Research Infrastructure Quality Assurance

GAW Report No. 252
WCC-Empa Report No. 19/3

System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide at the Global GAW Station Ushuaia, Argentina

November 2019

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Research Infrastructure Quality Assurance

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November 2019

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Acknowledgements

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 5th system and performance audit by WCC-Empa[1] at the global GAW station Ushuaia, which is run by the Servicio Meteorológico Nacional (SMN) of Argentina, was conducted from 12 to 19 November 2019 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at the Ushuaia 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
Ing Lino Condori	SMN Ushuaia, station manager
Mr Emilliano Petruzzi	SMN Ushuaia, station operator

The results and recommendations of the current audit were also presented and discussed at the SMN headquarters in Buenos Aires, involving the following SMN members:

Lic Maria de los Milagros Skansi	SMN Buenos Aires, Head of the Climatology Department
MSc Gerardo Carbajal Benítez	SMN Buenos Aires, Head of GAW Department
Ing María Elena Barlasina	SMN Buenos Aires, Head of Operation Ushuaia GAW
Mr Gustavo Copes	SMN Buenos Aires, scientist technician

Scientific Research Collaborator	
Dr Eija María Asmi	Finnish Meteorological Institute (FMI)

The discussion and recommendations were also followed by Dr Eija Asmi (FMI), who currently works as a guest scientist in Buenos Aires and collaborates with SMN.

This report summarizes the assessment of the Ushuaia GAW station in general, as well as the surface ozone, methane, carbon dioxide, and carbon monoxide measurements in particular. The report is distributed to the station manager, to the Head of GAW Department at SMN, the national focal point in Argentina 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 USH GAW station is jointly managed by SMN and the Government of the Tierra del Fuego province. Mainly SMN is responsible for the development of the station as well as for larger

[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.*

investments. The station is visited daily by a meteorological observer and, from Monday to Friday, by the station manager and a GAW station operator. The operation and maintenance of the station and the measurements improved significantly over the past few years. However, the current station manager has no long-term experience. Data evaluation is done in cooperation with the SMN headquarters in Buenos Aires. Data analysis and evaluation capabilities need to be improved. Continued training and education of all station staff must be of highest priority.

Recommendation 1 (*, critical, ongoing)**
SMN should explore all possibilities for training of station operators and scientists. Participation in GAWTEC as well as other training courses is highly recommended.

Recommendation 2 (*, critical, ongoing)**
USH data should scientifically be exploited. Collaboration with national and international partners needs to be re-established and/or intensified.

SMN significantly increased the funding for the operation of USH in the past years, which allowed the acquisition of a new instrument for CO, CH_4 and CO_2. This is regarded as highly valuable. However, it must be ensured that the financial planning includes the instrument maintenance costs as well as needed consumables such as calibration standards.

Recommendation 3 (*, critical, ongoing)**
In the past few years, the USH station has received significant support from SMN in terms of purchasing instruments and setting up new monitoring parameters, which are valuable additions for observational activities. Such support, however, is often not accompanied with relevant peripheral needs, such as calibration and maintenance cost and operational trainings. The financial planning for the USH operation must include these additional expenses for a successful and sustainable operation of USH.

Recommendation 4 (*, critical, ongoing)**
In case of instrument failures, a budget must be available to solve instrumental issues in due time. Estimated costs can be as high as USD 20'000 for a single case.

Recommendation 5 (*, critical, ongoing)**
Import/export procedures are time consuming and complicated in Argentina but critical in case of instrument failures. Although it might be beyond the control of SMN, it is encouraged to seek for solutions to optimise this process.

Station Location and Access

USH is located in Tierra del Fuego, Argentina (54.845°S, 68.311°W) roughly 10 km south-west of the city of Ushuaia in the vicinity of the Malvinas International Airport. The city has significantly grown during the last years, especially to the west-northwest of the station, and has now close to 60'000 inhabitants. The station is located on a coastal cliff at an altitude of 18 m a.s.l., on a remote sub-Antarctic marine coast. The situation has not been changed since the last audit by WCC-Empa in 2016 (Zellweger et al., 2016b). Access to the station is possible throughout the year with a special permit of the airport authorities. The location is adequate for the intended purpose, although local pollution episodes are possible mainly due to close vicinity of the airport and the city of Ushuaia.

Further information about the USH station is available from the GAW Station Information System (GAWSIS) (https://gawsis.meteoswiss.ch/GAWSIS/#/search/station/stationReportDetails/0-20008-0-USH).

Recommendation 6 (, important, ongoing)**
The USH station is located in the immediate vicinity of the international airport and close to the city of Ushuaia. This location enables research focusing both on the local and regional pollution and the remote troposphere. However, it is important that the processes influencing the station are well understood, and corresponding studies are strongly encouraged.

Station Facilities

The facilities at the site consist of the main building of 230 m^2, which provides space for offices, meeting rooms and laboratories. Basic kitchen and sanitary facilities are available. On the platform at the top of the roof, the air inlet and several radiation and meteorological equipment are mounted. The main laboratory is heated but no air conditioning is available. For the current measurements, this is acceptable, since the temperature variations remain small. Internet connection is available, but limited bandwidth (3/1 Mbit/s) constrains data transfer. The power supply is normally reliable, but short power cuts occur in irregular intervals. The main instruments are protected by individual UPS systems, which can bridge short power outages. Overall, USH is an ideal platform for continuous atmospheric research as well as for extensive measurement campaigns.

Recommendation 7 (, important, 2020)**
Depending on future measurements, air-conditioning might be needed. For the current set of measurements, the temperature variations are acceptable.

Recommendation 8 (, important, 2020)**
More bandwidth of the internet connection (at least 20 Mbit/s down and upload) is recommended.

Measurement Programme

USH was established in 1994 and comprises a slowly growing measurement programme that covers a few focal areas of the GAW programme. An overview on measured species is available from GAWSIS. The information available from GAWSIS was reviewed and updated as part of the audit.

Recommendation 9 (, 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 Management and Data Submission

Data evaluation is done at SMN in Buenos Aires in collaboration with the station manager. Once the data are visually inspected, quality controlled and calibrated, data need to be submitted to the designated GAW data repositories. As of March 2020, data of the scope of the audit has been submitted to the World Data Centres:

Submission to the World Data Centre for Greenhouse Gases (WDCGG):
SMN: CO (2009-2018); older data is currently not available due to re-evaluation.
NOAA: CO_2 (1994-2018), CH_4 (1994-2018), CO (1994-2018), N_2O (1995-2018)
Data of the Picarro G2401 instrument has not yet been submitted.

Submission to the World Data Centre for Reactive Gases (WDCRG):
SMN: O_3 (1994-2018)

Recommendation 10 (, important, 2020)**
The entire CO data series needs to be carefully re-evaluated and re-submitted to the World Data Centre for Greenhouse Gases (WDCGG).

Recommendation 11 (, important, 2020)**
Data of the Picarro instrument need to be submitted to the World Data Centre for Greenhouse Gases (WDCGG).

Recommendation 12 (*, 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.

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 on 5 March 2020. Summary plots findings are presented in the Appendix.

Documentation and Maintenance

Electronic log books and hand written notes are available for all parameters. The instrument manuals are available at the site. It was noted that the information was only partly comprehensive and up-to-date. A systematic log book for the new Cavity Ring-Down Spectrometer (CRDS) has not yet been started.

Checklists should be prepared and used for each instrument to ease the regular maintenance. Cylinder pressures of all gas cylinders should be regularly recorded in an electronic spreadsheet. Raw data should be regularly downloaded from the instruments (if available) and be copied to a robust backup solution.

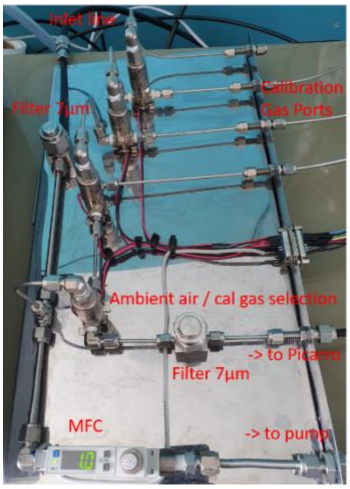
Recommendation 13 (*, important, ongoing)**
Documentation is an important QA aspect. It must be made sure that all relevant observations are entered in the corresponding log books. Electronic log books are recommended.

Air Inlet System

Different inlet systems are in use depending on the parameters measured at USH. Currently, the following inlet systems are in use:

Ozone and CO (NDIR): The air intake is located 7 m above ground (details see previous audit reports), and consists of two connected (U-shape) ½" PTFE tubes flushed at 11 l/min by a diaphragm pump. Short connections (~2 m) with ¼" PTFE tubing, including inlet filters, lead to the instruments. Residence time is estimated to be ~10 seconds. The ¼" connection including the inlet filter of the ozone instrument has been tested for O_3 loss at 500 ppb during the current audit, and no significant loss was found. The air intake is adequate for these measurements.

GHG and CO (CRDS): A new inlet system was installed together with the new analyser by SMN. The Inlet leads to the same location as the O_3 inlet with ⅜" tubing. This tube was inspected and was supposed to be Synflex-1300. However, the installed tubing was not Synflex-1300 and consisted of black plastic (unknown fabricate). It is recommended that this part of the inlet system is replaced by Synflex-1300, which is available at USH. This tube is connected to the valve control system of the Picarro G2401 instrument, which was also made by SMN. The flow rate is the inlet system is controlled by a mass flow controller (SMC PFM7 Series) at 1 l/min. The residence time in the inlet is estimated to be ~20 seconds.



Recommendation 14 (*, important, 2020)**
It is recommended to replace the ⅜" inlet tubing with Synflex-1300.

Surface Ozone Measurements

Surface ozone measurements at USH were established in 1994, and continuous time series are available since then.

Instrumentation. USH is currently equipped with two ozone analysers (Thermo Scientific 49C). In addition, a Thermo Scientific 49C-PS ozone calibrator with traceability to the WCC-Empa SRP#15 (calibrated in 2017 (Zellweger et al., 2017)) is available at the Regional Calibration Centre for Surface Ozone (RCC-III) in Buenos Aires. This instrument is shipped about once per year to check the USH analysers, and was also available at USH during the current audit. During the current audit, the station staff was trained in using the calibration system including the Thermo Scientific zero air system.

Recommendation 15 (, important, ongoing)**
The ozone calibrator of the RCC-III should be used to perform instrument checks and calibrations of the ozone analyser in yearly intervals. The electronic checklist provided during the audit should be used, including the A/B ozone check. The calibration settings of the ozone analyser however should not be changed. In case of a larger and unexpected bias (more than 1% from the current bias of the ozone analyser, which is reading approx. 1 ppb higher compared to the calibrator), the experiment should be repeated and if the bias is confirmed, the reason must be identified.

Data Acquisition. Instruments are equipped with individual data acquisition (DAQ) software. The previous LabView based DAQ developed by QA/SAC-Switzerland was replaced by custom made Python DAQ programmed by the USH station staff (Lino Condori). This system acquires the data of the ozone instruments with a time resolution of 1 min. The system is fully adequate.

Intercomparison (Performance Audit). The USH analysers and the calibrator of the RCC-III 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 randomized 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. No further corrections were applied to the data. The following equations characterize the bias of the instruments:

Thermo Scientific 49C #58546-318 (BKG -0.4 ppb, SPAN 1.012):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 0.74 ppb) / 1.0058 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.28 ppb^2 + 2.51e-05 * X_{O3}^2) (1b)

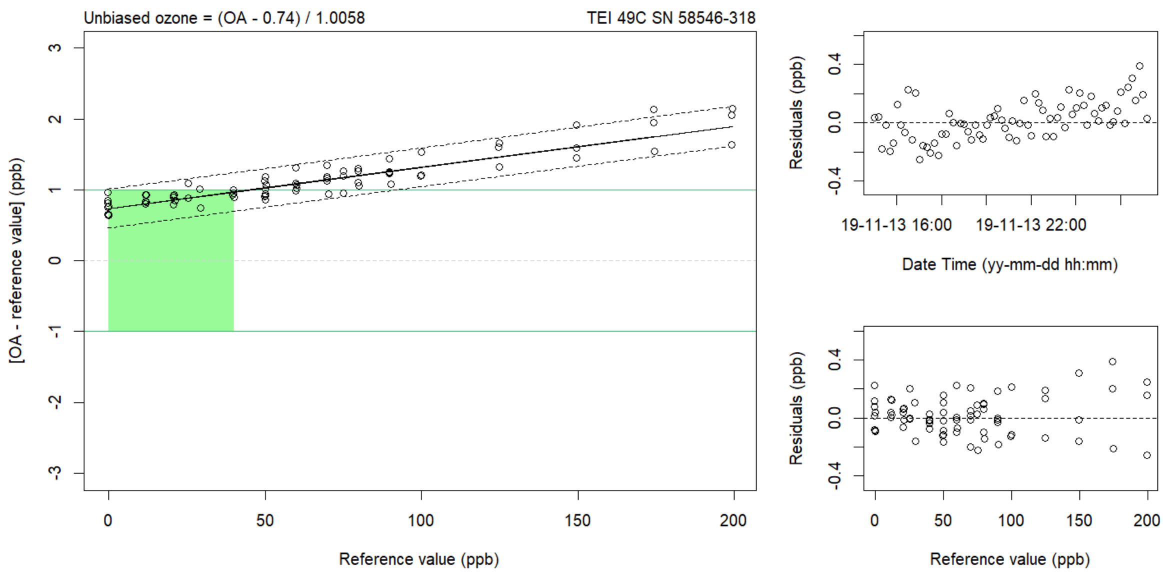


Figure 1. Left: Bias of the USH ozone analyser (Thermo Scientific 49C #58546-318) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with dark 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 49C #0330102717 (BKG +0.2 ppb, SPAN 1.024):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 0.48 ppb) / 1.0052 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.28 ppb^2 + 2.51e-05 * X_{O3}^2) (1d)

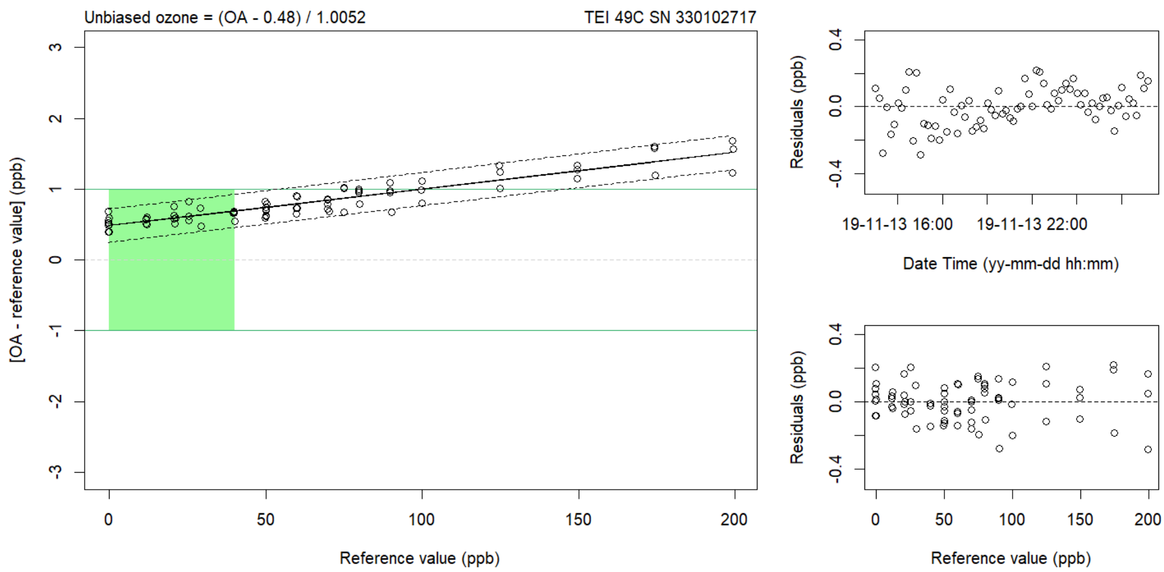


Figure 2. Same as above for the second USH ozone analyser (Thermo Scientific 49C #0330102717)

