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

REGIONAL GAW STATION ANMYEON-DO REPULIC OF KOREA JUNE 2017

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The second system and performance audit by WCC-Empa[1] at the regional GAW station Anmyeon-do was conducted from 14 - 16 June 2017 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). GAW activities in South Korea are coordinated by the Environmental Meteorology Research Division of the National Institute of Meteorological Sciences (NIMS). This has changed since the last audit by WCC-Empa. At that time, GAW related activities were coordinated by the Korea Global Atmosphere Watch Center (KGAWC).

A previous audits at the Anmyeon-do GAW station was made in October 2014 for CO_2 and CH_4 (Zellweger et al., 2014).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Han Sang Ok	NIMS, station manager
Ms. Haeyoung Lee	NIMS, scientist, measurement leader of GHGs
Ms. Sumin Kim	NIMS, scientist, measurement leader of reactive gases
Mr. Se Pyo Lee	NIMS, station operator
Mr. Hong Woo Choe	NIMS, station operator

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

The report is distributed to the Anmyeon-do station manager, the Korean GAW Country Contact and the World Meteorological Organization in Geneva. The report will be made available on the internet (https://www.empa.ch/web/s503/wcc-empa).

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

Station Management and Operation

The Anmyeon-do GAW station (AMY) is operated by NIMS, which is part of the Korea Meteorological Administration (KMA). The station is visited during weekdays by approximately 10 -15 scientists, technical and administrational staff. The operation and maintenance of the station is well organized, with clear assignments of responsibilities.

Station Location and Access

AMY (36.5383°N, 126.3300°E, 46 m a.s.l) is located on an island on the west coast of the Korean Peninsula. The station building itself is located on a hill at an elevation of 46 m above sea level, and comprises a 40 m tower. To the west the station is exposed to the open sea, with the Chinese mainland in a distance of 300-400 km. To the east of the station are several small farms producing mainly rice and sweet potatoes. Large parts of the area as well as the immediate surroundings of the station are covered by pine forests. The station is infrequently affected by local pollution, mainly during summer due to recreational activities, and autumn due to burning of crop residues. Further information is available from the GAW Station Information System (GAWSIS) (https://gawsis.meteoswiss.ch).

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

Station Facilities

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

Measurement Programme

AMY station comprises a comprehensive measurement programme that covers all six focal areas of the GAW programme. An overview on measured species is available from GAWSIS (https://gawsis.meteoswiss.ch).

> **Recommendation 1 (**, minor, 2018)**
> *GAWSIS needs to be updated. The information is not up to date for some of the measured parameters as well as for the station contacts.*

Data Submission

Data has been submitted to the corresponding data centres. WCC-Empa accessed the available data sets at different times. The first data set was downloaded on 3 October 2017. At that time, hourly data of surface O_3 (Jan/Feb 2014), CH_4 (1999-2014), CO_2 (1999-2014), and N_2O (1999-2014) data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). CO data has not yet been submitted. Ozone data of the whole year 2014 has been made available to the Tropospheric Ozone Assessment Report (TOAR) activity, also supported by WMO and data are accessible via the Jülich Open Web Interface (JOIN; https://join.fz-juelich.de/) after registration (Schultz et al., 2017). However, hourly data can only be visualized but not be downloaded. It was recognized that the data set accessed on 3 October 2017 contained questionable data, which has been communicated to the station.

At the time of the second access on 17 November 2017, these data series were updated at WDCGG. At that time, only daily values were available for CH_4 (1999-2017), CO_2 (1999-2017), and N_2O (1999-2017). The hourly data was removed from WDCGG.

The third access was made on 15 January 2018. At that time, CH_4 (1999-2017 and CO_2 (1999-2017) were available as hourly values, while other parameters have not yet been re-submitted.

> **Recommendation 2 (***, important, 2018)**
> *Data submission is an obligation of all GAW stations. It is recommended to submit data to the corresponding data centres at least in yearly intervals. One hourly data must be submitted for all parameters.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG were reviewed. Summary plots and a short description of the findings are presented in the Appendix. In contrast to the mainly good results of the current audit, the data review showed that some of the submitted past data was not plausible. This was immediately communicated, and the data was re-submitted by KMA. Some of the questionable data sets were in the meantime removed from WDCGG.

Recommendation 3 (*, critical, 2018)**
Part of the submitted data residing at WDCGG was not plausible. This was communicated to the station staff, and data series were re-visited and further quality controlled. WDCGG was informed immediately, and invalid data has been withdrawn. This happened already before the completion of the audit. To avoid future re-submissions, data needs to be carefully quality controlled before submission.

The data set accessed on 17 November 2017 contained only daily averages. The daily time series were also reviewed, and the data looks plausible. However, the data has been filtered, which is not clear from the data flags and the metadata. For example, during the ambient air comparison between WCC-Empa and AMY in 2014, several daily averages were exceeding 2000 ppb CH_4. These days are missing in the current data WDCGG data set. The agreement for the available days was on average within the WMO/GAW compatibility goals.

Recommendation 4 (*, critical, 2018)**
The data which is currently available from WDCGG was filtered, and data with high mole fractions were removed from the data set. Even though this is mentioned on the metadata, all valid data, including pollution episodes, need to be reported to the data centres. The current data sets need also to be revised.

CO_2 and CH_4 data were then again re-submitted and accessed on 15 January 2018 by WCC-Empa. These data sets contain again hourly values, and these two data sets look generally sound. However, data has been filtered, which is described in the metadata available from WDCGG. WCC-Empa strongly recommends submitting all valid data.

Documentation

All operation and maintenance actions are entered in electronic and hand written log books. The instrument manuals are available at the site, and weekly checklists are available. The reviewed information was comprehensive and up to date for the past few years (since 2014). However, going further back in time revealed some significant shortcomings. For example, the changes of the ozone calibration settings were not documented in the past, which makes post-correction of the data impossible.

Recommendation 5 (*, critical, ongoing)**
The station staff should be aware that documentation of all relevant information is of utmost importance for reliable data and measurements. The current practice is appropriate, but it has to be made sure that the information is archived together with the measurement data.

Air Inlet System

The air inlet systems were not changed since the last audit. A common air inlet system for GHG measurements is in place. Air is pumped from the 40 m tower to the laboratory building, and automatically dried to a dew point of -80°C using two cryogenic traps alternating every 24 hours. The stainless steel manifold is pressurized to approx. 2 bar, and instruments are directly connected to this manifold. This inlet is adequate but problems with the drying system were frequent during the period of the audit.

Recommendation 6 (, important, ongoing)**
It must be made sure that the automatic drying system is working to avoid unnecessary data gaps.

Ozone, CO and other reactive gases are sampled from a small tower approximately 5 m above the roof of the AMY laboratory. A 9 m long 30 mm outer diameter PFA tube is connected to a common manifold, from where instruments are connected by ¼ inch tubing and inlet filters. The manifold is flushed at 20 l/min. The residence time is estimated to be approximately 21 seconds based on the volume and flow rate of the inlet. Since ozone is known to be susceptible to losses in the inlet due to its high reactivity, tests should be performed to proof the suitability for ozone.

Recommendation 7 (, important, 2018)**
The residence time in the inlet system is relatively long for surface ozone measurements. It is recommended to re-design the inlet system to achieve a residence time of less than 5 seconds.

Recommendation 8 (, important, 2018)**
It is recommended to determine the ozone loss rate of the current inlet system.

Surface Ozone Measurements

Surface ozone measurements started in 1998 at AMY, and continuous time series are available since the current WCC-Empa audit. Past data are currently being carefully reviewed and made available if possible.

Instrumentation. AMY is equipped with one ozone analysers (TEI 49i), and an ozone generator (TEI 146i) is available for zero and span checks as well as for instrument diagnostics. The TEI 49i was installed at AMY in 2005; before this, measurements were made using an Ecotech instrument (model ML9812).

Recommendation 9 (*, critical, 2018)**
The response of the ozone instrument was tested using the TEI 146i ozone generator once per week. During these calibrations, the span settings of the instrument were changed. However, the TEI 146i is not suitable for ozone calibrations. It is important that this will not be done in future, and the TEI 146i will only be used for qualitative instrument checks.

Recommendation 10 (*, important, 2018)**
It is recommended to purchase on ozone calibrator (e.g. TEI 49i-PS), which needs further be calibrated against an ozone reference (e.g. at KRISS). Calibrations with the ozone calibrator should then be made every 6 months; however, changing of the calibration settings of the TEI 49i is not recommended.

Data Acquisition. Data (1-min time resolution) is currently manually downloaded using the TEI iPort software. All instrument parameters are available with iPort, but it requires manual intervention, and data is not available in near-real time and cannot be easily visualized and reviewed in the laboratory. The analogue signal is also acquired with a data logger (TECH KOREA KTE-1400D).

> **Recommendation 11 (**, important, 2018)**
> *The ozone instrument should be equipped with a dedicated data acquisition system that acquires the digital output of the instrument. The current praxis using iPort is intermediately appropriate but should not be a long term solution. All instrument parameters need to be recorded, and remote access must be possible.*

Intercomparison (Performance Audit). The AMY analyser was compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system, and no further corrections were applied. The following equations characterise the bias of the instruments:

The following equation characterises the bias of the instrument with unchanged settings:

TEI 49i #0932138786 (BKG -0.5 ppb, SPAN 1.081):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 0.33 ppb) / 1.0984 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.23 ppb^2 + 2.11e-05 * X_{O3}^2) (1b)

The calibration settings were adjusted after the first comparison, since the instrument did not meet the data quality objectives and has never been calibrated against an NIST traceable ozone reference.

The following equation characterises the bias of the instrument with new calibration settings:

TEI 49i #0932138786 (BKG 0.0 ppb, SPAN 1.006):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.23 ppb) / 1.0050 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.52e-05 * X_{O3}^2) (1d)

The results of the comparison are further presented in the following Figures.

The results of the surface ozone audit can be summarised as follows:

Good agreement between the WCC-Empa travelling instrument and the AMY analyser was found after adjustment of the calibration settings and the pressure sensor. It now is important that these settings are not changed, as recommended above. Calibrations must only be made using a transfer standard with traceability to the WMO/GAW reference.

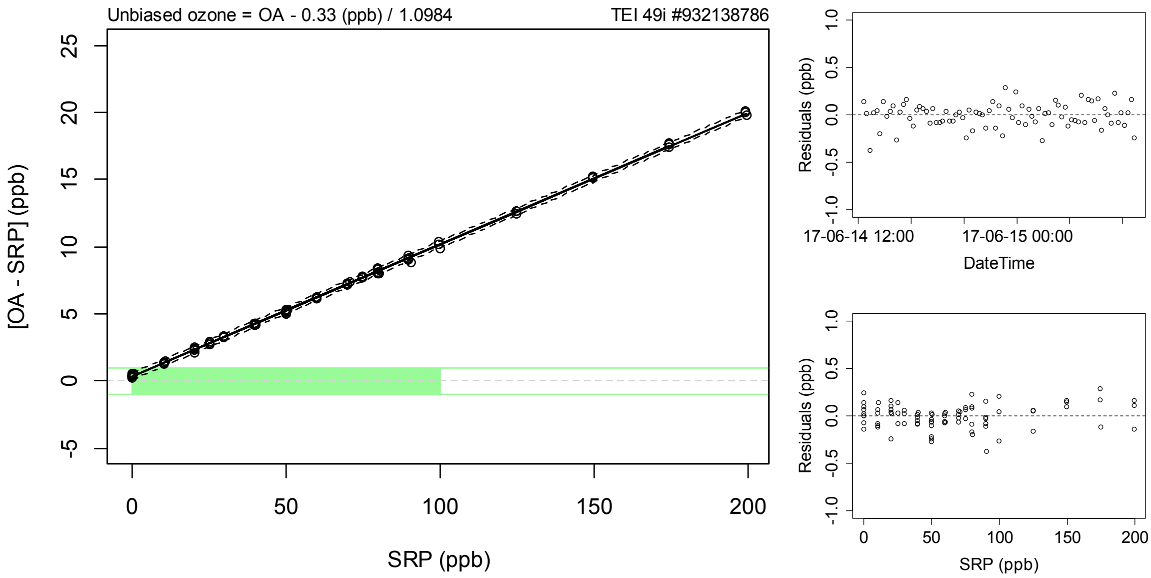

Figure 1. Left: Bias of the AMY ozone analyser (TEI 49i #0932138786) before adjustment of the calibration settings (BKG -0.5, COEF 1.081) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

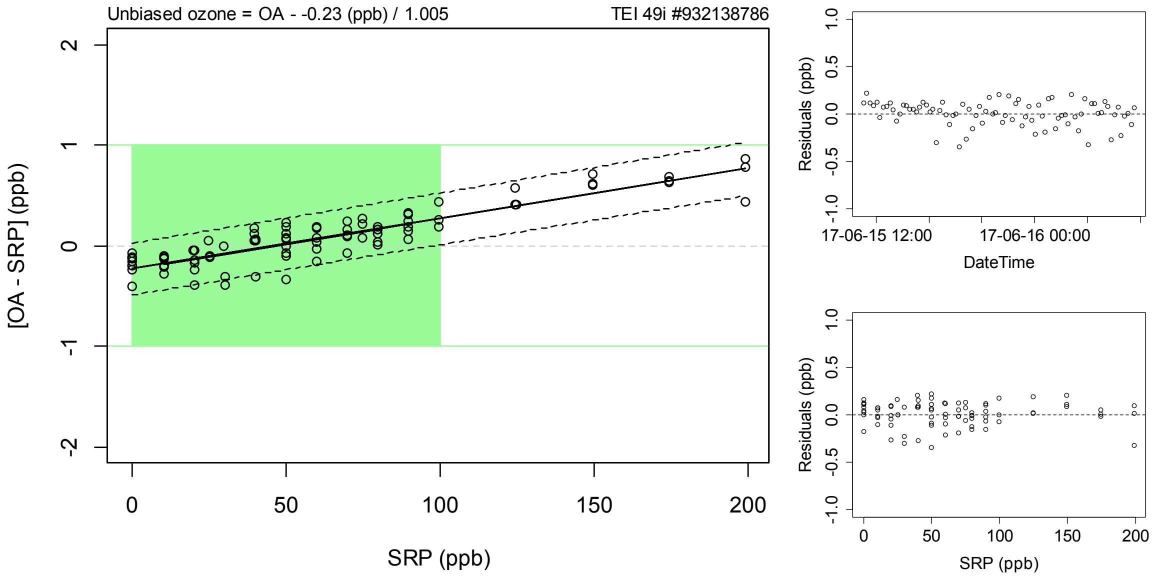

Figure 2. Same as above for the AMY ozone analyser (TEI 49i #0932138786) after adjustment of the calibration settings (BKG 0.0, COEF 1.006).

Carbon Monoxide Measurements

Carbon monoxide measurements at Anmyeon-do were established in 1998, and continuous time series are available since the current WCC-Empa audit. Past data are currently being carefully reviewed and made available if possible.

Instrumentation. AMY is equipped with a Thermo TEI 48i-TLE NDIR instrument as well as with a Los Gatos LGR N_2O/CO-30-EP QCL analyser.

