Research Infrastructure Quality Assurance

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Research Infrastructure Quality Assurance – System and Performance audit of Surface Ozone, Carbon Monoxide, Methane, and Carbon Dioxide at the Global GAW Station Sonnblick, Austria, July 2020

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

GLOBAL GAW STATION SONNBLICK AUSTRIA JULY 2020

Submitted to the World Meteorological Organization by

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WCC-Empa Report 20/2

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WCC-Empa Report 20/2

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The second system and performance audit by WCC-Empa[1] at the global GAW station Sonnblick (SNB) was conducted from 14–16 July 2020 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at SNB and the corresponding audit reports is available from the WCC-Empa website (www.empa.ch/gaw).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Dr Elke Ludewig	ZAMG Sonnblick, station manager
Mr Gerhard Schauer	ZAMG Sonnblick, station system engineer
Ms Iris Buxbaum	UBA Wien, head of the Austrian background air quality monitoring network
Mr Andreas Wolf	UBA Wien, calibration laboratory manager
Mr Franz Zimmerl	UBA Wien, technician

This report summarizes the assessment of the Sonnblick GAW station in general, as well as the surface ozone (O_3), carbon monoxide (CO), methane (CH_4) and carbon dioxide (CO_2) measurements in particular.

The report is distributed to the Sonnblick station manager, the head of the Austrian background air quality monitoring network, the national focal point for GAW in Austria, 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 a priority level (with *** indicating the highest priority) and suggested completion date are indicated for each recommendation.

Station management and operation

The Sonnblick (SNB) observatory was established in 1886 and is run by the Central Institute for Meteorology and Geodynamics (ZAMG). ZAMG employs the station staff and coordinates scientific activities at SNB. The observatory and its infrastructure are owned by the Sonnblick association (Sonnblick-Verein). Measurements and research projects are carried out by different institutions. The Environment Agency Austria (UBA) makes atmospheric trace gas observations at SNB in collaboration with ZAMG. The station is visited by scientists and technical staff as needed, and two technicians are permanently at the station on a 15-day rotating schedule.

Station location and access

SNB (47.054°N, 12.959°E, 3106 m a.s.l) is located in the central Austrian Alps on top of Hoher Sonnblick, a mountain in Hohe Tauern National Park, which covers 1 856 km² in the Austrian Alps. The nearest settlements are Heiligenblut (10 km to the west, 1288 m a.s.l, ~1 000 inhabitants) and Rauris (20 km to the north, 950 m a.s.l, ~3 000 inhabitants). Year-round access to SNB is possible either by cable car from the north (not open to the public) or by hiking from the Rauris valley to the north or Heiligenblut to the south (about 5 hours from both sides). Due to the remote location, the station is often exposed to clean air masses not affected by regional anthropogenic emissions and representative of the free troposphere. The location is fully adequate for the intended purpose.

Further information is available from GAWSIS (https://gawsis.meteoswiss.ch) and from the station website (https://www.sonnblick.net).

[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 based on mutual agreement.

Station facilities

The facilities at the site consist of a laboratory, an office, and sanitary and kitchen facilities. Additional space (such as for storage) is available. The SNB observatory is an ideal platform for continuous atmospheric research and measurement campaigns. Accommodation is available at Zittelhaus (https://www.alpenverein.at/zittelhaus/informationen.php), which is attached to the observatory.

Measurement programme

The SNB station comprises a comprehensive measurement programme that covers the main areas of the GAW programme. An overview of measured species is available from GAWSIS and the station website (https://www.sonnblick.net). The information available from GAWSIS was reviewed as part of the audit.

> **Recommendation 1 (***, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. Part of the reviewed information (such as the site description) needs to be updated. GAWSIS support should be contacted for updates that are not possible through the web interface, such as deleting station contacts.*

Data submission

As of September 2020, data on the scope of the audit has been submitted to the World Data Centres by SNB:

Submission to the World Data Centre for Reactive Gases (WDCRG):
O_3 (1995-2019)

Submission to the World Data Centre for Greenhouse Gases (WDCGG):
CO (1999-2019), CH_4 (2012-2019), CO_2 (1999-2019)

> **Recommendation 2 (***, important, ongoing)**
> *Data have been submitted punctually for all parameters covered by the scope of the audit. Data submission is compulsory for all GAW stations. It is recommended to continue with the current practice of submitting data to the corresponding data centres at least yearly. 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 was reviewed. Summary plots and a short description of the findings are presented in the appendix. The data used for this report were accessed on 18 September 2020. In general, all accessed data looked sound with respect to the mole fraction, trend, and seasonal and diurnal variation. At present, no further corrective actions are needed.

Documentation

All information is entered in electronic and handwritten logbooks. The instrument manuals are available at the site. The reviewed information was comprehensive and up to date.

Air inlet system

The air inlet for the gas measurements is located on the roof of the observatory. It consists of a heated steel construction, which is coated on the inside with PTFE. The total length is approximately 2.6 m, with an inner diameter of 0.2 m. The whole system is flushed with a high flow rate. The instruments are directly connected to the inlet system using stainless steel tubing (CO_2 and CH_4) and perfluoroalkoxy (PFA) plastic (CO and O_3). The inlet system is adequate in terms of the materials and residence times, and no change is required.

Data acquisition

A commercial system (UWEDAT, Austrian Institute of Technology (AIT)) is used for the data acquisition of all instruments covered by the scope of the audit. Data are automatically transferred and backed up on UBA servers. In addition, a redundant system programmed using KNIME and connected to an oracle database is available. The data acquisition systems are appropriate; however, the resolutions of the CO and CH_4 measurements need to be enlarged.

Recommendation 3 (*, minor, 2020)
The current resolution of the data acquisition system is 10 nmol mol^{-1} for 1-min data for CO and 1 nmol mol^{-1} for CH_4. It is recommended to increase the resolutions to at least 1 nmol mol^{-1} for CO and 0.1 nmol mol^{-1} for CH_4.

Surface ozone measurements

Surface O_3 measurements at SNB were established in 1989, and continuous time series with few interruptions have been available since 1995.

Instrumentation. SNB is currently equipped with two O_3 analysers (OAs): Thermo Scientific 49i and Teledyne API T400. The API T400 is only running for testing purposes, and the data generated are not considered for submission to data centres.

Standards. No O_3 standard is available at the site; however, a Thermo Scientific 49i-PS O_3 standard with traceability to the WMO/GAW reference is available at UBA and is regularly used at SNB for O_3 calibrations. The standard was also available during the current audit at SNB.

Recommendation 4 (*, minor, ongoing)
The current practice for quality control (QC) of O_3 measurements should be continued. Adjustments to the calibration settings based on regular comparisons with the travelling standard (TS) should not be made.

Intercomparison (Performance Audit). The two SNB analysers and the UBA O_3 calibrator were compared against the WCC-Empa TS with traceability to a standard reference photometer (SRP). The internal O_3 generator of the TS was used for generation of a randomized sequence of O_3 levels ranging from 0 to 200 nmol mol^{-1}. 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 (O_3 calibrator) and the SNB data acquisition system. The following equations characterize the bias of instruments and the remaining uncertainty after compensation for the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the O_3 absorption cross section of 11.476×10^{-18} cm^2 molecule^{-1} (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the O_3 absorption cross section.

Thermo Scientific 49i #CM1126i008 (BKG -0.6 nmol mol^{-1}, SPAN 1.011):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = OA − 0.86 nmol mol^{-1}) / 0.9883(1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.12e-05 × X_{O3}^2)(1b)

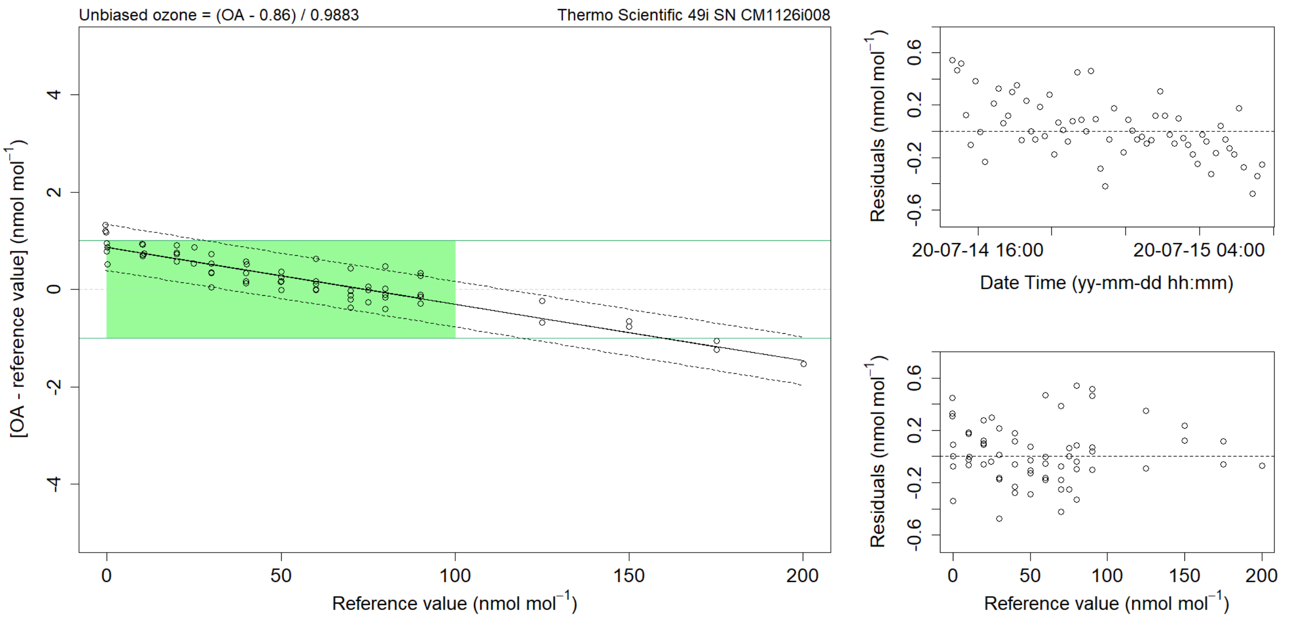

Figure 1. *Left: Bias of the SNB OA (Thermo Scientific 49i #CM1126i008) with respect to the SRP as a function of the mole fraction. Each point represents the average of the last five 1-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working–Hotelling 95% confidence bands. Right: Regression residuals of the O_3 comparisons as a function of time (top) and the mole fraction (bottom)*

Teledyne API T400 #4686, instrument only used for testing (BKG -0.1, SPAN 0.998):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = OA − 0.12 nmol mol^{-1}) / 1.0138(1c)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.14e-05 × X_{O3}^2)(1d)

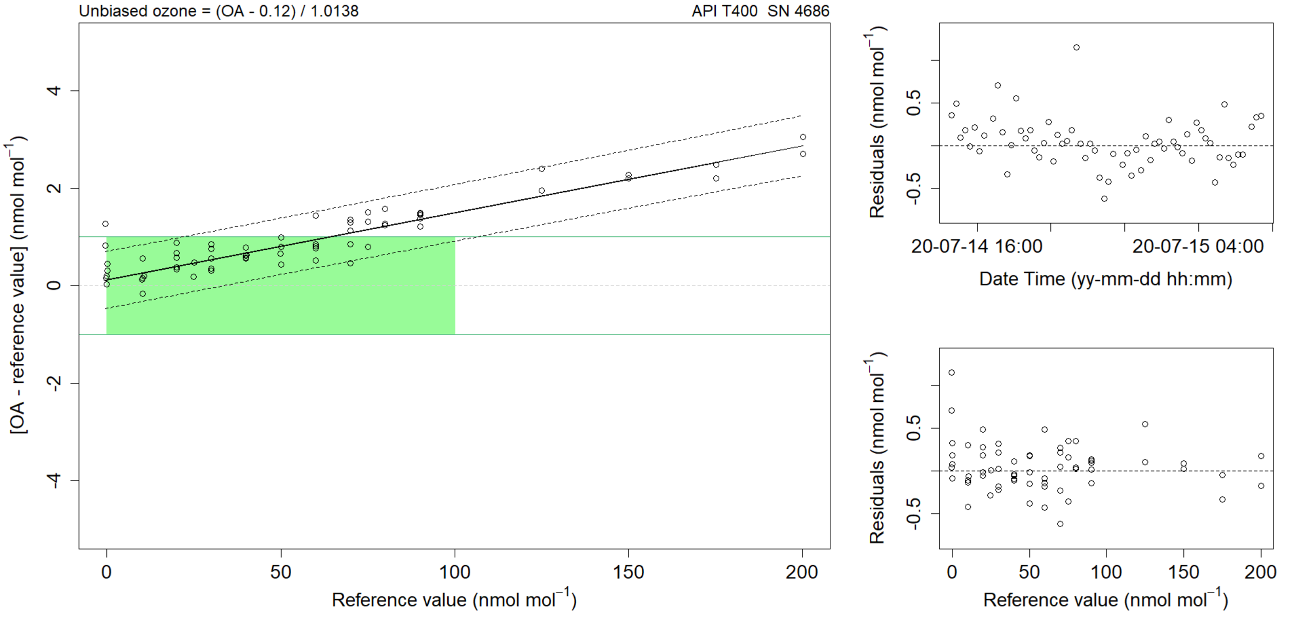

Figure 2. *Same as above for the SNB Teledyne API T400 SN 4686 OA (test instrument)*