Thermo Scientific 49C-PS #56084-306 (BKG -0.5 ppb, SPAN 1.015):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OC] + 0.00 ppb) / 1.0020 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.30 ppb^2 + 2.54e-05 * X_{O3}^2) (1f)

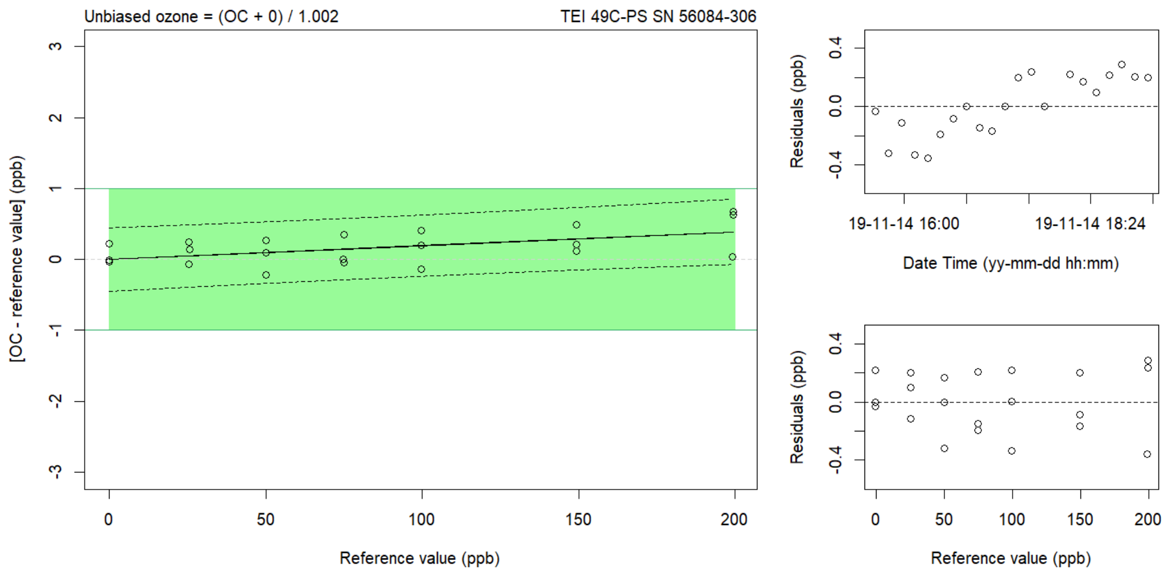


Figure 3. Same as above for the RCC-III ozone calibrator (Thermo Scientific 49C-PS #56084-306)

The results of the comparisons can be summarized as follows:

Perfect agreement between the WCC-Empa travelling instrument and the USH calibrator was found, which confirms the validity of the last calibration made by WCC-Empa during the RCC-III comparison campaign in 2017.

Slightly larger deviations were found for the two USH analysers. These deviations were, within the uncertainties, not different from the last audit in 2016. This confirms that the instrument is still in a good working condition, and no further action is required.

Carbon Monoxide Measurements

Ongoing measurement of carbon monoxide at Ushuaia commenced in 1994, and continuous data series are available since then. Carbon monoxide measurements at Ushuaia were made using non-dispersive near infrared absorption (NDIR) technique, and the system has not changed since the last audit by WCC-Empa in 2014. In 2017, a cavity Ring-Down spectrometer (CRDS) capable of measuring CO was added.

***Instrumentation*.** Horiba APMA-360 NDIR analyser and since 2017 a Picarro G2401 CRDS instrument.

The Picarro instrument was manually calibrated using three standard gases in monthly intervals until the current audit. During the audit, the calibration scheme was changed to automatic measurements of the three calibration gases every 15 days, and measurements of a working standard every 25 hours.

Data Acquisition. Instruments are equipped with individual data acquisition (DAQ) software. The previous LabView based DAQ developed by QA/SAC-Switzerland was replaced by custom made Python DAQ programmed by the USH station staff (Lino Condori). This system acquires the data of the NDIR carbon monoxide instrument with a time resolution of 1 min. The system is fully adequate. The Picarro software is used to acquire data and control the calibration system of the Picarro G2401 instrument.

Standards. Three standard gases are available for the Picarro instrument. Two of them were delivered by WCC-Empa in 2016, and an additional standard was delivered by the Finnish Meteorological Institute (FMI). The Horiba is calibrated using a 2.582 ppm standard, and automatic zero and span checks are made with a dilution system. A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the USH instruments with randomized carbon monoxide levels using WCC-Empa travelling standards. The following equations characterize the instrument bias, and the results are further illustrated in Figures 4 to 6 with respect to the WMO GAW DQOs (WMO, 2014).

The results presented below were processed by WCC-Empa using the calibration standards of the USH Picarro. The same method is also in use at SMN for the data processing since the current WCC-Empa audit.

Picarro G2401 #2634-CFKADS2238:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO - 2.1) / 0.9827 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.7 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

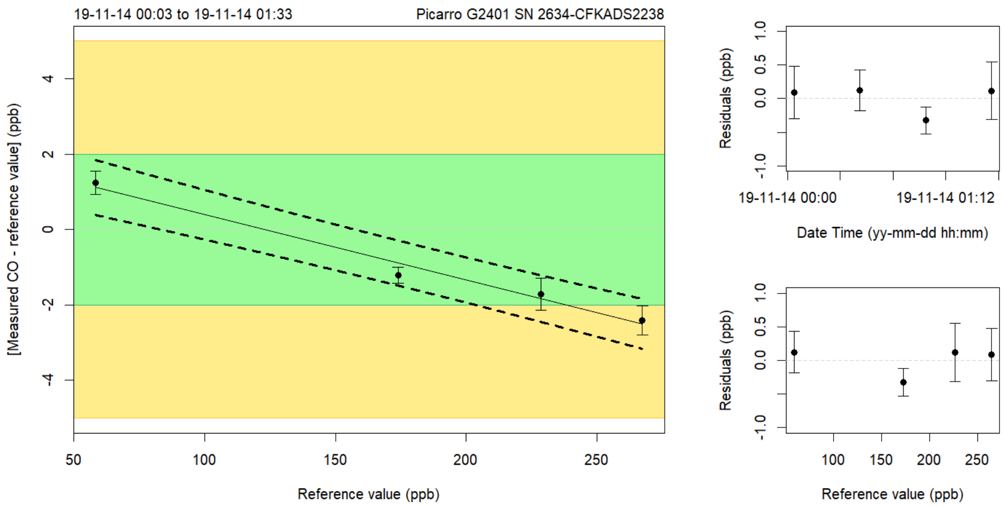


Figure 4. Left: Bias of the USH Picarro G2401 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dark green and orange lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for USH. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

Horiba APMA-360 (Zero -3, SPAN 1.032, zero corrected):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 3.4) / 1.0041 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (11.3 ppb_2 + 1.01e-04 * X_{CO2}) (2d)

Horiba APMA-360 (Zero -3, SPAN 1.032, zero corr./calibrated (080808_CA08220 2.582 ppm CO)):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 3.1) / 1.0538 (2e)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (12.3 ppb_2 + 1.01e-04 * X_{CO2}) (2f)

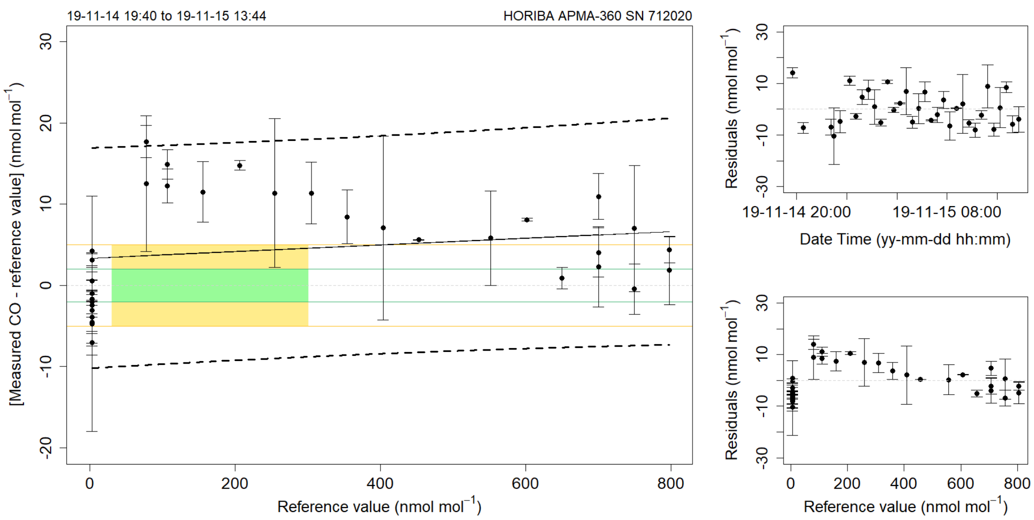


Figure 5. Same as above, for the Horiba APMA-360 carbon monoxide analyser with correction of the zero offset

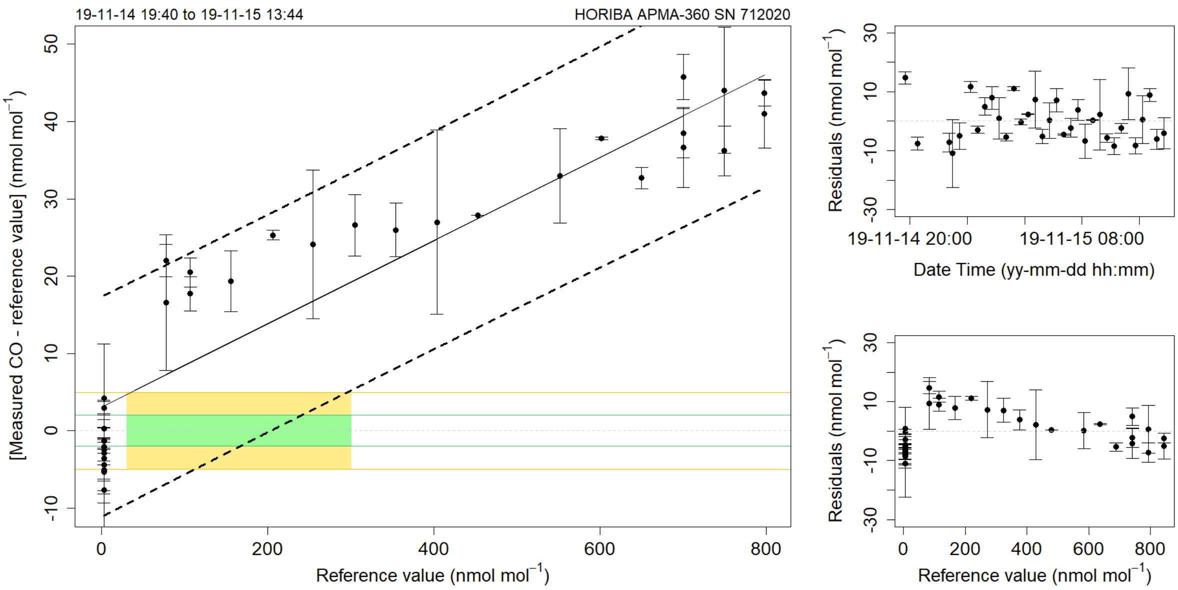


Figure 6. Same as above, for the Horiba APMA-360 carbon monoxide analyser after calibration and correction of the zero offset

The results of the comparisons can be summarized as follows:

Picarro G2401: The comparison results were partly exceeding the WMO/GAW network compatibility goals of 2 ppb but were well within the extended goals of 5 ppb. This is acceptable in light of the relatively high uncertainties of the CO calibration standards. However, it was noticed that the internal water vapour correction of the instrument is not working well, and therefore, drying of the air is recommended. This has already been implemented during the audit. The results of the corresponding water interference test are shown in the Appendix.

Horiba APMA-360: The instrument seems to be non-linear and lost sensitivity at higher CO mole fraction. This is in contrast to the previous audit by WCC-Empa in 2016 where the instrument was found in good working condition. A potential reason for the observed could be decreasing efficiency of the internal catalyst. It now has to be carefully checked if this is also reflected in the automatic span checks, and if available, in the manual measurements of calibration standards. If this is the case, data may be corrected. However, the instrument has definitely reached the end of its lifetime. It is no longer appropriate for CO measurements at USH. If it will be further used elsewhere, manual and automatic span checks are of utmost importance.

Recommendation 16 (, important, 2020)**
The Picarro G2401 CRDS analyser is giving more reliable CO values compared to the Horiba NDIR analyser. Available resources should focus on the CRDS technique. It is strongly recommended to decommission the Horiba CO analyser as it has reached the end of its lifetime.

Similar results were also observed during the ambient air comparison with the WCC-Empa travelling instrument, which are shown further below. For the CRDS analyser these measurements confirmed the results of the performance audit and showed that the Picarro instrument is producing reliable CO data. The results of the Horiba APMA-360 analyser however were in better agreement with the WCC-Empa reference during the ambient air comparison.

Methane Measurements

Continuous measurements of CH_4 at USH started in 2017 using a CRDS analyser. Flask measurements made on behalf of NOAA are available since 1994.

Instrumentation. Picarro G2401 (since 2017). By default, the mole fractions given by the Picarro G2401 only rely on factory calibration settings which become inaccurate when instrument sensitivity is changing over time. Thus, calibration is done using the three laboratory standards and a working standard. An instrument specific water vapour correction function has been determined during the audit. Further details are given in the Appendix.

Recommendation 17 (*, important, ongoing)**
Since the internal water vapour correction is not accurate enough for meeting the WMO/GAW network compatibility goals, the instrument specific water vapour correction (see Appendix) function should be applied to all CH_4 and CO_2 data.

Recommendation 18 (*, important, yearly)**
It is recommended to monitor the stability of the water vapour correction by making a droplet test (see Rella et al. (2013)) in yearly intervals.

Data Acquisition. Currently the software of the Picarro instrument is used as the data acquisition system.

Standards. Three standard gases are available for the Picarro instrument. Two of them were delivered by WCC-Empa in 2016, and an additional standard was delivered by the Finnish Meteorological Institute (FMI). A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the USH instruments with randomized 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 is further illustrated in Figure 7 with respect to the relevant mole fraction range and the WMO/GAW network compatibility goals and extended network compatibility goals (WMO, 2018).

The results presented below were processed by WCC-Empa using the calibration standards of the USH Picarro. The same method is also in use at SMN for the data processing since the current WCC-Empa audit.