Standards. NDIR: KRISS CO in N_2 standard, 8008.5 ppm, which is diluted to 9.8 ppm with the TEI 146i calibrator. QCL: A set of NOAA standards is available. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 3 and 4 with respect to the WMO GAW DQOs (WMO, 2014):

TEI 48i-TLE #0706520050 (BKG 1.845, COEF 1.181):

Unbiased CO mixing ratio:	X_{CO} (ppb) = (CO + 42.2) / 1.0797	(2a)
Remaining standard uncertainty:	u_{CO} (ppb) = sqrt (183.7 ppb^2 + 1.01e-04 * X_{CO}^2)	(2b)

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

Unbiased CO mixing ratio:	X_{CO} (ppb) = (CO – 1.3) / 0.9963	(2c)
Remaining standard uncertainty:	u_{CO} (ppb) = sqrt (0.3 ppb^2 + 1.01e-04 * X_{CO}^2)	(2d)

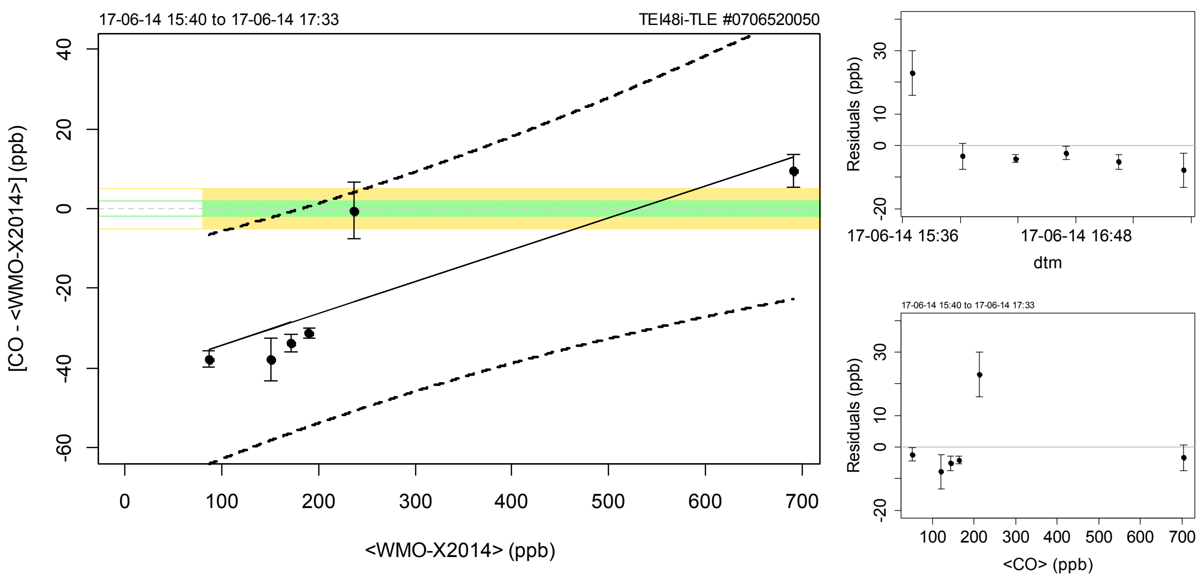

Figure 3. *Left: Bias of the AMY TEI 48i-TLE carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

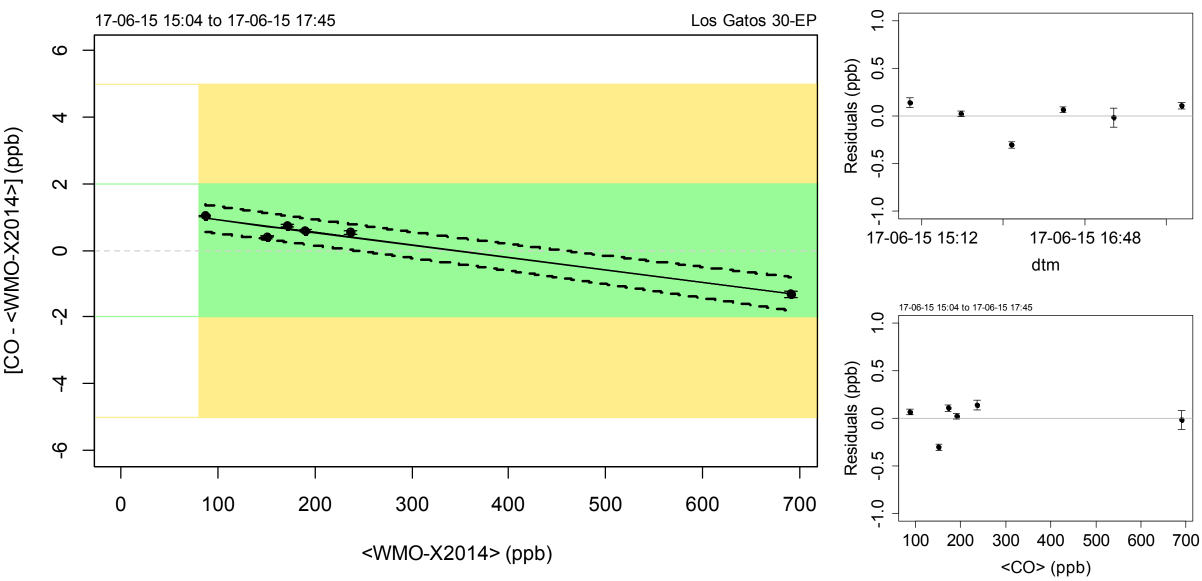

Figure 4. *Same as above, for the Picarro LGR N2O/CO-30-EP.*

The results of the comparisons can be summarised as follows:

The bias of the TEI 48i-TLE NDIR instrument was large and far outside the WMO/GAW DQOs, which is common for this particular type of analyser. The TEI 48i-TLE instrument is known for temperature dependent zero drift, as well as sensitivity to pressure changes and water vapour interference. Results might only be acceptable if the sample air is dried. Furthermore, care has to be taken that the pressure of the sample and calibration gas are the same. In case of unstable laboratory temperature, frequent zeroing is required. This has all not been implemented at AMY. The instrument is clearly not appropriate for CO measurements at a regional GAW station. Due to the availability of an alternative instrument (LGR N2O/CO-30-EP), this is not recommended to invest in the NDIR system.

In contrast, excellent results were obtained with the LGR N2O/CO-30-EP analyser. This instrument is state of the art, and only CO data from this instrument should be considered for future data submission.

Recommendation 12 (*, important, 2018)**
The audit showed that the TEI 48i-TLE instrument is not suitable for CO measurements with the current set-up.

Methane Measurements

Measurements of methane started in 1999, and data series are available since then. Initially, these measurements were made using a GC/FID system (Agilent 6890N) for CH_4. In 2011, a Picarro G2301 CRDS instrument was installed, and since the beginning of 2015, data of this instrument is considered for submission to the WMO/GAW data centre. Comparisons of the two different analytical systems for methane were published (KMA, 2013).

Instrumentation. Cavity Ring Down Spectroscopy (CRDS) (Picarro G2301) (since 2012). The instrumentation is adequate for CH_4 measurements.

Standards. NOAA standards are available at AMY. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instrument with randomised CH_4 levels from travelling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 5 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2301 #2490-CFKADS2216:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 7.2 ppb) / 0.9967 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.2 ppb^2 + 1.30e-07 * $X_{CH4}{}^2$) (3b)

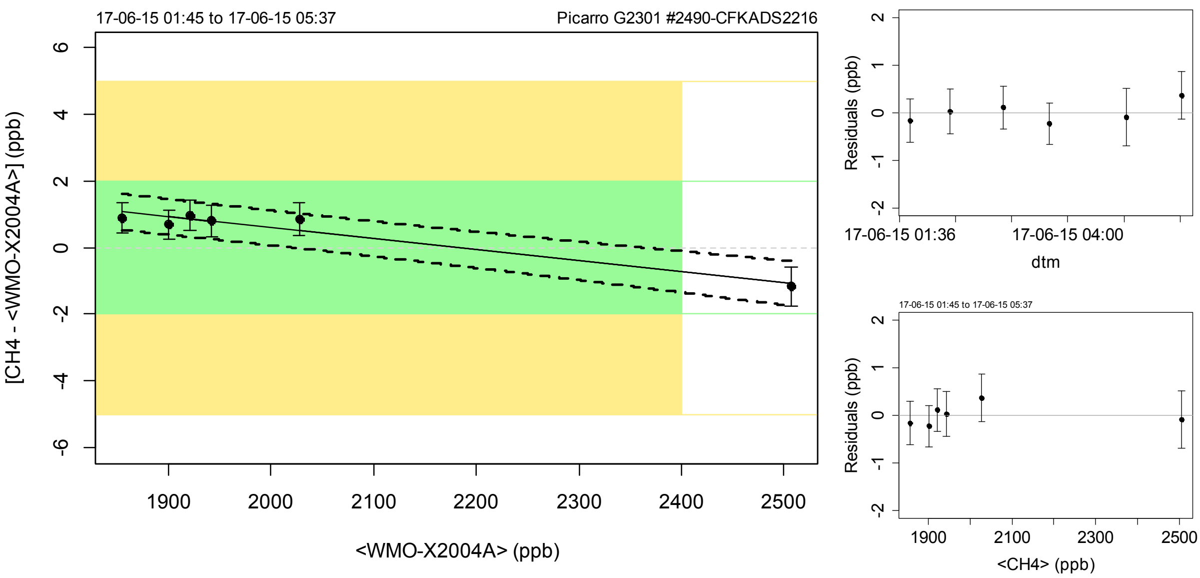

Figure 5. *Left: Bias of the* G2301 #2490-CFKADS2216 *methane instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The bias of the AMY CH_4 instrument was within the WMO/GAW compatibility goal over the entire relevant mole fraction range. This confirms that the instrumentation is fully adequate for CH_4 measurements, and no further action is required.

Carbon Dioxide Measurements

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

Instrumentation. Cavity Ring Down Spectroscopy (CRDS) (Picarro G2301) (since 2012). The instrumentation is adequate for CO_2 measurements.

Standards. NOAA standards are available at AMY. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instrument with randomised CO_2 levels from travelling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 6 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2301 #2490-CFKADS2216:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 1.27 ppm) / 0.99708 (4a)

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

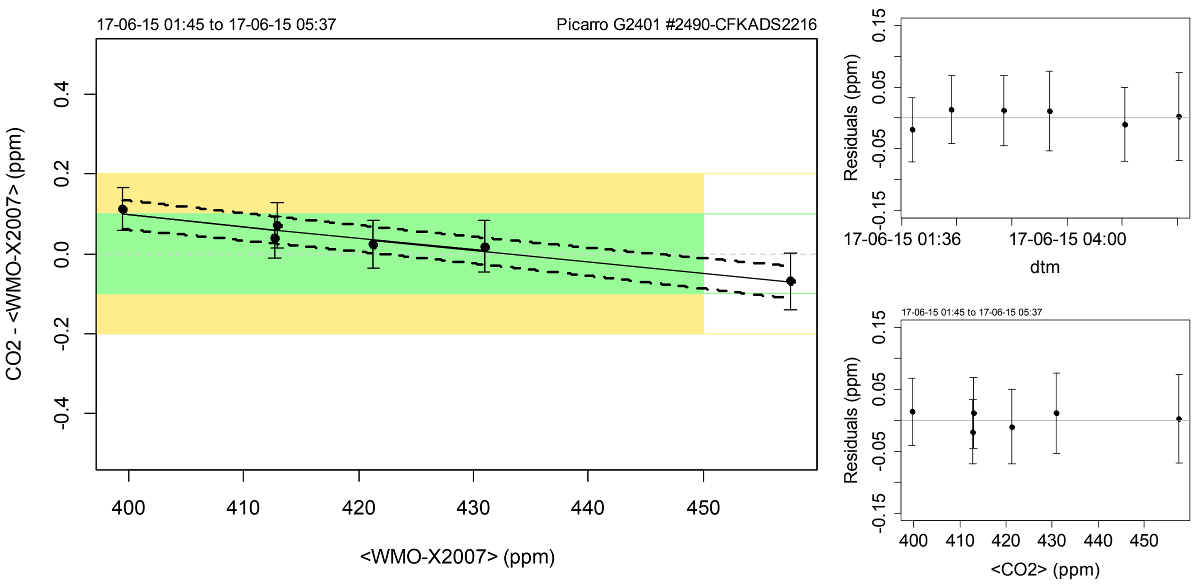

Figure 6. *Left: Bias of the PICARRO G2301 #2490-CFKADS2216 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The bias of the AMY methane instrument was within the WMO/GAW compatibility goal over the entire relevant mole fraction range. This confirms that the instrumentation is fully adequate for CO_2 measurements, and no further action is required. However, it should be considered to calibrate the zero offset of the instruments by determining the signal when measuring CO_2 free air and applying a user calibration. This has to be done only once, since the calibration of these instruments remains usually stable over time.

Recommendation 13 (*, minor, 2018)
It is recommended to apply an instrument specific CO_2 offset in the user calibration option of the Picarro instruments using CO_2 free air. Afterwards, the zero calibration should be checked at least once per year and adjusted if needed.

Nitrous Oxide Measurements

Measurements of nitrous oxide commenced at AMY in 1999, and continuous data series are available since then.

Instrumentation. Currently two instruments are available for N2O measurements. A gas chromatograph with Electron Capture Detector (GC/ECD), and a QCL laser spectrometer (Los Gatos 30-EP). The current instrumentation is adequate for N_2O measurement.

Standards. NOAA standards are available at AMY. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the AMY instruments with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 7 and 8 with respect to the WMO GAW DQOs (WMO, 2014):

GC/ECD instrument:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 30.38) / 0.9059 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.18 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

Los Gatos 30-EP:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O - 6.42) / 0.9809 (5c)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.04 ppb^2 + 1.01e-07 * X_{N2O}^2) (5d)

The result of the comparison can be summarised as follows:

Deviations from the WMO/GAW compatibility goals were found for both the GC/ECD and the QCL instruments but the results of the QCL system were significantly better compared to the GC instrument. On average, the QCL instrument was within the extended WMO/GAW compatibility goal. Compared to results at other GAW station, the deviation is small.

Recommendation 14 (*, minor, 2018)
The QCL instrumentation is fully adequate for N_2O measurements. Since the performance of the QCL analyser is significantly better compared to the CG/ECD instrument, it should be considered as the main AMY N_2O instrument.