Thermo Scientific 49i-PS #1162110060 (BKG 0 nmol mol^{-1}, SPAN 0.996):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OC] − 0.02 nmol mol^{-1}) / 0.9989(1e)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.10e-05 × X_{O3}^2)(1f)

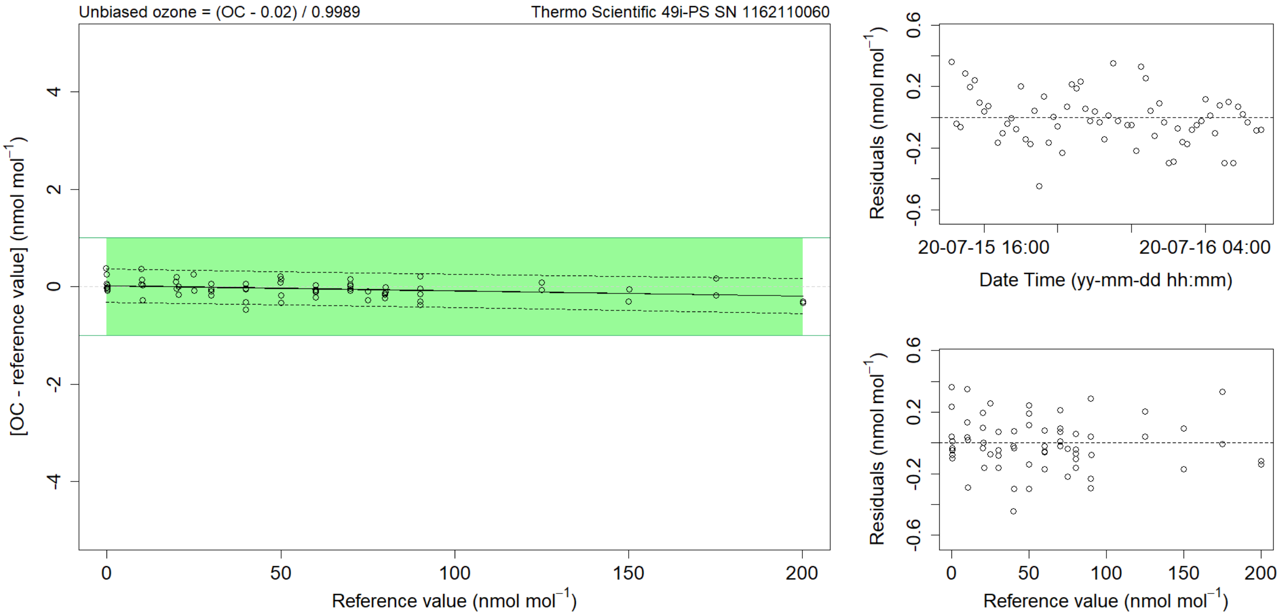

Figure 3. *Same as above for the Thermo Scientific 49i-PS #1162110060 O_3 calibrator*

The results of the comparisons can be summarized as follows:

The main SNB OA as well as the UBA O_3 calibrator agreed within the WMO/GAW DQOs in the relevant mole fraction range. The deviation was slightly higher for the test instrument; however, this instrument is not used for surface O_3 measurements at SNB, so the result is less relevant. Due to the good results, no further action is required.

Carbon monoxide measurements

Continuous measurements of CO at SNB started in 1999, and continuous time series have been available since 2002.

Instrumentation. Horiba APMA-360 Non-Dispersive Infrared (NDIR) CO analyser

Standards. A commercial calibration gas (produced by Air Liquide) with approximately 1.5 ppm of CO in synthetic air is available. This standard was calibrated at UBA using CO standards from the Dutch National Metrology Institute (NMI). In addition, a zero-air system is available. Calibrations of the Horiba are made manually. A list of available standards is given in the appendix.

Intercomparison (performance audit). The comparison involved repeated challenges of the SNB instruments with randomized CO levels using WCC-Empa TSs. The following equations characterize the instrument bias, and the results are further illustrated in Figure 4 with respect to the WMO GAW DQOs (WMO, 2020):

Horiba APMA-360 #913012:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 5.7) / 1.0297(2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (45.6 + 1.01e-04 × X_{CO}^2)(2b)

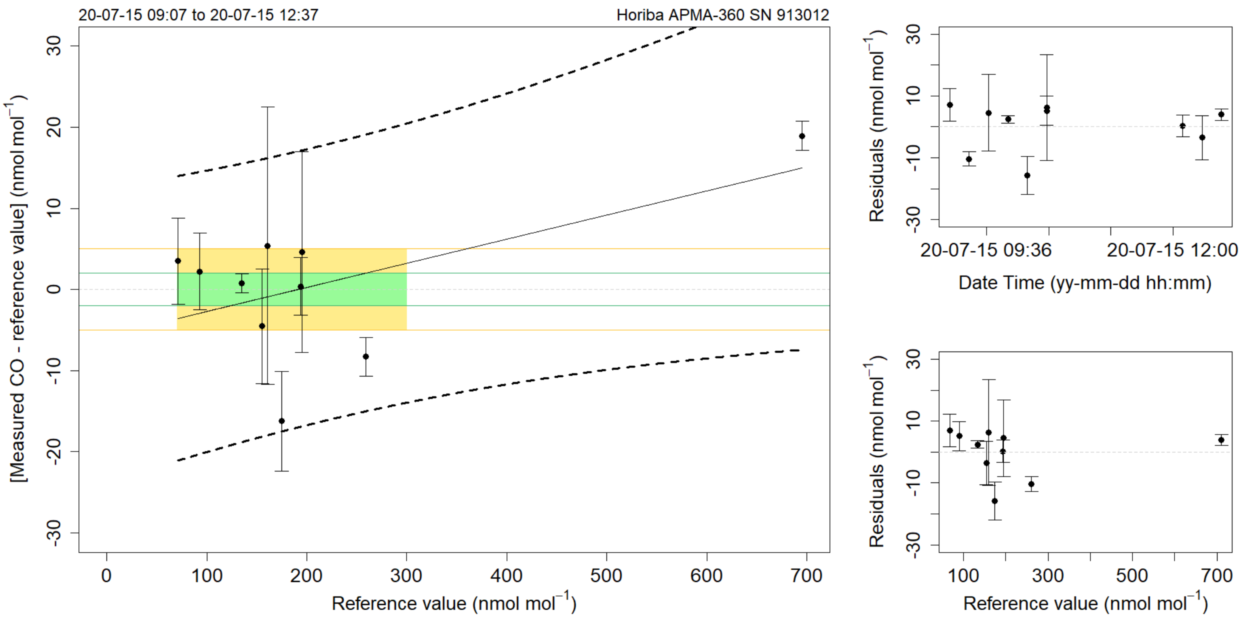

Figure 4. *Left: Bias of the SNB Horiba APMA-360 CO instrument with respect to the WMO-X2014A reference scale as a function of the mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. 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 SNB. The dashed lines around the regression lines are the Working–Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence)*

The results of the comparisons can be summarized as follows:

The uncertainty of the measurements with the Horiba APMA-360 NDIR analyser is large, especially compared with more advanced measurement techniques. Therefore, the current analytical technique is not adequate for CO measurements in the unpolluted troposphere, and replacement of the system is recommended. The following recommendations are made regarding CO measurements:

> **Recommendation 5 (***, critical, 2021)**
> *The current instrumentation for CO measurements is not adequate due to its high noise and uncertainty. Replacement with another analytical technique (e.g. instruments based on cavity ring-down spectroscopy (CRDS) in the near infrared (IR) or other spectroscopic techniques based on quantum cascade lasers (QCL) in the mid-IR) is recommended.*
>
> **Recommendation 6 (**, important, 2021)**
> *CO measurements at SNB are not linked to the WMO/GAW reference but have traceability to standards certified by national metrology institutes. It is recommended to purchase standards from the Central Calibration Laboratory (CCL), or to establish traceability to the WMO/GAW reference by other means (e.g. through the Integrated Carbon Observation System).*

Methane measurements

Measurements of CH_4 at SNB started in 2012, and continuous data series have been available since then.

Instrumentation. Two Picarro G2301 analysers (humid measurements) are available. One instrument runs continuously, and the other serves as a backup system. Only the main instrument was considered for the audit. Ambient-air comparisons of the two systems made by the SNB operators showed excellent agreement between the two systems.

Standards. The station is equipped with a standard that was calibrated at WCC-Empa in 2013 with a nominal CH_4 amount fraction of 1823.24 ± 2.09 nmol mol^{-1}. This value was referenced to the WMO-X2004 calibration scale, which has now been superseded by the WMO-X2004A scale. In addition, high-purity nitrogen (N_2 60) is available to calibrate the zero offset of the instrument. Calibrations using these two standards have been manually made in irregular intervals several times per year. During each calibration, the calibration settings of the instrument were adjusted. No further correction was then applied to the data, and the dry fraction of CH_4 based on the built-in water vapour compensation was used. In principle, the calibration scheme using zero air (or high-purity N_2) and one standard gas is appropriate due to the excellent linearity of the CRDS system. However, the current practice potentially compromises the accuracy of the system by small-step changes at each calibration. The following recommendations are made:

> **Recommendation 7 (***, critical, 2021)**
> *SNB CH_4 measurements need to be referenced to the latest version of the WMO/GAW calibration scale (WMO-X2004A). Calibration standards should be purchased from the CCL.*
> **Recommendation 8 (**, important, 2021)**
> *Manual calibrations should be replaced with automated measurements of calibration gases and postprocessing of the data. Furthermore, regular measurements of working standards (to account for short-term drift) and target cylinders (treated as ambient air, as a QC measure to monitor the stability of the system) is highly recommended.*
>
> **Recommendation 9 (**, important, 2021)**
> *If humid measurements are made, it is recommended to apply water vapour corrections that were determined for each instrument individually using the water droplet method described by Rella et al. (2013).*

Intercomparison (performance audit). The comparison involved repeated challenges of the SNB instrument with randomized CH_4 levels from TSs. The results of the comparison measurements for the individual measurement parameters are summarized and illustrated below.

The following equation characterizes the instrument bias. The results are further illustrated in Figure 5 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2301 #883-CFADS2188:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 0.28 nmol mol^{-1}) / 1.0008(3a)

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

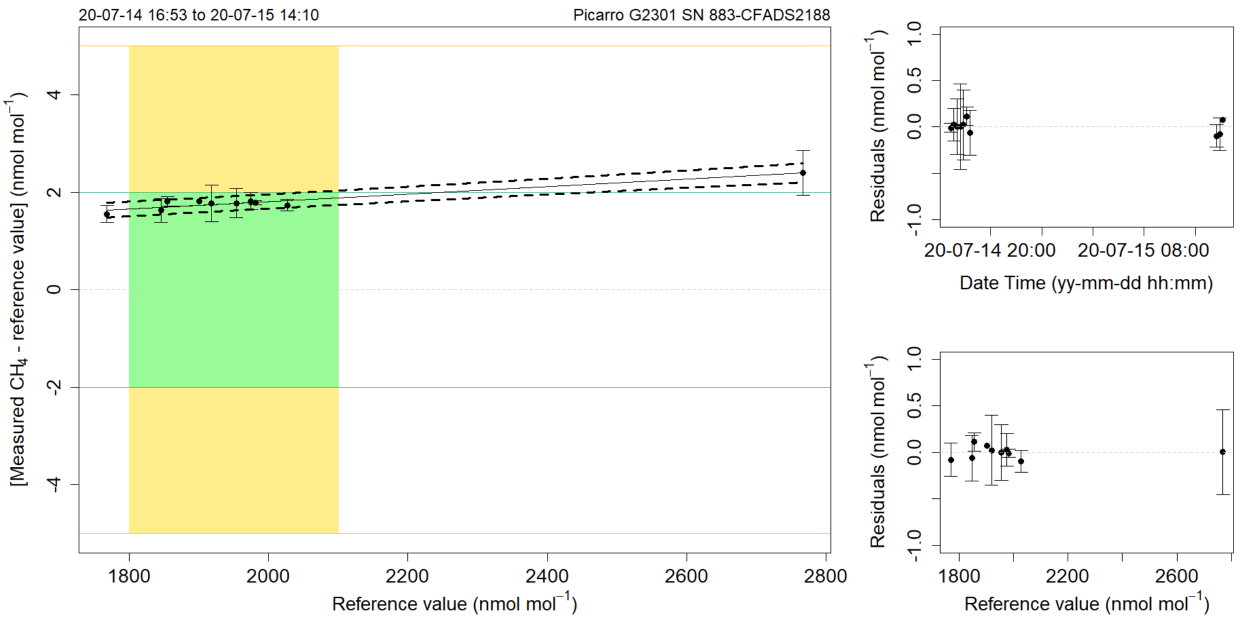

Figure 5. *Left: Bias of the Picarro G2301 #883-CFADS2188 instrument with respect to the WMO-X2004A CH_4 reference scale as a function of the mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 SNB. 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:

Although SNB refers to the outdated WMO-X2004 CH_4 calibration scale, the bias was within the WMO/GAW network compatibility goals in the relevant amount fraction range. Updating the values to the latest CH_4 calibration scale would further improve the result.

Carbon dioxide measurements

Continuous measurements of CO_2 at SNB commenced in 1999, and data have been available since 2000. Initial measurements were made using the NDIR technique (first with a Fuji ZRC, then, since 2000, with an URAS 14). In 2012, measurements using CRDS (Picarro G2301) commenced and the NDIR system was decommissioned.

Instrumentation. Same as for CH_4.