Picarro G2401 #2634-CFKADS2238:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 + 0.16 ppb) / 1.0002 (3a)

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

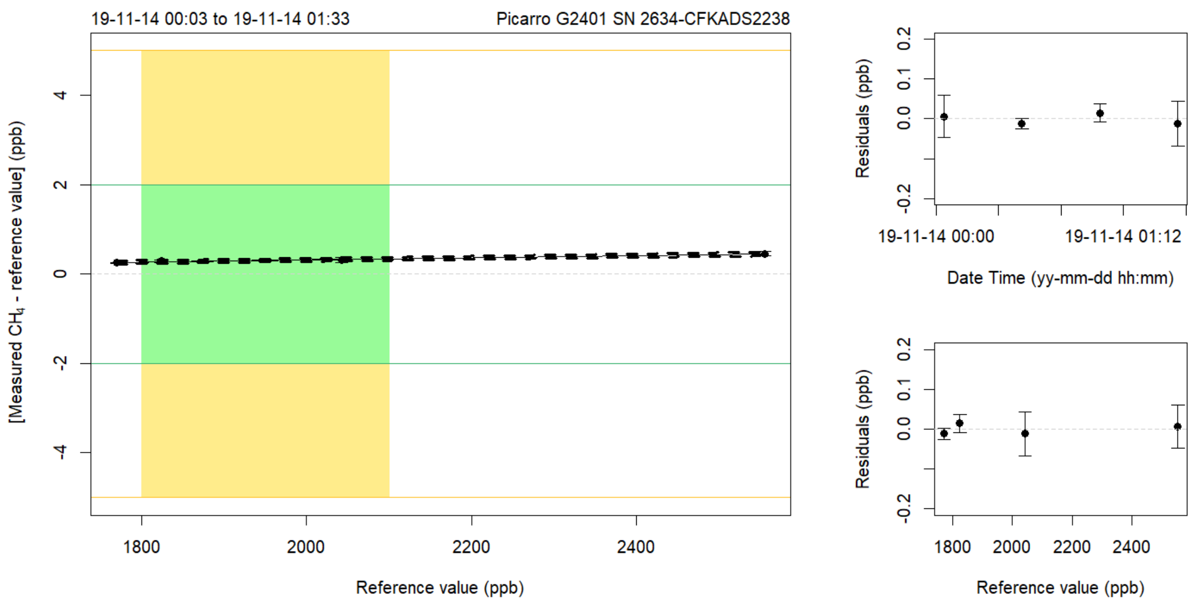


Figure 7. Left: Bias of the Picarro G2401 methane instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points.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

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

Perfect agreement, with no significant bias, was also observed during the ambient air comparison, which confirms the results of the performance audit based on travelling standards.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at USH started in 2017 using a CRDS analyser. Flask measurements made on behalf of NOAA are available since 1994.

Instrumentation, Standards and Data Acquisition. CO_2 is measured by the same instrument as CH_4. See above for details on instruments and calibration.

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

The following equation characterizes the instrument bias. The result is further illustrated in Figure 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

The results presented below were processed by WCC-Empa using the calibration standards of the USH Picarro. The same method is also in use at SMN for the data processing since the current WCC-Empa audit.

Picarro G2401 #2634-CFKADS2238:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.35 ppm) / 0.99921 (4a)

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

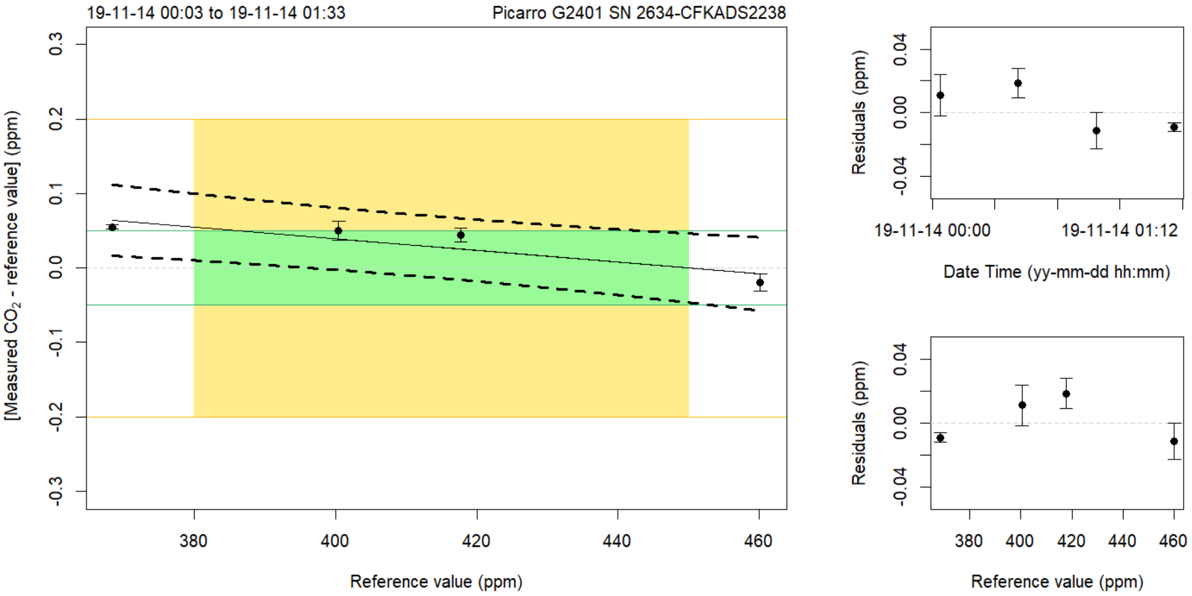


Figure 8. Left: Bias of the Picarro G2401 CO_2 instrument (USH) with respect to the WMO-X2007 CO_2 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points.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

The result of the comparison can be summarized as follows:

The USH instrument showed agreement within the WMO/GAW compatibility goals in the relevant mole fraction range, and no further action is required. However, it has to be noted that the data of the comparison was processed by WCC-Empa. The same method was implemented after the audit by SMN. An initial data evaluation made by SMN yielded larger deviations.

Recommendation 19 (*, important, ongoing)**
The data evaluation implemented by SMN using the information of the automatic calibrations based on a Python script proofed to be appropriate. Continuation of this method of data processing is recommended.

Recommendation 20 (*, important, 2020)**
CO, CH_4 and CO_2 data acquired in the period before the current (starting in 2017) need to be carefully re-processed before submission. The information of the monthly calibrations should be considered for the reprocessing of the data.

Similar results were also observed during the ambient air comparison with the WCC-Empa travelling instrument, which are shown further below.

USH PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the USH 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. (2016a) for CO_2 and CH_4, and Zellweger et al. (2019) for CO and N_2O, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2017 meeting (WMO, 2018) for CO_2, CH_4 and CO and refer to conditions usually found in unpolluted air masses. For surface ozone the mole fraction range of 0 -100 ppb was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 9 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, CO, CH_4, and CO_2. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current USH audit are shown as coloured dots in Figure 9, 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 the RCC ozone calibrator and one ozone analyser, CH_4 and CO_2. The results of the CRDS were within the extended DQOs for CO. The NDIR CO instrument showed only partly compliance with the extended compatibility goals. This is in contrast to the better results observed during the ambient air comparison. A potential reason is sensitivity of this analyser to the way on how air is sampled. Small changes in the inlet pressure may affect the sensitivity and/or the offset of the instrument. The CRDS is much more robust, and therefore easier to calibrate. Therefore, as recommended above, it should be considered to decommission the NDIR CO analyser.

One of the ozone analyser was also slightly exceeding the DQOs. This is only a matter of calibration, and the instrument itself is in a good working condition. For the reason of continuity it was decided not to adjust the calibration settings of the instrument, and post correction should be made.

Table 1. USH 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	USH within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]	% of audits outside eDQOs
O_3 (TEI 49C #330102717)	0 -100	ppb	✓	65	NA	35
O_3 (TEI 49C #58546-318)	0 -100	ppb	✗[2]	65	NA	35
O_3 (RCC calibrator)	0 -100	ppb	✓	65	NA	35
CO (Horiba)	30 - 300	ppb	(✓)	22	47	53
CO (Picarro)	30 - 300	ppb	✓	22	47	53
CH_4 (Picarro)	1750 - 2100	ppb	✓	65	93	7
CO_2 (Picarro)	380 - 450	ppm	✓	38	66	34

[1] *Percentage of stations within the eDQO and DQO*
[2] *Instrument is within DQOs in the relevant mole fraction range of USH*

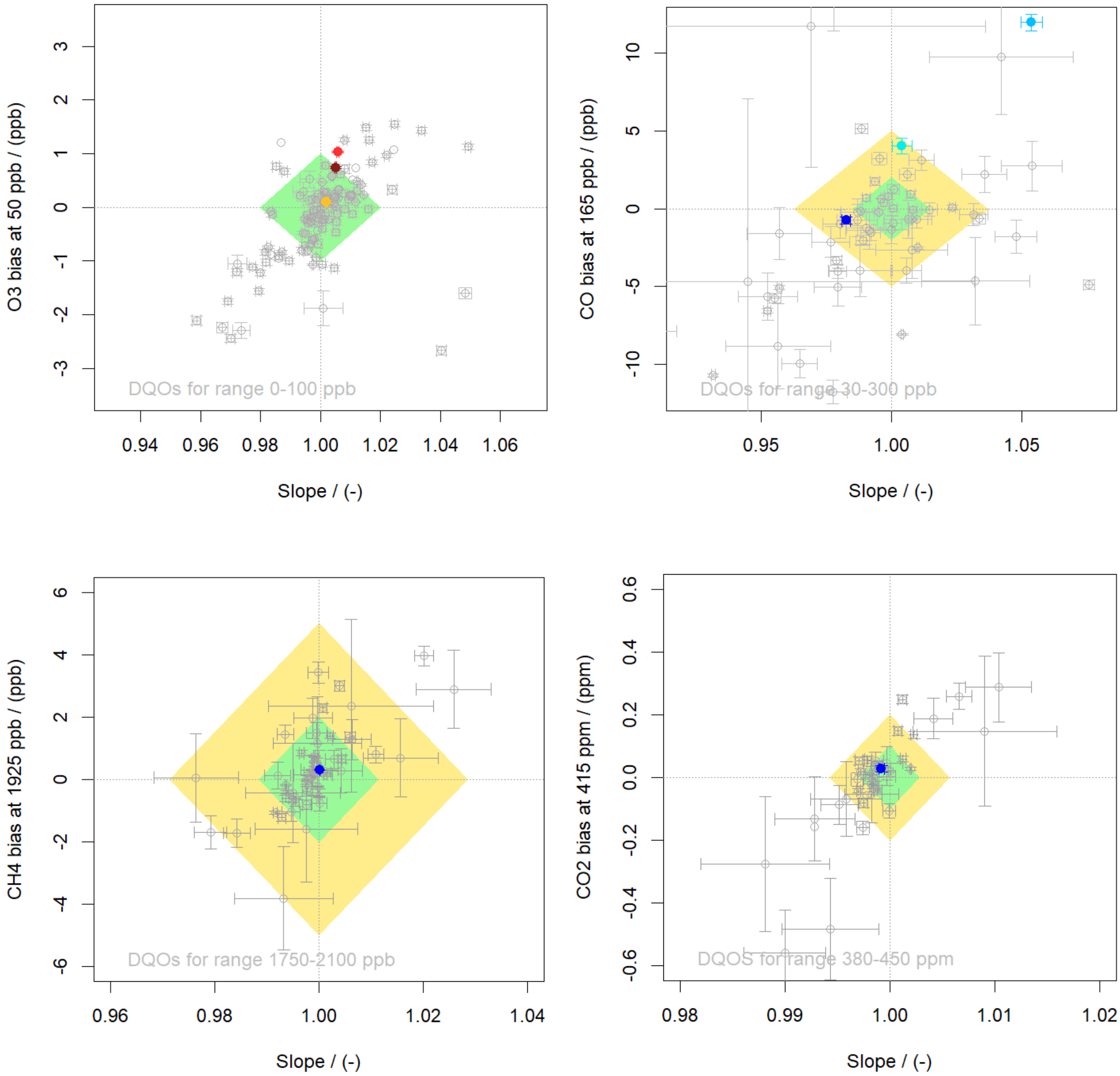


Figure 9. O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show USH results (orange: TEI 49C-PS #56084-306, dark red: TEI 49C #330102717, red: TEI 49C #58546-318, blue: Picarro G2410, cyan: Horiba APMA-360 zero corrected, light blue: Horiba APMA-360 zero and span corrected). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).

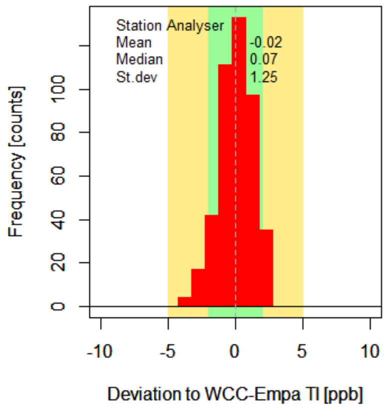
PARALLEL MEASUREMENTS OF AMBIENT AIR

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 15 November 2019 through 7 January 2020; however, on 5 December 2019, water entered the WCC-Empa system, which affected the flow in the system until the end of the campaign. Consequently, only data until 5 December 2019 was used for the comparison. The TI was connected to a separate independent inlet line sampling from the same location as the USH analyser. The TI was sampling air using the following sequence: 305 min ambient air followed by 30 min measurement of three standard gases, each 10 min, and then 1440 min ambient air. The sample air was dried by a Nafion dryer (Model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum in 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 CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below. The USH data shown here were processed by SMN.

Carbon Monoxide

Figure 10 shows the comparison of hourly CO between the WCC-Empa TS and the USH Picarro G2401 and the Horiba APMA-360. The corresponding deviation histograms are shown in Figure 11.

Figure 10. Comparison of the Picarro G2401 analyser (top) and the Horiba APMA-360 (bottom) with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.



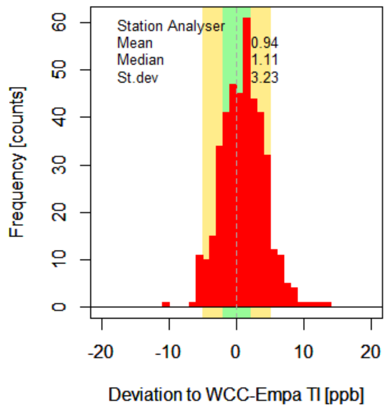


Figure 11. Carbon monoxide deviation histograms for the USH Picarro G2401 analyser (left) and the Horiba APMA-360 (right).

Both instruments showed agreement within the WMO/GAW network compatibility goals. Interestingly, the Horiba instrument also performed well during the ambient air comparison, in contrast to the comparisons of the performance audit. A potential reason is the sensitivity of the analyser to pressure changes. During the comparison with travelling standards, the input pressure of the sample gas is slightly different compared to ambient air measurements, which might explain the difference. Despite the good results of the ambient air comparison, the recommendation to decommission the Horiba instrument remains valid, since the QA/QC requirements are much more challenging compared to the Picarro analyser.

Methane

Figure 12 shows the comparison of hourly CH_4 between the WCC-Empa TS USH Picarro. The corresponding deviation histograms are shown in Figure 13. Excellent agreement within the WMO/GAW network compatibility goals for the Southern Hemisphere was found between the TI and the USH instrument, which confirms the results of the performance audit using travelling standards. The temporal variation was well captured by both instruments.