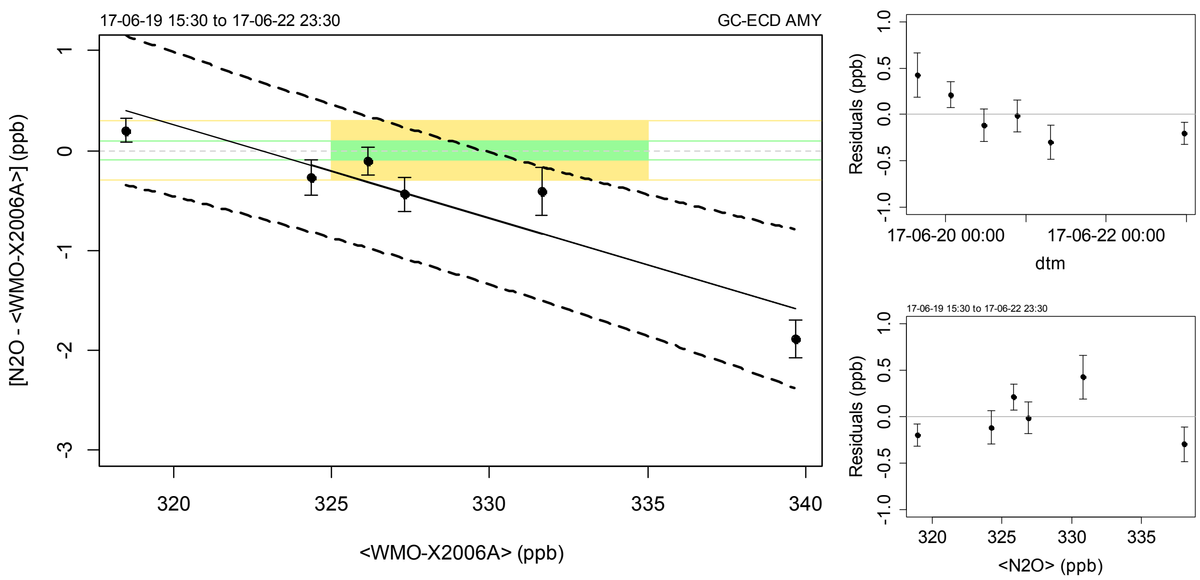

Figure 7. *Left: Bias of the AMY GC/ECD nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for AMY. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

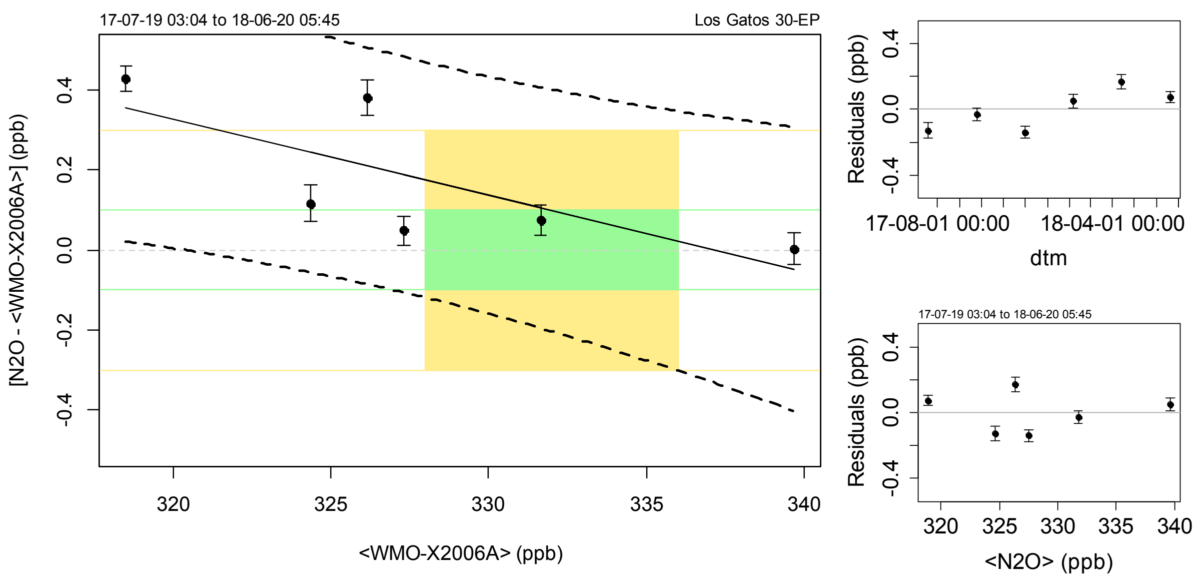

Figure 8. *Same as above for the AMY Los Gatos 30-EP nitrous oxide instrument.*

AMY PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the AMY performance audit to other station audits made by WCC-Empa. The method used to describe the results in context to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, 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 given in the recommendation of the GGMT-2015 meeting (WMO, 2016) for the greenhouse gases and CO and refer to conditions usually found in unpolluted air masses, and as 0 -100 ppb for surface ozone (Table 1). This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility goals in a certain mole fraction range. Figure 9 shows the bias vs. the slope of the performance audits audits made by WCC-Empa for CO, CH_4, CO_2 and N_2O, while the results for O_3 are shown in Figure 10. The grey dots show all comparison results 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. Figure 9 and 10 further highlight the results of the current audit (coloured dots), which are discussed below.

Figure 9 (top left) shows the CO bias at 165 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 2 ppb for the relevant range of CO, and the yellow area represents the extended compatibility goal of 5 ppb. To date, 22% of all CO audits complied with the 2 ppb goal, 22% met the 5 ppb goal, and 56% were exceeding the WMO/GAW compatibility goal in the relevant range. The AMY performance audit results are shown in the same graph as a red (TEI 48i-TLE) and blue (Los Gatos 30-EP) dot. The QCL system was entirely within the extended WMO/GAW compatibility goal, while the TEI 48i-TLE was clearly exceeding the goal. This demonstrates the far superior performance of the QCL instrument in comparison to the NDIR analyser.

Figure 9 (top right) shows the CH_4 bias at 1925 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 2 ppb for the relevant range of CH_4, and the yellow area represents the extended compatibility goal of 5 ppb. To date, 61% of all CH_4 audits complied with the 2 ppb goal, 30% met the 5 ppb goal, and 9% were exceeding the WMO/GAW compatibility goal in the relevant range. The AMY performance audit results are shown in the same graph as a blue dot. The result of the AMY performance audit fully complies with the WMO/GAW compatibility goal.

Figure 9 (bottom left) shows the CO_2 bias at 415 ppm vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 0.1 ppm for the relevant range of CO_2, and the yellow area represents the extended compatibility goal of 0.2 ppm. To date, 34% of all CO_2 audits complied with the 0.1 ppm goal, 25% met the 0.2 ppm goal, and 41 % were exceeding the WMO/GAW compatibility goal in the relevant range. The AMY performance audit result is shown in the same graph as a blue dot. The result of the AMY performance audit complies with the extended WMO/GAW compatibility goal of 0.2 ppm over the entire relevant range.

Figure 9 (bottom right) shows the N_2O bias at 330 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 0.1 ppb for the relevant range of N_2O, and the yellow area represents the extended compatibility goal of 0.3 ppb. To date, none of the WCC-Empa N_2O audits complied with the 0.1 ppb goal, while 38% met the 0.3 ppb goal, and 62 % were exceeding the WMO/GAW compatibility goal in the relevant range. The AMY performance audit results are shown in the same graph as red (GC/ECD) and blue (QCL) dots. The result of the AMY performance audit complies with the extended

WMO/GAW compatibility goal of 0.3 ppb over the entire relevant range for the QCL instrument, while the GC/ECD was not able to meet the WMO/GAW compatibility goals.

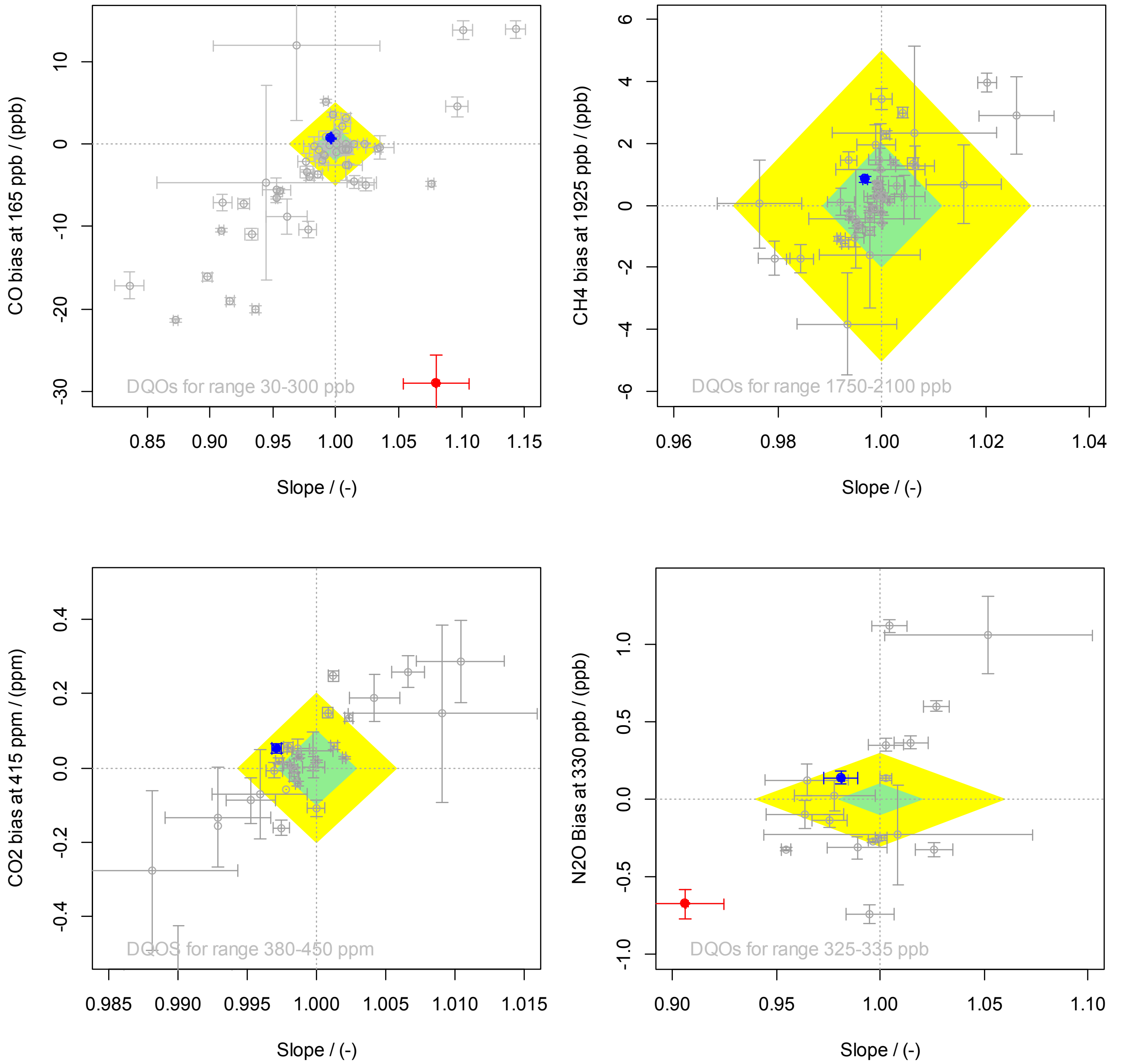

Figure 9. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to the results of all performance audits made until now, while the coloured dots show AMY results. Blue dots: AMY QCL instrument for N_2O and CO, Picarro for CH_4 and CO_2. Red dots: NDIR instrument for CO, GC/ECD for N_2O. The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

Figure 10 shows surface ozone audit results by WCC-Empa from 1996 until 2017. The green area corresponds to the data quality objective of 1 ppb (WMO, 2013) in the range of 0 – 100 ppb O_3. To date, 54% of all ozone audits complied with this goal. The AMY results are shown in the same graph as a red dot (before adjustment of the calibration settings) and blue dots (after adjustment). The results of the AMY ozone instrument with the new calibration settings meet the WMO/GAW compatibility goals in the range 0 – 100 ppb ozone, while they were significantly exceeded before adjustment.

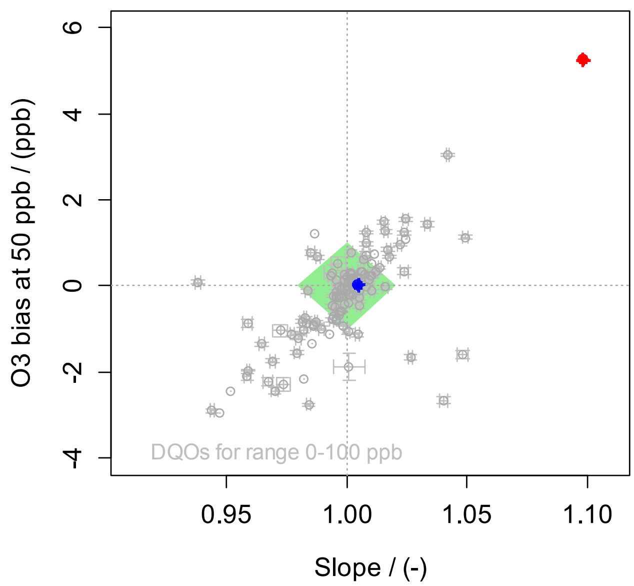

Figure 10. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to the results of all performance audits made until now, while the coloured dots show AMY results (red: TEI 49i before adjustments of the calibration settings, blue: TEI 49i after adjustment). The green area corresponds to the WMO/GAW compatibility goal.*

Table 1. Relevant mole fraction range for different parameters.

Compound	**Range**	**Unit**
CO	30 - 300	ppb
CH_4	1750 - 2100	ppb
CO_2	380 - 450	ppm
N_2O	325 - 335	ppb
O_3	0 -100	ppb

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 SN # 1497-CFKADS2098). The TI was running from 31 July 2017 through 5 September 2017. The TI was connected to a spare sample port of the AMY manifold (description see above). The TI was sampling using the following sequence: 1740 min ambient air followed by 30 min measurement of three standard gases (10 min each). To account for the effect of water vapour a correction function (Rella et al., 2013; Zellweger et al., 2012) was applied to the TI data. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below.

Carbon Monoxide:

Figure 11 shows the comparison of hourly CO data of the AMY TEI 48i-TLE NDIR instrument with the TI, and Figure 12 shows the comparison of the Los Gatos 30-EP QCL analyser with the TI. One hourly averages are shown for both comparisons. The corresponding deviation histograms are shown in Figure 13.

The median bias was within the WMO/GAW compatibility goal of 2 ppb for the Los Gatos 30-EP instrument, which confirms the good agreement found during the comparisons of the performance audit. The TEI 48i-TLE however was on average measuring 20 ppb higher compared to the WCC-Empa TI, with a high variability. This confirms that the TEI 48i-TLE is highly sensitive to temperature and pressure changes. As recommended above, only the data of the Los Gatos instrument should be considered for data submission.

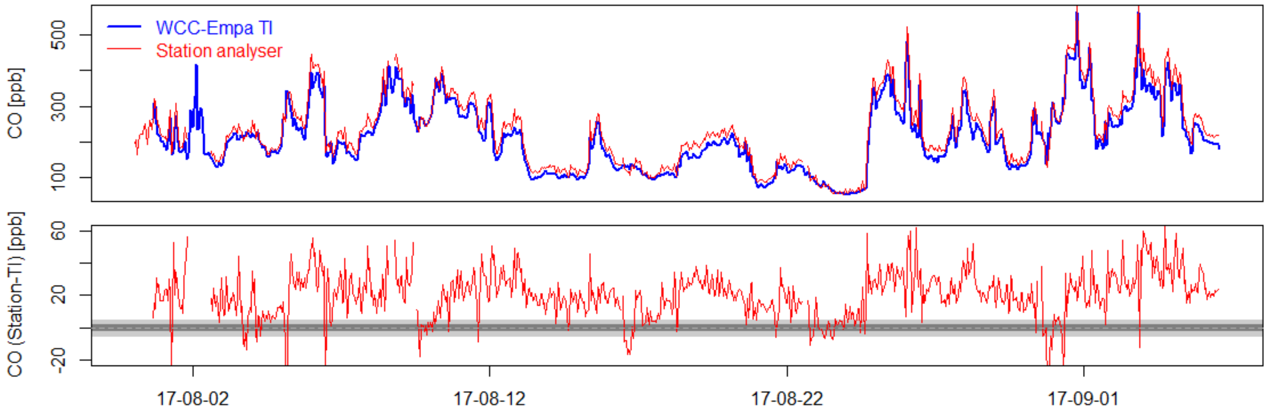

Figure 11. CO comparison at AMY between the WCC-Empa travelling instrument and the AMY TEI 48i-TLE. Upper panel: CO time series (1 h data). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

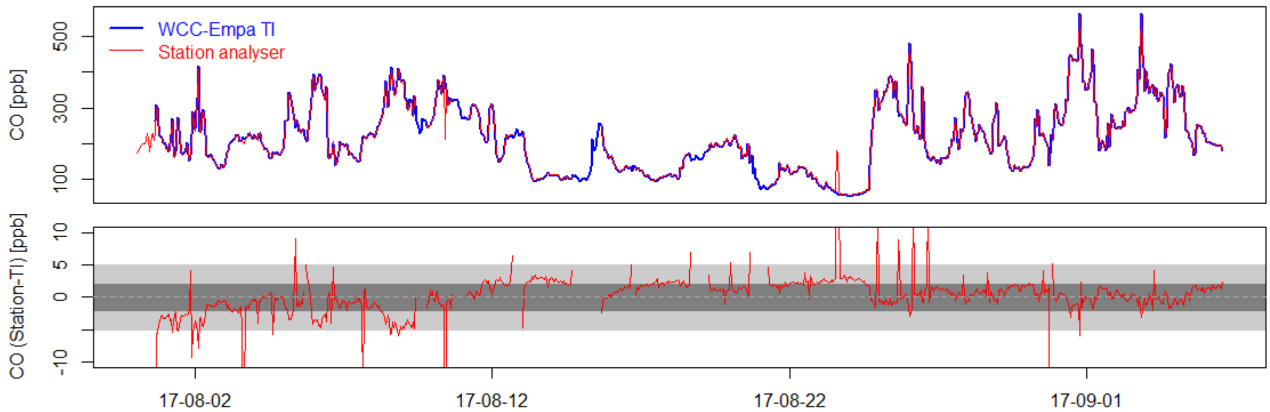

Figure 12. CO comparison at AMY between the WCC-Empa travelling instrument and the AMY Los Gatos 30-EP QCL instrument. Upper panel: CO time series (1 h data). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

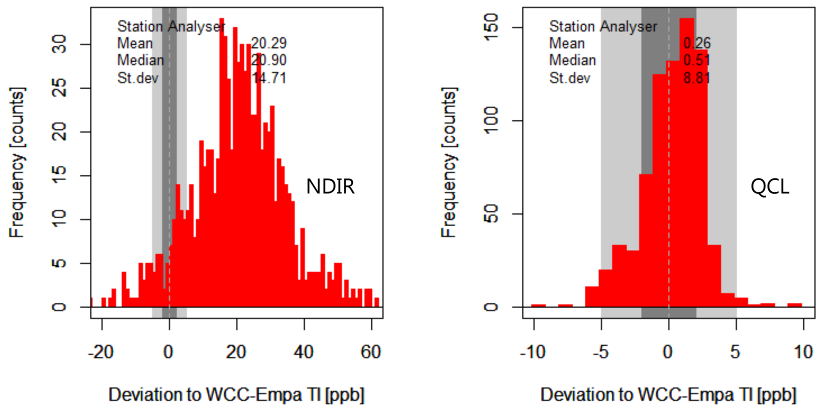

Figure 13. CO deviation histograms (1 h data, station analyser – TI) for the AMY TEI 48i-TLE (left) and for the AMY Los Gatos 30-EP instrument (right).