Standards. The station is equipped with a standard that was calibrated at WCC-Empa in 2013 with a nominal CO_2 amount fraction of 409.20±0.82 μmol mol^{-1} on the WMO-X2007 calibration scale. The calibration and data treatment scheme used is the same as for CH_4. The recommendations made above with respect to water vapour correction and automation of the calibration procedure are also valid for CO_2. In addition, it is also recommended that SNB should maintain a direct link to the current WMO/GAW reference using standard gases from the CCL.

> **Recommendation 10 (**, important, 2021)**
> *CO_2 calibration standards from the CCL should be available at SNB. It is recommended to purchase calibration standards from the CCL covering at least the relevant amount fraction range of SNB.*

Intercomparison (performance audit). The comparison involved repeated challenges of the SNB instrument with randomized CO_2 levels from TSs. The results of the comparison measurements for the individual measurement parameters are summarized and illustrated below.

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

Picarro G2301 #883-CFADS2188:

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.08 µmol mol^{-1}) / 0.99982 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.002 + 3.28e-08 × X_{CO2}^2) (4b)

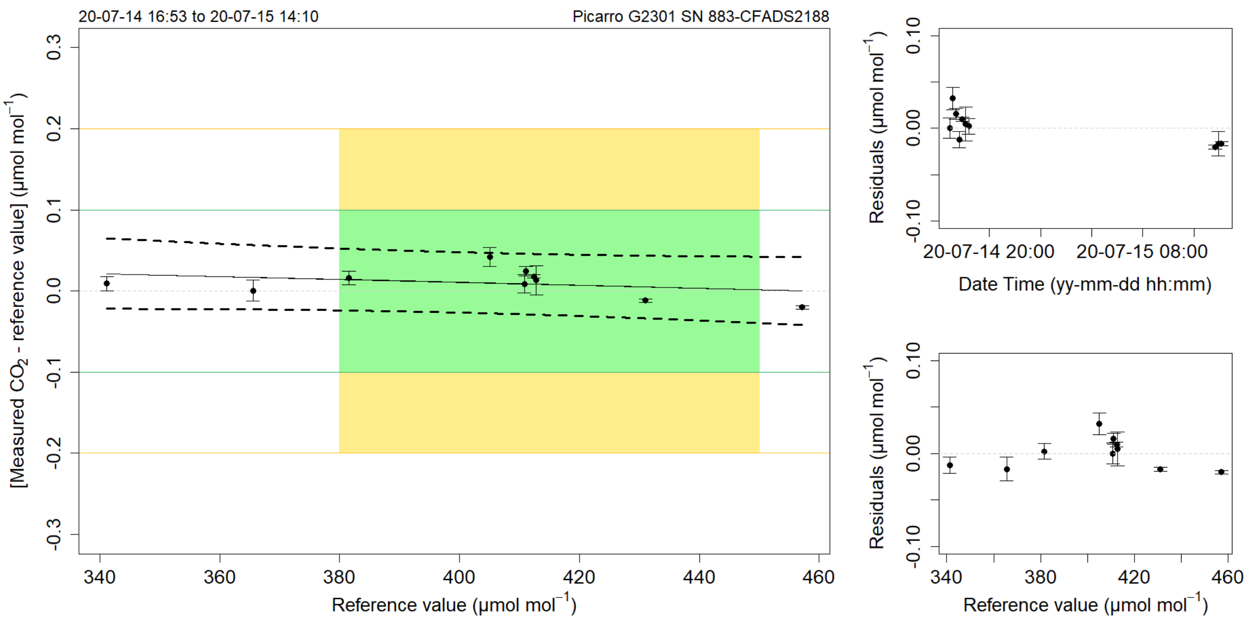

Figure 6. *Left: Bias of the Picarro G2301 #883-CFADS2188 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of the mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 SNB. 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 SNB Picarro G2401 instrument showed agreement within the WMO/GAW compatibility goals in the assessed mole fraction range. Due to the excellent result, no immediate action is required, but recommendations made above regarding calibration standards, water vapour correction and automatic measurements of standards also apply to CO_2 measurements.

SNB PERFORMANCE AUDIT RESULTS COMPARED WITH OTHER STATIONS' RESULTS

This section compares the results of the SNB performance audit with those of other station audits conducted by WCC-Empa. The method used to compare the results with those of other audits is described by the developers in Zellweger et al. (2016) (for CO_2 and CH_4) and Zellweger et al. (2019) (for CO and N_2O), but it 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. For CO_2, CH_4 and CO, the relevant mole fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) and refer to conditions usually found in unpolluted air masses. For surface O_3, the mole fraction range selected was 0-100 ppb, since this range covers most of the natural O_3 abundance in the troposphere. The resulting well-defined bias/slope combinations meet the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 7 shows the bias versus the slope of the performance audits conducted by WCC-Empa for O_3, CO, CH_4 and CO_2. The grey dots show all comparison results obtained during WCC-Empa audits for the main station analysers but exclude cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current SNB audit are shown as coloured dots in Figure 7 and are summarized in Table 1, which also shows the percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs).

The results were within the DQOs for the main O_3 instrument and for the CO_2 and CH_4 instruments; the extended WMO/GAW network compatibility goals were reached for CO, even though the instrument showed large variations.

Table 1. *SNB performance audit results compared with those of other stations. Column 4 indicates whether the results of the latest audit were within the DQO (green tick mark), within the extended DQO (orange tick mark) or outside the DQOs (red cross). Columns 5–7 show the percentage of all WCC-Empa audits between 1996 (O_3), 2005 (CO and CH_4) or 2010 (CO_2) and May 2020 that fell within these criteria.*

Compound / Instrument	**Range**	**Unit**	**SNB within DQO/eDQO**	**% of audits within DQOs**	**% of audits within eDQOs[1]**	**% of audits outside eDQOs**
O_3 (Thermo Scientific 49i #CM1126i008)	0– 100	nmol mol^{-1}	✓	64	NA[2]	36
O_3 (Teledyne API T400 #4686)	0–100	nmol mol^{-1}	✗	64	NA	36
O_3 (Thermo Scientific 49i-PS #1162110060)	0–100	nmol mol^{-1}	✓	64	NA	36
CO (Horiba APMA-360 #913012)	30–300	nmol mol^{-1}	✓	21	50	50
CH_4 (Picarro G2301 #883-CFADS2188)	1750–2100	nmol mol^{-1}	✓	70	93	7
CO_2 (Picarro G2301 #883-CFADS2188)	380–450	µmol mol^{-1}	✓	40	67	33

[1] Percentage of stations within the eDQO and DQO

[2] Not available

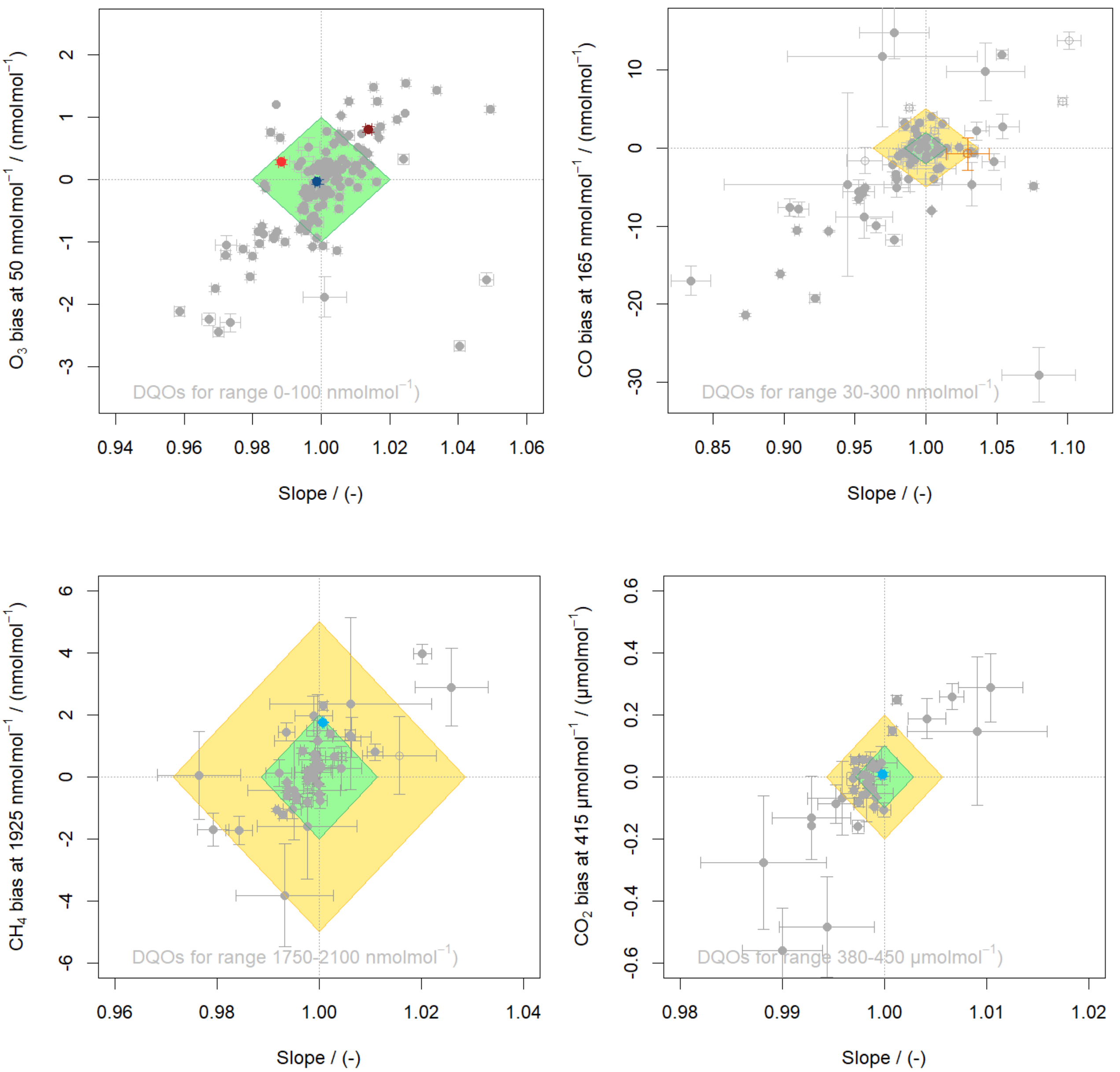

Figure 7. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the centre of the relevant mole fraction range versus the slope of the performance audits by WCC-Empa. The grey dots show past performance audits by WCC-Empa at various stations, while the coloured dots show SNB results (red: Thermo Scientific 49i #CM1126i008; dark red: Teledyne API T400 #4686; dark blue: Thermo Scientific 49i-PS #1162110060; orange: Horiba APMA-360 #913012; light blue: Picarro G2301 #883-CFADS2188). Filled symbols refer to a comparison with the same calibration scale at the station and the WCC, while open symbols indicate a scale difference. The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

PARALLEL MEASUREMENTS OF AMBIENT AIR

As part of the audit, parallel ambient-air CO_2, CH_4 and CO measurements were performed using a WCC-Empa travelling instrument (TI) (Picarro G2401). The TI operated from 14 July to 17 August 2020. It sampled air from an independent inlet leading to the same air intake location as that of the SNB analyser. It sampled air using the following sequence: 305 min of ambient air followed by 30 min of three standard gases (10 min each), followed by 1 440 min of ambient air. The air was dried using a Nafion dryer (Model MD-070-48S-4) in reflux mode with the Picarro pump used for the vacuum in the purge air flow. To account for the remaining bias due to water vapour, a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the CO_2 and CH_4 data of the TI. Details of the calibration of the TI are given in the appendix. The results of the ambient-air comparison are presented below.

Carbon monoxide

Figure 8 shows the comparison of hourly CO between the WCC-Empa TI and the SNB Horiba APMA-360. The corresponding deviation histograms are shown in Figure 9.

Both instruments captured the temporal variability, but unlike in the TS comparison, the Horiba APMA-360 produced a higher reading than the WCC-Empa TI. This bias may be due to water vapour inference, which is a well-known issue with the NDIR technique. On average, the agreement between the SNB instrument and the TI was within the extended WMO/GAW network compatibility goal. Nevertheless, replacement of the Horiba APMA-360 is recommended due to the larger analytical noise compared with other techniques.