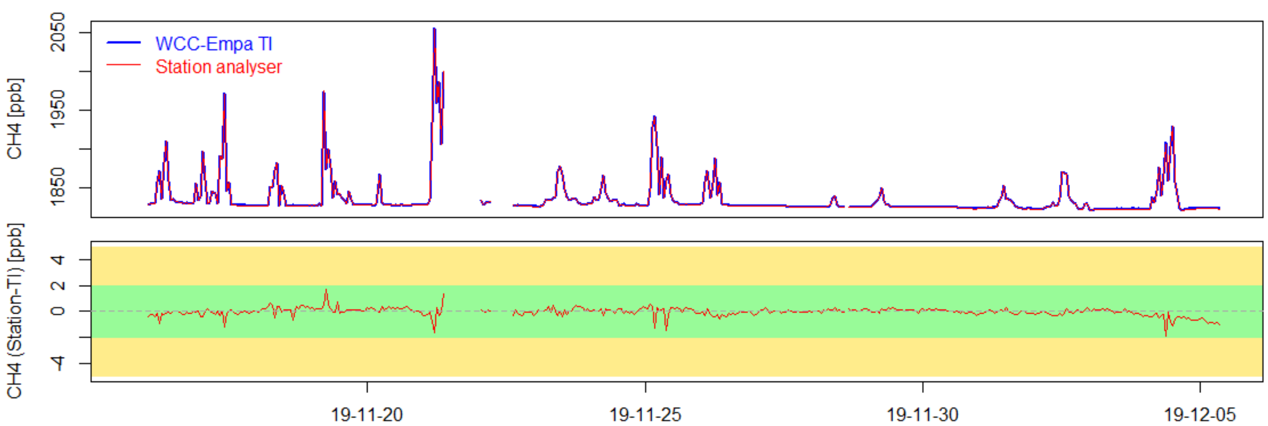


Figure 12. Comparison of the USH Picarro G2401 with the WCC-Empa travelling instrument for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

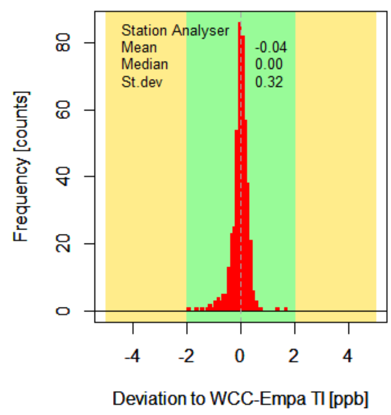


Figure 13. Methane deviation histogram for the USH Picarro G2401

Carbon Dioxide

Figure 14 shows the comparison of hourly CO_2 between the WCC-Empa TI and the USH Picarro, and Figure 15 shows the corresponding deviation histogram. The temporal variability is well captured by both instruments, and no dependency of the bias on the amount fraction was observed Excellent agreement was found between the TI and the USH instrument, which confirms the results of the performance audit using travelling standards.

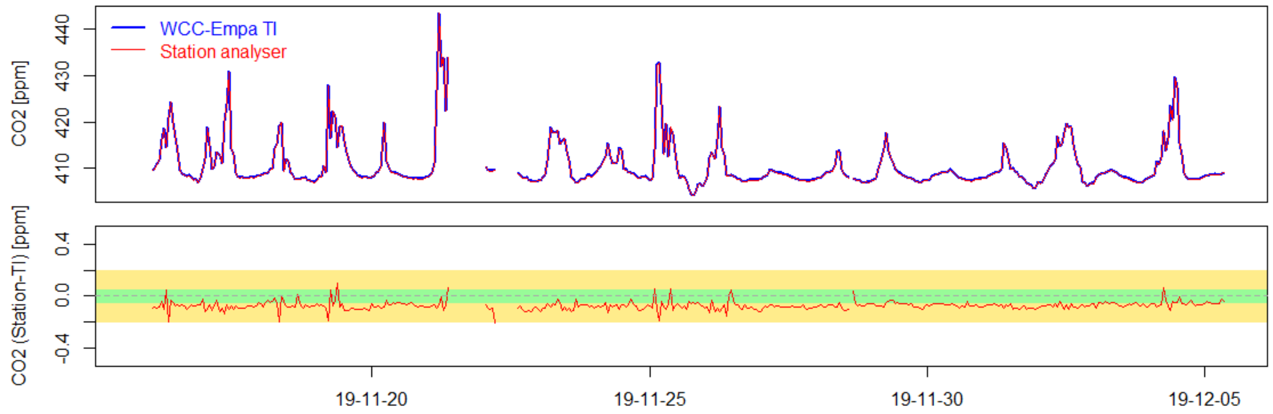


Figure 14. Comparison of the USH Picarro G2401 with the WCC-Empa travelling instrument for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

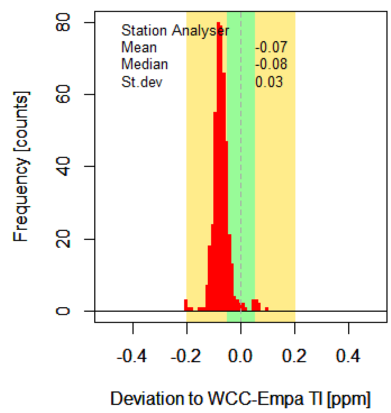


Figure 15. Carbon dioxide deviation histogram of the USH Picarro G2041 compared to WCC-Empa

The good results of the ambient air comparison demonstrates that the data processing by SMN is now fully appropriate. As recommended above, the current data processing method using Python based scripts should be continued.

CONCLUSIONS

The global GAW station Ushuaia provides excellent infrastructure for long-term continuous observations in all WMO/GAW focal areas as well as for research projects. USH contributes significantly to the GAW programme with observations made in a data sparse area of the world. However, continued support, both technically and financially, from the SMN headquarters is required for an ongoing and sustainable operation of the station. Furthermore, the skills of the station staff need to be strengthened, both technically and scientifically. Collaboration with external partners, both national and international, should be continued and intensified.
The continuation of the Ushuaia measurement series is highly important for GAW. Measurements of atmospheric constituents in this data sparse region 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 mole fraction range. Table 2 summarizes the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Note that Table 2 refers only to the mole fractions relevant to USH, 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 Main Analyser	O_3 Backup Analyser	O_3 Calibrator	CO Horiba	CO Picarro	CH_4 Picarro	CO_2 Picarro
Audit with TS	✓	✓	✓	✗	✓	✓	✓
Ambient air comparison	NA	NA	NA	✓	✓	✓	✓

NA no ambient air comparison was made for ozone

SUMMARY RANKING OF THE USHUAIA GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(3)	Small but growing programme
Access	(5)	Year round access
Facilities		
Laboratory and office space	(5)	Adequate, including space for additional research campaigns
Internet access	(3)	Low bandwidth
Air Conditioning	(4)	Only heating, temperature stability acceptable
Power supply	(4)	Mostly reliable, backup UPS
Safety aspects	(3)	High-pressure gas cylinders should be better secured
General Management and Operation		
Organization	(3)	Well-coordinated, budgetary issues
Competence of staff	(3)	Further training needed
Air Inlet System	(4)	Mostly adequate systems
Instrumentation		
Ozone	(4)	Adequate but old instrumentation
CH_4/CO_2 (Picarro)	(5)	State of the art instrumentation
CO (Picarro)	(4)	Adequate instrumentation
CO (Horiba)	(2)	Decommission recommended
Standards		
O_3	(4)	NIST traceable standard at RCC-III
CO, CO_2, CH_4	(3)	NOAA traceable standards from Empa and FMI, no local supplier
Data Management		
Data acquisition	(4)	Adequate systems, no data base
Data processing	(2)	Automatization needed (Phython,R), now implemented
Data submission	(3)	Data partly submitted, with more than 2 years delay, partly dependent on help of external partners

#*0: inadequate thru 5: adequate.*

Dübendorf, March 2020

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APPENDIX

Data Review

The following figures show summary plots of USH data accessed on 5 March 2019 from WDCGG and 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 by USH/SMN:

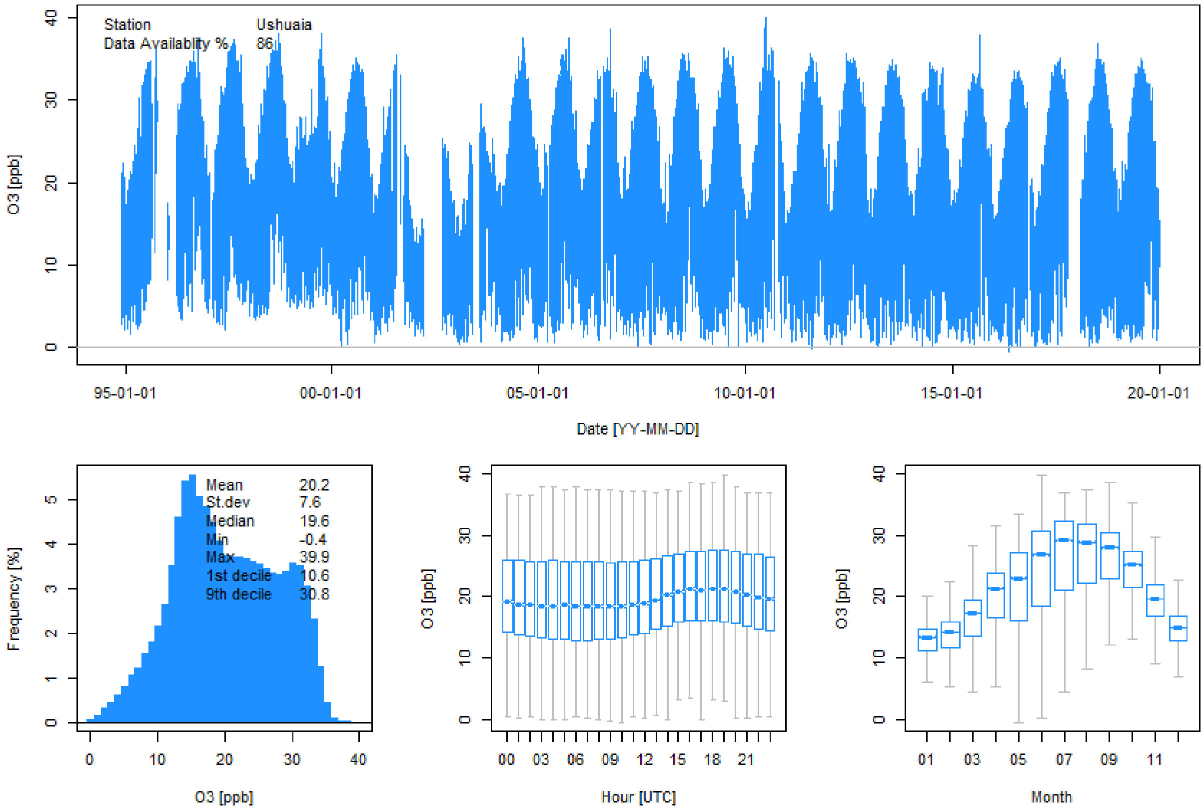

Figure 16. USH O_3 data accessed from WDCRG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

Ozone data submitted by SMN:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- The lowest values of the early period (before 2000) are significantly higher than afterwards. It should be checked if this is an instrument or data treatment artefact.

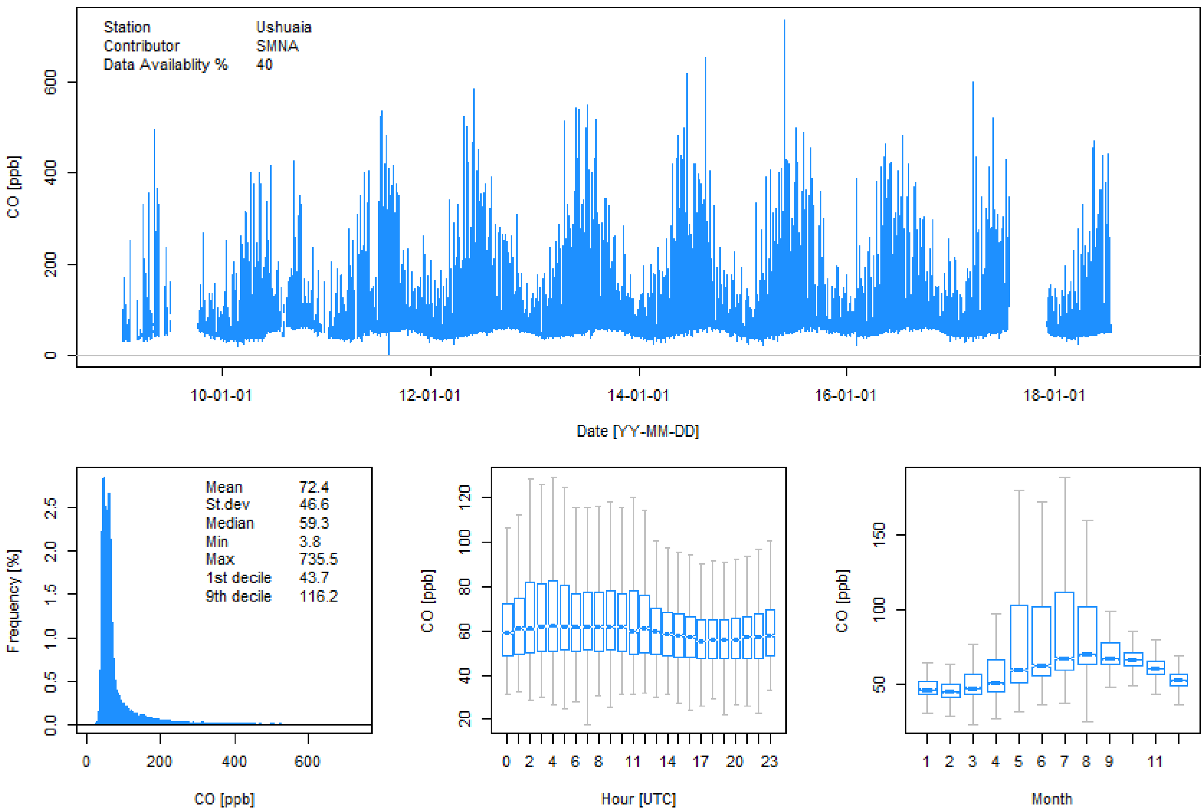

Figure 17. Hourly USH CO data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

CO data submitted by SMN:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Some of the lowest values are potentially invalid and should be flagged.

Flask data submitted by USH/NOAA:

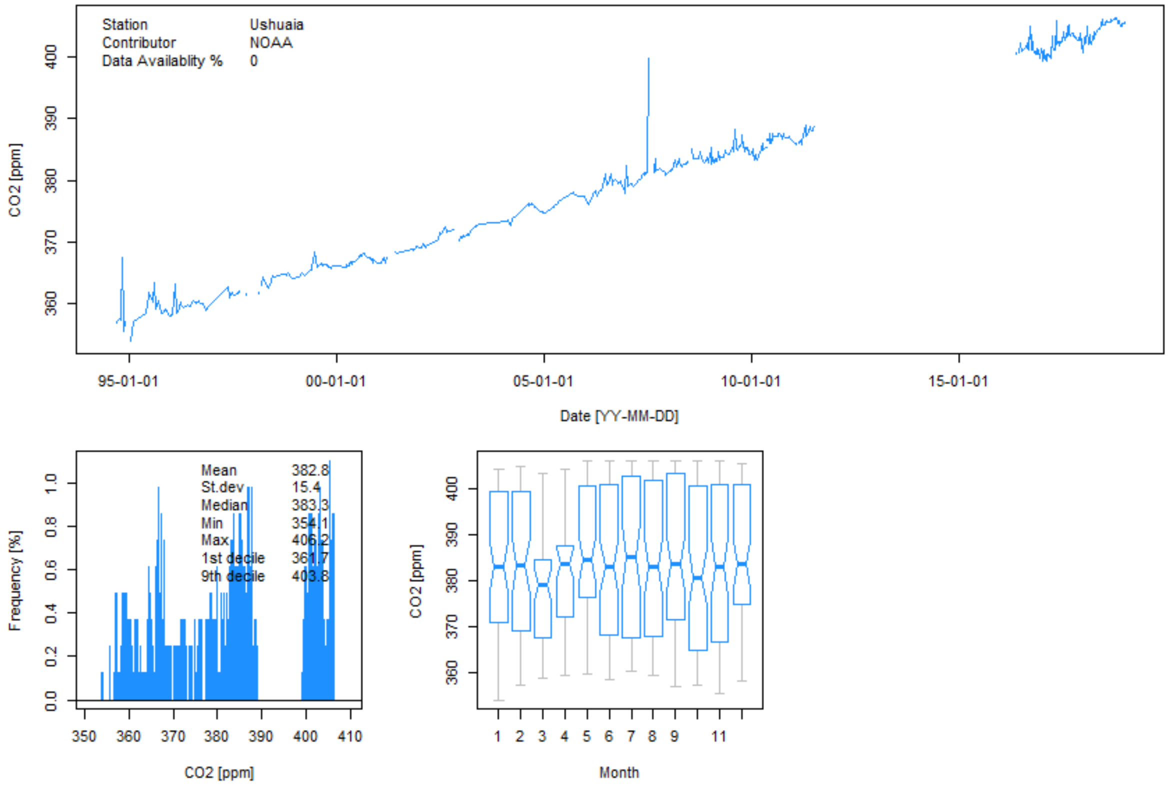

Figure 18. NOAA CO_2 flask data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Right: seasonal variation; the horizontal blue lines denotes to the median, and the blue boxes show the inter-quartile range.