Methane and Carbon Dioxide:

Figure 14 and 15 show the comparison of hourly CH_4 and CO_2 data of the AMY Picarro G2301 instrument with the TI. The corresponding deviation histograms are shown in Figure 16.

Good agreement was found between the AMY Picarro G2301 and the WCC-Empa TI for both CH_4 and CO_2, with a median bias of the AMY instrument of +0.01 ppb for CH_4, and -0.01 ppm for CO_2. This is well within the WMO/GAW compatibility goals of 2 ppb (CH_4) and 0.1 ppm (CO_2). The temporal variation was also well captured by both instruments. The results confirm the good agreement observed during the performance audit and demonstrate that the whole measurement set-up is appropriate. No further action is required.

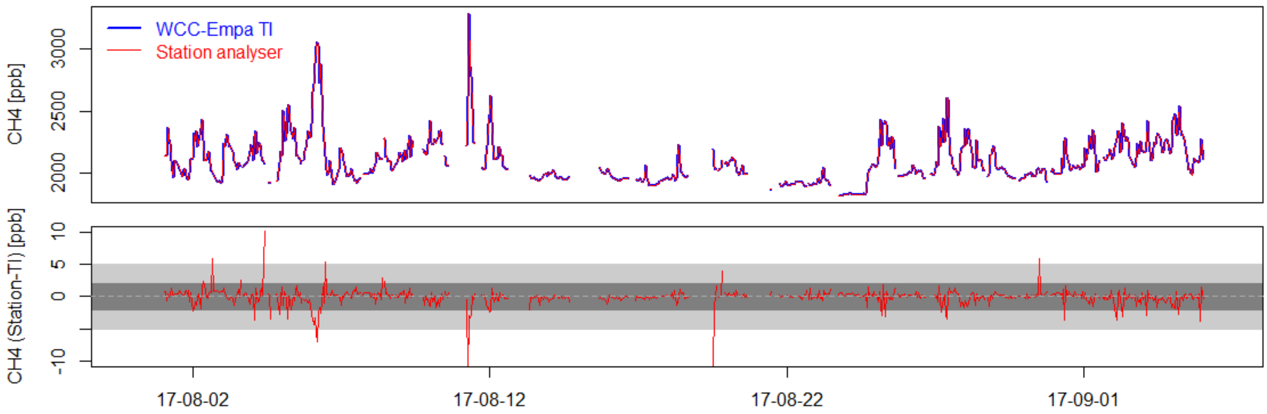

Figure 14. CH_4 comparison at AMY between the WCC-Empa travelling instrument and the AMY Picarro G2301. Upper panel: CH_4 time series (1 h data). Lower panel: CH_4 bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

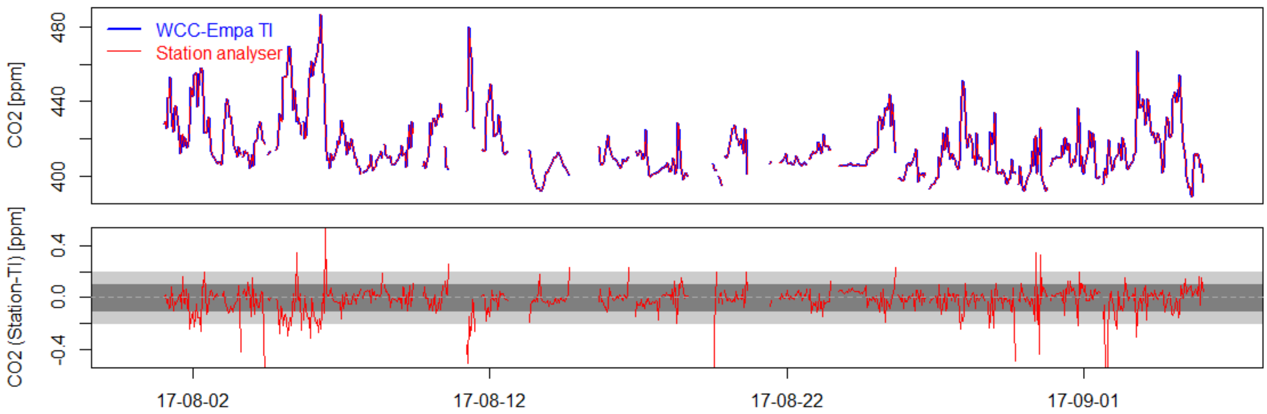

Figure 15. Same as above for CO_2.

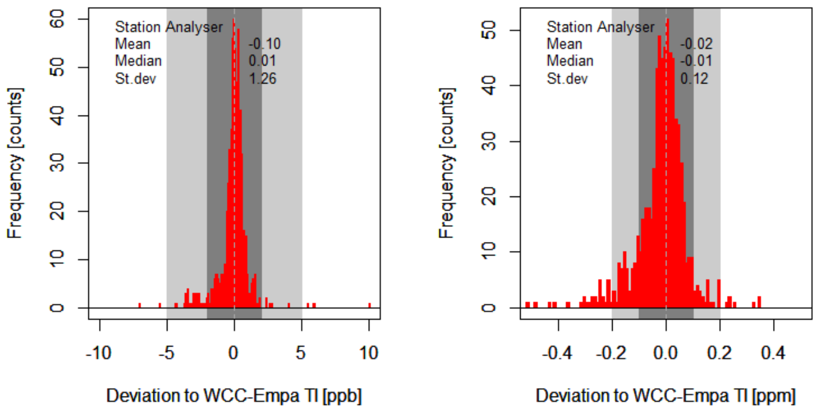

Figure 16. CH_4 (left) and CO_2 (right) deviation histograms (1 h data, station analyser – TI) for the AMY Picarro G2301.

Discussion of the ambient air comparison results

The ambient air comparison confirmed the results of the performance audit. Agreement within the WMO/GAW compatibility goals was found for all parameters for the median of the hourly bias for the AMY Picarro and Los Gatos analysers. However, the NDIR CO instrument was not meeting the compatibility goals, which has also been seen during the performance audit.

CONCLUSIONS

The regional GAW station Anmyeon-do is located at a very important location for the GAW programme, which makes the available data a very significant contribution. Significant progress has been made since the last audit by WCC-Empa in 2014 with regard to data submission. However, some of the submitted data needs to be re-assessed.

Most assessed measurements were of high data quality and met the WMO/GAW compatibility or extended compatibility goals in the relevant mole fraction range. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals.

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 X indicates results outside the compatibility goals.

Comparison type	O_3 initial	O_3 final	CO NDIR	CO QCL	CH_4	CO_2	N_2O GC/ECD	N_2O QCL
Performance audit with TS	✗ #	✓ *	✗	✓	✓	✓	(✓)	✓
Ambient air comparison	NA	NA	✗	✓	✓	✓		NA

NA no ambient air comparison was made for ozone and nitrous oxide
\# Initial comparison before adjustment of the calibration settings.
* Final comparison with new calibration settings.

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

SUMMARY RANKING OF THE ANMYEON-DO GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access by road.
Facilities		
Laboratory and office space	(5)	Adequate, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable with very few power cuts
General Management and Operation		
Organisation	(5)	Well-coordinated
Competence of staff	(4)	Skilled staff, further training with respect to reactive gases needed
Air Inlet System	(4)	Adequate but prone to leakage due to the drying system for GHG
Instrumentation		
Ozone	(5)	Adequate instrumentation
CO/N_2O (Los Gatos 30-EP)	(5)	Adequate instrumentation
CO (TEI 48i-TLE)	(2)	Drifting due to pressure and temperature sensitivity
N_2O (GC/ECD)	(3)	Performs not as good as QCL
CH_4 / CO_2 (Picarro G2301)	(5)	Adequate instrumentation
Standards		
Ozone	(0)	No standard available
CO, CO_2, CH_4, N_2O	(5)	NOAA standards / working standards available
Data Management		
Data acquisition	(4)	Fully adequate system except for ozone with manual data download
Data processing	(3)	Experienced staff, but re-processing of some data series is needed
Data submission	(2)	Data submission has been made for all parameters except for CO. Data are partly not plausible.

#0: inadequate thru 5: adequate.

Dübendorf, January 2018

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APPENDIX

Data Review

The following figures show summary plots of AMY data accessed on 3 October 2017 from WDCGG (CH4 and CO_2). The plots show time series of daily data, frequency distribution, diurnal and seasonal variations.

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

Ozone:

- Data has not been submitted, and therefore no review is possible. Ozone data (since the current audit) will be made available soon, and older data is currently reviewed.

Methane:

- Data set looks generally sound except for several periods in 2009 and 2010 with clearly invalid data.
- Therefore, the whole data series need to be re-checked, with a focus on the low values in 2009/10. This has already been done, which is reflected in the newer versions shown below.

Carbon dioxide:

- Data set looks generally sound.
- Seasonal cycle and trend looks plausible.

Nitrous oxide:

- The data set in general does not look plausible.
- The whole data set needs to be revised. In the meantime, data should be withdrawn from WDCGG. This was done immediately after communication to the station staff, and this version of the data set is no longer accessible from WDCGG. Since the data was not valid and needs further review, it is not shown here.

Carbon monoxide:

- Data has not been submitted, and therefore no review is possible.

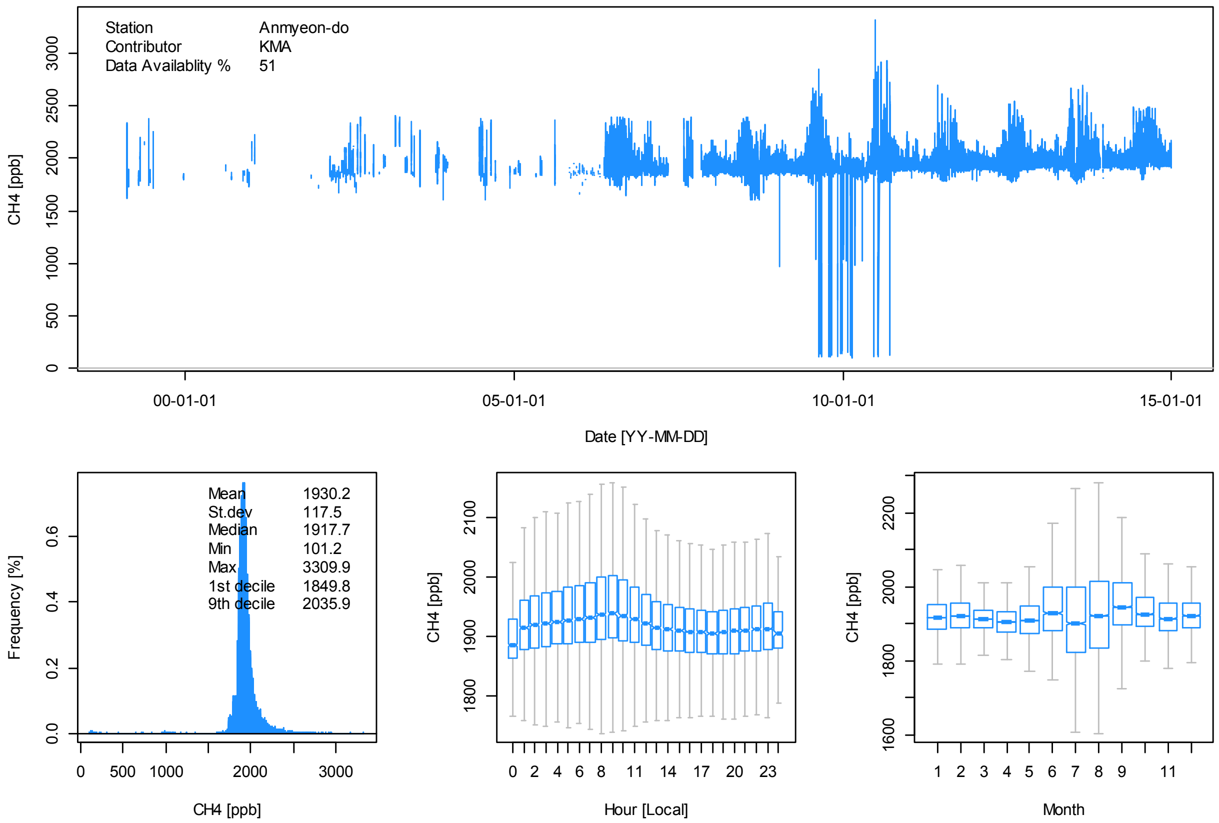


Figure 17. *CH_4 data accessed from WDCGG (3 October 2017). Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Middle: Diurnal variation. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

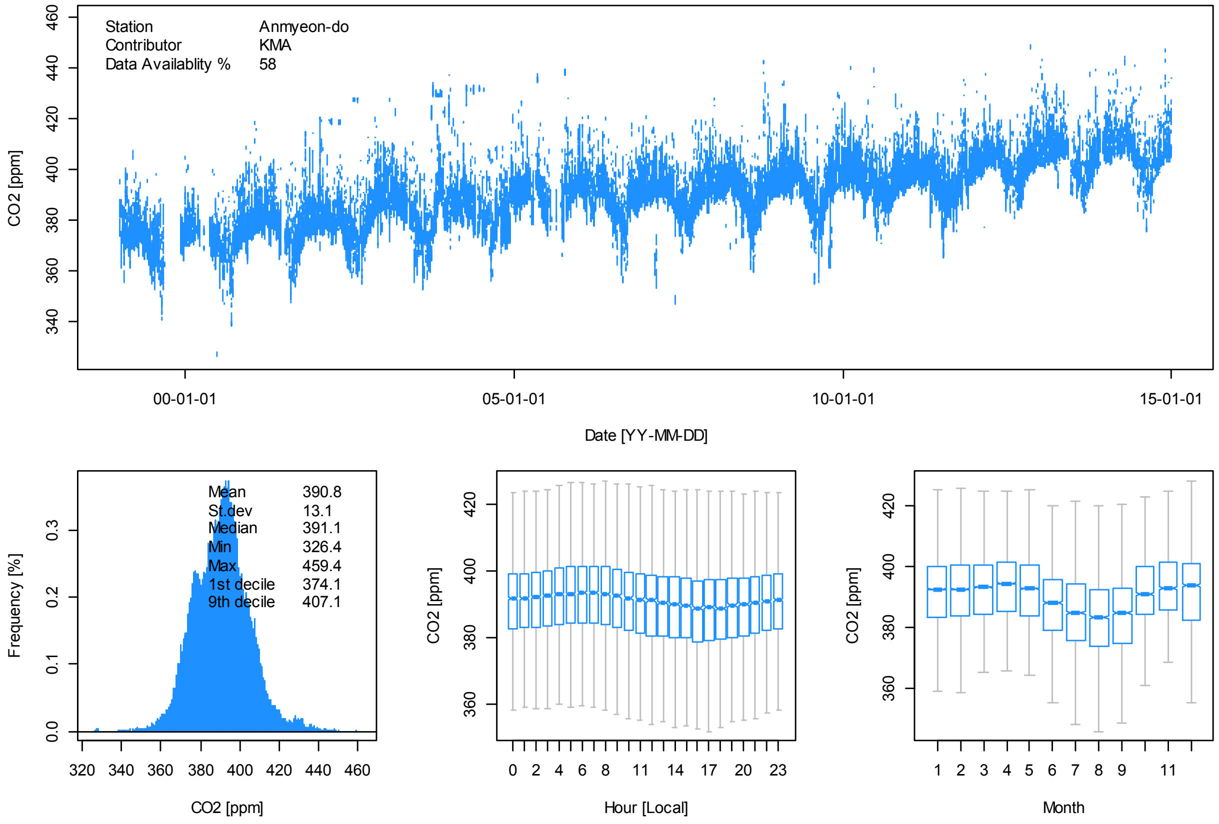


Figure 18. *Same as above for CO_2.*

The GHG data set was then removed from WDCGG, and only daily averages were available. Data accessed on 17 November 2017 from WDCGG (CH4, CO2 and N2O) are shown in the following figures. The plots show time series of daily data, frequency distribution and seasonal variations.