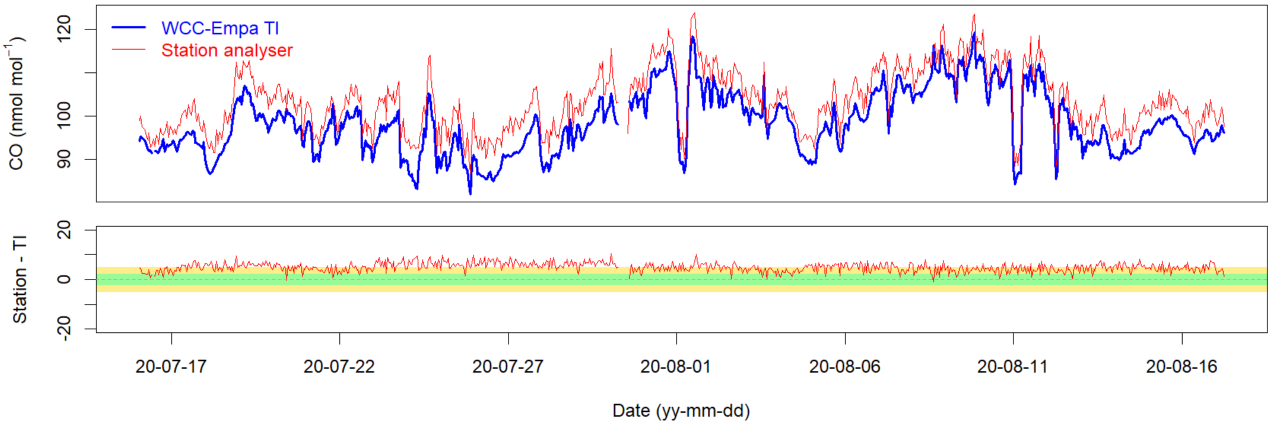

Figure 8. *Comparison of the Horiba APMA-360 analyser with the WCC-Empa TI for CO. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas show the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

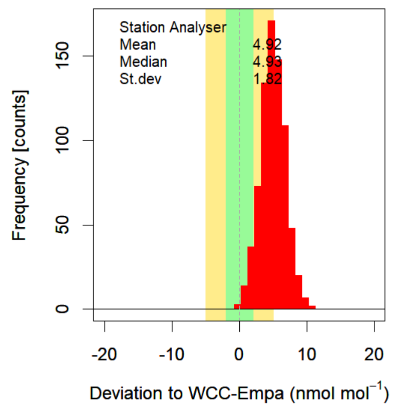

Figure 9. *CO deviation histogram for the SNB Horiba APMA-360*

Methane

Figure 10 shows the comparison of hourly CH_4 between the WCC-Empa TI and the SNB Picarro G2301. The corresponding deviation histogram is shown in Figure 11. The temporal variation was well captured by both the WCC-Empa and the SNB instruments. Agreement within the WMO/GAW network compatibility goals was found between the TI and the SNB instrument; the average bias of 0.84 nmol mol^{-1} was slightly smaller compared with the TS comparison.

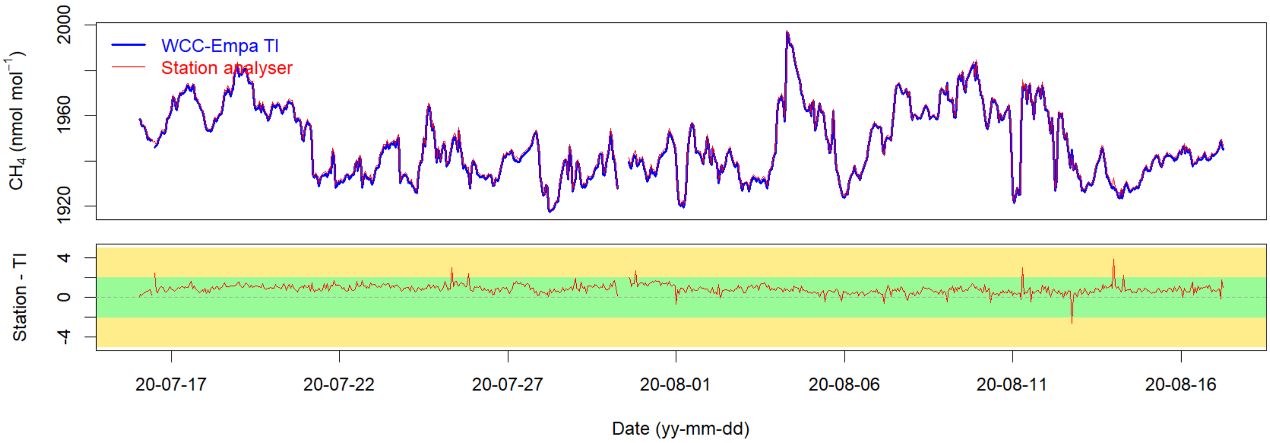

Figure 10. *Comparison of the SNB Picarro G2301 with the WCC-Empa TI for CH_4. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas show the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

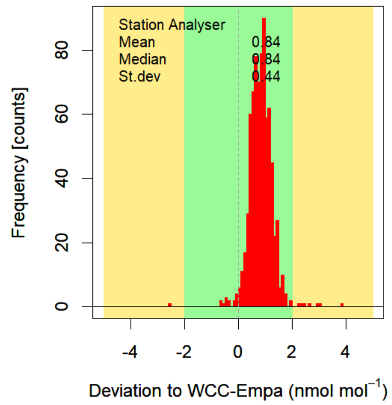

Figure 11. *CH4 deviation histogram for the SNB Picarro G2301*

Carbon dioxide

Figure 12 shows the comparison of hourly CO_2 between the WCC-Empa TI and the SNB Picarro G2301, and Figure 13 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 within the WMO/GAW network compatibility goal was found between the TI and the SNB instrument, which confirms the results of the performance audit using TSs.

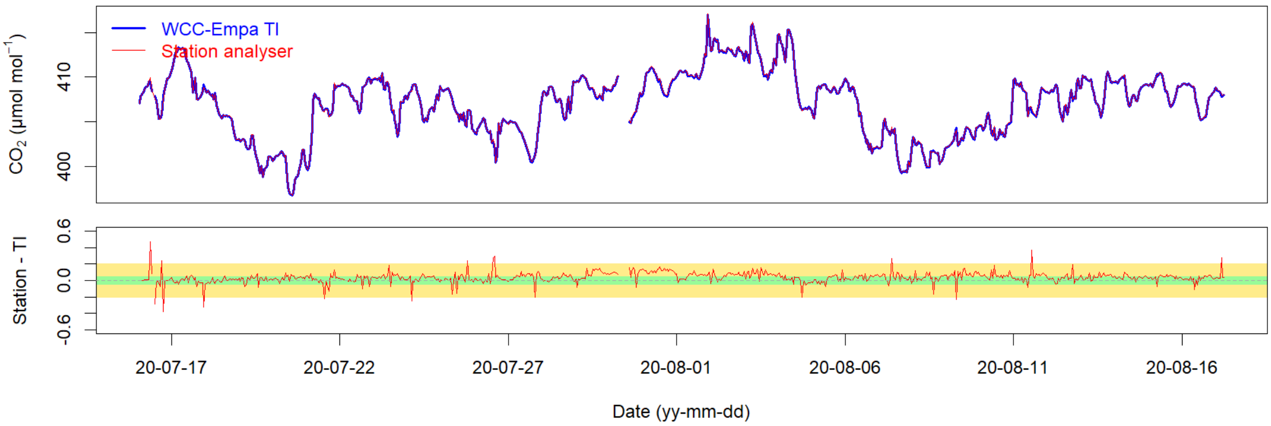

Figure 12. *Comparison of the SNB Picarro G2301 with the WCC-Empa TI for CO_2. Time series based on hourly data as well as the difference between the station instrument and the TI are shown. The coloured horizontal areas show the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.*

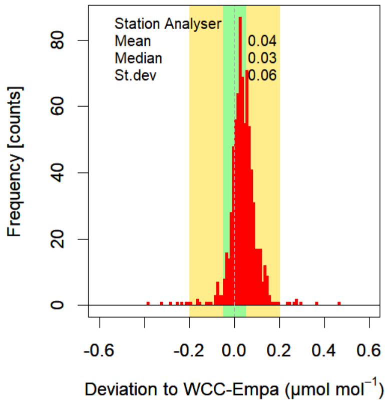

Figure 13. *Carbon dioxide deviation histogram for the SNB Picarro G2301 compared with WCC-Empa*

CONCLUSIONS

The global GAW station Sonnblick 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 important contribution to the GAW programme.

Most assessed measurements were of high quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant mole fraction range. However, the CO instrument currently in use at SNB is no longer adequate, and replacement by a more up-to-date analytical technique is recommended. Table 2 summarizes the results of the performance audit and the ambient-air comparison with respect to the WMO/GAW compatibility goals. Table 2 refers only to the mole fractions relevant to SNB, whereas Table 1 covers a wider mole fraction range.

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

Comparison type	**O_3 (Thermo Scientific 49i)**	**O_3 (Thermo Scientific 49i-PS)**	**O_3 (Teledyne API T400)**	**CO (Horiba APMA-360)**	**CH_4 (Picarro G2301)**	**CO_2 (Picarro G2301)**
Audit with TS	✓	✓	✗	✓	✓	✓
Ambient-air comparison	NA	NA	NA	✓	✓	✓

NA no ambient-air comparisons were made for surface O_3

The continuation of the observations made at Sonnblick is highly important for GAW. The large number of measured atmospheric constituents combined with the high data quality enables state-of-the-art research to be carried out.

SUMMARY RANKING OF THE SONNBLICK GAW STATION

System audit aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme
Access	(5)	Year-round access; new cable car
Facilities		
Laboratory and office space	(5)	Adequate, with limited space for additional research campaigns
Internet access	(5)	Sufficient bandwidth
Air conditioning	(5)	Adequate system; temperature fluctuation of 3 °C during the audit
Power supply	(4)	Reliable but old power line; replacement foreseen
General management and operation		
Organization	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air inlet system	(4)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
Methane/carbon dioxide	(5)	State-of-the-art instrumentation
Carbon monoxide	(2)	Current technique not adequate, replacement recommended
Calibration standards		
Ozone	(5)	Traceability to SRP via UBA transfer standard; regular calibrations
Carbon dioxide, methane	(3)	Insufficient number of standards but adequate calibration strategy
Carbon monoxide	(3)	Measurements are not reported on WMO/GAW calibration scales
Data management		
Data acquisition	(4)	Adequate system; decimal resolution needs to be enlarged
Data processing	(5)	Skilled staff; appropriate procedures
Data submission	(5)	All data are submitted at yearly intervals

#0: inadequate thru 5: adequate.

Dübendorf, January 2021

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APPENDIX

Data review

The following figures show summary plots of SNB data accessed on 18 September 2020 from WDCRG and WDCGG. The plots show time series of hourly data, frequency distribution, and diurnal and seasonal variations.

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

Surface ozone:

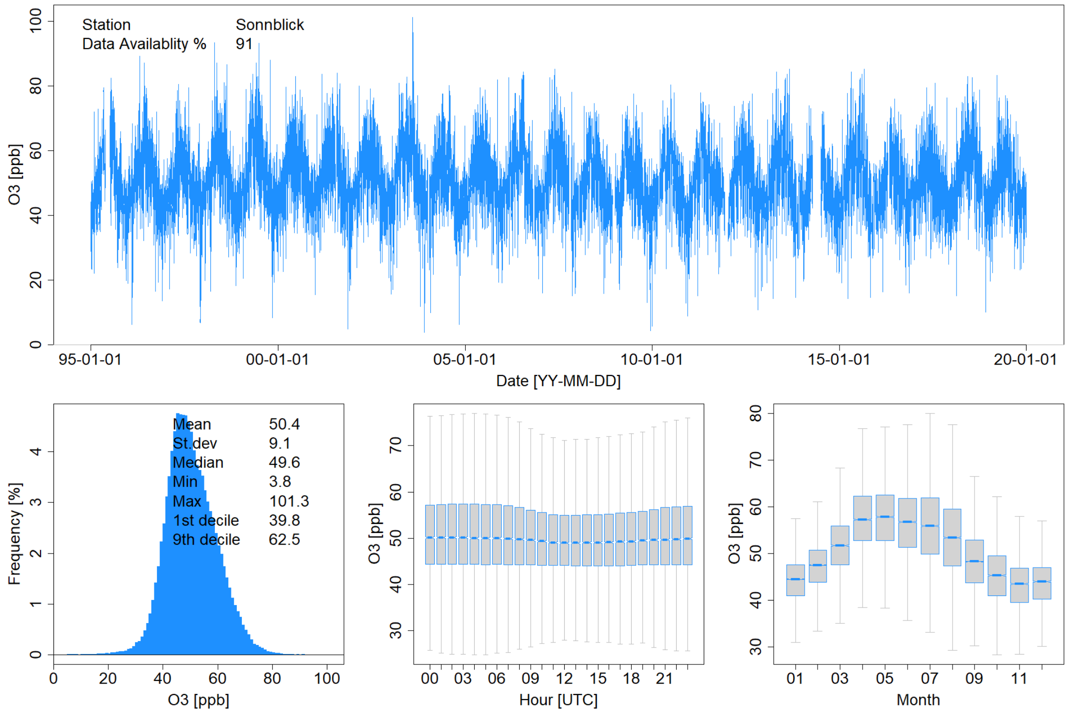

Figure 14. *O_3 data for the period from 1995 to 2019 accessed from WDCRG. Top: time series showing hourly averages. Bottom: left: frequency distribution; middle: diurnal variation; right: seasonal variation (the horizontal blue line denotes the median, and the grey boxes show the inter-quartile range on the middle and right plots)*

- The data sets look sound with respect to the mole fraction, trend, and seasonal and diurnal variation.

