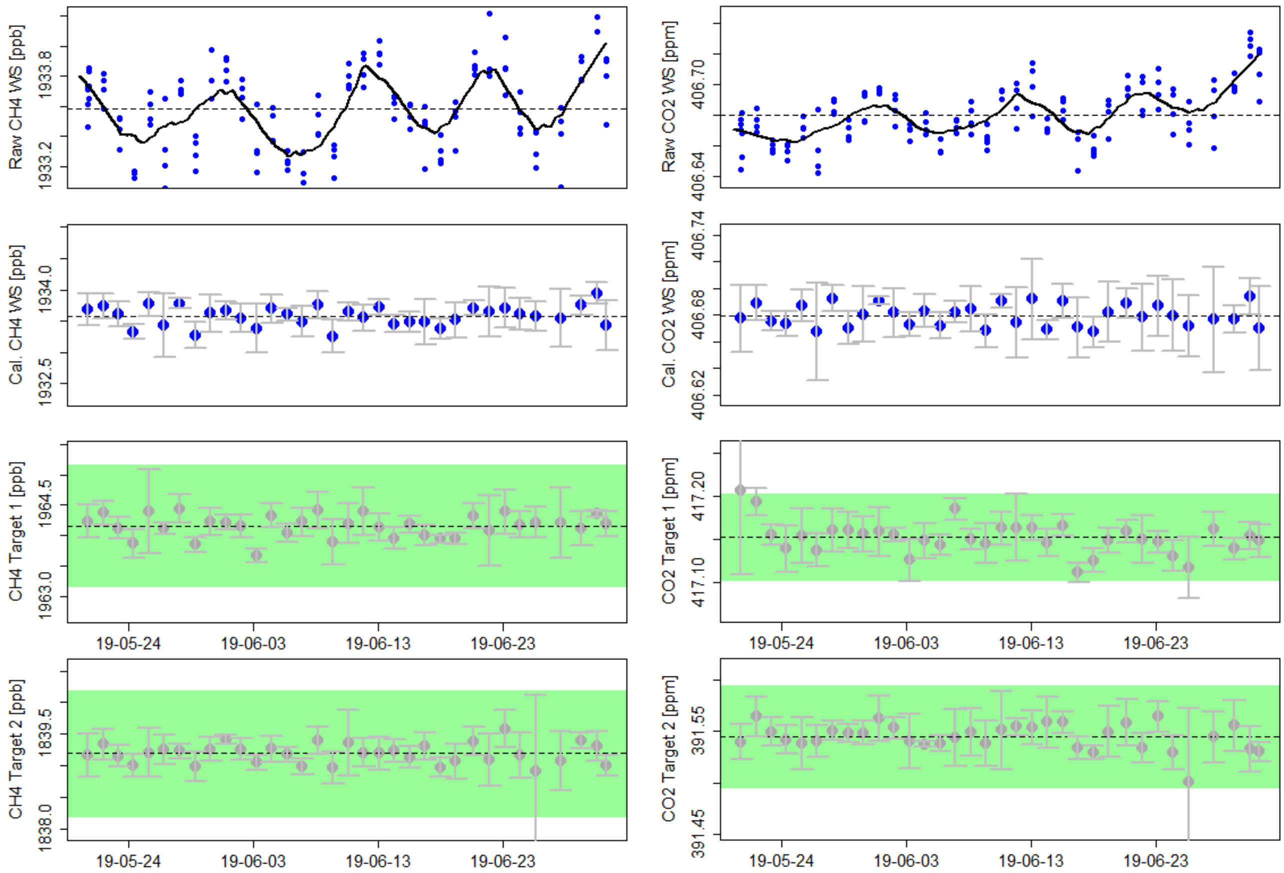

Figure 34. CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

For CO, the Picarro G2401 was calibrated every 1745 min with three WCC-Empa TS used as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

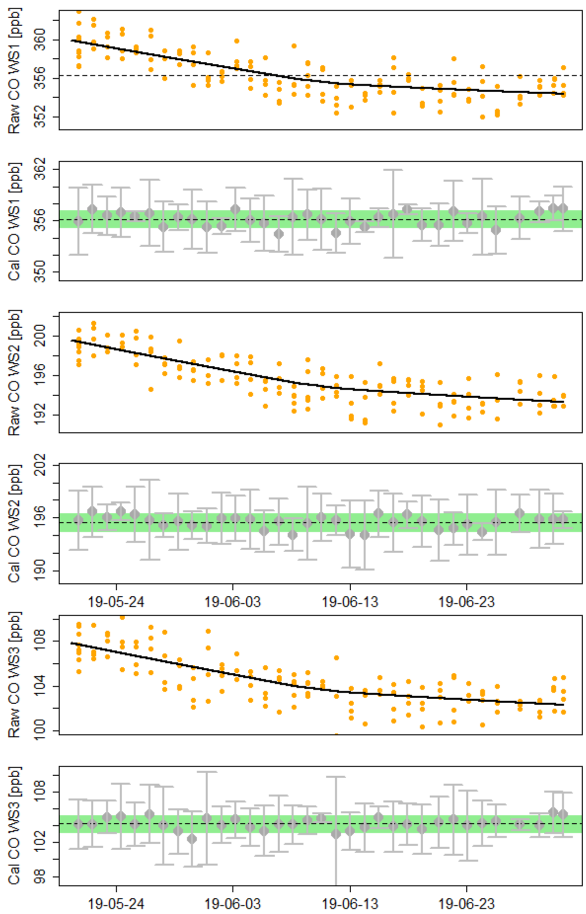

Figure 35. CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

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LIST OF ABBREVIATIONS

AEMET	State Meteorological Agency of Spain
AERONET	Aerosol robotic network
a.s.l	above sea level
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
IARC	Izaña Atmospheric Research Centre
IZO	Izaña GAW Station
LS	Laboratory Standard
NA	Not Applicable
NDACC	Network for the Detection of Atmospheric Composition Change
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PI	Principle Investigator
QCL	Quantum Cascade Laser
SCO	St. Cruz GAW Station
SOP	Standard Operating Procedure
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

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