The main findings for this new data set can be summarised as follows:

Methane:

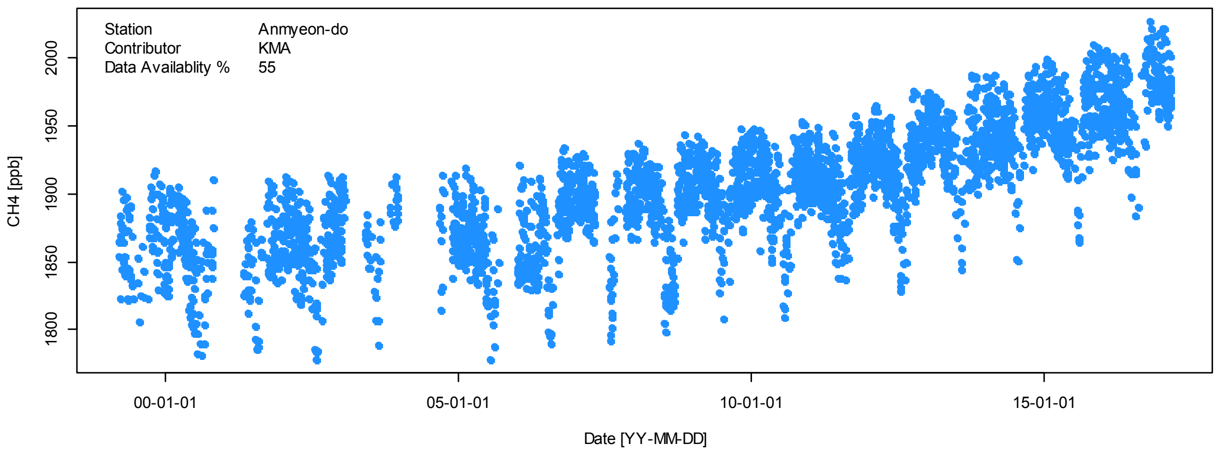
- Data set looks generally sound, but from comparison with other available data (parallel measurements by WCC-Empa in 2014 and 2017, NOAA flasks) it is clear that the data is filtered.
- Even though data processing method is mentioned in metadata of WDCGG, the entire hourly data set, without filtering and including valid data of high mole fraction, must be made available.

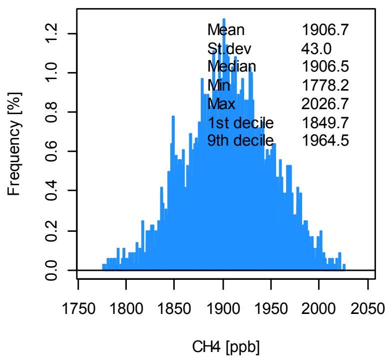
Carbon dioxide:

- Same as for CH_4. Data seems to be filtered, days with high CO_2 mole fractions were removed from the data set.
- Even though data processing method is mentioned in metadata of WDCGG, the entire hourly data set, without filtering and including valid data of high mole fraction, must be made available.

Nitrous oxide:

- Data seems to be filtered, with a time dependent lower and upper cut off.
- Hourly data needs to be submitted.





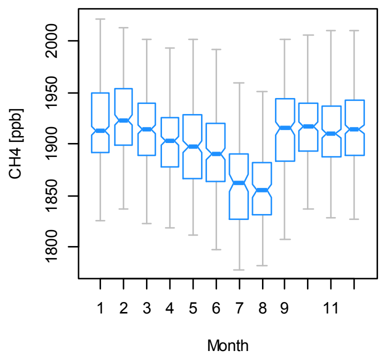


Figure 19. *CH_4 data accessed from WDCGG (17 November 2017). Top: Time series, daily averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

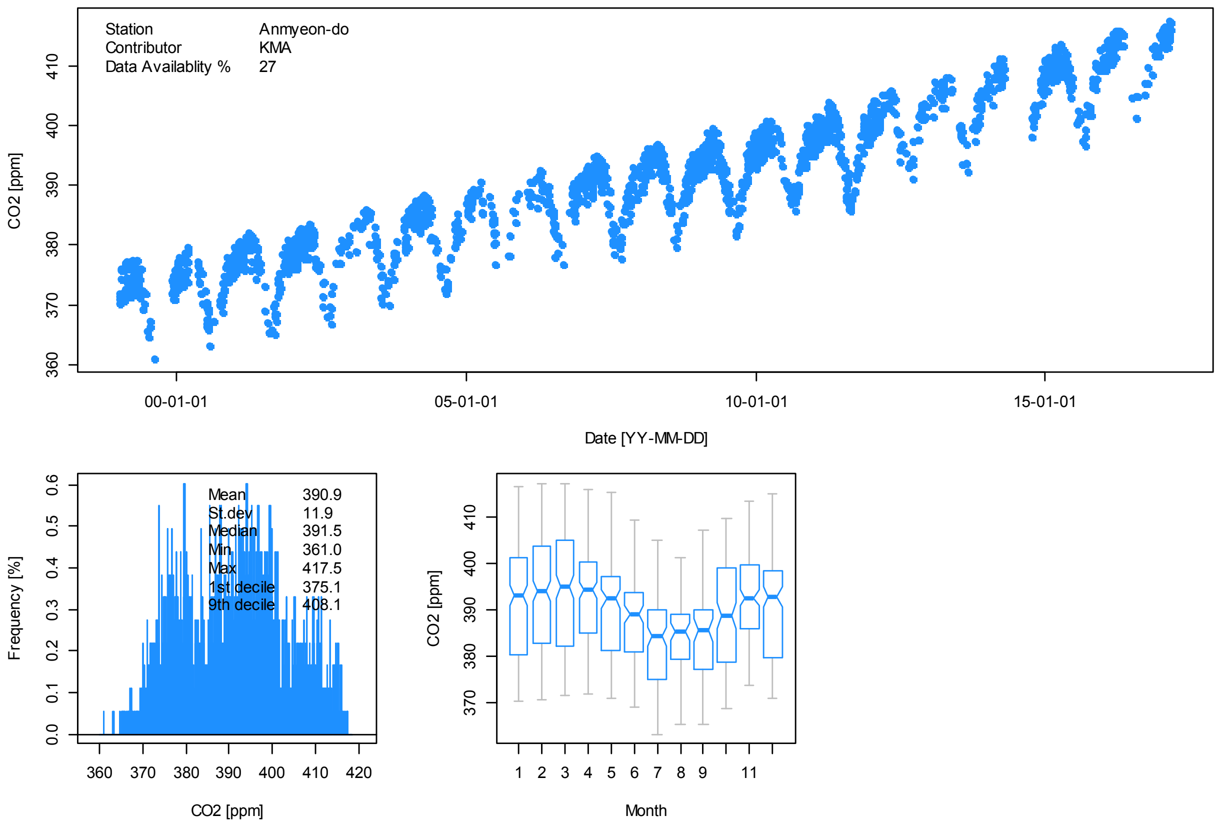


Figure 20. *Same as above for CO_2.*

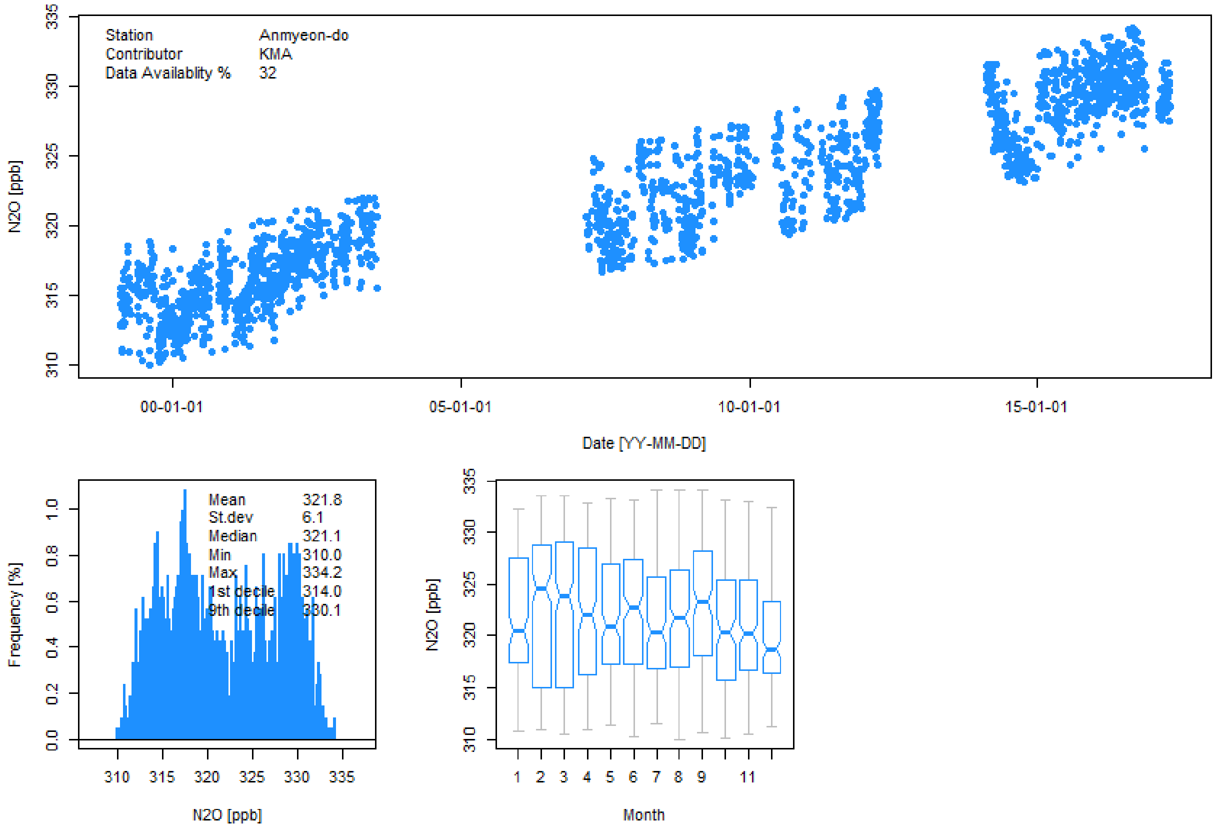


Figure 21. *Same as above for N_2O.*

The CH_4 and CO_2 data sets described above were also removed from WDCGG after communication to KMA, and re-submission was made shortly afterwards. The new data set accessed on 15 January 2018 contained again hourly values. The following plots show time series of daily data, frequency distribution, and diurnal and seasonal variations.

The main findings for this new data set can be summarised as follows:

Methane:

- Data set looks generally sound.

Carbon dioxide:

- Data set looks generally sound.
- Seasonal cycle and trend looks plausible.

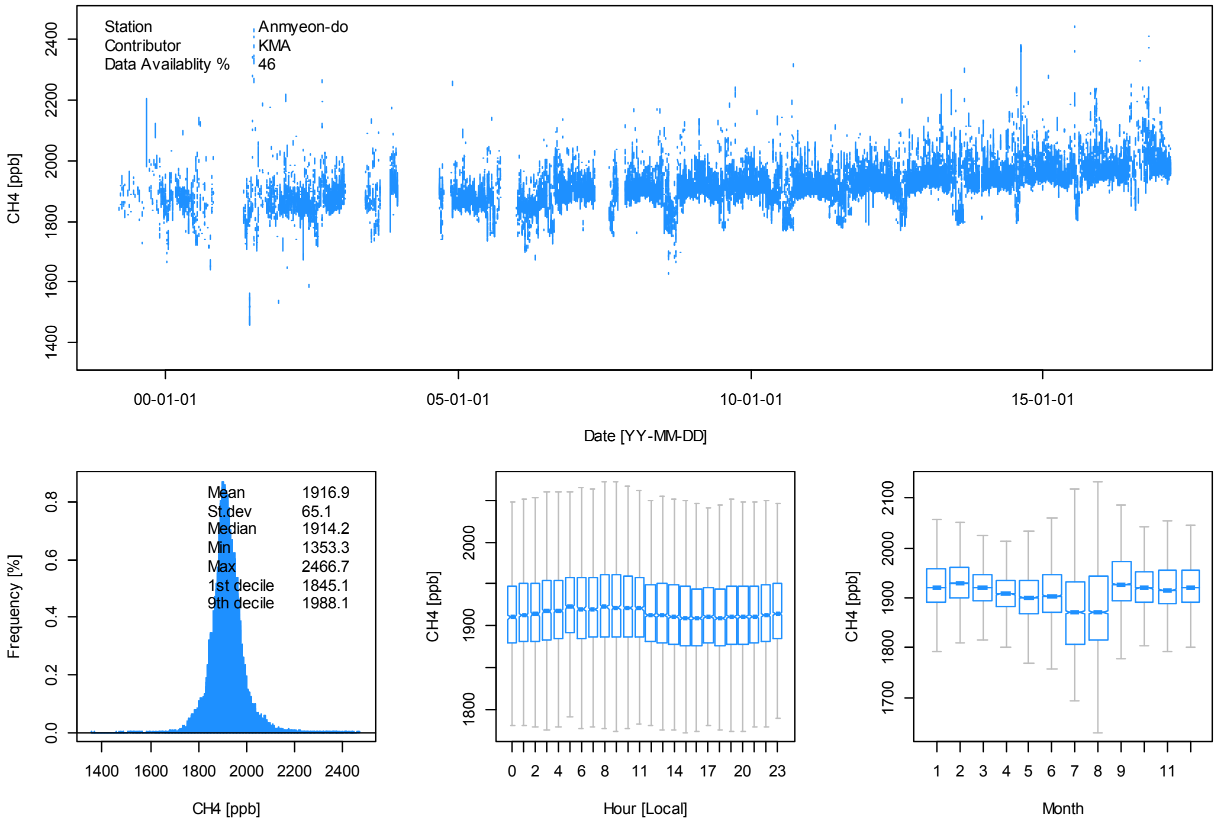


Figure 22. *CH_4 data accessed from WDCGG (15 January 2018). Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Middle: Diurnal variation. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