Carbon monoxide:

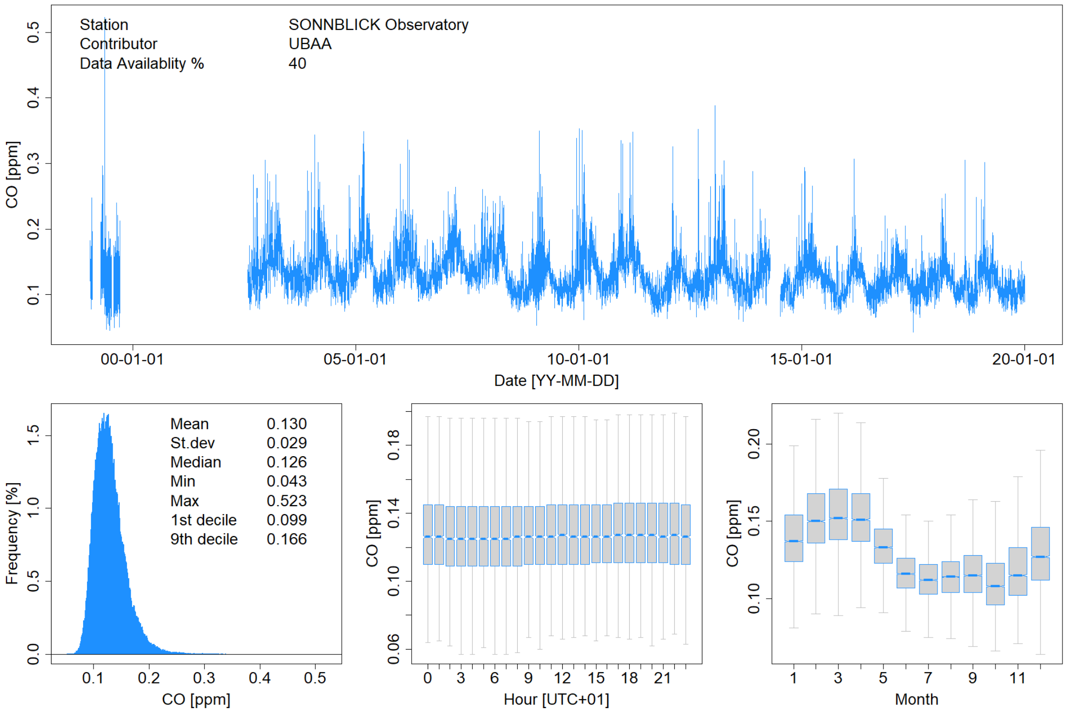

Figure 15. *In situ CO data submitted by UBA. All valid data are shown. Top: time series showing hourly averages. Bottom: left: frequency distribution; middle: diurnal variation; right: seasonal variation (the horizontal blue line denotes the median and the grey boxes show the inter-quartile range)*

- The data sets look generally sound with respect to the mole fraction, trend, and seasonal and diurnal variation.
- Early data (before 2000) seem to be subject to higher noise and uncertainty.

Methane:

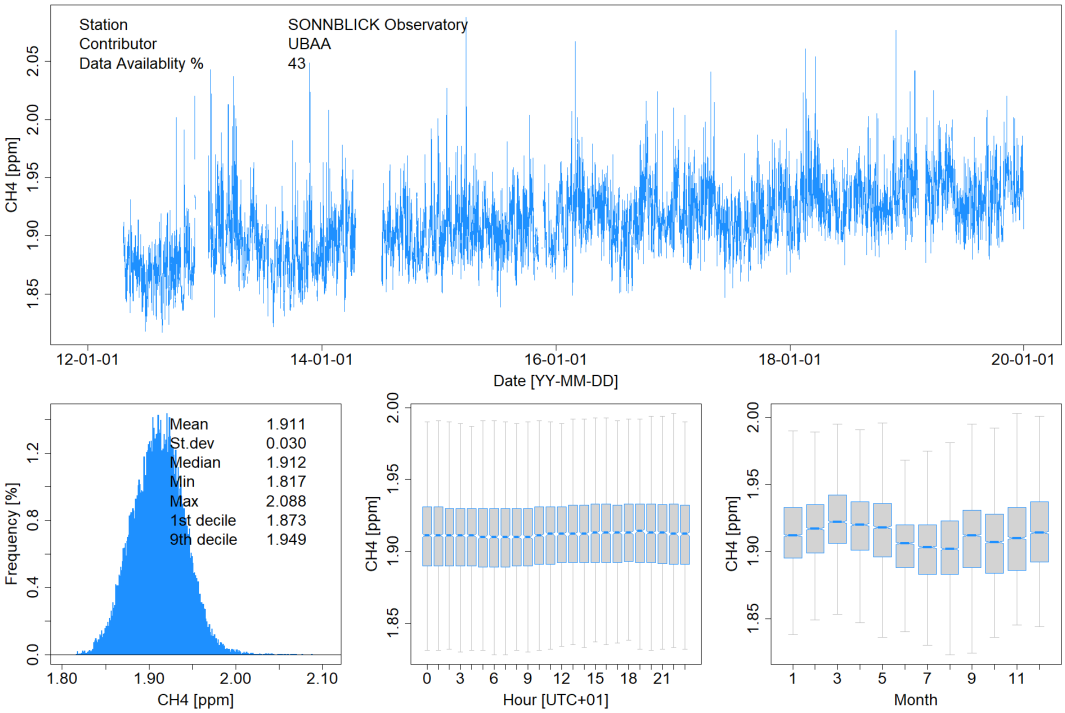

Figure 16. *In situ CH_4 data submitted by UBA. All valid data are shown. Top: time series showing hourly averages. Bottom: left: frequency distribution; middle: diurnal variation; right: seasonal variation; (the horizontal blue line denotes the median and the grey boxes show the inter-quartile range)*

- The data sets look sound with respect to the mole fraction, trend, and seasonal and diurnal variation.

Carbon dioxide:

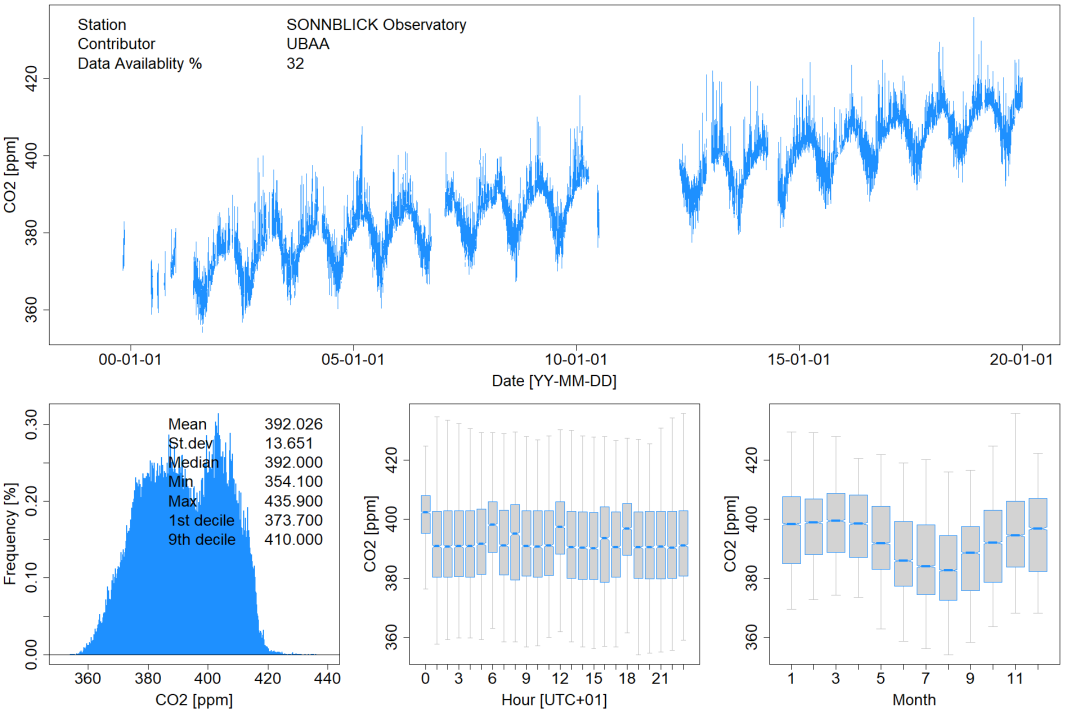

Figure 17. *In situ CO_2 data submitted by UBA. All valid data are shown. Top: time series showing hourly averages. Bottom: left: frequency distribution; middle: diurnal variation; right: seasonal variation (the horizontal blue line denotes the median and the grey boxes show the inter-quartile range)*

- The data sets look sound with respect to the mole fraction, trend, and seasonal and diurnal variation. Irregularities in the mean diurnal variation are due to calibrations at fixed times until 2010.

Surface ozone comparisons

All procedures were conducted according to the WCC-Empa SOP and included comparisons of the TS with the SRP at Empa before and after the comparison of the analyser.

The internal O_3 generator of the WCC-Empa transfer standard was used to generate a randomized sequence of O_3 levels ranging from 0 to 200 nmol mol^{-1}. Zero-air was generated using a custom-built zero-air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approximately 1.5 m of PFA tubing. Table 3 details the experimental set-up during the comparisons of the TS with the station analysers. The data used for the evaluation were recorded by the WCC-Empa and SNB data acquisition systems.

Table 3. *Experimental details of the O_3 comparison*

Travelling standard (TS)	
Model, serial number	Thermo Scientific 49i-PS #0810-153 (WCC-Empa)
Settings	BKG 0.0, COEF 1.004
Pressure readings (hPa)	Ambient 699.0 TS 700.1, adjusted to 699.1 before the comparison
SNB station analyser (OA)	
Model, serial number	Thermo Scientific 49i #CM1126i008
Principle	UV absorption
Range	0-1 μmol mol^{-1}
Settings	BKG +0.0 nmol mol^{-1}, COEF 0.996
Pressure readings (hPa)	Ambient 699.1; ozone analyser 706.1 (no adjustment was made)
SNB test analyser (OA)	
Model, serial number	Teledyne API T400 SN 4686
Principle	UV absorption
Range	0-1 μmol mol^{-1}
Settings	BKG -0.19 nmol mol^{-1}, COEF 0.998
Pressure readings (hPa)	Not available
UBA ozone calibrator (OC)	
Model, serial number	Thermo Scientific 49i-PS #1162110060
Principle	UV absorption
Range	0-1 μmol mol^{-1}
Settings	BKG +0.0 nmol mol^{-1}, COEF 0.996
Pressure readings (hPa)	Ambient 698.2; ozone analyser 698.1 (no adjustment was made)

Results

Each O_3 level was applied for 15 minutes, and the last five 1-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. The readings of the TS were compensated for bias with respect to the SRP prior to the evaluation of the OA values.

The results of the assessment are shown in the following tables (individual measurement points) and are further presented in the Executive Summary.

Table 4. *Five-minute aggregates computed from the last five of a total of fifteen 1-minute values for the comparison of the SNB OA Thermo Scientific 49i #CM1126i008 with the bias-corrected WCC-Empa TS*

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
14.7.2020 14:37	79.99	0.09	80.46	0.29	0.47	0.59
14.7.2020 14:52	60.00	0.14	60.63	0.45	0.63	1.05
14.7.2020 15:07	89.98	0.13	90.32	0.49	0.34	0.38
14.7.2020 15:22	19.97	0.21	20.72	0.22	0.75	3.76
14.7.2020 15:37	49.99	0.06	50.16	0.16	0.17	0.34
14.7.2020 15:52	70.01	0.27	70.44	0.26	0.43	0.61
14.7.2020 16:07	10.61	0.30	11.34	0.35	0.73	6.88
14.7.2020 16:22	39.99	0.10	40.15	0.10	0.16	0.40
14.7.2020 16:52	29.93	0.10	30.66	0.18	0.73	2.44
14.7.2020 17:07	−0.38	0.50	0.82	0.16	1.20	NA
14.7.2020 17:22	75.03	0.07	75.08	0.23	0.05	0.07
14.7.2020 17:37	175.06	0.19	174.00	0.58	−1.06	−0.61
14.7.2020 17:52	25.03	0.27	25.91	0.28	0.88	3.52
14.7.2020 18:07	125.05	0.08	124.81	0.19	−0.24	−0.19
14.7.2020 18:22	200.03	0.10	198.49	0.25	−1.54	−0.77
14.7.2020 18:37	150.03	0.11	149.38	0.27	−0.65	−0.43
14.7.2020 18:52	0.10	0.41	0.97	0.09	0.87	NA
14.7.2020 19:07	40.00	0.24	40.33	0.34	0.33	0.82
14.7.2020 19:22	10.02	0.41	10.96	0.25	0.94	9.38
14.7.2020 19:37	79.97	0.10	79.87	0.17	−0.10	−0.13
14.7.2020 19:52	19.93	0.33	20.84	0.29	0.91	4.57
14.7.2020 20:07	59.95	0.17	59.94	0.26	−0.01	−0.02
14.7.2020 20:22	90.01	0.08	89.89	0.39	−0.12	−0.13
14.7.2020 20:37	29.96	0.10	30.48	0.12	0.52	1.74
14.7.2020 20:52	69.99	0.04	69.96	0.20	−0.03	−0.04
14.7.2020 21:07	49.98	0.13	50.34	0.22	0.36	0.72
14.7.2020 21:22	−0.44	0.24	0.88	0.02	1.32	NA
14.7.2020 21:37	79.98	0.10	80.00	0.49	0.02	0.03
14.7.2020 21:52	60.03	0.12	60.19	0.13	0.16	0.27
14.7.2020 22:07	90.03	0.10	90.30	0.38	0.27	0.30
14.7.2020 22:22	19.98	0.13	20.71	0.16	0.73	3.65
14.7.2020 22:37	50.01	0.12	50.00	0.29	−0.01	−0.02
14.7.2020 22:52	69.96	0.14	69.59	0.39	−0.37	−0.53
14.7.2020 23:07	10.19	0.32	10.87	0.46	0.68	6.67
14.7.2020 23:22	39.90	0.25	40.48	0.21	0.58	1.45
14.7.2020 23:52	29.98	0.16	30.33	0.16	0.35	1.17
15.7.2020 00:07	−0.01	0.18	0.94	0.16	0.95	NA
15.7.2020 00:22	75.04	0.11	75.03	0.35	−0.01	−0.01