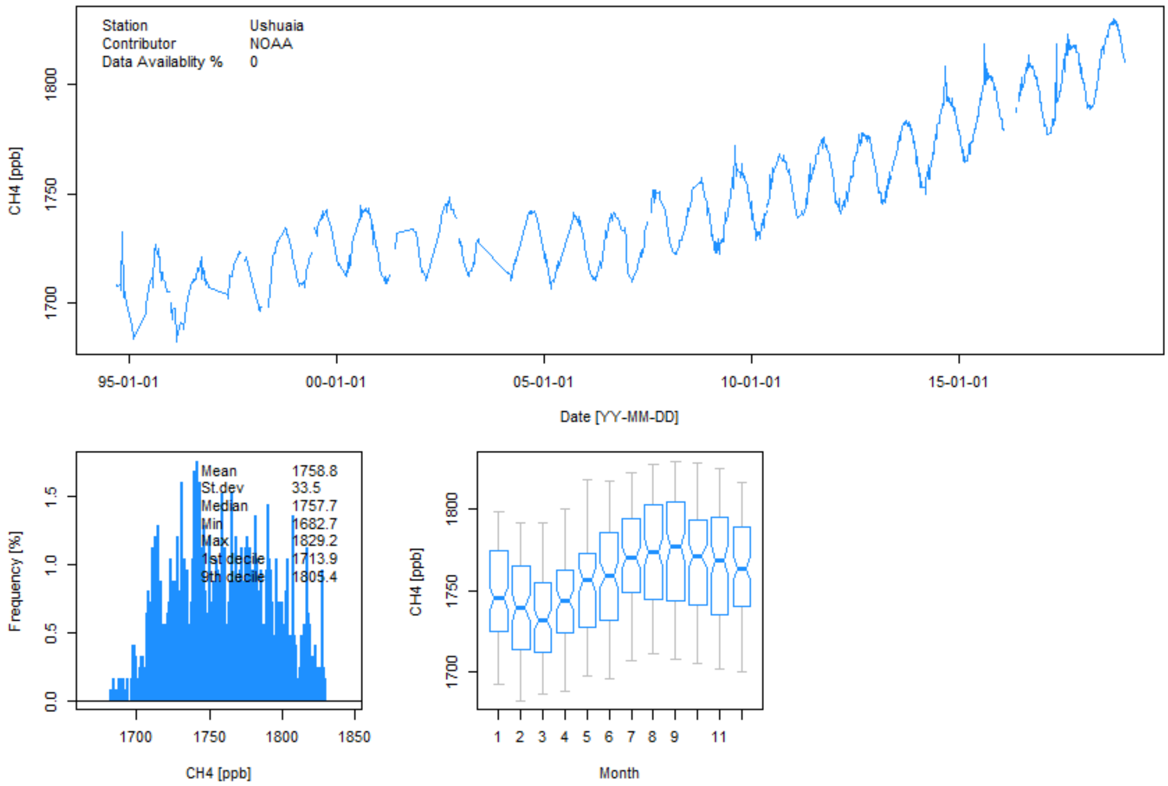

Figure 19. Same as above for CH_4

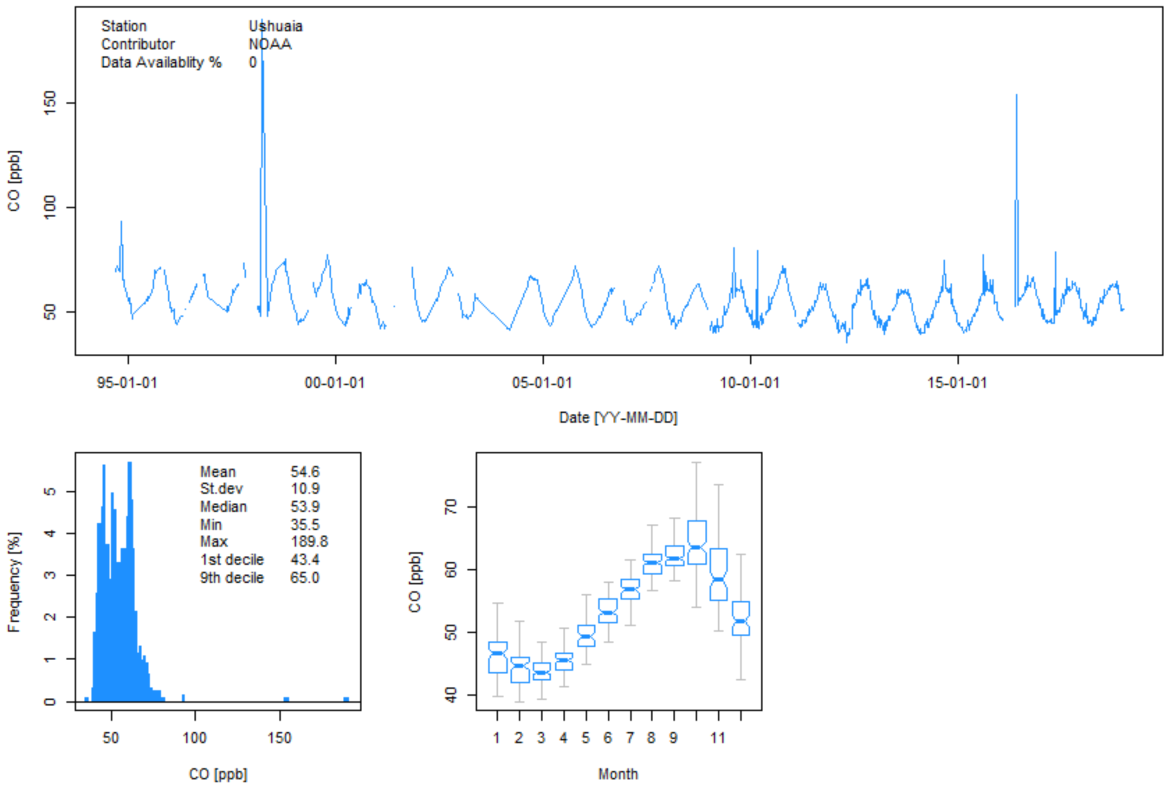

Figure 20. Same as above for CO

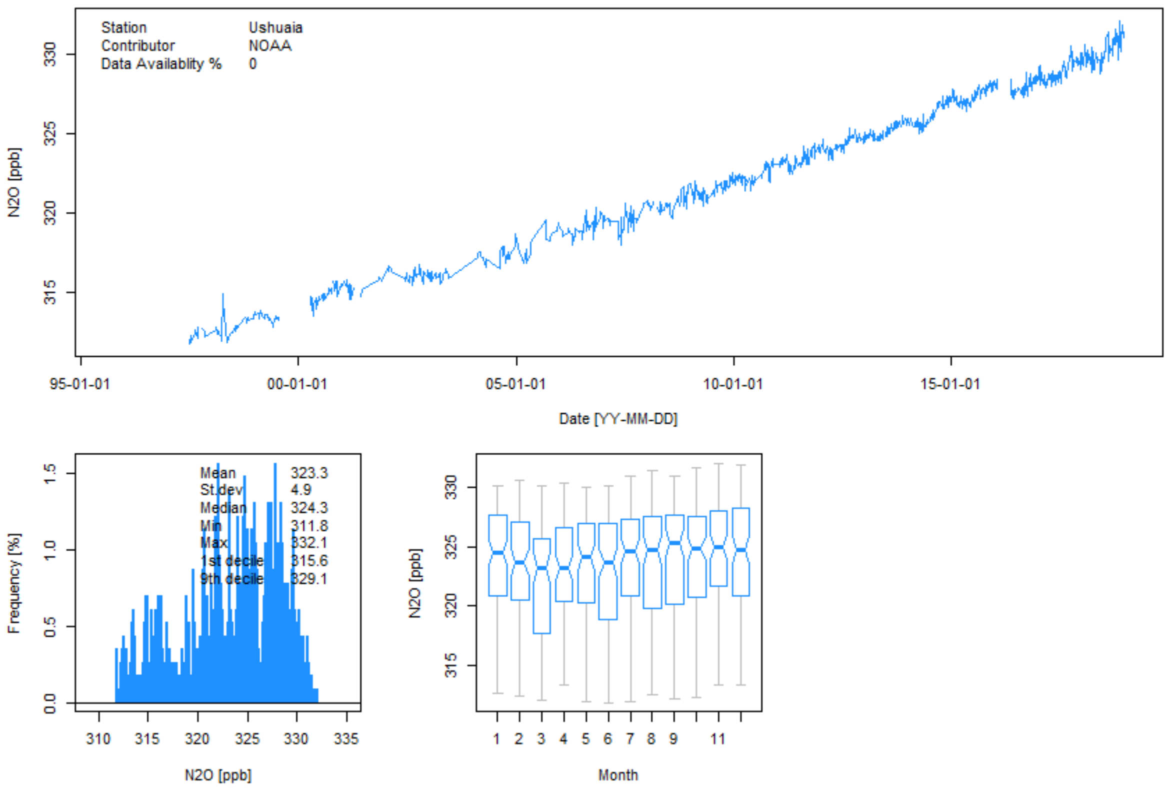

Figure 21. Same as above for N_2O

NOAA flask data:

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

Surface Ozone Comparisons

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

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomized 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 49C-PS #54509-300 (WCC-Empa)
Settings	BKG -0.3, COEF 1.009
Pressure readings (hPa)	Ambient 999.2; TS 998.7 (no adjustment was made)
USH Station analyser (OA)	
Model, S/N	Thermo Scientific 49C #58546-318
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.4 ppb, COEF 1.012
Pressure readings (hPa)	Ambient 999.0; OA 988.5 (no adjustment was made)
USH Station analyser (OA)	
Model, S/N	Thermo Scientific 49C #0330102717
Principle	UV absorption
Range	0-1 ppm
Settings	BKG +0.0 ppb, COEF 1.024
Pressure readings (hPa)	Ambient 998.9; OA 998.6 (no adjustment was made)
RCC-III ozone calibrator (OC)	
Model, S/N	Thermo Scientific 49C-PS #56084-306
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.5 ppb, COEF 1.015
Pressure readings (hPa)	Ambient 998.4; OC 994.3 (no adjustment was made)

Results

Each ozone level was applied for 15 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 15 one-minute values for the comparison of the USH ozone analyser (OA) Thermo Scientific 49C #58546-318 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 (%)
2019-11-13 15:03	1	0	-0.10	0.77	0.04	0.08	0.87	NA
2019-11-13 15:13	1	50	50.35	51.46	0.08	0.13	1.11	2.2
2019-11-13 15:23	1	90	90.24	91.32	0.07	0.18	1.08	1.2
2019-11-13 15:33	1	20	21.08	22.00	0.34	0.35	0.92	4.4
2019-11-13 15:43	1	70	70.19	71.16	0.09	0.06	0.97	1.4
2019-11-13 15:53	1	80	80.15	81.22	0.06	0.10	1.07	1.3
2019-11-13 16:03	1	10	11.62	12.63	0.39	0.48	1.01	8.7
2019-11-13 16:13	1	40	39.75	40.76	0.71	0.66	1.01	2.5
2019-11-13 16:23	1	60	60.06	61.10	0.15	0.09	1.04	1.7
2019-11-13 16:33	2	0	-0.31	0.75	0.10	0.08	1.06	NA
2019-11-13 16:43	2	100	99.96	101.15	0.08	0.04	1.19	1.2
2019-11-13 16:53	2	25	25.49	26.65	0.24	0.16	1.16	4.6
2019-11-13 17:03	2	200	199.36	200.88	0.09	0.08	1.52	0.8
2019-11-13 17:13	2	150	149.56	150.94	0.14	0.13	1.38	0.9
2019-11-13 17:23	2	50	50.18	51.08	0.13	0.07	0.90	1.8
2019-11-13 17:33	2	175	174.60	176.05	0.09	0.05	1.45	0.8
2019-11-13 17:43	2	125	125.04	126.32	0.09	0.13	1.28	1.0
2019-11-13 17:53	2	75	75.12	76.08	0.08	0.04	0.96	1.3
2019-11-13 18:03	3	0	-0.24	0.51	0.04	0.15	0.75	NA
2019-11-13 18:13	3	40	40.01	40.96	0.10	0.11	0.95	2.4
2019-11-13 18:23	3	80	79.81	81.08	0.07	0.11	1.27	1.6
2019-11-13 18:33	3	10	11.79	12.68	0.69	0.63	0.89	7.5
2019-11-13 18:43	3	30	29.38	30.19	0.31	0.36	0.81	2.8
2019-11-13 18:53	3	90	89.71	90.96	0.07	0.20	1.25	1.4
2019-11-13 19:03	3	60	59.94	61.04	0.05	0.20	1.10	1.8
2019-11-13 19:13	3	20	20.55	21.42	0.29	0.28	0.87	4.2
2019-11-13 19:23	3	50	49.70	50.65	0.11	0.18	0.95	1.9
2019-11-13 19:33	3	70	69.85	71.00	0.04	0.11	1.15	1.6
2019-11-13 19:43	4	0	-0.18	0.56	0.06	0.09	0.74	NA
2019-11-13 19:53	4	50	50.02	50.98	0.13	0.17	0.96	1.9
2019-11-13 20:03	4	90	89.71	90.95	0.08	0.07	1.24	1.4
2019-11-13 20:13	4	20	20.73	21.70	0.30	0.31	0.97	4.7
2019-11-13 20:23	4	70	69.85	71.06	0.06	0.16	1.21	1.7
2019-11-13 20:33	4	80	79.83	81.14	0.07	0.12	1.31	1.6
2019-11-13 20:43	4	10	11.87	12.77	0.55	0.63	0.90	7.6
2019-11-13 20:53	4	40	39.66	40.65	0.16	0.35	0.99	2.5
2019-11-13 21:03	4	60	59.86	60.87	0.06	0.06	1.01	1.7
2019-11-13 21:13	5	0	-0.30	0.55	0.04	0.03	0.85	NA
2019-11-13 21:23	5	100	99.79	100.97	0.08	0.16	1.18	1.2
2019-11-13 21:33	5	25	25.41	26.36	0.29	0.34	0.95	3.7
2019-11-13 21:43	5	200	199.43	201.35	0.06	0.09	1.92	1.0
2019-11-13 21:53	5	150	149.56	151.08	0.11	0.09	1.52	1.0
2019-11-13 22:03	5	50	50.06	51.04	0.10	0.06	0.98	2.0
2019-11-13 22:13	5	175	174.32	176.18	0.07	0.14	1.86	1.1
2019-11-13 22:23	5	125	124.83	126.39	0.13	0.13	1.56	1.2