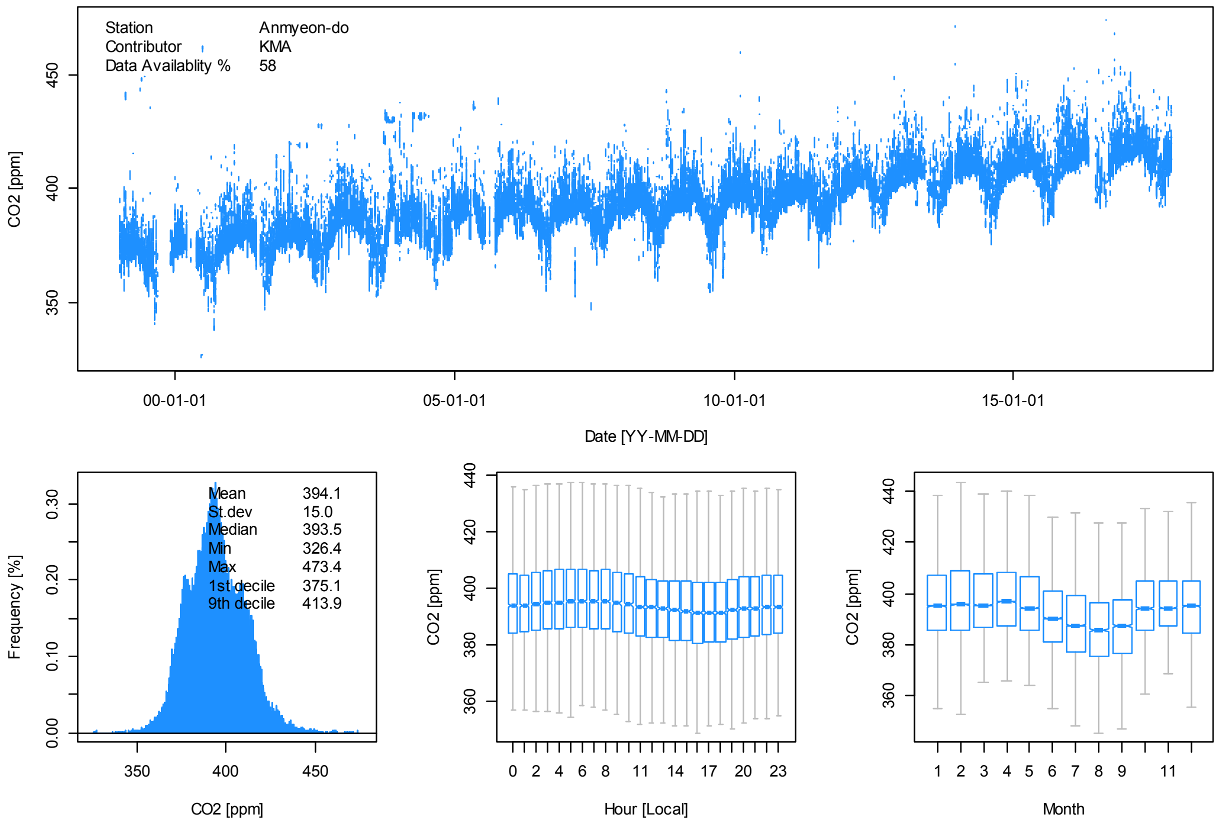


Figure 23. *Same as above for CO_2.*

Surface Ozone Comparisons

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

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. Zero air was generated using a custom built zero air generator (Nafion drier, activated charcoal, Purafil). 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 data acquisition system.

Table 3. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
Settings	BKG -0.3, COEF 1.009
Pressure readings (mmHg)	Ambient 760.1; TS 754.7 (adjusted to ambient)
Station analyser (OA)	
Model, S/N	TEI 49i #0932138786
Principle	UV absorption
Range	0-1 ppm
Settings	Initial: BKG -0.5 ppb, COEF 1.081 Final: BKG +0.0 ppb, COEF 1.006
Pressure readings (hPa)	Ambient 760.1; OA 747.1 (adjusted to ambient for the second comparison with new calibration settings)

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 readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

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 AMY ozone analyser (OA) TEI 49i #0932138786 (initial comparison, BKG -0.5, COEF 1.081) with the WCC-Empa travelling standard (TS).

Date - Time (UTC+9)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2017-06-14 12:24	1	0	0.24	0.87	0.03	0.08	0.63	NA
2017-06-14 12:39	1	50	50.59	55.95	0.04	0.10	5.36	10.6
2017-06-14 12:54	1	90	90.52	99.32	0.10	0.10	8.80	9.7
2017-06-14 13:09	1	20	20.44	22.90	0.05	0.09	2.46	12.0
2017-06-14 13:24	1	70	70.83	78.16	0.17	0.21	7.33	10.3
2017-06-14 13:39	1	80	80.25	88.23	0.06	0.10	7.98	9.9

Date - Time (UTC+9)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2017-06-14 13:54	1	10	10.61	12.25	0.09	0.10	1.64	15.5
2017-06-14 14:09	1	40	39.81	44.09	0.08	0.10	4.28	10.8
2017-06-14 14:24	1	60	60.02	66.30	0.12	0.11	6.28	10.5
2017-06-14 14:39	2	0	0.09	0.67	0.04	0.04	0.58	NA
2017-06-14 14:54	2	100	100.00	109.82	0.08	0.08	9.82	9.8
2017-06-14 15:09	2	25	25.06	27.98	0.08	0.11	2.92	11.7
2017-06-14 15:24	2	200	199.56	219.32	0.07	0.05	19.76	9.9
2017-06-14 15:39	2	150	149.82	164.85	0.09	0.16	15.03	10.0
2017-06-14 15:54	2	50	50.08	55.33	0.10	0.11	5.25	10.5
2017-06-14 16:09	2	175	174.65	191.79	0.06	0.14	17.14	9.8
2017-06-14 16:24	2	125	124.88	137.41	0.09	0.07	12.53	10.0
2017-06-14 16:39	2	75	75.05	82.82	0.06	0.10	7.77	10.4
2017-06-14 16:54	3	0	0.09	0.64	0.06	0.10	0.55	NA
2017-06-14 17:09	3	40	39.97	44.32	0.05	0.10	4.35	10.9
2017-06-14 17:24	3	80	79.84	87.90	0.05	0.07	8.06	10.1
2017-06-14 17:39	3	10	10.18	11.70	0.13	0.12	1.52	14.9
2017-06-14 17:54	3	30	29.91	33.17	0.09	0.08	3.26	10.9
2017-06-14 18:09	3	90	89.79	98.80	0.13	0.22	9.01	10.0
2017-06-14 18:24	3	60	59.97	66.13	0.12	0.09	6.16	10.3
2017-06-14 18:39	3	20	20.06	22.50	0.05	0.09	2.44	12.2
2017-06-14 18:54	3	50	49.84	55.04	0.12	0.13	5.20	10.4
2017-06-14 19:09	3	70	69.87	77.00	0.10	0.06	7.13	10.2
2017-06-14 19:24	4	0	0.07	0.56	0.09	0.08	0.49	NA
2017-06-14 19:39	4	50	49.88	55.18	0.09	0.12	5.30	10.6
2017-06-14 19:54	4	90	89.81	98.88	0.07	0.06	9.07	10.1
2017-06-14 20:09	4	20	20.14	22.30	0.14	0.09	2.16	10.7
2017-06-14 20:24	4	70	69.79	77.03	0.10	0.15	7.24	10.4
2017-06-14 20:39	4	80	79.88	87.85	0.05	0.18	7.97	10.0
2017-06-14 20:54	4	10	10.21	11.70	0.15	0.06	1.49	14.6
2017-06-14 21:09	4	40	39.88	44.20	0.09	0.06	4.32	10.8
2017-06-14 21:24	4	60	59.82	66.04	0.13	0.08	6.22	10.4
2017-06-14 21:39	5	0	0.11	0.46	0.10	0.08	0.35	NA
2017-06-14 21:54	5	100	99.78	109.88	0.09	0.23	10.10	10.1
2017-06-14 22:09	5	25	25.01	28.02	0.11	0.08	3.01	12.0
2017-06-14 22:24	5	200	199.65	219.17	0.08	0.11	19.52	9.8
2017-06-14 22:39	5	150	149.61	164.56	0.09	0.09	14.95	10.0
2017-06-14 22:54	5	50	50.00	55.06	0.19	0.10	5.06	10.1
2017-06-14 23:09	5	175	174.48	192.00	0.06	0.13	17.52	10.0
2017-06-14 23:24	5	125	124.80	137.33	0.04	0.10	12.53	10.0
2017-06-14 23:39	5	75	74.89	82.53	0.05	0.17	7.64	10.2
2017-06-14 23:54	6	0	-0.09	0.62	0.05	0.13	0.71	NA
2017-06-15 00:09	6	40	39.87	44.09	0.07	0.10	4.22	10.6
2017-06-15 00:24	6	80	79.79	88.02	0.05	0.10	8.23	10.3
2017-06-15 00:39	6	10	10.23	11.58	0.14	0.10	1.35	13.2
2017-06-15 00:54	6	30	29.79	33.18	0.11	0.05	3.39	11.4
2017-06-15 01:09	6	90	89.80	98.89	0.13	0.18	9.09	10.1
2017-06-15 01:24	6	60	59.85	66.00	0.09	0.18	6.15	10.3
2017-06-15 01:39	6	20	20.01	22.47	0.05	0.14	2.46	12.3

Date - Time (UTC+9)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2017-06-15 01:54	6	50	49.93	54.93	0.05	0.05	5.00	10.0
2017-06-15 02:09	6	70	69.79	76.98	0.07	0.03	7.19	10.3
2017-06-15 02:24	7	0	0.01	0.51	0.07	0.04	0.50	NA
2017-06-15 02:39	7	50	49.90	55.06	0.10	0.15	5.16	10.3
2017-06-15 02:54	7	90	89.79	99.04	0.08	0.11	9.25	10.3
2017-06-15 03:09	7	20	20.08	22.58	0.14	0.12	2.50	12.5
2017-06-15 03:24	7	70	69.76	76.92	0.06	0.10	7.16	10.3
2017-06-15 03:39	7	80	79.83	88.05	0.14	0.04	8.22	10.3
2017-06-15 03:54	7	10	10.28	11.62	0.25	0.14	1.34	13.0
2017-06-15 04:09	7	40	39.81	44.06	0.16	0.16	4.25	10.7
2017-06-15 04:24	7	60	59.89	66.05	0.12	0.05	6.16	10.3
2017-06-15 04:39	8	0	-0.03	0.36	0.10	0.14	0.39	NA
2017-06-15 04:54	8	100	99.77	110.03	0.06	0.18	10.26	10.3
2017-06-15 05:09	8	25	24.99	27.79	0.06	0.09	2.80	11.2
2017-06-15 05:24	8	200	199.40	219.20	0.07	0.15	19.80	9.9
2017-06-15 05:39	8	150	149.58	164.57	0.12	0.16	14.99	10.0
2017-06-15 05:54	8	50	49.97	55.18	0.06	0.12	5.21	10.4
2017-06-15 06:09	8	175	174.49	191.90	0.08	0.19	17.41	10.0
2017-06-15 06:24	8	125	124.81	137.11	0.09	0.18	12.30	9.9
2017-06-15 06:39	8	75	74.91	82.65	0.10	0.14	7.74	10.3
2017-06-15 06:54	9	0	0.01	0.49	0.04	0.12	0.48	NA
2017-06-15 07:09	9	40	39.84	44.05	0.08	0.09	4.21	10.6
2017-06-15 07:24	9	80	79.76	88.12	0.11	0.03	8.36	10.5
2017-06-15 07:39	9	10	10.34	11.72	0.14	0.32	1.38	13.3
2017-06-15 07:54	9	30	29.88	33.25	0.10	0.07	3.37	11.3
2017-06-15 08:09	9	90	89.84	98.84	0.11	0.08	9.00	10.0
2017-06-15 08:24	9	60	59.90	66.16	0.14	0.09	6.26	10.5
2017-06-15 08:39	9	20	20.02	22.58	0.04	0.07	2.56	12.8
2017-06-15 08:54	9	50	49.94	54.97	0.08	0.10	5.03	10.1

Table 5. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the AMY ozone analyser (OA) TEI 49i #0932138786 (final comparison, BKG 0.0, COEF 1.006) with the WCC-Empa travelling standard (TS).

Date - Time (UTC+9)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2017-06-15 11:03	1	0	-0.02	0.00	0.09	0.10	0.02	NA
2017-06-15 11:18	1	50	49.85	50.10	0.08	0.07	0.25	0.5
2017-06-15 11:33	1	90	89.84	90.11	0.10	0.10	0.27	0.3
2017-06-15 11:48	1	20	20.05	20.09	0.04	0.09	0.04	0.2
2017-06-15 12:03	1	70	69.84	70.06	0.07	0.09	0.22	0.3
2017-06-15 12:18	1	80	79.87	79.96	0.04	0.18	0.09	0.1
2017-06-15 12:33	1	10	10.27	10.28	0.11	0.11	0.01	0.1
2017-06-15 12:48	1	40	39.98	40.07	0.04	0.18	0.09	0.2
2017-06-15 13:03	1	60	59.88	60.06	0.13	0.14	0.18	0.3
2017-06-15 13:18	2	0	-0.01	-0.07	0.08	0.11	-0.06	NA
2017-06-15 13:33	2	100	99.74	99.84	0.11	0.08	0.10	0.1

Date - Time (UTC+9)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2017-06-15 13:48	2	25	24.99	24.96	0.13	0.14	-0.03	-0.1
2017-06-15 14:03	2	200	199.47	200.04	0.10	0.09	0.57	0.3
2017-06-15 14:18	2	150	149.74	150.15	0.08	0.12	0.41	0.3
2017-06-15 14:33	2	50	49.99	50.08	0.12	0.07	0.09	0.2
2017-06-15 14:48	2	175	174.59	175.03	0.11	0.07	0.44	0.3
2017-06-15 15:03	2	125	124.69	124.97	0.10	0.09	0.28	0.2
2017-06-15 15:18	2	75	74.86	75.05	0.09	0.08	0.19	0.3
2017-06-15 15:33	3	0	-0.04	-0.02	0.09	0.13	0.02	NA
2017-06-15 15:48	3	40	39.89	40.00	0.07	0.07	0.11	0.3
2017-06-15 16:03	3	80	79.84	79.99	0.16	0.15	0.15	0.2
2017-06-15 16:18	3	10	10.24	10.22	0.06	0.08	-0.02	-0.2
2017-06-15 16:33	3	30	29.93	29.62	0.13	0.08	-0.31	-1.0
2017-06-15 16:48	3	90	89.76	89.96	0.08	0.08	0.20	0.2
2017-06-15 17:03	3	60	59.84	60.03	0.08	0.15	0.19	0.3
2017-06-15 17:18	3	20	20.01	19.96	0.13	0.12	-0.05	-0.2
2017-06-15 17:33	3	50	49.85	49.78	0.05	0.10	-0.07	-0.1
2017-06-15 17:48	3	70	69.85	69.94	0.16	0.09	0.09	0.1
2017-06-15 18:03	4	0	-0.04	-0.14	0.17	0.10	-0.10	NA
2017-06-15 18:18	4	50	49.86	49.55	0.11	0.07	-0.31	-0.6
2017-06-15 18:33	4	90	89.74	90.00	0.07	0.12	0.26	0.3
2017-06-15 18:48	4	20	20.06	19.75	0.03	0.08	-0.31	-1.5
2017-06-15 19:03	4	70	69.78	69.93	0.08	0.06	0.15	0.2
2017-06-15 19:18	4	80	79.84	79.82	0.05	0.06	-0.02	0.0
2017-06-15 19:33	4	10	10.22	10.13	0.12	0.13	-0.09	-0.9
2017-06-15 19:48	4	40	39.81	39.91	0.07	0.09	0.10	0.3
2017-06-15 20:03	4	60	59.91	59.89	0.06	0.08	-0.02	0.0
2017-06-15 20:18	5	0	-0.04	-0.11	0.10	0.10	-0.07	NA
2017-06-15 20:33	5	100	99.76	100.12	0.05	0.15	0.36	0.4
2017-06-15 20:48	5	25	24.97	24.95	0.12	0.05	-0.02	-0.1
2017-06-15 21:03	5	200	199.56	200.05	0.17	0.18	0.49	0.2
2017-06-15 21:18	5	150	149.61	150.14	0.08	0.17	0.53	0.4
2017-06-15 21:33	5	50	49.97	49.93	0.07	0.16	-0.04	-0.1
2017-06-15 21:48	5	175	174.58	174.97	0.11	0.12	0.39	0.2
2017-06-15 22:03	5	125	124.71	125.16	0.09	0.07	0.45	0.4
2017-06-15 22:18	5	75	75.03	75.09	0.05	0.06	0.06	0.1
2017-06-15 22:33	6	0	-0.09	-0.08	0.11	0.09	0.01	NA
2017-06-15 22:48	6	40	39.84	40.01	0.11	0.11	0.17	0.4
2017-06-15 23:03	6	80	79.88	79.88	0.10	0.13	0.00	0.0
2017-06-15 23:18	6	10	10.26	10.15	0.13	0.11	-0.11	-1.1
2017-06-15 23:33	6	30	29.85	29.92	0.08	0.12	0.07	0.2
2017-06-15 23:48	6	90	89.80	89.89	0.10	0.11	0.09	0.1
2017-06-16 00:03	6	60	59.94	59.79	0.06	0.05	-0.15	-0.3
2017-06-16 00:18	6	20	19.93	19.98	0.08	0.08	0.05	0.3
2017-06-16 00:33	6	50	49.95	49.97	0.07	0.05	0.02	0.0
2017-06-16 00:48	6	70	69.90	69.81	0.13	0.10	-0.09	-0.1
2017-06-16 01:03	7	0	-0.14	-0.08	0.08	0.08	0.06	NA
2017-06-16 01:18	7	50	49.85	50.07	0.10	0.03	0.22	0.4
2017-06-16 01:33	7	90	89.91	89.91	0.09	0.05	0.00	0.0