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
15.7.2020 00:37	175.11	0.07	173.87	0.37	−1.24	−0.71
15.7.2020 00:52	24.86	0.20	25.40	0.28	0.54	2.17
15.7.2020 01:07	125.00	0.17	124.32	0.51	−0.68	−0.54
15.7.2020 01:22	200.09	0.11	198.55	0.44	−1.54	−0.77
15.7.2020 01:37	150.03	0.14	149.27	0.40	−0.76	−0.51
15.7.2020 01:52	−0.18	0.13	0.99	0.16	1.17	NA
15.7.2020 02:07	40.04	0.07	40.56	0.27	0.52	1.30
15.7.2020 02:22	10.26	0.45	10.98	0.40	0.72	7.02
15.7.2020 02:37	80.01	0.05	79.85	0.26	−0.16	−0.20
15.7.2020 02:52	19.95	0.19	20.68	0.07	0.73	3.66
15.7.2020 03:07	59.98	0.22	60.09	0.22	0.11	0.18
15.7.2020 03:22	90.03	0.16	89.74	0.22	−0.29	−0.32
15.7.2020 03:37	29.97	0.22	30.30	0.25	0.33	1.10
15.7.2020 03:52	70.03	0.14	69.83	0.14	−0.20	−0.29
15.7.2020 04:07	50.08	0.23	50.34	0.28	0.26	0.52
15.7.2020 04:22	−0.07	0.27	0.72	0.17	0.79	NA
15.7.2020 04:37	80.00	0.10	79.60	0.24	−0.40	−0.50
15.7.2020 04:52	60.00	0.10	60.00	0.27	0.00	0.00
15.7.2020 05:07	90.03	0.17	89.88	0.21	−0.15	−0.17
15.7.2020 05:22	19.98	0.22	20.55	0.24	0.57	2.85
15.7.2020 05:37	49.96	0.24	50.11	0.45	0.15	0.30
15.7.2020 05:52	70.03	0.11	69.90	0.19	−0.13	−0.19
15.7.2020 06:07	10.17	0.47	11.09	0.39	0.92	9.05
15.7.2020 06:22	39.98	0.07	40.10	0.25	0.12	0.30
15.7.2020 06:52	29.95	0.09	29.99	0.48	0.04	0.13
15.7.2020 07:07	0.19	0.19	0.71	0.11	0.52	NA
15.7.2020 07:22	75.04	0.18	74.78	0.61	−0.26	−0.35

Table 5. *Five-minute aggregates computed from the last five of a total of fifteen 1-minute values for the comparison of the SNB OA Teledyne API T400 SN 4686 with the bias-corrected WCC-Empa TS*

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
14.7.2020 14:37	79.99	0.09	81.56	0.36	1.57	1.96
14.7.2020 14:52	60.00	0.14	61.43	0.24	1.43	2.38
14.7.2020 15:07	89.98	0.13	91.44	0.30	1.46	1.62
14.7.2020 15:22	19.97	0.21	20.55	0.39	0.58	2.90
14.7.2020 15:37	49.99	0.06	50.78	0.16	0.79	1.58
14.7.2020 15:52	70.01	0.27	71.30	0.07	1.29	1.84
14.7.2020 16:07	10.61	0.30	10.81	0.23	0.20	1.89
14.7.2020 16:22	39.99	0.10	40.77	0.14	0.78	1.95
14.7.2020 16:52	29.93	0.10	30.78	0.26	0.85	2.84
14.7.2020 17:07	−0.38	0.50	0.44	0.79	0.82	NA
14.7.2020 17:22	75.03	0.07	76.34	0.54	1.31	1.75
14.7.2020 17:37	175.06	0.19	177.25	0.45	2.19	1.25
14.7.2020 17:52	25.03	0.27	25.51	0.39	0.48	1.92

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
14.7.2020 18:07	125.05	0.08	127.45	0.23	2.40	1.92
14.7.2020 18:22	200.03	0.10	203.08	0.21	3.05	1.52
14.7.2020 18:37	150.03	0.11	152.30	0.41	2.27	1.51
14.7.2020 18:52	0.10	0.41	0.41	0.26	0.31	NA
14.7.2020 19:07	40.00	0.24	40.61	0.25	0.61	1.52
14.7.2020 19:22	10.02	0.41	10.15	0.30	0.13	1.30
14.7.2020 19:37	79.97	0.10	81.22	0.26	1.25	1.56
14.7.2020 19:52	19.93	0.33	20.60	0.44	0.67	3.36
14.7.2020 20:07	59.95	0.17	60.71	0.16	0.76	1.27
14.7.2020 20:22	90.01	0.08	91.49	0.57	1.48	1.64
14.7.2020 20:37	29.96	0.10	30.51	0.37	0.55	1.84
14.7.2020 20:52	69.99	0.04	71.13	0.25	1.14	1.63
14.7.2020 21:07	49.98	0.13	50.96	0.32	0.98	1.96
14.7.2020 21:22	−0.44	0.24	0.82	0.29	1.26	NA
14.7.2020 21:37	79.98	0.10	81.22	0.37	1.24	1.55
14.7.2020 21:52	60.03	0.12	60.83	0.11	0.80	1.33
14.7.2020 22:07	90.03	0.10	91.41	0.47	1.38	1.53
14.7.2020 22:22	19.98	0.13	20.32	0.19	0.34	1.70
14.7.2020 22:37	50.01	0.12	50.44	0.27	0.43	0.86
14.7.2020 22:52	69.96	0.14	70.42	0.15	0.46	0.66
14.7.2020 23:07	10.19	0.32	10.03	0.34	−0.16	−1.57
14.7.2020 23:22	39.90	0.25	40.48	0.32	0.58	1.45
14.7.2020 23:52	29.98	0.16	30.29	0.67	0.31	1.03
15.7.2020 00:07	−0.01	0.18	0.02	0.12	0.03	NA
15.7.2020 00:22	75.04	0.11	75.84	0.10	0.80	1.07
15.7.2020 00:37	175.11	0.07	177.59	0.42	2.48	1.42
15.7.2020 00:52	24.86	0.20	25.04	0.35	0.18	0.72
15.7.2020 01:07	125.00	0.17	126.95	0.32	1.95	1.56
15.7.2020 01:22	200.09	0.11	202.79	0.62	2.70	1.35
15.7.2020 01:37	150.03	0.14	152.24	0.47	2.21	1.47
15.7.2020 01:52	−0.18	0.13	−0.02	0.44	0.16	NA
15.7.2020 02:07	40.04	0.07	40.67	0.27	0.63	1.57
15.7.2020 02:22	10.26	0.45	10.82	0.50	0.56	5.46
15.7.2020 02:37	80.01	0.05	81.28	0.26	1.27	1.59
15.7.2020 02:52	19.95	0.19	20.33	0.47	0.38	1.90
15.7.2020 03:07	59.98	0.22	60.84	0.46	0.86	1.43
15.7.2020 03:22	90.03	0.16	91.52	0.15	1.49	1.66
15.7.2020 03:37	29.97	0.22	30.32	0.60	0.35	1.17
15.7.2020 03:52	70.03	0.14	71.39	0.35	1.36	1.94
15.7.2020 04:07	50.08	0.23	51.08	0.35	1.00	2.00
15.7.2020 04:22	−0.07	0.27	0.13	0.31	0.20	NA
15.7.2020 04:37	80.00	0.10	81.25	0.27	1.25	1.56
15.7.2020 04:52	60.00	0.10	60.52	0.24	0.52	0.87
15.7.2020 05:07	90.03	0.17	91.25	0.38	1.22	1.36
15.7.2020 05:22	19.98	0.22	20.86	0.35	0.88	4.40
15.7.2020 05:37	49.96	0.24	50.62	0.43	0.66	1.32
15.7.2020 05:52	70.03	0.11	70.88	0.31	0.85	1.21
15.7.2020 06:07	10.17	0.47	10.32	0.30	0.15	1.47

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OA (nmol mol⁻¹)	sdOA (nmol mol⁻¹)	OA-TS (nmol mol⁻¹)	OA-TS (%)
15.7.2020 06:22	39.98	0.07	40.55	0.23	0.57	1.43
15.7.2020 06:52	29.95	0.09	30.70	0.35	0.75	2.50
15.7.2020 07:07	0.19	0.19	0.64	0.23	0.45	NA
15.7.2020 07:22	75.04	0.18	76.54	0.42	1.50	2.00

Table 6. *Five-minute aggregates computed from the last five of a total of fifteen 1-minute values for the comparison of the UBA OC Thermo Scientific 49i-PS #1162110060 with the bias-corrected WCC-Empa TS*

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OC (nmol mol⁻¹)	sdOC (nmol mol⁻¹)	OC-TS (nmol mol⁻¹)	OC-TS (%)
15.7.2020 14:15	−0.28	0.21	0.11	0.19	0.39	NA
15.7.2020 14:30	80.02	0.09	79.91	0.58	−0.11	−0.14
15.7.2020 14:45	59.95	0.12	59.84	0.19	−0.11	−0.18
15.7.2020 15:00	90.01	0.09	90.22	0.23	0.21	0.23
15.7.2020 15:15	20.00	0.20	20.19	0.39	0.19	0.95
15.7.2020 15:30	49.96	0.14	50.17	0.20	0.21	0.42
15.7.2020 15:45	69.98	0.11	70.02	0.32	0.04	0.06
15.7.2020 16:00	9.86	0.18	9.90	0.13	0.04	0.41
15.7.2020 16:15	40.01	0.16	40.07	0.29	0.06	0.15
15.7.2020 16:45	29.94	0.19	29.76	0.35	−0.18	−0.60
15.7.2020 17:00	0.18	0.19	0.10	0.20	−0.08	NA
15.7.2020 17:15	75.01	0.07	74.91	0.31	−0.10	−0.13
15.7.2020 17:30	175.05	0.10	174.88	0.20	−0.17	−0.10
15.7.2020 17:45	25.00	0.07	24.92	0.17	−0.08	−0.32
15.7.2020 18:00	125.06	0.08	125.15	0.14	0.09	0.07
15.7.2020 18:15	200.05	0.11	199.71	0.45	−0.34	−0.17
15.7.2020 18:30	150.04	0.06	149.73	0.41	−0.31	−0.21
15.7.2020 18:45	−0.05	0.25	0.01	0.08	0.06	NA
15.7.2020 19:00	39.98	0.11	39.51	0.22	−0.47	−1.18
15.7.2020 19:15	9.98	0.33	10.12	0.36	0.14	1.40
15.7.2020 19:30	80.01	0.15	79.78	0.28	−0.23	−0.29
15.7.2020 19:45	20.65	1.01	20.65	1.14	0.00	0.00
15.7.2020 20:00	59.98	0.11	59.88	0.36	−0.10	−0.17
15.7.2020 20:15	89.99	0.06	89.68	0.31	−0.31	−0.34
15.7.2020 20:30	30.01	0.11	30.07	0.30	0.06	0.20
15.7.2020 20:45	69.98	0.08	70.14	0.28	0.16	0.23
15.7.2020 21:00	50.01	0.13	50.16	0.18	0.15	0.30
15.7.2020 21:15	−0.05	0.12	0.21	0.19	0.26	NA
15.7.2020 21:30	80.06	0.09	80.05	0.29	−0.01	−0.01
15.7.2020 21:45	60.02	0.23	59.96	0.32	−0.06	−0.10
15.7.2020 22:00	90.02	0.09	89.98	0.22	−0.04	−0.04
15.7.2020 22:15	19.96	0.15	19.93	0.32	−0.03	−0.15
15.7.2020 22:30	49.99	0.14	49.82	0.22	−0.17	−0.34
15.7.2020 22:45	70.03	0.06	69.99	0.35	−0.04	−0.06
15.7.2020 23:00	9.79	0.21	10.15	0.30	0.36	3.68
15.7.2020 23:15	39.95	0.25	39.90	0.39	−0.05	−0.13

Date – Time	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	OC (nmol mol⁻¹)	sdOC (nmol mol⁻¹)	OC-TS (nmol mol⁻¹)	OC-TS (%)
15.7.2020 23:45	29.99	0.20	29.93	0.34	−0.06	−0.20
16.7.2020 00:00	0.01	0.23	−0.02	0.08	−0.03	NA
16.7.2020 00:15	75.00	0.08	74.73	0.23	−0.27	−0.36
16.7.2020 00:30	175.05	0.10	175.22	0.28	0.17	0.10
16.7.2020 00:45	24.99	0.25	25.24	0.26	0.25	1.00
16.7.2020 01:00	125.02	0.06	124.95	0.37	−0.07	−0.06
16.7.2020 01:15	200.10	0.13	199.79	0.16	−0.31	−0.15
16.7.2020 01:30	150.06	0.05	150.01	0.57	−0.05	−0.03
16.7.2020 01:45	0.06	0.20	0.05	0.13	−0.01	NA
16.7.2020 02:00	40.01	0.18	39.69	0.26	−0.32	−0.80
16.7.2020 02:15	10.33	0.34	10.05	0.16	−0.28	−2.71
16.7.2020 02:30	79.98	0.04	79.85	0.20	−0.13	−0.16
16.7.2020 02:45	20.68	0.94	20.52	0.90	−0.16	−0.77
16.7.2020 03:00	59.98	0.03	59.76	0.23	−0.22	−0.37
16.7.2020 03:15	90.06	0.10	89.90	0.49	−0.16	−0.18
16.7.2020 03:30	30.04	0.27	29.98	0.38	−0.06	−0.20
16.7.2020 03:45	69.99	0.05	69.92	0.17	−0.07	−0.10
16.7.2020 04:00	49.96	0.17	50.04	0.37	0.08	0.16
16.7.2020 04:15	0.02	0.14	0.05	0.16	0.03	NA
16.7.2020 04:30	79.96	0.06	79.79	0.36	−0.17	−0.21
16.7.2020 04:45	59.97	0.05	60.01	0.26	0.04	0.07
16.7.2020 05:00	90.03	0.09	89.65	0.36	−0.38	−0.42
16.7.2020 05:15	19.88	0.14	19.98	0.29	0.10	0.50
16.7.2020 05:30	49.98	0.11	49.65	0.23	−0.33	−0.66
16.7.2020 05:45	69.98	0.23	69.99	0.33	0.01	0.01
16.7.2020 06:00	10.29	0.48	10.32	0.26	0.03	0.29
16.7.2020 06:15	39.99	0.17	39.93	0.14	−0.06	−0.15
16.7.2020 06:45	29.94	0.03	29.85	0.45	−0.09	−0.30
16.7.2020 07:00	0.18	0.32	0.12	0.19	−0.06	NA

Carbon monoxide comparisons

All procedures were conducted according to the SOP (WMO, 2007) and included comparing the TSs at Empa before comparing the analysers. Details of the traceability of the TSs to the WMO/GAW Reference Standard at the National Oceanic and Atmospheric Administration / Earth System and Research Laboratory (NOAA/ESRL) are given further below.