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-11-13 22:33	5	75	74.93	76.21	0.06	0.20	1.28	1.7
2019-11-13 22:43	6	0	-0.17	0.57	0.08	0.07	0.74	NA
2019-11-13 22:53	6	40	39.82	40.87	0.05	0.09	1.05	2.6
2019-11-13 23:03	6	80	79.69	80.80	0.05	0.12	1.11	1.4
2019-11-13 23:13	6	10	11.61	12.54	0.52	0.59	0.93	8.0
2019-11-13 23:23	6	30	29.10	30.18	0.44	0.40	1.08	3.7
2019-11-13 23:33	6	90	89.69	90.91	0.07	0.15	1.22	1.4
2019-11-13 23:43	6	60	59.88	61.22	0.09	0.06	1.34	2.2
2019-11-13 23:53	6	20	20.71	21.70	0.28	0.36	0.99	4.8
2019-11-14 00:03	6	50	49.81	50.98	0.14	0.18	1.17	2.3
2019-11-14 00:13	6	70	69.83	71.20	0.18	0.08	1.37	2.0
2019-11-14 00:23	7	0	-0.32	0.63	0.05	0.10	0.95	NA
2019-11-14 00:33	7	50	50.03	51.08	0.15	0.10	1.05	2.1
2019-11-14 00:43	7	90	89.80	91.24	0.06	0.08	1.44	1.6
2019-11-14 00:53	7	20	20.96	21.96	0.54	0.33	1.00	4.8
2019-11-14 01:03	7	70	69.86	71.03	0.04	0.06	1.17	1.7
2019-11-14 01:13	7	80	79.86	81.18	0.05	0.17	1.32	1.7
2019-11-14 01:23	7	10	11.90	12.92	0.61	0.65	1.02	8.6
2019-11-14 01:33	7	40	39.76	40.77	0.19	0.19	1.01	2.5
2019-11-14 01:43	7	60	59.93	61.05	0.11	0.11	1.12	1.9
2019-11-14 01:53	8	0	-0.28	0.63	0.08	0.04	0.91	NA
2019-11-14 02:03	8	100	99.88	101.40	0.07	0.17	1.52	1.5
2019-11-14 02:13	8	25	25.31	26.26	0.22	0.09	0.95	3.8
2019-11-14 02:23	8	200	199.48	201.50	0.12	0.12	2.02	1.0
2019-11-14 02:33	8	150	149.56	151.41	0.08	0.09	1.85	1.2
2019-11-14 02:43	8	50	50.18	51.41	0.10	0.11	1.23	2.5
2019-11-14 02:53	8	175	174.40	176.44	0.17	0.10	2.04	1.2
2019-11-14 03:03	8	125	124.88	126.49	0.06	0.17	1.61	1.3
2019-11-14 03:13	8	75	75.03	76.25	0.09	0.16	1.22	1.6

Table 5. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the USH ozone analyser (OA) Thermo Scientific 49C #0330102717 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 (%)
2019-11-13 15:03	1	0	-0.10	0.59	0.04	0.08	0.69	NA
2019-11-13 15:13	1	50	50.35	51.19	0.08	0.07	0.84	1.7
2019-11-13 15:23	1	90	90.24	90.91	0.07	0.07	0.67	0.7
2019-11-13 15:33	1	20	21.08	21.74	0.34	0.32	0.66	3.1
2019-11-13 15:43	1	70	70.19	70.90	0.09	0.10	0.71	1.0
2019-11-13 15:53	1	80	80.15	80.95	0.06	0.11	0.80	1.0
2019-11-13 16:03	1	10	11.62	12.27	0.39	0.50	0.65	5.6
2019-11-13 16:13	1	40	39.75	40.48	0.71	0.71	0.73	1.8
2019-11-13 16:23	1	60	60.06	60.98	0.15	0.09	0.92	1.5
2019-11-13 16:33	2	0	-0.31	0.48	0.10	0.07	0.79	NA
2019-11-13 16:43	2	100	99.96	100.74	0.08	0.06	0.78	0.8

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-11-13 16:53	2	25	25.49	26.38	0.24	0.13	0.89	3.5
2019-11-13 17:03	2	200	199.36	200.47	0.09	0.08	1.11	0.6
2019-11-13 17:13	2	150	149.56	150.65	0.14	0.09	1.09	0.7
2019-11-13 17:23	2	50	50.18	50.85	0.13	0.15	0.67	1.3
2019-11-13 17:33	2	175	174.60	175.71	0.09	0.23	1.11	0.6
2019-11-13 17:43	2	125	125.04	126.01	0.09	0.30	0.97	0.8
2019-11-13 17:53	2	75	75.12	75.81	0.08	0.10	0.69	0.9
2019-11-13 18:03	3	0	-0.24	0.38	0.04	0.10	0.62	NA
2019-11-13 18:13	3	40	40.01	40.61	0.10	0.10	0.60	1.5
2019-11-13 18:23	3	80	79.81	80.82	0.07	0.04	1.01	1.3
2019-11-13 18:33	3	10	11.79	12.39	0.69	0.60	0.60	5.1
2019-11-13 18:43	3	30	29.38	29.92	0.31	0.35	0.54	1.8
2019-11-13 18:53	3	90	89.71	90.66	0.07	0.11	0.95	1.1
2019-11-13 19:03	3	60	59.94	60.70	0.05	0.07	0.76	1.3
2019-11-13 19:13	3	20	20.55	21.25	0.29	0.22	0.70	3.4
2019-11-13 19:23	3	50	49.70	50.34	0.11	0.15	0.64	1.3
2019-11-13 19:33	3	70	69.85	70.59	0.04	0.06	0.74	1.1
2019-11-13 19:43	4	0	-0.18	0.31	0.06	0.07	0.49	NA
2019-11-13 19:53	4	50	50.02	50.68	0.13	0.28	0.66	1.3
2019-11-13 20:03	4	90	89.71	90.68	0.08	0.11	0.97	1.1
2019-11-13 20:13	4	20	20.73	21.38	0.30	0.37	0.65	3.1
2019-11-13 20:23	4	70	69.85	70.66	0.06	0.10	0.81	1.2
2019-11-13 20:33	4	80	79.83	80.84	0.07	0.16	1.01	1.3
2019-11-13 20:43	4	10	11.87	12.46	0.55	0.58	0.59	5.0
2019-11-13 20:53	4	40	39.66	40.38	0.16	0.26	0.72	1.8
2019-11-13 21:03	4	60	59.86	60.61	0.06	0.10	0.75	1.3
2019-11-13 21:13	5	0	-0.30	0.20	0.04	0.11	0.50	NA
2019-11-13 21:23	5	100	99.79	100.77	0.08	0.11	0.98	1.0
2019-11-13 21:33	5	25	25.41	26.10	0.29	0.32	0.69	2.7
2019-11-13 21:43	5	200	199.43	200.98	0.06	0.10	1.55	0.8
2019-11-13 21:53	5	150	149.56	150.82	0.11	0.09	1.26	0.8
2019-11-13 22:03	5	50	50.06	50.85	0.10	0.13	0.79	1.6
2019-11-13 22:13	5	175	174.32	175.83	0.07	0.13	1.51	0.9
2019-11-13 22:23	5	125	124.83	126.13	0.13	0.12	1.30	1.0
2019-11-13 22:33	5	75	74.93	75.96	0.06	0.05	1.03	1.4
2019-11-13 22:43	6	0	-0.17	0.43	0.08	0.12	0.60	NA
2019-11-13 22:53	6	40	39.82	40.55	0.05	0.10	0.73	1.8
2019-11-13 23:03	6	80	79.69	80.67	0.05	0.07	0.98	1.2
2019-11-13 23:13	6	10	11.61	12.27	0.52	0.55	0.66	5.7
2019-11-13 23:23	6	30	29.10	29.90	0.44	0.41	0.80	2.7
2019-11-13 23:33	6	90	89.69	90.77	0.07	0.18	1.08	1.2
2019-11-13 23:43	6	60	59.88	60.81	0.09	0.11	0.93	1.6
2019-11-13 23:53	6	20	20.71	21.54	0.28	0.30	0.83	4.0
2019-11-14 00:03	6	50	49.81	50.68	0.14	0.08	0.87	1.7
2019-11-14 00:13	6	70	69.83	70.71	0.18	0.14	0.88	1.3
2019-11-14 00:23	7	0	-0.32	0.34	0.05	0.14	0.66	NA
2019-11-14 00:33	7	50	50.03	50.78	0.15	0.11	0.75	1.5
2019-11-14 00:43	7	90	89.80	90.77	0.06	0.10	0.97	1.1

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-11-14 00:53	7	20	20.96	21.55	0.54	0.45	0.59	2.8
2019-11-14 01:03	7	70	69.86	70.72	0.04	0.07	0.86	1.2
2019-11-14 01:13	7	80	79.86	80.82	0.05	0.12	0.96	1.2
2019-11-14 01:23	7	10	11.90	12.59	0.61	0.53	0.69	5.8
2019-11-14 01:33	7	40	39.76	40.48	0.19	0.21	0.72	1.8
2019-11-14 01:43	7	60	59.93	60.61	0.11	0.14	0.68	1.1
2019-11-14 01:53	8	0	-0.28	0.31	0.08	0.11	0.59	NA
2019-11-14 02:03	8	100	99.88	100.98	0.07	0.16	1.10	1.1
2019-11-14 02:13	8	25	25.31	25.94	0.22	0.18	0.63	2.5
2019-11-14 02:23	8	200	199.48	200.92	0.12	0.04	1.44	0.7
2019-11-14 02:33	8	150	149.56	150.78	0.08	0.15	1.22	0.8
2019-11-14 02:43	8	50	50.18	50.92	0.10	0.16	0.74	1.5
2019-11-14 02:53	8	175	174.40	175.88	0.17	0.17	1.48	0.8
2019-11-14 03:03	8	125	124.88	126.08	0.06	0.08	1.20	1.0
2019-11-14 03:13	8	75	75.03	76.07	0.09	0.07	1.04	1.4

Table 6. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the USH ozone calibrator (OC) Thermo Scientific 49C-PS #56084-306 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2019-11-14 15:40	1	0	-0.16	-0.10	0.04	0.06	0.06	NA
2019-11-14 15:50	1	50	50.12	49.93	0.18	0.21	-0.19	-0.4
2019-11-14 16:00	1	25	25.30	25.31	0.21	0.24	0.01	0.0
2019-11-14 16:10	1	100	99.65	99.49	0.09	0.11	-0.16	-0.2
2019-11-14 16:20	1	200	199.24	199.14	0.17	0.11	-0.10	-0.1
2019-11-14 16:30	1	75	74.96	74.93	0.10	0.16	-0.03	0.0
2019-11-14 16:40	1	150	149.46	149.59	0.19	0.15	0.13	0.1
2019-11-14 16:50	2	0	-0.18	-0.08	0.08	0.09	0.10	NA
2019-11-14 17:00	2	75	74.78	74.79	0.08	0.04	0.01	0.0
2019-11-14 17:10	2	150	149.40	149.45	0.10	0.17	0.05	0.0
2019-11-14 17:20	2	100	99.84	100.02	0.06	0.15	0.18	0.2
2019-11-14 17:30	2	25	25.45	25.77	0.22	0.29	0.32	1.3
2019-11-14 17:40	2	200	199.52	200.02	0.15	0.18	0.50	0.3
2019-11-14 17:50	2	50	50.07	50.20	0.15	0.11	0.13	0.3
2019-11-14 18:19	3	50	50.17	50.48	0.05	0.13	0.31	0.6
2019-11-14 18:30	3	25	25.71	25.92	0.44	0.41	0.21	0.8
2019-11-14 18:40	3	100	99.65	100.05	0.11	0.15	0.40	0.4
2019-11-14 18:45	3	0	-0.20	0.11	0.08	0.08	0.31	NA
2019-11-14 18:50	3	200	199.48	200.03	0.12	0.16	0.55	0.3
2019-11-14 19:10	3	150	149.51	149.93	0.07	0.08	0.42	0.3
2019-11-14 19:15	3	75	74.93	75.30	0.21	0.26	0.37	0.5

Water vapour of the USH Picarro G2401 as determined during the current audit

The water vapour correction function was determined by WCC-Empa during the audit according to the method described by Rella et al. (2013) (see Figure 22). It is recommended that this function is confirmed in at least yearly intervals by USH staff.

Carbon monoxide is only reported as a water vapour corrected mole fraction by the Picarro G2401 instrument (here called *COcorr*). The ratio of COcorr/COdry should be equal to 1 over the entire water vapour range. This was not the case, which indicates that the implemented water vapour correction for CO is not appropriate. This is frequently observed (Zellweger et al., 2019), and therefore, sample air drying as implement at USH, is recommended.

The following functions (5a-b) were obtained to compensate for the humidity interference:

$$CO_2(dry) = CO_2(wet) / (1 - 0.015157 * H_{rep} + 0.000053 * H_{rep2}) \quad (5a)$$

$$CH_4(dry) = CH_4\ (wet) / (1 - 0.012043 * H_{rep} - 0.000026 * H_{rep2}) \quad (5b)$$

Where H_{rep} corresponds to the Picarro reported water mixing ratio in %.

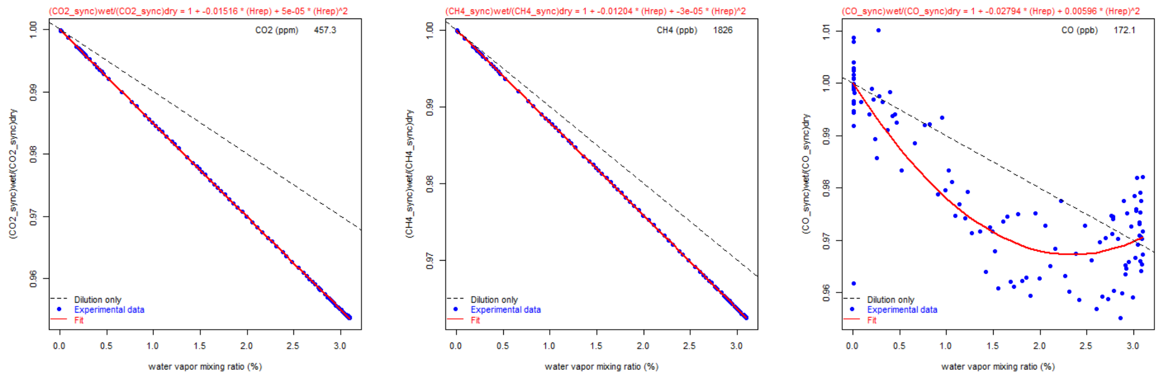

Figure 22. Quadratic fits for the USH Picarro G2401 instrument of CO_2wet/CO_2dry, COcorr/COdry and CH_4wet/CH_4dry vs. H_2O mixing ratios.

The internal water vapour correction does not sufficiently account for the influence of H_2O on the spectroscopy, as shown in Figure 23. Significant deviations were observed for all parameters.

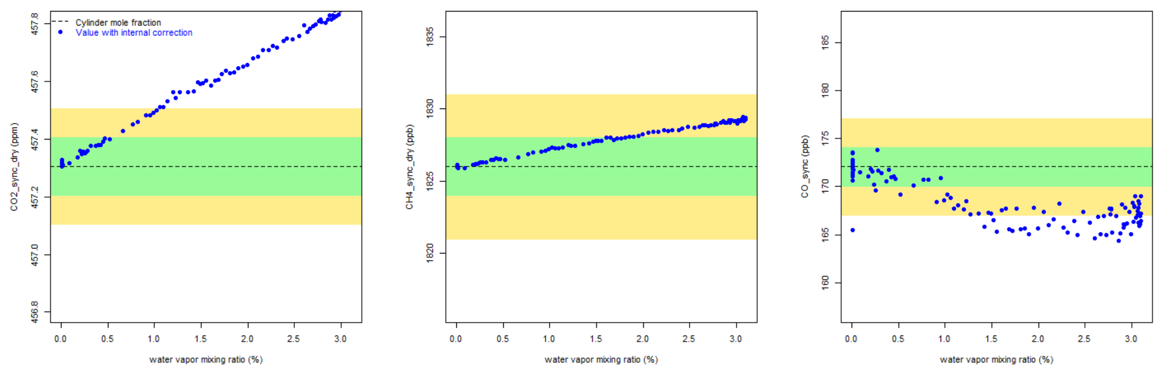

Figure 23. H_2O dependency for CO_2, CH_4 and CO of a working tank measured by the USH Picarro G2401. The blue dots are internally corrected values measured by the Picarro G2401. The green and yellow areas correspond to the WMO network compatibility and extended network compatibility goals.

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 **7** 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 USH data acquisition system. The standards used for the calibration of the USH instruments are shown in Table 8.

Table 7. Experimental details of USH CO comparison

Travelling standard (TS)	
The USH Picarro instrument was audited using WCC-Empa Travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air). Assigned values and standard uncertainties see Table 17. The NDIR instrument was audited using a CO in air standard (CA05309, 98.8 ppm CO, 1900 psi, Scott Marin has been used in combination with a dilution system. Levels ranging from 0 to 800 ppb (steps of 50 ppb) were generated in random order and were simultaneously measured by the USH instrument and the WCC-Empa Picarro G2401, which was calibrated using three calibration standards. The calibrated Picarro readings were taken as the reference value. Details of the standards used for the calibration of the Picarro are given in Table 17.	
Station Analyser (CRDS)	
Model, S/N	Picarro G2401 #2634-CFKADS2238
Principle	CRDS
Drying system	Perma Pure Nafion dryer (model PD-50T-12MPS) operated in reflux mode. The dryer was not yet installed during the TS comparison.
Station Analyser (NDIR)	
Model, S/N	Horiba APMA-360 #712020
Principle	NDIR, cross flow modulation
Drying system	Perma Pure Nafion dryer
Connection	TS were directly delivered to the sample ports of the instruments.

Table 8. Reference standards available at USH. Calibration scales: CH_4: WMOX2004A, N_2O: WMOX2006A, CO: WMOX2014A, CO_2: WMOX2007

Cylinder ID	CH_4 (ppb)		N_2O (ppb)		CO (ppb)		CO_2 (ppb)		Pressure (psi)	Use
CA05309[1]	NA	NA	NA	NA	98800.0	990.0	NA	NA	1900	CO dilution
080808_CA08220[2]	NA	NA	NA	NA	2582.0	52.0	NA	NA	1400	CO NDIR
120614_CB09197	1778.03	0.08	321.66	0.09	90.45	1.01	329.53	0.02	1090	Picarro LS
130822_CB10205	2397.66	0.13	326.81	0.04	278.47	0.19	427.18	0.02	1400	Picarro LS
82549	1948.63	NA	331.51	NA	143.79	0.06	419.13	NA	2300	Picarro LS
130821_CB10215	2042.46	0.09	345.67	0.07	228.58	0.54	368.32	0.01	1820	Stock*
150520_CB11214	2555.44	0.1	306.24	0.09	267.33	0.26	400.42	0.04	1820	Stock*
190605_CC703023	1769.08	0.09	339.96	0.04	58.22	0.74	417.72	0.01	1820	Stock*
190611_CC702887	1823.25	0.07	366.72	0.05	173.90	0.59	460.19	0.01	1800	Picarro WS[#]

[1] *NIST scale*
[2] *WMO-X2000 scale*
** Used for the calibration of the TI during the ambient air comparison of the current audit*
[#] *Installation during this audit*

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 9. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2634-CFKADS2238 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 (%)
(19-11-14 00:03:00)	150520_CB11214	267.3	0.3	264.9	0.4	4	-2.4	-0.9
(19-11-14 00:33:00)	190605_CC703023	58.2	0.7	59.5	0.3	4	1.2	2.1
(19-11-14 01:03:00)	190611_CC702887	173.9	0.6	172.7	0.2	4	-1.2	-0.7
(19-11-14 01:33:00)	130821_CB10215	228.6	0.5	226.9	0.4	4	-1.7	-0.8

Table 10. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Horiba APMA-360 instrument (AL) with the WCC-Empa dilution system / Picarro G2401 (WMO-X2014A CO scale). Horiba data was corrected for zero offset during this comparison.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-11-14 22:59:00)	Dilution system	2.5	0.6	-4.6	10.9	2	-7.1	NA
(19-11-14 23:29:00)	Dilution system	797.9	0.5	799.7	4.2	2	1.8	0.2
(19-11-14 19:40:00)	Dilution system	77.2	2.0	94.9	2.0	2	17.7	23.0
(19-11-14 20:32:00)	Dilution system	2.5	0.6	-1.4	2.0	2	-3.9	NA
(19-11-14 22:44:00)	Dilution system	749.4	1.1	749.0	3.1	2	-0.5	-0.1
(19-11-15 00:14:00)	Dilution system	106.6	0.0	121.5	1.8	2	14.9	14.0
(19-11-15 00:44:00)	Dilution system	2.5	0.6	3.0	1.1	2	0.5	NA
(19-11-15 01:14:00)	Dilution system	700.0	0.5	710.9	2.8	2	11.0	1.6
(19-11-15 01:44:00)	Dilution system	155.4	1.3	166.9	3.7	2	11.5	7.4
(19-11-15 02:14:00)	Dilution system	2.5	0.6	6.7	6.7	2	4.3	NA
(19-11-15 02:44:00)	Dilution system	649.9	1.4	650.8	1.3	2	0.9	0.1

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-11-15 03:14:00)	Dilution system	206.1	1.8	220.9	0.6	2	14.8	7.2
(19-11-15 03:44:00)	Dilution system	2.5	0.6	5.6	0.9	2	3.1	NA
(19-11-15 04:14:00)	Dilution system	601.4	1.5	609.5	0.2	2	8.1	1.3
(19-11-15 04:44:00)	Dilution system	254.3	1.5	265.6	9.2	2	11.4	4.5
(19-11-15 05:14:00)	Dilution system	2.5	0.6	0.8	2.3	2	-1.7	NA
(19-11-15 05:44:00)	Dilution system	551.5	1.6	557.3	5.8	2	5.8	1.1
(19-11-15 06:14:00)	Dilution system	304.6	2.0	316.0	3.8	2	11.4	3.7
(19-11-15 06:44:00)	Dilution system	2.5	0.6	1.5	0.2	2	-1.0	NA
(19-11-15 07:14:00)	Dilution system	700.0	0.5	704.0	3.0	2	4.1	0.6
(19-11-15 07:44:00)	Dilution system	354.0	1.3	362.4	3.3	2	8.5	2.4
(19-11-15 08:14:00)	Dilution system	2.5	0.6	-0.6	5.5	2	-3.1	NA
(19-11-15 08:44:00)	Dilution system	452.4	1.3	458.0	0.0	2	5.6	1.2
(19-11-15 09:14:00)	Dilution system	403.3	1.1	410.4	11.3	2	7.1	1.8
(19-11-15 09:44:00)	Dilution system	2.5	0.6	0.4	1.4	2	-2.1	NA
(19-11-15 10:14:00)	Dilution system	2.5	0.6	-2.3	2.7	2	-4.8	NA
(19-11-15 10:44:00)	Dilution system	797.9	0.5	802.2	1.6	2	4.4	0.6
(19-11-15 11:14:00)	Dilution system	77.2	2.0	89.7	8.4	2	12.5	16.3
(19-11-15 11:44:00)	Dilution system	2.5	0.6	-2.1	2.6	2	-4.6	NA
(19-11-15 12:14:00)	Dilution system	749.4	1.1	756.4	7.8	2	7.0	0.9
(19-11-15 12:44:00)	Dilution system	106.6	0.0	118.9	2.1	2	12.3	11.5
(19-11-15 13:13:00)	Dilution system	2.5	0.6	0.0	3.2	2	-2.5	NA
(19-11-15 13:44:00)	Dilution system	700.0	0.5	702.3	5.0	2	2.3	0.3

Table 11. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Horiba APMA-360 instrument (AL) with the WCC-Empa dilution system / Picarro G2401 (WMO-X2014A CO scale). Horiba data was corrected for zero offset, and a span factor was applied based on the measurement of the calibration standard during this comparison.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-11-14 22:59:00)	Dilution system	2.5	0.6	-5.3	11.5	2	-7.7	NA
(19-11-14 23:29:00)	Dilution system	797.9	0.5	838.9	4.5	2	41.0	5.1
(19-11-14 19:40:00)	Dilution system	77.2	2.0	99.2	2.1	2	22.0	28.5
(19-11-14 20:32:00)	Dilution system	2.5	0.6	-1.9	2.1	2	-4.4	NA
(19-11-14 22:44:00)	Dilution system	749.4	1.1	785.6	3.2	2	36.2	4.8
(19-11-15 00:14:00)	Dilution system	106.6	0.0	127.1	1.9	2	20.5	19.2
(19-11-15 00:44:00)	Dilution system	2.5	0.6	2.7	1.2	2	0.3	NA
(19-11-15 01:14:00)	Dilution system	700.0	0.5	745.7	2.9	2	45.7	6.5
(19-11-15 01:44:00)	Dilution system	155.4	1.3	174.8	3.9	2	19.4	12.5
(19-11-15 02:14:00)	Dilution system	2.5	0.6	6.6	7.1	2	4.2	NA
(19-11-15 02:44:00)	Dilution system	649.9	1.4	682.6	1.4	2	32.7	5.0
(19-11-15 03:14:00)	Dilution system	206.1	1.8	231.4	0.6	2	25.3	12.3
(19-11-15 03:44:00)	Dilution system	2.5	0.6	5.4	1.0	2	3.0	NA
(19-11-15 04:14:00)	Dilution system	601.4	1.5	639.3	0.2	2	37.8	6.3
(19-11-15 04:44:00)	Dilution system	254.3	1.5	278.3	9.6	2	24.1	9.5
(19-11-15 05:14:00)	Dilution system	2.5	0.6	0.4	2.4	2	-2.0	NA
(19-11-15 05:44:00)	Dilution system	551.5	1.6	584.5	6.1	2	33.0	6.0
(19-11-15 06:14:00)	Dilution system	304.6	2.0	331.2	4.0	2	26.6	8.7

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-11-15 06:44:00)	Dilution system	2.5	0.6	1.2	0.2	2	-1.3	NA
(19-11-15 07:14:00)	Dilution system	700.0	0.5	738.4	3.2	2	38.5	5.5
(19-11-15 07:44:00)	Dilution system	354.0	1.3	379.9	3.5	2	26.0	7.3
(19-11-15 08:14:00)	Dilution system	2.5	0.6	-1.1	5.8	2	-3.5	NA
(19-11-15 08:44:00)	Dilution system	452.4	1.3	480.2	0.0	2	27.9	6.2
(19-11-15 09:14:00)	Dilution system	403.3	1.1	430.3	11.9	2	27.0	6.7
(19-11-15 09:44:00)	Dilution system	2.5	0.6	0.0	1.5	2	-2.5	NA
(19-11-15 10:14:00)	Dilution system	2.5	0.6	-2.8	2.9	2	-5.3	NA
(19-11-15 10:44:00)	Dilution system	797.9	0.5	841.5	1.7	2	43.7	5.5
(19-11-15 11:14:00)	Dilution system	77.2	2.0	93.7	8.8	2	16.6	21.5
(19-11-15 11:44:00)	Dilution system	2.5	0.6	-2.6	2.7	2	-5.1	NA
(19-11-15 12:14:00)	Dilution system	749.4	1.1	793.4	8.1	2	44.0	5.9
(19-11-15 12:44:00)	Dilution system	106.6	0.0	124.4	2.2	2	17.7	16.6
(19-11-15 13:13:00)	Dilution system	2.5	0.6	-0.5	3.4	2	-2.9	NA
(19-11-15 13:44:00)	Dilution system	700.0	0.5	736.6	5.2	2	36.7	5.2

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 8, and Table 12 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 12. Experimental details of USH CH_4 comparison

Travelling standard (TS)	
WCC-Empa Travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 17.	
Station Analyser	
Model, S/N	Picarro G2401 #2634-CFKADS2238.
Principle	CRDS
Drying system	Perma Pure Nafion dryer (model PD-50T-12MPS) operated in reflux mode. The dryer was not yet installed during the TS comparison.
Connection	TS were directly delivered to the sample ports of the instruments.

Results

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

Table 13. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the USH Picarro G2401 #2634-CFKADS2238 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 (%)
(19-11-14 00:03:00)	150520_CB11214	2555.44	0.10	2555.89	0.05	4	0.45	0.02
(19-11-14 00:33:00)	190605_CC703023	1769.08	0.09	1769.33	0.01	4	0.25	0.01
(19-11-14 01:03:00)	190611_CC702887	1823.25	0.07	1823.54	0.02	4	0.29	0.02
(19-11-14 01:33:00)	130821_CB10215	2042.46	0.09	2042.77	0.06	4	0.31	0.02

Carbon Dioxide Comparisons

Comparison details see CH_4.

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 14. CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the USH Picarro G2401 #2634-CFKADS2238 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 (%)
(19-11-14 00:03:00)	150520_CB11214	400.42	0.04	400.47	0.01	4	0.05	0.01
(19-11-14 00:33:00)	190605_CC703023	417.72	0.01	417.76	0.01	4	0.04	0.01
(19-11-14 01:03:00)	190611_CC702887	460.19	0.01	460.17	0.01	4	-0.02	0.00
(19-11-14 01:33:00)	130821_CB10215	368.32	0.01	368.37	0.00	4	0.05	0.01

WCC-Empa Travelling Standards

Ozone

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

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

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

Zero air source: 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 15. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 24). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed

(Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

X_{TS} (ppb) = ([TS] + 0.10 ppb) / 1.0011 (6a)

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

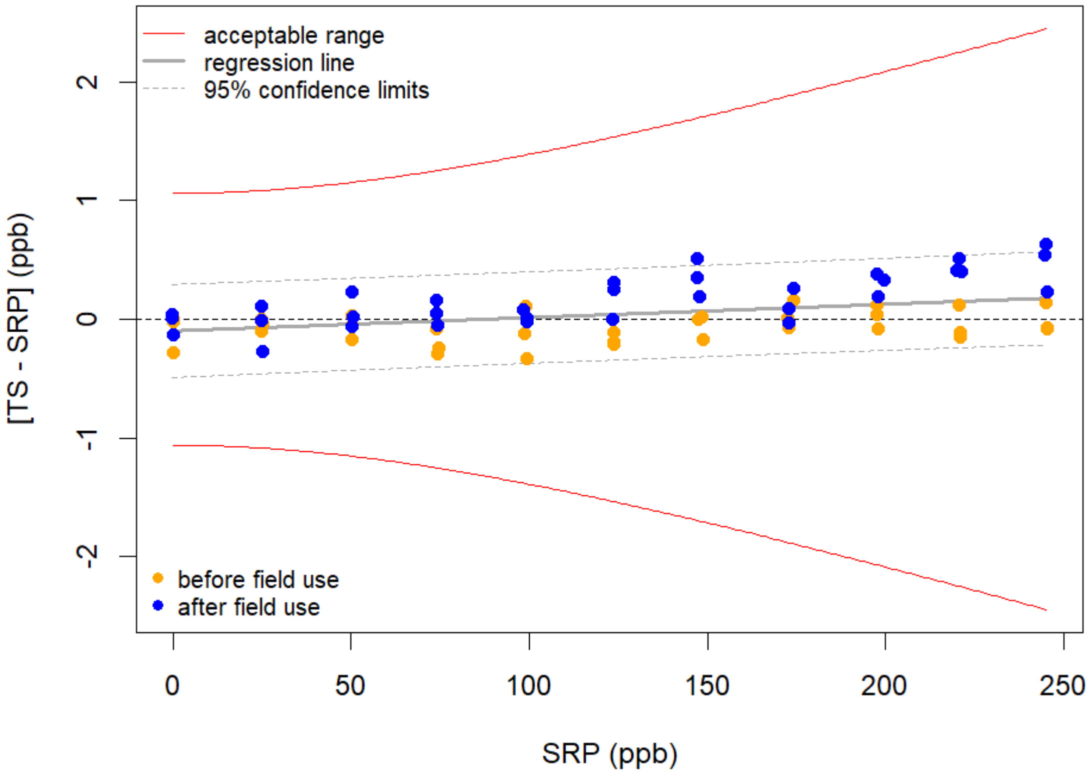

Figure 24. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site

Table 15. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard (TS)

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2019-07-04	1	25	25.08	0.24	25.04	0.14
2019-07-04	1	175	172.83	0.23	172.76	0.10
2019-07-04	1	125	123.86	0.19	123.66	0.10
2019-07-04	1	0	0.22	0.23	-0.05	0.11
2019-07-04	1	150	148.80	0.31	148.63	0.19
2019-07-04	1	75	74.64	0.15	74.40	0.07
2019-07-04	1	220	220.86	0.32	220.72	0.10
2019-07-04	1	100	98.98	0.27	99.09	0.11
2019-07-04	1	200	197.98	0.22	197.90	0.10
2019-07-04	1	50	50.14	0.34	50.10	0.11
2019-07-04	1	245	245.25	0.21	245.18	0.12
2019-07-04	2	170	172.45	0.28	172.46	0.10
2019-07-04	2	0	-0.01	0.30	-0.01	0.09
2019-07-04	2	150	148.59	0.27	148.61	0.18
2019-07-04	2	50	50.34	0.29	50.17	0.09

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2019-07-04	2	100	99.28	0.23	98.95	0.07
2019-07-04	2	25	24.89	0.35	24.90	0.07
2019-07-04	2	220	220.83	0.21	220.72	0.14
2019-07-04	2	125	123.71	0.23	123.50	0.12
2019-07-04	2	200	197.53	0.19	197.65	0.11
2019-07-04	2	75	74.14	0.28	73.85	0.14
2019-07-04	2	245	245.38	0.28	245.30	0.11
2019-07-04	3	100	98.60	0.32	98.49	0.06
2019-07-04	3	75	74.12	0.41	74.04	0.14
2019-07-04	3	220	220.63	0.26	220.75	0.09
2019-07-04	3	0	0.04	0.19	0.02	0.08
2019-07-04	3	175	174.05	0.41	174.21	0.43
2019-07-04	3	125	123.70	0.16	123.59	0.13
2019-07-04	3	25	24.98	0.35	24.88	0.09
2019-07-04	3	50	50.25	0.18	50.28	0.04
2019-07-04	3	200	197.56	0.33	197.60	0.11
2019-07-04	3	145	147.41	0.16	147.41	0.14
2019-07-04	3	245	244.95	0.22	245.09	0.18
2020-02-14	4	25	98.41	0.30	98.50	0.09
2020-02-14	4	175	73.93	0.18	74.10	0.09
2020-02-14	4	125	220.11	0.31	220.52	0.10
2020-02-14	4	0	-0.09	0.27	-0.09	0.11
2020-02-14	4	150	174.05	0.64	174.31	0.47
2020-02-14	4	75	123.51	0.31	123.51	0.14
2020-02-14	4	220	24.82	0.19	24.81	0.10
2020-02-14	4	100	50.54	0.31	50.56	0.09
2020-02-14	4	200	197.44	0.21	197.83	0.10
2020-02-14	4	50	147.15	0.26	147.66	0.15
2020-02-14	4	245	244.72	0.48	245.26	0.16
2020-02-14	5	170	74.09	0.32	74.14	0.09
2020-02-14	5	0	0.01	0.35	-0.12	0.08
2020-02-14	5	150	221.13	0.41	221.53	0.31
2020-02-14	5	50	123.57	0.26	123.89	0.13
2020-02-14	5	100	172.85	0.21	172.81	0.19
2020-02-14	5	25	197.76	0.26	197.96	0.08
2020-02-14	5	220	25.16	0.49	24.90	0.12
2020-02-14	5	125	50.26	0.20	50.49	0.05
2020-02-14	5	200	99.32	0.24	99.30	0.10
2020-02-14	5	75	147.71	0.31	147.90	0.07
2020-02-14	5	245	245.46	0.35	245.70	0.26
2020-02-14	6	100	74.29	0.36	74.24	0.06
2020-02-14	6	75	172.86	0.30	172.96	0.17
2020-02-14	6	220	24.84	0.33	24.96	0.15
2020-02-14	6	0	99.25	0.35	99.25	0.08
2020-02-14	6	175	220.46	0.36	220.97	0.11
2020-02-14	6	125	147.04	0.31	147.39	0.08
2020-02-14	6	25	50.22	0.45	50.16	0.05
2020-02-14	6	50	-0.27	0.45	-0.23	0.07
2020-02-14	6	200	199.64	0.59	199.98	0.76
2020-02-14	6	145	123.70	0.25	123.95	0.10
2020-02-14	6	245	245.02	0.17	245.64	0.09

#*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 travelling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-X2014A scale (Novelli et al., 2003)
CO_2: WMO-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, CO_2 and CH_4: Picarro G2401 (Cavity Ring-Down Spectroscopy).

Table 15 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 16, and Figure 25 shows the analysis of the TS over time.

Table 15. NOAA/ESRL laboratory standards and CO working standard 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
190618_CC703041*	3244.00	2258.07	NA	419.61

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

Table 16. Calibration summary of the WCC-Empa travelling standards. CO (A) refers to CO measurements on the Aerodyne, CO (P) on the Picarro instrument

TS	Press. (psi)	CH_4 (ppb)	sd	CO_2 (ppm)	sd	N_2O (ppb)	sd	CO (A) (ppb)	sd	CO (P) (ppb)	sd
130821_CB10215	1940	2042.46	0.09	368.32	0.01	345.67	0.07	229.64	0.19	228.58	0.54
150520_CB11214	1900	2555.44	0.1	400.42	0.04	306.24	0.09	267.88	0.12	267.33	0.26
190605_CC703023	1920	1769.08	0.09	417.72	0.01	339.96	0.04	59.96	0.36	58.22	0.74
190611_CC702887	1920	1823.25	0.07	460.19	0.01	366.72	0.05	175.25	0.23	173.9	0.59

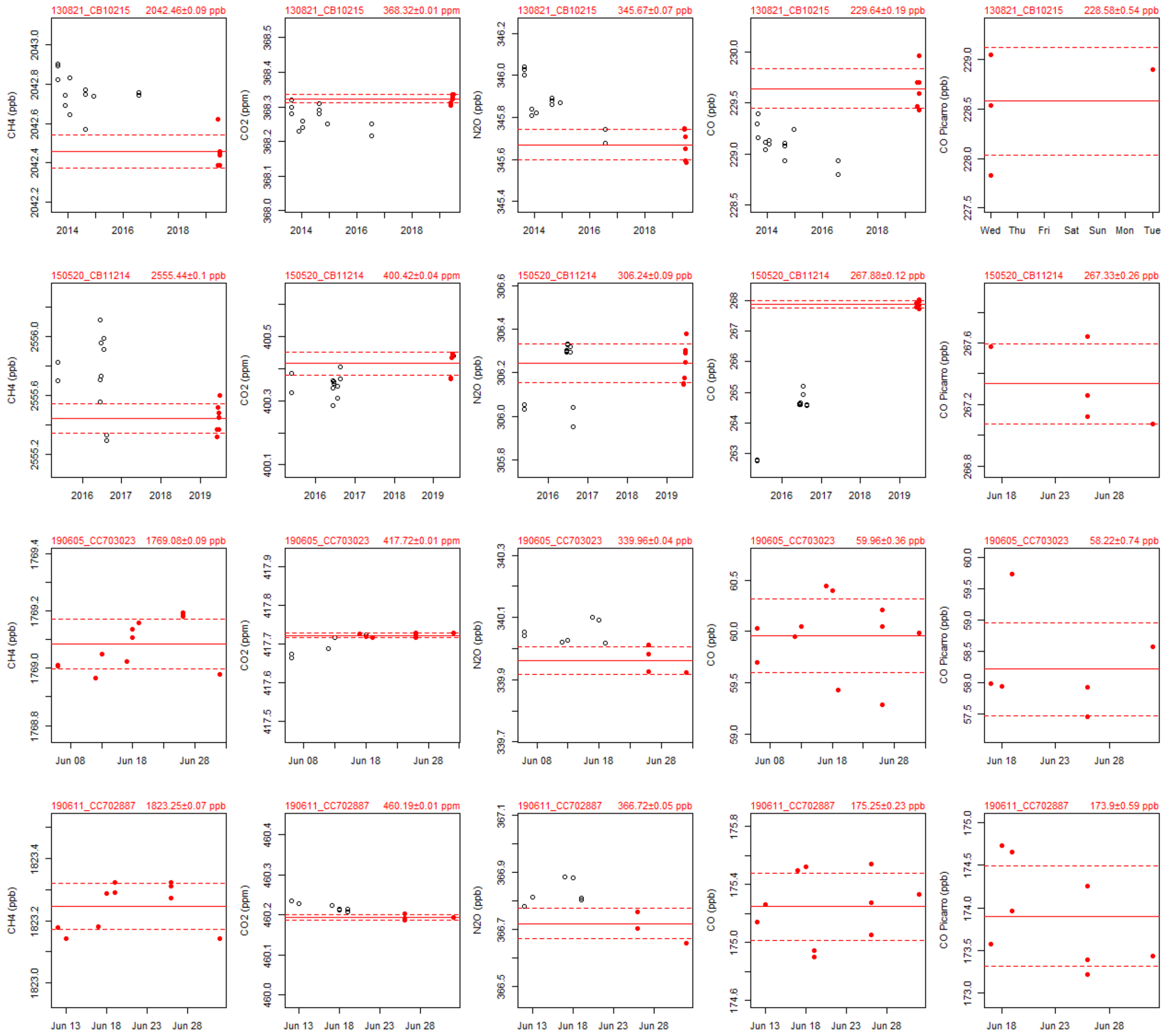

Figure 25. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.

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. 1.5 ppb for CH_4 and 0.05 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

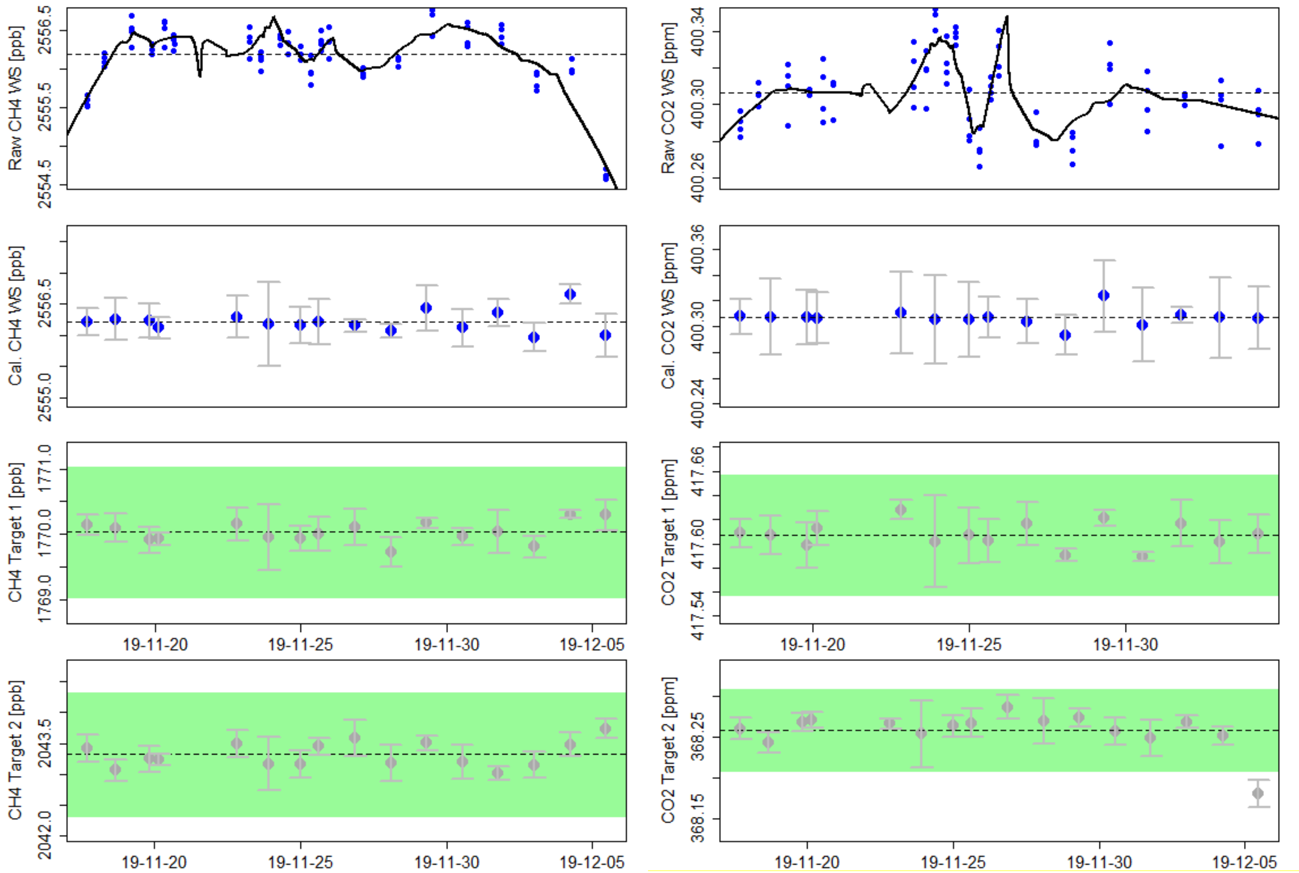

Figure 26. CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel 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 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.

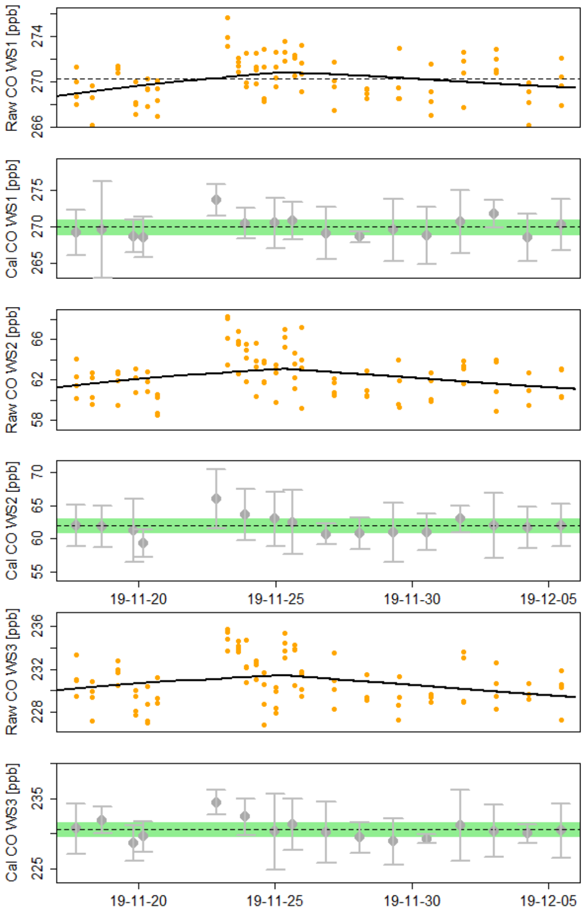

Figure 27. CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels 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

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
FMI	Finnish Meteorological Institute
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
QA	Quality Assurance
QC	Quality Control
QCL	Quantum Cascade Laser
SMN	Servicio Meteorológico Nacional
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Travelling Standard
USH	Ushuaia GAW Station
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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248. Twelfth Intercomparison Campaign of the Regional Brewer Calibration Center Europe, El Arenosillo Atmospheric Sounding Station, Huelva, Spain, 27 May–9 June 2017, 2019.

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