Date - Time (UTC+9)	**Run #**	**Level (ppb)**	**TS (ppb)**	**OA (ppb)**	**sdTS (ppb)**	**sdOA (ppb)**	**OC-TS (ppb)**	**OC-TS (%)**
2017-06-16 01:48	7	20	20.03	19.95	0.07	0.11	-0.08	-0.4
2017-06-16 02:03	7	70	69.81	69.89	0.12	0.09	0.08	0.1
2017-06-16 02:18	7	80	79.86	79.99	0.08	0.07	0.13	0.2
2017-06-16 02:33	7	10	10.30	10.12	0.13	0.09	-0.18	-1.7
2017-06-16 02:48	7	40	39.77	39.99	0.04	0.16	0.22	0.6
2017-06-16 03:03	7	60	59.94	59.99	0.06	0.11	0.05	0.1
2017-06-16 03:18	8	0	0.09	-0.19	0.14	0.09	-0.28	NA
2017-06-16 03:33	8	100	99.77	99.95	0.06	0.23	0.18	0.2
2017-06-16 03:48	8	25	24.91	25.04	0.08	0.08	0.13	0.5
2017-06-16 04:03	8	200	199.54	199.69	0.12	0.14	0.15	0.1
2017-06-16 04:18	8	150	149.72	150.16	0.13	0.06	0.44	0.3
2017-06-16 04:33	8	50	50.07	50.22	0.04	0.13	0.15	0.3
2017-06-16 04:48	8	175	174.52	174.92	0.03	0.28	0.40	0.2
2017-06-16 05:03	8	125	124.77	125.05	0.07	0.06	0.28	0.2
2017-06-16 05:18	8	75	74.88	75.13	0.09	0.06	0.25	0.3
2017-06-16 05:33	9	0	-0.07	-0.09	0.06	0.10	-0.02	NA
2017-06-16 05:48	9	40	39.91	39.65	0.12	0.13	-0.26	-0.7
2017-06-16 06:03	9	80	79.80	79.92	0.11	0.13	0.12	0.2
2017-06-16 06:18	9	10	10.13	10.13	0.04	0.09	0.00	0.0
2017-06-16 06:33	9	30	29.94	29.70	0.14	0.28	-0.24	-0.8
2017-06-16 06:48	9	90	89.73	89.86	0.09	0.02	0.13	0.1
2017-06-16 07:03	9	60	59.92	59.99	0.13	0.21	0.07	0.1
2017-06-16 07:18	9	20	20.12	19.96	0.07	0.06	-0.16	-0.8
2017-06-16 07:33	9	50	49.89	50.00	0.08	0.10	0.11	0.2

Carbon Monoxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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 6 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the AMY data acquisition system. The standards used for the calibration of the AMY analyser are shown in Table 7.

Table 6. Experimental details of AMY 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 21.	
Station Analyser AMY (AL)	
Model, S/N	TEI48i-TLE #0706520050
Principle	NDIR / gas filter correlation
Drying system	none
Station Analyser AMY (AL)	
Model, S/N	Los Gatos 30-EP
Principle	QCL
Drying system	Cryo trap (-80°C)
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports

Table 7. CO Standards available at AMY.

Cylinder ID	Manufacturer	Use	CO	Scale
KRISS (high CO)	KRISS	TEI 48i-TLE, dilution	8005.5 ppm	KRISS, 1% uncert.
CB11394	NOAA/ESRL	Los Gatos 30-EP	137.27 ppb	WMO-CO-X2014A

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 8. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the TEI 48I-TLE #0706520050 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 (%)
(17-06-14 15:40:00)	160622_FA02474	236.3	0.1	235.8	7.0	3	-0.5	-0.2
(17-06-14 16:01:00)	150601_FA02466	691.6	0.2	701.1	4.1	3	9.5	1.4
(17-06-14 16:23:00)	160825_FB03887	190.3	0.1	159.1	1.2	3	-31.2	-16.4
(17-06-14 16:44:00)	160926_FB03367	86.1	0.2	48.4	2.1	3	-37.8	-43.8
(17-06-14 17:06:00)	160825_FB03365	171.7	0.7	138.0	2.2	3	-33.7	-19.6
(17-06-14 17:33:00)	130819_FB03853	150.9	0.6	112.9	5.4	3	-38.0	-25.2

Table 9. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Los Gatos 30-EP 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 (%)
(17-06-15 15:04:57)	160622_FA02474	236.3	0.1	236.9	0.1	68	0.6	0.2
(17-06-15 15:35:01)	160825_FB03887	190.3	0.1	190.9	0.0	67	0.6	0.3
(17-06-15 16:04:59)	130819_FB03853	150.9	0.6	151.3	0.0	67	0.4	0.3
(17-06-15 16:35:10)	160926_FB03367	86.1	0.2	87.2	0.0	66	1.0	1.2
(17-06-15 17:04:57)	150601_FA02466	691.6	0.2	690.3	0.1	68	-1.3	-0.2
(17-06-15 17:45:03)	160825_FB03365	171.7	0.7	172.5	0.0	68	0.8	0.4

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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 10 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the AMY data acquisition system. The standards used for the calibration of the AMY analyser are shown in Table 11.

Table 10. Experimental details of AMY 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 21.	
Station Analyser AMY (AL)	
Model, S/N	Picarro G2301 #2490-CFKADS2216
Principle	CRDS
Drying system	Cryo trap (-80°C)
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports

The standards used for the calibration of the AMY analyser are shown in Table 11.

Table 11. CH_4 Standards available at AMY.

Cylinder ID	Manufacturer	Use	CH_4 (ppb)	Scale
CB09838	NOAA/ESRL	LS	1673.89	WMO-X2004A
CB09738	NOAA/ESRL	LS	1874.89	WMO-X2004A
CB09906	NOAA/ESRL	LS	1995.39	WMO-X2004A
CB09734	NOAA/ESRL	LS	1810.43	WMO-X2004A
CB10932	NOAA/ESRL	LS	1710.62	WMO-X2004A
CB10922	NOAA/ESRL	LS	1904.00	WMO-X2004A
CB10982	NOAA/ESRL	LS	2005.10	WMO-X2004A
CB11151	NOAA/ESRL	LS	2227.96	WMO-X2004A

Results

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

Table 12. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2301 #2490-CFKADS2216 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 (%)
(17-06-15 01:45:00)	160926_FB03367	1855.03	0.07	1855.94	0.45	541	0.91	0.05
(17-06-15 02:19:30)	130819_FB03853	1942.25	0.12	1943.06	0.47	984	0.81	0.04
(17-06-15 03:05:01)	160825_FB03365	1920.93	0.14	1921.89	0.45	539	0.96	0.05
(17-06-15 03:44:31)	150601_FA02466	1900.46	0.05	1901.15	0.43	492	0.69	0.04
(17-06-15 04:50:07)	160622_FA02474	2506.99	0.11	2505.82	0.60	546	-1.17	-0.05
(17-06-15 05:37:29)	160825_FB03887	2027.15	0.16	2028.02	0.49	293	0.87	0.04

Carbon Dioxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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.

The Picarro G2301 described above is also used for CO_2 measurements. The standards used for the calibration of the AMY analyser are shown in Table 13.

Table 13. CO_2 Standards available at AMY.

Cylinder ID	Manufacturer	Use	CO_2 (ppm)	Scale
CB09838	NOAA/ESRL	LS	351.72	WMO-X2007A
CB09738	NOAA/ESRL	LS	410.93	WMO-X2007A
CB09906	NOAA/ESRL	LS	448.67	WMO-X2007A
CB09734	NOAA/ESRL	LS	381.11	WMO-X2007A
CB10932	NOAA/ESRL	LS	351.29	WMO-X2007A
CB10922	NOAA/ESRL	LS	389.84	WMO-X2007A
CB10982	NOAA/ESRL	LS	410.68	WMO-X2007A
CB11151	NOAA/ESRL	LS	453.94	WMO-X2007A

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 Picarro G2301 #2490-CFKADS2216 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 (%)
(17-06-15 01:45:00)	160926_FB03367	412.70	0.04	412.74	0.05	541	0.04	0.01
(17-06-15 02:19:30)	130819_FB03853	399.52	0.03	399.63	0.05	984	0.11	0.03
(17-06-15 03:05:01)	160825_FB03365	412.92	0.03	412.99	0.06	539	0.07	0.02
(17-06-15 03:44:31)	150601_FA02466	430.95	0.03	430.97	0.06	492	0.02	0.00
(17-06-15 04:50:07)	160622_FA02474	421.29	0.03	421.31	0.06	546	0.02	0.00
(17-06-15 05:37:29)	160825_FB03887	457.60	0.01	457.53	0.07	293	-0.07	-0.02

Nitrous Oxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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 10 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the AMY data acquisition system. The standards used for the calibration of the AMY analyser are shown in Table 16.

Table 15. Experimental details of AMY N_2O comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 21.	
Station Analyser AMY (AL)	
Model, S/N	Agilent GC/ECD System
Principle	GC/ECD
Drying system	Cryo trap (-80°C)
Station Analyser AMY (AL)	
Model, S/N	Los Gatos 30-EP
Principle	QCL
Drying system	Cryo trap (-80°C)
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports

Table 16. N_2O Standards available at AMY.

Cylinder ID	Manufacturer	Use	N_2O (ppb)	Scale
CB10848	NOAA/ESRL	LS	323.20	WMO-X2004A
CB10922	NOAA/ESRL	LS	327.30	WMO-X2004A
CB10982	NOAA/ESRL	LS	336.94	WMO-X2004A
CB11151	NOAA/ESRL	LS	340.50	WMO-X2004A
CB1139	NOAA/ESRL	LS	329.05	WMO-X2004A

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

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(17-06-19 15:30:00)	160825_FB03887	331.65	0.03	331.24	0.24	4	-0.41	-0.12
(17-06-20 01:30:00)	150601_FA02466	326.16	0.01	326.05	0.14	4	-0.11	-0.03
(17-06-20 11:30:00)	160622_FA02474	324.37	0.01	324.11	0.18	4	-0.26	-0.08
(17-06-20 21:30:00)	130819_FB03853	327.31	0.01	326.87	0.17	4	-0.44	-0.13
(17-06-21 07:30:00)	160926_FB03367	339.69	0.02	337.80	0.19	4	-1.89	-0.56
(17-06-22 23:30:00)	160825_FB03365	318.51	0.01	318.71	0.12	4	0.20	0.06

Table 18. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Los Gatos 30-EP instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(17-07-19 03:04:57)	160622_FA02474	324.37	0.01	324.49	0.05	68	0.12	0.04
(17-09-24 15:35:01)	160825_FB03887	331.65	0.03	331.73	0.04	67	0.08	0.02
(17-11-30 16:04:59)	130819_FB03853	327.31	0.01	327.36	0.04	67	0.05	0.02
(18-02-05 04:35:10)	160926_FB03367	339.69	0.02	339.69	0.04	66	0.00	0.00
(18-04-13 05:04:57)	150601_FA02466	326.16	0.01	326.54	0.04	68	0.38	0.12
(18-06-20 05:45:03)	160825_FB03365	318.51	0.01	318.94	0.03	68	0.43	0.14

WCC-Empa Traveling Standards

Ozone

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

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

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

Zero air source: Pressurized air – 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 19. 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] + 0.13 ppb) / 1.0021 (6a)