Table 7 shows details of the experimental set-up during the comparison of the transfer standard and the station analysers. The data used for the evaluation were recorded by the SNB data acquisition system. The standards used for the calibration of the SNB instrument are shown in Table 8.

Table 7. Experimental details of SNB 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 16).	
Station analyser	
Model, serial number	Horiba APMA-360 #913012
Principle	NDIR
Drying system	No drying system available
Comparison procedures	
Connection	WCC-Empa travelling standards were connected to spare calibration gas ports.

Table 8 *CO standards at SNB as of July 2020*

Cylinder ID	CO (nmol mol⁻¹)	Calibration scale
DOTHE	1510±100	Traceable to VSL # 5605794

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 9. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Horiba APMA-360 #913012 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale)*

Date / Time	TS cylinder	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	AL (nmol mol⁻¹)	sdAL (nmol mol⁻¹)	N	AL-TS (nmol mol⁻¹)	AL-TS (%)
20.7.15 09:07:30	181129_FB03383	71.1	0.7	74.6	5.3	2	3.5	4.9
20.7.15 09:22:30	140514_FB03899	259.1	0.5	250.8	2.4	2	−8.3	−3.2

Date / Time	TS cylinder	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	AL (nmol mol⁻¹)	sdAL (nmol mol⁻¹)	N	AL-TS (nmol mol⁻¹)	AL-TS (%)
20.7.15 09:37:30	140514_FB03894	195.0	0.4	199.6	12.4	2	4.6	2.4
20.7.15 09:52:30	110512_FB03348	135.1	1.0	135.8	1.2	2	0.8	0.6
20.7.15 10:07:30	160825_FB03382	174.8	0.7	158.5	6.2	2	−16.3	−9.3
20.7.15 10:22:30	160926_FB03367	92.8	1.1	95.0	4.7	2	2.2	2.4
20.7.15 10:22:30	140515_FB03384	160.9	1.2	166.3	17.1	2	5.4	3.4
20.7.15 12:07:30	160825_FB03358	193.8	0.7	194.2	3.5	2	0.4	0.2
20.7.15 12:22:30	140515_FB03377	155.4	0.9	150.8	7.1	2	−4.6	−2.9
20.7.15 12:37:30	150601_FA02466	695.6	0.4	714.6	1.8	2	18.9	2.7

Methane comparisons

All procedures were conducted according to the SOP (WMO, 2007) and included comparing the TSs at Empa before comparing the analysers. Details of the traceability of the TSs to the WMO/GAW Reference Standard at NOAA/ESRL are given further below. Table 10 shows details of the experimental set-up during the comparison of the transfer standards and the station analysers. The standards used for the calibration of the SNB instruments are shown in Table 11. The values of the SNB D0084 L3WN3 calibration standard were assigned in 2013 by WCC-Empa (calibration certificate 2013-UBA-GHG from January 2013). The standard was reanalysed during the current audit using WCC-Empa TS, and values were slightly changed due to a change in the CH_4 calibration scale.

Table 10. *Experimental details of the SNB 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 16).	
Station analyser	
Model, serial number	Picarro G2301 #883-CFADS2188
Principle	CRDS
Drying system	No dryer; sample is measured humid and corrected for water interference using the instrument’s built-in correction function
Comparison procedures	
Connection	WCC-Empa travelling standards were connected to spare calibration gas ports.

Table 11. *CH_4 and CO_2 standards at SNB as of July 2020*

Cylinder ID	CH_4 (nmol mol^{-1})	CO_2 (µmol mol^{-1})	Calibration scale
D0084 L3WN3	1823.24±2.09	409.20±0.82	CH_4: WMO-X2004 CO_2: WMO-X2007 WCC-Empa certificate from 2013
D0084 L3WN3	1822.26±0.36	409.35±0.04	CH_4: WMO-X2004A CO_2: WMO-X2007 WCC-Empa measurements during this audit
N_2 60	0	0	NA

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 12. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2301 #883-CFADS2188 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale)*

Date / Time	TS cylinder	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)	AL (nmol mol⁻¹)	sdAL (nmol mol⁻¹)	N	AL-TS (nmol mol⁻¹)	AL-TS (%)
20.7.14 16:53:00	181129_FB03383	1981.2	0.02	1983.03	0.05	3	1.79	0.09
20.7.14 17:08:00	140514_FB03899	1974.7	0.05	1976.53	0.18	3	1.82	0.09
20.7.14 17:23:00	140514_FB03894	1953.8	0.06	1955.67	0.30	3	1.78	0.09
20.7.14 17:38:00	110512_FB03348	2766.9	0.09	2769.34	0.46	3	2.40	0.09
20.7.14 17:53:00	160825_FB03382	1918.7	0.04	1920.47	0.38	3	1.77	0.09
20.7.14 18:08:00	160926_FB03367	1855.1	0.05	1856.94	0.10	3	1.81	0.10
20.7.14 18:23:00	140515_FB03384	1845.7	0.07	1847.36	0.24	3	1.63	0.09
20.7.15 13:40:30	160825_FB03358	2027.1	0.03	2028.91	0.12	2	1.73	0.09
20.7.15 13:55:30	140515_FB03377	1768.7	0.04	1770.30	0.18	2	1.56	0.09
20.7.15 14:10:30	150601_FA02466	1900.4	0.02	1902.25	0.00	2	1.81	0.10

Carbon dioxide comparisons

The comparison procedure was the same as for CH_4 (see above).

Results

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

Table 13. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the Picarro G2301 #883-CFADS2188 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale)

Date / Time	TS cylinder	TS (µmol mol⁻¹)	sdTS (µmol mol⁻¹)	AL (µmol mol⁻¹)	sdAL (µmol mol⁻¹)	N	AL-TS (µmol mol⁻¹)	AL-TS (%)
20.7.14 16:53:00	181129_FB03383	410.79	0.05	410.80	0.01	3	0.01	0.00
20.7.14 17:08:00	140514_FB03899	405.02	0.03	405.06	0.01	3	0.04	0.01
20.7.14 17:23:00	140514_FB03894	411.06	0.01	411.08	0.01	3	0.02	0.00
20.7.14 17:38:00	110512_FB03348	341.18	0.01	341.19	0.01	3	0.01	0.00
20.7.14 17:53:00	160825_FB03382	412.38	0.01	412.40	0.00	3	0.02	0.00
20.7.14 18:08:00	160926_FB03367	412.78	0.01	412.79	0.02	3	0.01	0.00
20.7.14 18:23:00	140515_FB03384	381.54	0.01	381.56	0.01	3	0.02	0.01
20.7.15 13:40:30	160825_FB03358	457.18	0.03	457.16	0.00	2	−0.02	0.00
20.7.15 13:55:30	140515_FB03377	365.56	0.03	365.56	0.01	2	0.00	0.00
20.7.15 14:10:30	150601_FA02466	431.04	0.04	431.03	0.00	2	−0.01	0.00

WCC-Empa travelling standards

Ozone

The WCC-Empa TS was compared with the SRP before and after the audit. The following instruments were used:

WCC-Empa O3 reference: National Institute of Standards and Technology SRP #15 (Master)

WCC-Empa TS: Thermo Scientific 49C-PS #0810-153, BKG 0.0, COEF 1.004

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 14. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (see Figure 18). The data were pooled and evaluated by linear regression analysis, with consideration for uncertainties in both instruments. From this, the unbiased O_3 mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (see equation 19 in Klausen et al., 2003).

X_{TS} (nmol mol^{-1}) = ([TS] − 0.03 nmol mol^{-1}) / 0.9995(5a)

u_{TS} (nmol mol^{-1}) = sqrt ((0.43 nmol mol^{-1})^2 + (0.0034 × X)^2)(5b)

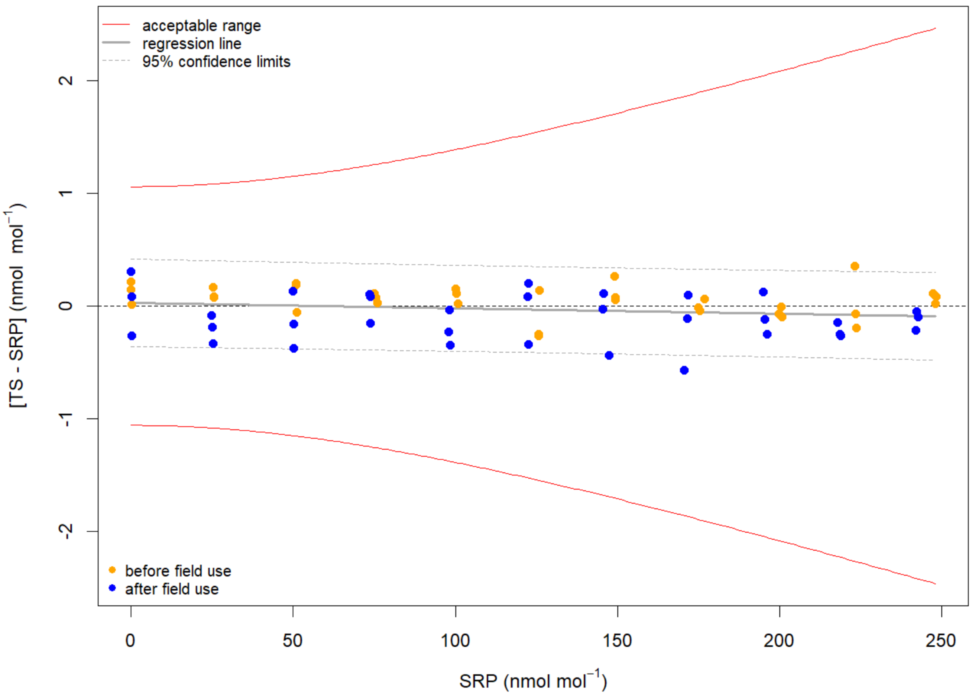

Figure 18. *Deviations between the TS and the SRP before and after use of the TS at the field site*

***Table 14**. Five-minute aggregates computed from ten valid 30-second values for comparison of the SRP with the WCC-Empa TS*

Date	Run	Level[1]	SRP (nmol mol⁻¹)	sdSRP (nmol mol⁻¹)	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)
24.1.2020	1	25	25.52	0.26	25.60	0.09
24.1.2020	1	0	0.00	0.25	0.15	0.12
24.1.2020	1	75	75.86	0.27	75.89	0.08
24.1.2020	1	125	125.89	0.35	126.03	0.15
24.1.2020	1	100	100.80	0.39	100.82	0.14
24.1.2020	1	175	175.42	0.18	175.39	0.10
24.1.2020	1	200	200.67	0.20	200.58	0.18
24.1.2020	1	150	149.19	0.17	149.46	0.13
24.1.2020	1	225	223.54	0.34	223.47	0.15
24.1.2020	1	50	50.99	0.40	50.94	0.13
24.1.2020	1	250	248.23	0.49	248.31	0.20
24.1.2020	2	150	149.30	0.16	149.38	0.14
24.1.2020	2	0	−0.01	0.26	0.21	0.09
24.1.2020	2	175	176.79	0.44	176.85	0.35
24.1.2020	2	100	100.45	0.20	100.56	0.12
24.1.2020	2	200	200.58	0.36	200.57	0.17
24.1.2020	2	25	25.38	0.20	25.55	0.11
24.1.2020	2	75	75.57	0.28	75.65	0.07
24.1.2020	2	125	125.68	0.26	125.42	0.13
24.1.2020	2	50	50.98	0.28	51.17	0.15
24.1.2020	2	225	223.73	0.31	223.53	0.17
24.1.2020	2	250	248.13	0.26	248.14	0.27
24.1.2020	3	25	25.54	0.29	25.62	0.08
24.1.2020	3	125	125.71	0.38	125.46	0.16
24.1.2020	3	175	174.92	0.28	174.91	0.18
24.1.2020	3	75	75.02	0.32	75.13	0.15
24.1.2020	3	0	0.14	0.29	0.16	0.07
24.1.2020	3	225	223.32	0.38	223.67	0.42
24.1.2020	3	150	149.26	0.23	149.32	0.14
24.1.2020	3	50	50.89	0.25	51.09	0.10
24.1.2020	3	100	100.04	0.20	100.19	0.13
24.1.2020	3	200	199.89	0.37	199.82	0.15
24.1.2020	3	245	247.37	0.29	247.48	0.29
15.7.2020	4	170	171.51	0.45	171.40	0.29
15.7.2020	4	0	0.10	0.30	−0.16	0.25
15.7.2020	4	145	147.37	0.49	146.93	0.31
15.7.2020	4	50	50.09	0.12	49.93	0.17
15.7.2020	4	100	98.35	0.21	98.00	0.12
15.7.2020	4	25	25.18	0.18	24.85	0.16
15.7.2020	4	220	218.90	0.26	218.64	0.32
15.7.2020	4	125	122.52	0.20	122.73	0.20
15.7.2020	4	195	196.21	0.11	195.96	0.17
15.7.2020	4	75	73.78	0.29	73.63	0.13
15.7.2020	4	245	242.79	0.32	242.69	0.31
15.7.2020	5	100	98.21	0.21	98.18	0.23
15.7.2020	5	75	73.78	0.35	73.86	0.13
15.7.2020	5	220	218.58	0.26	218.33	0.07
15.7.2020	5	0	0.18	0.31	0.26	0.32
15.7.2020	5	170	171.90	0.63	171.99	0.47
15.7.2020	5	120	122.31	0.26	122.40	0.25
15.7.2020	5	25	25.09	0.19	24.91	0.13

Date	Run	Level[1]	SRP (nmol mol⁻¹)	sdSRP (nmol mol⁻¹)	TS (nmol mol⁻¹)	sdTS (nmol mol⁻¹)
15.7.2020	5	50	49.86	0.18	50.00	0.17
15.7.2020	5	195	194.88	0.25	195.01	0.14
15.7.2020	5	145	145.74	0.33	145.85	0.15
15.7.2020	5	240	242.27	0.31	242.22	0.18
15.7.2020	6	75	73.54	0.22	73.64	0.16
15.7.2020	6	0	−0.18	0.30	0.12	0.23
15.7.2020	6	220	217.98	0.24	217.83	0.25
15.7.2020	6	120	122.43	0.28	122.10	0.12
15.7.2020	6	170	170.67	0.44	170.10	0.23
15.7.2020	6	195	195.40	0.31	195.28	0.23
15.7.2020	6	25	24.81	0.38	24.72	0.19
15.7.2020	6	50	50.04	0.19	49.67	0.20
15.7.2020	6	100	97.84	0.22	97.61	0.28
15.7.2020	6	145	145.55	0.22	145.52	0.24
15.7.2020	6	240	242.13	0.19	241.92	0.20

[1] The level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the CCL of the WMO/GAW Programme 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 through TSs 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 Global Monitoring Division 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).
CO, CO_2 and CH_4: Picarro G2401 CRDS.

Table 15 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results, including standard deviations of the WCC-Empa TS, are listed in Table 16, and Figure 19 shows the analysis of the TS over time.

Table 15. *NOAA/ESRL laboratory standards and working standards at WCC-Empa*

Cylinder	CO (nmol mol⁻¹)	CH_4 (nmol mol⁻¹)	N_2O (nmol mol⁻¹)	CO_2 (µmol mol⁻¹)
CC339478[1]	463.76	2485.25	357.19	484.39
CB11499[1]	141.03	1933.77	329.15	407.33
CB11485[1]	110.88	1844.78	328.46	394.30
CA02789[2]	448.67	2097.48	342.18	495.85
190618_CC7030	3244.00	2258.07	NA	419.61
120307_CB0896	485.76	2470.72	322.91	363.64

[1] used for calibrations of CO_2, CH_4 and N_2O
[2] used for calibrations of CO

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

TS	**Press. (psi)**	**CH_4 (nmol mol^{-1})**	**sd**	**CO_2 (μmol mol^{-1})**	**sd**	**N_2O (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**	**CO (P) (nmol mol^{-1})**	**sd**
110512_FB03348	1000	2766.94	0.09	341.18	0.01	323.83	0.03	135.18	0.26	135.05	0.98
140514_FB03894	820	1953.89	0.06	411.06	0.01	329.15	0.04	195.46	0.28	194.95	0.42
140514_FB03899	600	1974.71	0.05	405.02	0.03	328.59	0.06	258.43	0.45	259.14	0.51
140515_FB03377	790	1768.74	0.04	365.56	0.03	317.4	0.06	155.18	0.26	155.38	0.85
140515_FB03384	1100	1845.73	0.07	381.54	0.01	326.04	0.04	160.98	0.16	160.85	1.15
150601_FA02466	210	1900.44	0.02	431.04	0.04	326.58	0.09	694.65	0.66	695.64	0.43
160825_FB03358	1500	2027.18	0.03	457.18	0.03	331.7	0.03	193.59	0.09	193.79	0.71
160825_FB03382	1020	1918.7	0.04	412.38	0.01	318.28	0.05	173.98	0.22	174.76	0.69
160926_FB03367	380	1855.13	0.05	412.78	0.01	339.64	0.04	92.44	0.47	92.78	1.06
181129_FB03383	1910	1981.24	0.02	410.79	0.05	327.58	0.04	71.07	0.28	71.08	0.65

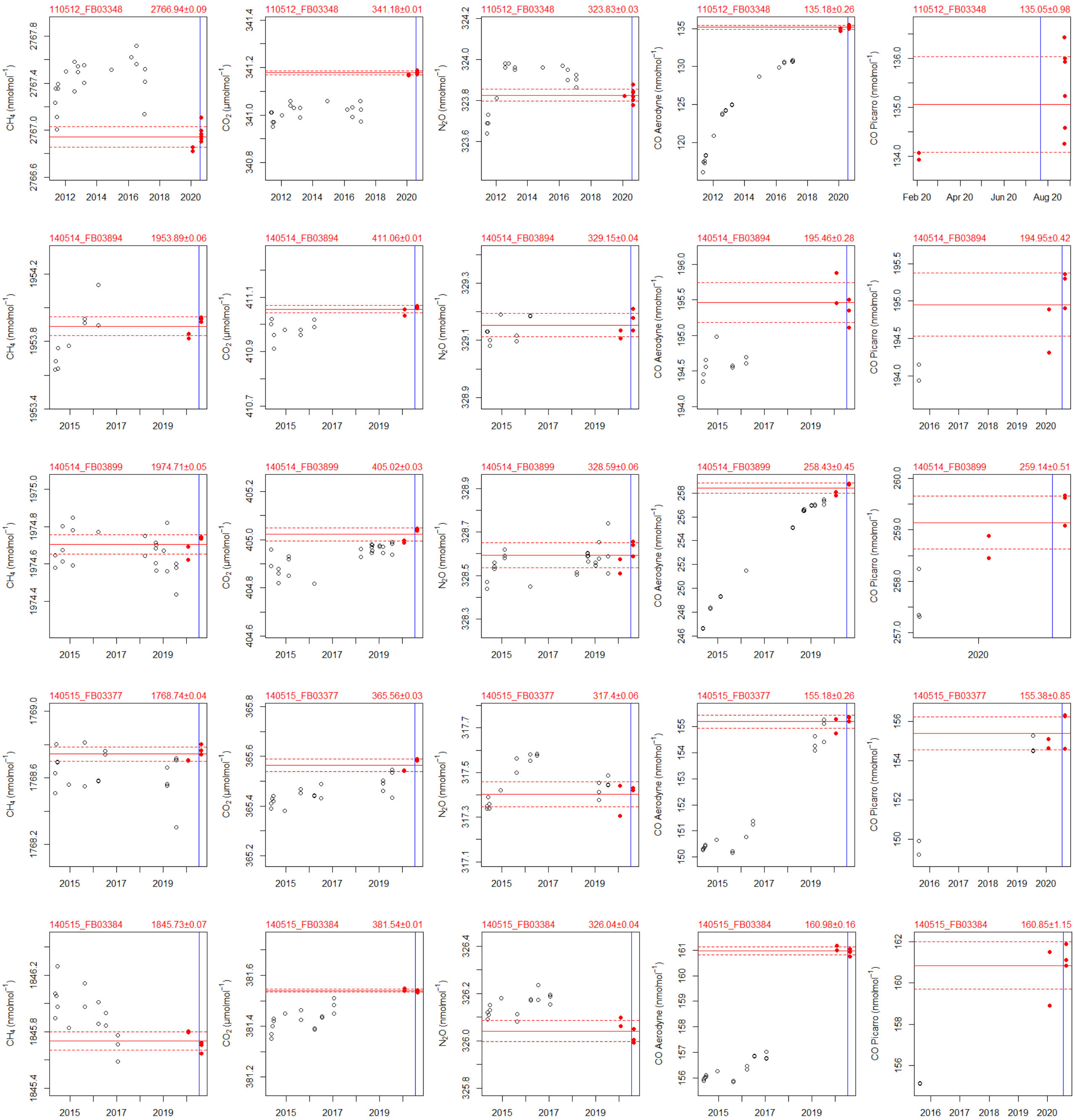

***Figure 19.** Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid lines show the average of the points that were considered for the assignment of the values; the red dotted lines show the standard deviation of the measurement. The blue vertical lines indicate the date of the audit.*

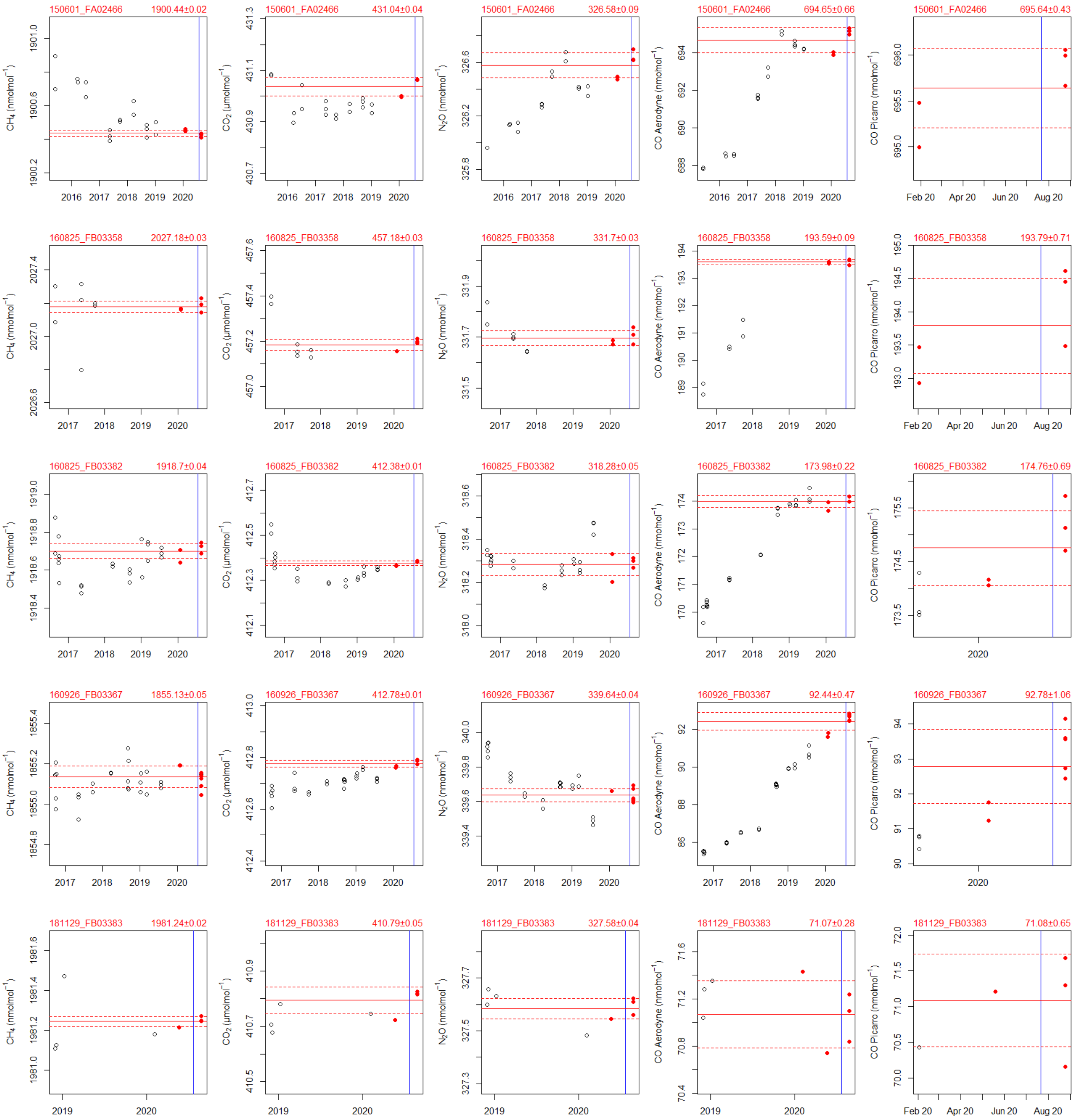

Figure 20. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid lines show the average of the points that were considered for the assignment of the values; the red dotted line shows the standard deviation of the measurement. The blue vertical lines indicate the date of the audit.*

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