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

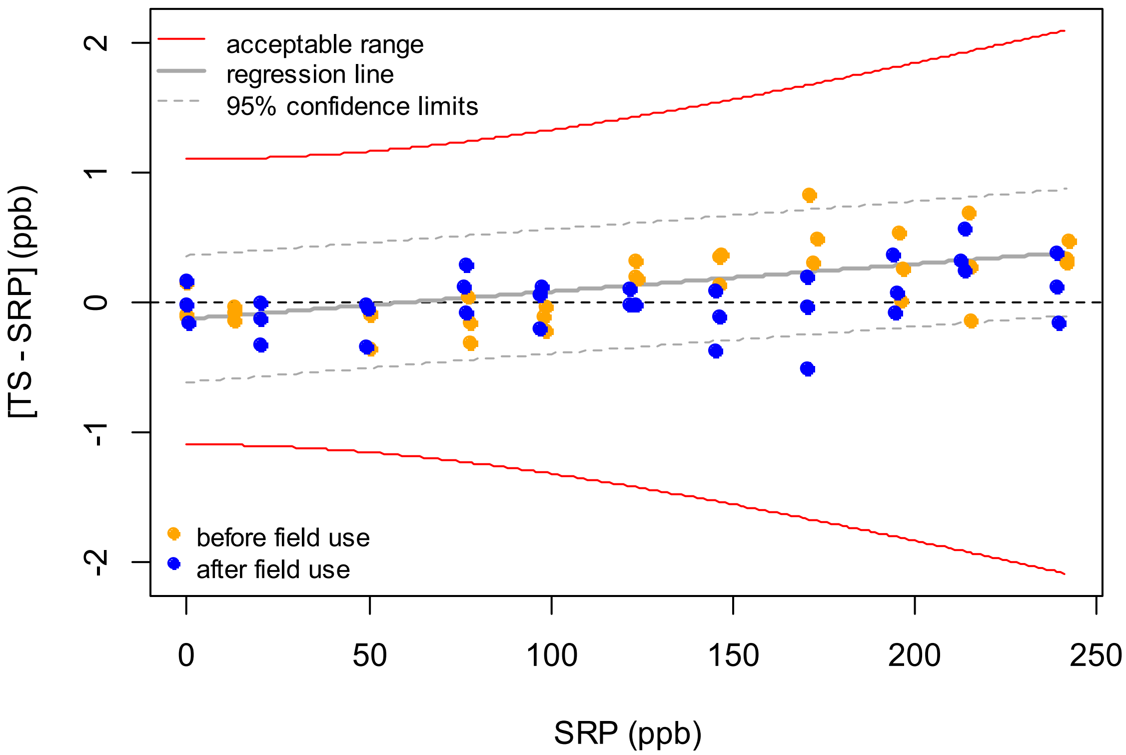


Figure 24. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 19. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2017-05-10	1	0	-0.11	0.17	-0.23	0.12
2017-05-10	1	175	173.24	0.43	173.73	0.27
2017-05-10	1	195	196.58	0.27	196.83	0.22
2017-05-10	1	75	77.36	0.22	77.41	0.11
2017-05-10	1	50	50.14	0.19	50.07	0.14
2017-05-10	1	125	123.10	0.34	123.43	0.18
2017-05-10	1	100	98.05	0.31	97.94	0.16
2017-05-10	1	215	215.32	0.22	215.60	0.19
2017-05-10	1	145	145.93	0.17	146.28	0.17
2017-05-10	1	15	13.11	0.31	12.97	0.17
2017-05-10	1	240	241.90	0.54	242.38	0.79
2017-05-10	2	215	215.07	0.54	214.93	0.21
2017-05-10	2	15	13.01	0.33	12.97	0.10
2017-05-10	2	125	123.62	0.23	123.79	0.23
2017-05-10	2	170	171.66	0.30	171.96	0.18
2017-05-10	2	145	146.08	0.30	146.22	0.19
2017-05-10	2	195	195.82	0.27	195.84	0.20
2017-05-10	2	75	77.42	0.27	77.10	0.24
2017-05-10	2	50	50.03	0.35	49.68	0.16
2017-05-10	2	100	98.51	0.18	98.28	0.12
2017-05-10	2	0	0.00	0.16	-0.10	0.13
2017-05-10	2	240	241.33	0.28	241.63	0.30
2017-05-10	3	125	122.99	0.24	123.19	0.08
2017-05-10	3	80	77.53	0.35	77.38	0.07
2017-05-10	3	50	50.02	0.24	49.92	0.10
2017-05-10	3	215	214.62	0.41	215.32	0.18
2017-05-10	3	195	195.56	0.23	196.09	0.17
2017-05-10	3	170	170.87	0.08	171.70	0.12
2017-05-10	3	0	-0.16	0.17	-0.02	0.10
2017-05-10	3	100	98.76	0.29	98.73	0.13
2017-05-10	3	145	146.47	0.34	146.83	0.18
2017-05-10	3	15	13.28	0.35	13.19	0.17
2017-05-10	3	240	241.70	0.68	242.03	0.79
2017-10-03	4	75	76.50	0.26	76.79	0.06
2017-10-03	4	50	49.66	0.29	49.61	0.07
2017-10-03	4	0	-0.20	0.25	-0.04	0.08
2017-10-03	4	125	123.38	0.51	123.35	0.22
2017-10-03	4	215	213.78	0.30	214.34	0.20
2017-10-03	4	145	145.24	0.28	145.33	0.12
2017-10-03	4	95	97.12	0.33	97.25	0.17
2017-10-03	4	170	170.03	0.36	170.23	0.32
2017-10-03	4	20	20.27	0.25	19.93	0.09
2017-10-03	4	195	194.92	0.14	194.99	0.31
2017-10-03	4	240	238.85	0.27	238.98	0.12
2017-10-03	5	75	76.58	0.28	76.50	0.05
2017-10-03	5	195	194.21	0.45	194.13	0.22
2017-10-03	5	50	49.44	0.24	49.10	0.13
2017-10-03	5	20	20.15	0.27	20.03	0.09
2017-10-03	5	170	170.36	0.26	169.85	0.15
2017-10-03	5	0	0.02	0.34	-0.01	0.11

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2017-10-03	5	215	213.54	0.48	213.78	0.63
2017-10-03	5	145	145.11	0.30	144.74	0.18
2017-10-03	5	120	121.71	0.38	121.69	0.12
2017-10-03	5	95	97.03	0.23	96.82	0.13
2017-10-03	5	240	238.63	0.36	239.01	0.37
2017-10-03	6	75	76.28	0.44	76.40	0.13
2017-10-03	6	20	20.04	0.26	20.03	0.13
2017-10-03	6	215	212.71	0.45	213.03	0.43
2017-10-03	6	195	193.85	0.56	194.21	0.17
2017-10-03	6	95	96.71	0.40	96.76	0.13
2017-10-03	6	120	121.66	0.40	121.76	0.22
2017-10-03	6	0	0.19	0.25	0.03	0.12
2017-10-03	6	145	145.92	0.36	145.81	0.31
2017-10-03	6	170	170.22	0.52	170.18	0.19
2017-10-03	6	50	49.43	0.60	49.40	0.09
2017-10-03	6	240	239.05	0.49	238.89	0.43
2017-05-10	1	0	-0.11	0.17	-0.23	0.12
2017-05-10	1	175	173.24	0.43	173.73	0.27
2017-05-10	1	195	196.58	0.27	196.83	0.22
2017-05-10	1	75	77.36	0.22	77.41	0.11
2017-05-10	1	50	50.14	0.19	50.07	0.14
2017-05-10	1	125	123.10	0.34	123.43	0.18

#the level is only indicative.

Greenhouse gases and carbon monoxide

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

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

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

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

Table 20 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 21, and Figure 25 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS.

Table 20. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO (ppb)	CH_4 (ppb)	N_2O (ppb)	CO_2 (ppm)
CC339478	463.76	2485.25	357.19	484.39
CB11499	141.03	1933.77	329.15	407.33
CB11485	110.88	1844.78	328.46	394.3

Table 21. Calibration summary of the WCC-Empa travelling standards.

TS	CO (ppb)	sdCO (ppb)	CH_4 (ppb)	sdCH_4 (ppb)	CO_2 (ppm)	sdCO_2 (ppm)	N_2O (ppb)	sdN_2O (ppb)
130819_FB03853	150.88	0.59	1942.25	0.12	399.51	0.02	327.28	0.03
150601_FA02466	691.59	0.21	1900.46	0.05	430.94	0.03	326.27	0.14
160622_FA02474	236.3	0.05	2506.99	0.11	421.27	0.04	324.36	0.02
160825_FB03365	171.74	0.66	1920.93	0.14	412.9	0.04	318.49	0.04
160825_FB03887	190.31	0.09	2027.15	0.16	457.61	0.02	331.64	0.02
160926_FB03367	86.13	0.22	1855.03	0.07	412.68	0.03	339.65	0.06

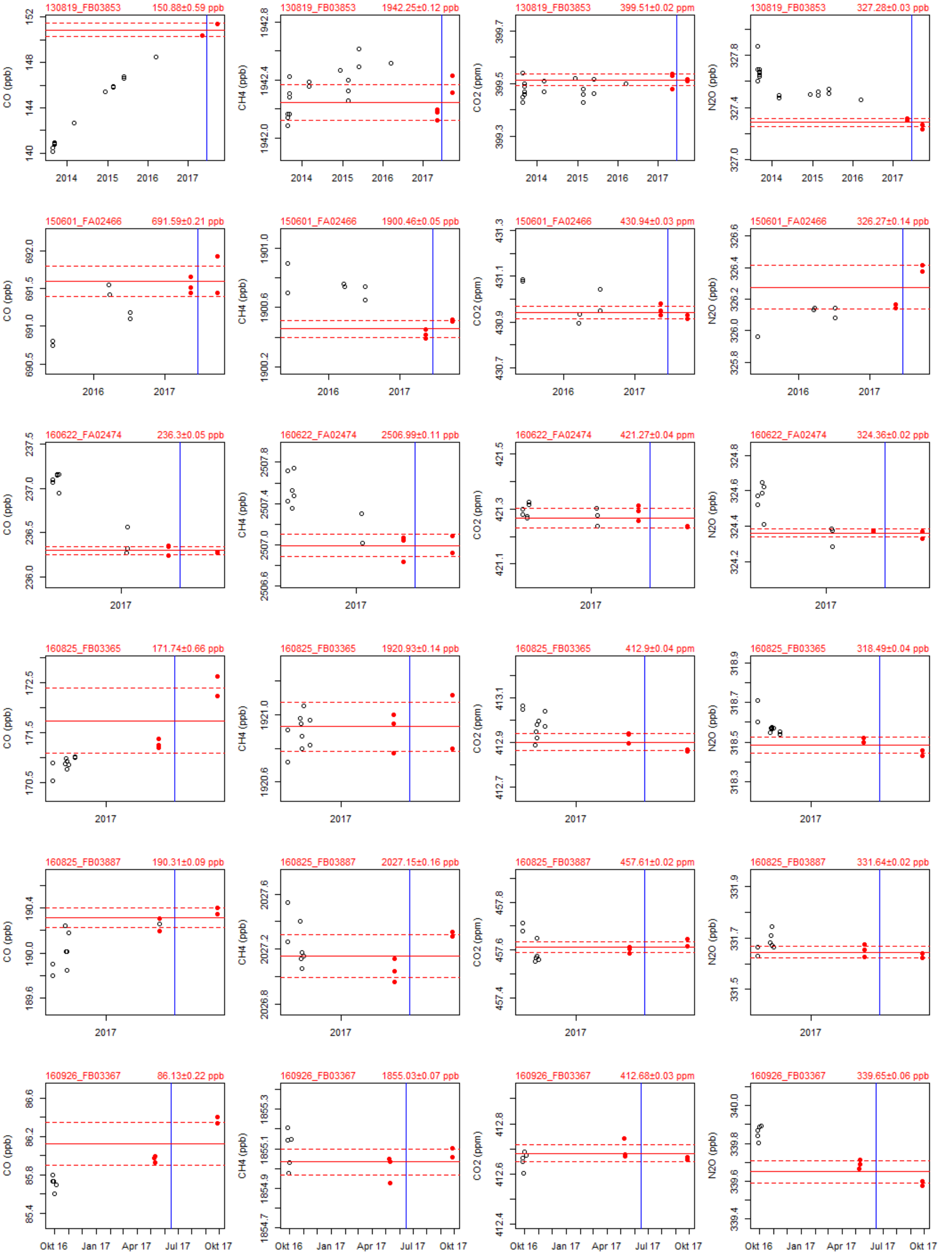


Figure 25. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

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 was calibrated every 1740 min using one WCC-Empa TS as a working standard, and two TS were used as targets. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 0.7 ppb for CH_4 and 0.04 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

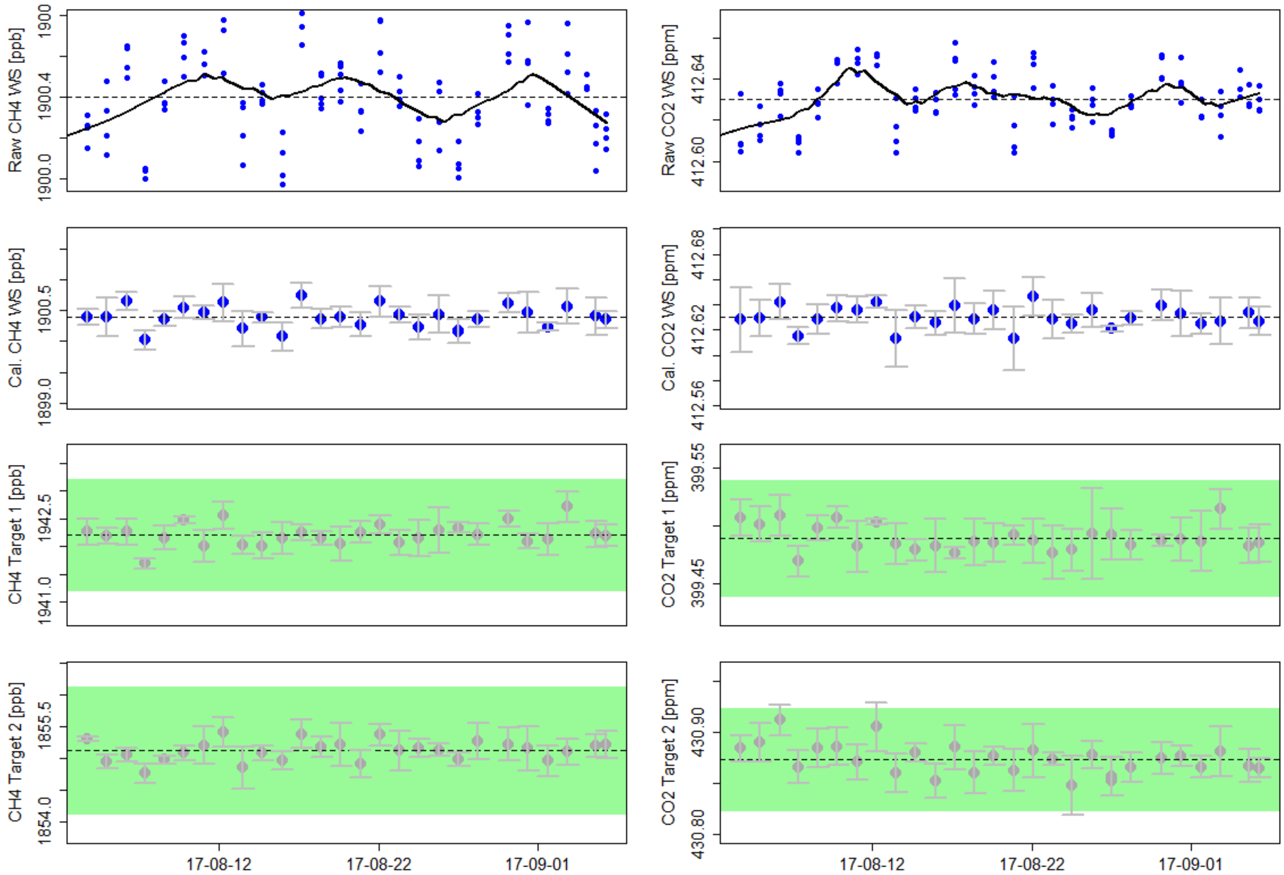


Figure 26. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1-min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 1740 min 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.

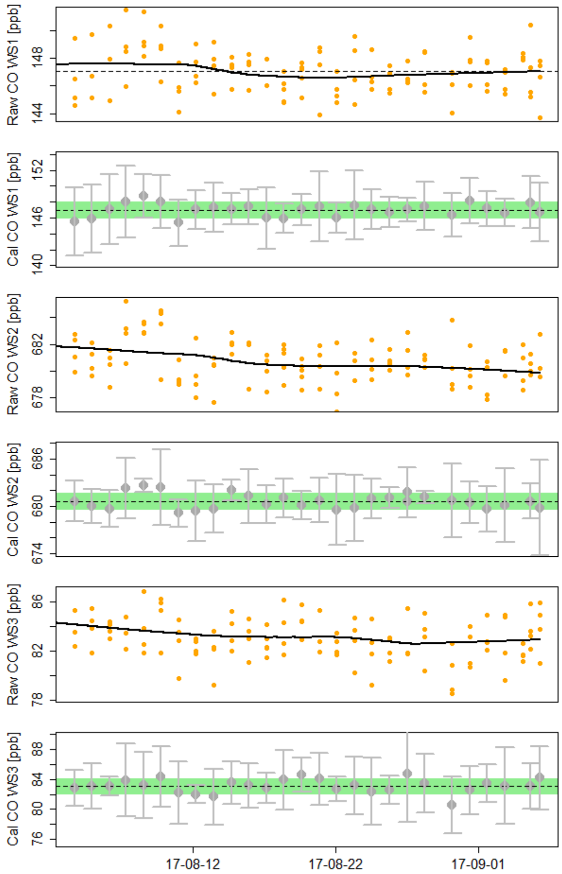


Figure 27. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels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

AMY	Anmyeon-do GAW Station
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
KGAWC	Korea Global Atmosphere Watch Center
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NIMS	National Institute of Meteorological Sciences
NOAA	National Oceanic and Atmospheric Administration
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization