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

GLOBAL GAW STATION MT. WALIGUAN CHINA SEPTEMBER 2016

Submitted to the World Meteorological Organization by

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The fourth system and performance audit by WCC-Empa[1] at the Global GAW station Mt. Waliguan was conducted from 3 - 6 September 2016 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). Monitoring and research activities at the Mt. Waliguan (WLG) global GAW station are coordinated by the China Meteorological Administration (CMA). The measurements at WLG are run by the Qinghai Meteorological Bureau (QMB) and the Centre for Atmosphere Watch and Services (CAWAS), which both are part of CMA. The local infrastructure as well as the routine operation of WLG is maintained by QMB, Xining, which operates the China Global Atmosphere Watch Baseline Observatory (CGAWBO). The scientific and technical support, training, QA/QC and data management is provided by the newly established Meteorological Operation Centre (MOC), which is part of CAWAS.

WCC-Empa also made an audit at the central calibration facilities of MOC and the regional GAW station Linan, which are presented in a separate report.

Previous audits at the Mt. Waliguan GAW observatory were conducted in September 2000 (Zellweger et al., 2000), October 2004 (Zellweger et al., 2004) and in June 2009 (Zellweger et al., 2009). The current audit includes CO_2 for the first time.

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Michael Müller	Empa Dübendorf, National Air Pollution Monitoring Network
Mr. Xiaochun Zhang	MOC, Group Leader CAWAS
Dr. Shuangxi Fang	MOC, Group Leader GHG
Dr. Weili Lin	MOC, Reactive Gases Analysis
Dr. Miao Liang	MOC, GHG Analysis
Ms. Jingjing Pan	MOC, Operator
Mr. Zhang Guo Qing	WLG, Station Manager, Supervisor CGAWBO
Mr. Wang Jian Qiong	WLG, Team leader operation division
Mr. Wu Hao	WLG, Deputy team leader operation division

This report summarises the assessment of the Mt. Waliguan 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 WLG station, the MOC and CAWAS, the Chinese GAW Country Contact and the World Meteorological Organization in Geneva. The report will be posted on the internet.

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 daily operation is coordinated by QMB/ CGAWBO, and the station is permanently staffed with two operators. All other aspects are directly addressed by MOC, which was recently established for

[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.

all operational aspects of the Chinese GAW programme. MOC also serves as the central calibration laboratory for all GAW stations in China.

Recommendation 1 (*, important, ongoing)**
The current operation scheme has recently been established after a period with unclear responsibilities. It is important for the successful operation of the station that responsibilities are clearly defined and communicated.

Recommendation 2 (*, important, ongoing)**
The current station management and operation focuses on operational and monitoring aspects, while scientific use of the data is not within the scope of MOC. However, the GHG group within MOC is responsible for both the operation and the scientific use of the GHG data. It is encouraged that the data is also scientifically used, and scientific collaboration with internal and external partners is strongly recommended.

Station Location and Access

WLG (36.283°N, 100.900°E, 3810m a.s.l) is situated on the top of Mt. Waliguan, on the Tibetan plateau in Western China. WLG is a remote site, located away from major industrial sources. The closest major settlement with 30000 inhabitants is located 30 km to the west. The surrounding area is covered with grass (no trees). The station is all year accessible by road. Further information is available in the GAW Station Information System (GAWSIS, www.gaw.empa.ch/gawsis). No significant changes were made since the last audit by WCC-Empa.

Station Facilities

The Mt. Waliguan station comprises extensive laboratory space. Basic 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

The WLG station comprises a comprehensive measurement programme that covers all focal areas of the GAW programme. An overview on measured species is available from GAWSIS and the station web site (links above). However, it was noticed that access to GAWSIS is not possible from China due to restricted internet access within China.

Recommendation 3 (*, critical, 2017)**
CMA is encouraged to explore with government officials if unblocking of the GAWSIS website is possible.

Recommendation 4 (, minor, 2017)**
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 only been partly submitted to the corresponding data centres. Surface O_3 (1994-2013), CH_4 (1994-2015), and CO_2 (1994-2015) data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Only daily and monthly averaged data has been submitted.

> **Recommendation 5 (***, critical, 2017)**
> *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. Submission of O_3, CH_4, and CO_2 data with 1 h time resolution needs to be made.*
>
> **Recommendation 6 (***, critical, 2017)**
> *CO and N_2O data must be submitted to WDCGG with hourly resolution for the entire available time period.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG were reviewed. The review was only partly possible due to the fact that CO and N_2O have not yet been submitted, and only one hourly data is available for the other parameters. The reviewed data looks plausible, but submission of missing data must be regarded as of highest priority. Summary plots and a short description of the findings are presented in the Appendix.

Documentation

All information is entered in electronic log and hand written books. The instrument manuals are available at the site, and weekly checklists are available. The reviewed information was comprehensive and up to date.

PERFORMANCE AUDIT

Surface Ozone Measurements

Surface ozone measurements started in 1994 at WLG, and continuous time series are available since then.

Instrumentation. WLG is equipped with two ozone analysers (TEI 49i) and an ozone calibrator (TEI 49i-PS). The WLG instruments were compared against the WCC-Empa travelling standard with traceability to a Standard Reference Photometer (SRP). The results of the comparison are summarised below.

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. CMA is currently in the process of upgrading the data acquisition system.

> **Recommendation 7 (**, important, 2017)**
> *The ozone instruments need to be equipped with dedicated data acquisition systems. All instrument parameters need to be recorded, and remote access must be possible.*

Air Inlet. Unchanged since the audit made by WCC-Empa in 2004. Materials as well as the residence time of the inlet system are adequate for surface ozone measurements.

Intercomparison (Performance Audit). The WLG analysers and calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). 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:

TEI 49i-PS #1160770024 (BKG 0.0 ppb, SPAN 1.035) – station calibrator:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OC] + 0.68 ppb) / 1.0065 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.35 ppb^2 + 2.56e-05 * X_{O3}^2) (1b)

TEI 49i #1031445279 (BKG +0.4 ppb, SPAN 1.054) – station analyser:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.83 ppb) / 1.0161 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.45 ppb^2 + 2.58e-05 * X_{O3}^2) (1d)

TEI 49i #15500012 (BKG 0.0 ppb, SPAN 1.010) – station analyser:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.01 ppb) / 1.0172 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.39 ppb^2 + 2.54e-05 * X_{O3}^2) (1f)

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

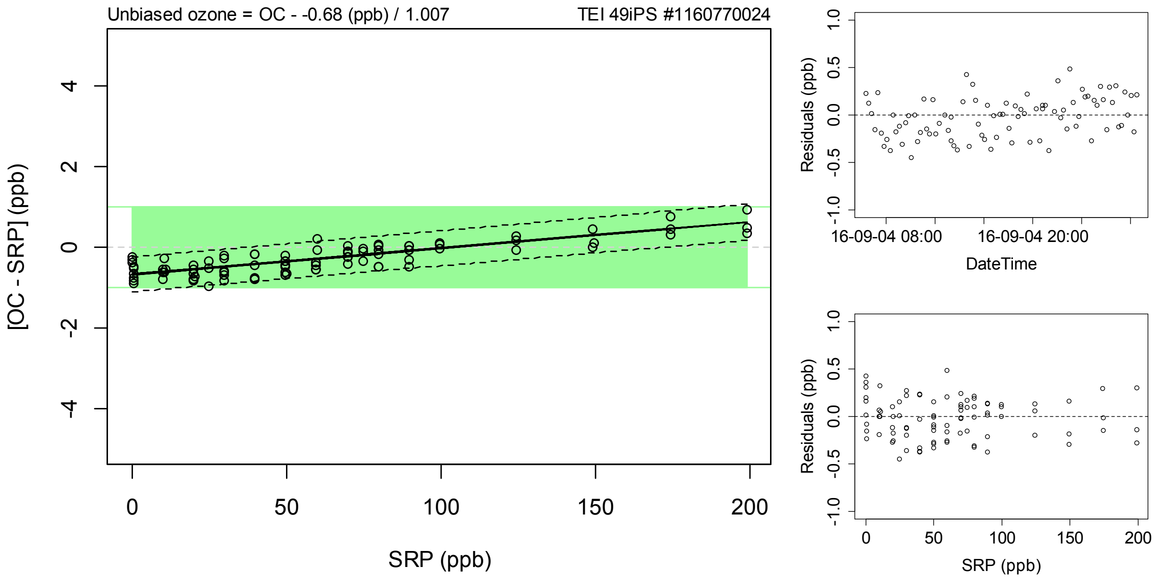

Figure 1. Left: Bias of the WLG ozone calibrator (TEI 49i-PS #1160770024) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the DQOs. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

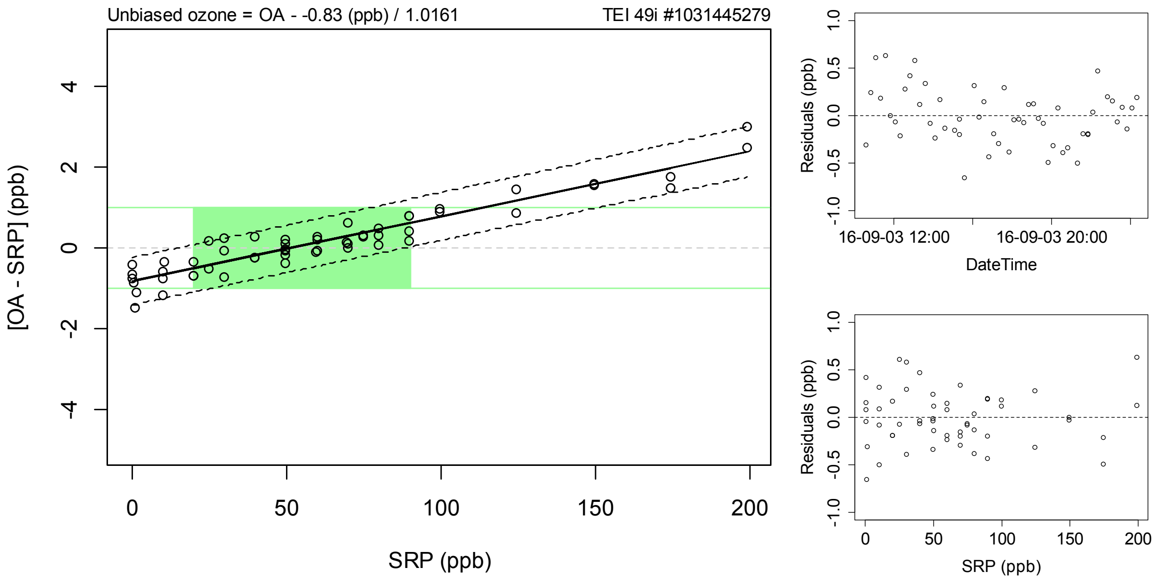

Figure 2. Same as Figure 1, for the TEI 49i #1031445279 station analyser.

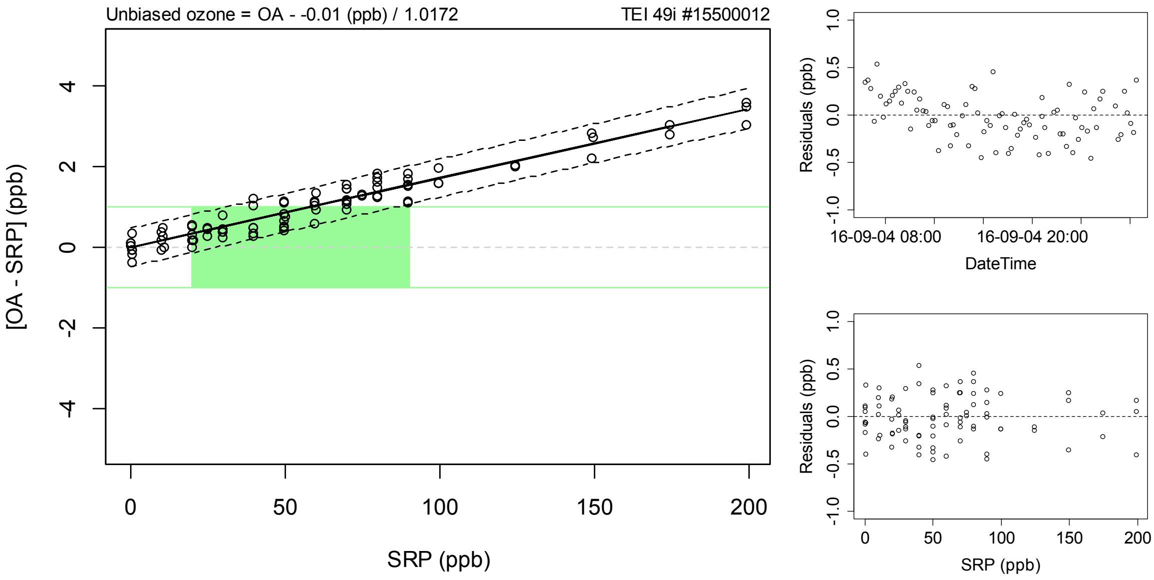

Figure 3. Same above, for the TEI 49i #15500012 station analyser.

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

Good agreement between the WCC-Empa travelling instrument and the WLG calibrator was found. The two station analysers overestimate the ozone at higher mole fractions, while the agreement was within the DQO at the relevant range for one of the instruments. The ozone data of WLG should be corrected accordingly, and it also should be considered to adjust calibration settings based on a calibration with the station calibrator.

Recommendation 8 (, minor, 2017)**
Calibration of the two station analysers with the station calibrator should be considered. It further needs to be made sure that the ozone data is corrected based on the findings of the current audit.

Carbon Monoxide Measurements

Carbon monoxide measurements at Mt. Waliguan were established in 1997, and continuous time series but with some data gaps are available since then.

Instrumentation. Two gas chromatographs with FID/methanizer (Agilent 6890N and 7890A) and Cavity Ring Down Spectroscopy (CRDS) (Picarro G2401) (since 2016). The current instrumentation is adequate for CO measurement. At the time of the audit one of the GC systems had a problem, and the TS were only analysed on the Agilent 6890N.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at WLG. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from both the Picarro and the GC instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 80 m tower trough a 120 m long Synflex 1300 tube with an inner diameter of 10 mm. The flow rate in the sample line is 7 l/min, controlled by a KNF PM24385-022 pump. The overall residence time is approx. 80 s. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the WLG 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 4 and 5 with respect to the WMO GAW DQOs (WMO, 2016):

AGILENT 6890N #US10719008:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 0.4) / 0.9903 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (2.2 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

Picarro G2401 #2490-CFKADS2216:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 6.1) / 1.0336 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.4 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

Recommendation 9 (, important, 2017)**

It is recommended to re-calibrate the CRDS instrument, and the reason for the differing results of the GC and CRDS instruments needs to be explored.

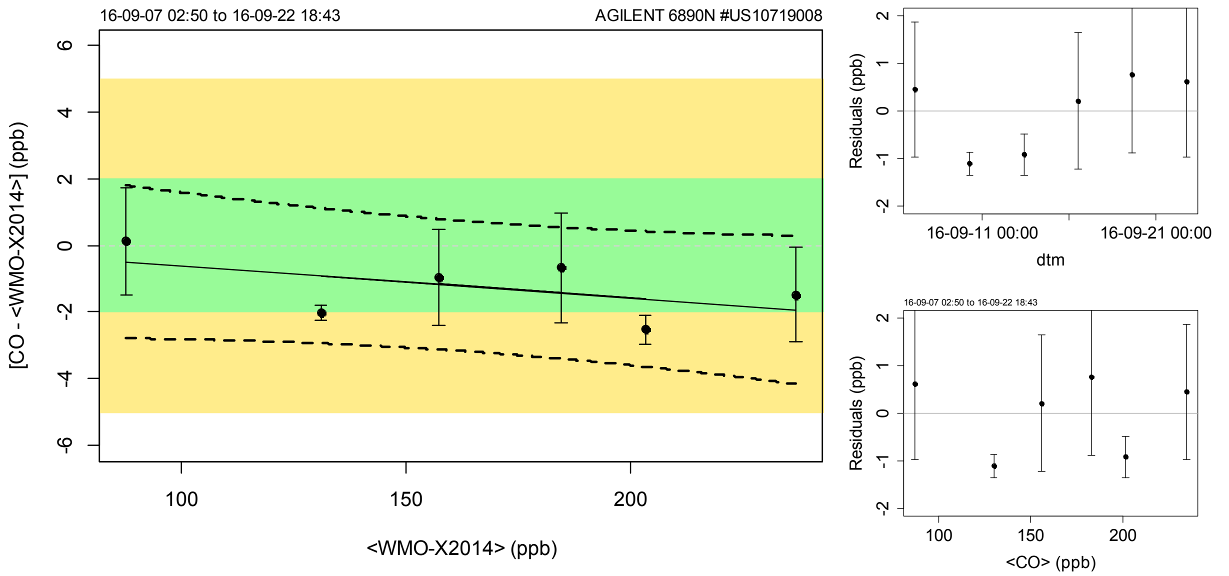

Figure 4. *Left: Bias of the WLG AGILENT 6890N carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 WLG. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

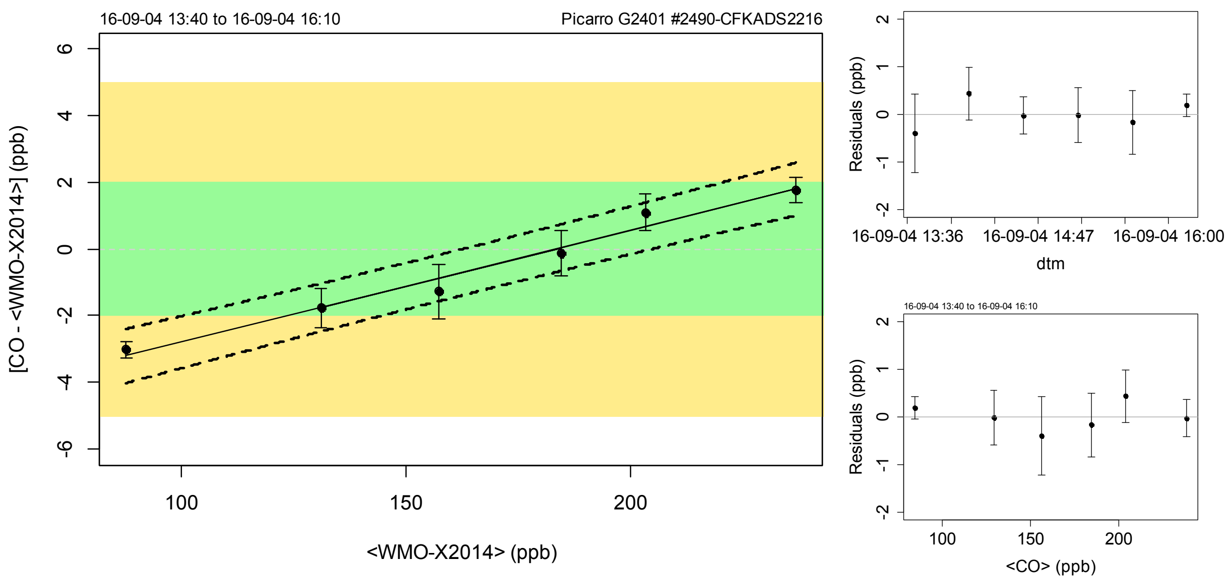

Figure 5. *Same as above, for the Picarro G2401 #2490-CFKADS2216.*

The results of the comparisons can be summarised as follows:

The comparison showed good agreement within the WMO/GAW compatibility goals for the mole fraction range from 120 to 250 ppb for both the CRDS and the GC/FID instrument. However, the CRDS instrument was underestimating mole fractions below 120 ppb, while the GC/FID instrument was within the DQOs over the entire relevant mole fraction range.

Methane Measurements

Methane measurements at Mt. Waliguan were established in 1994, and continuous time series are available since then.

Instrumentation. Two gas chromatographs with FID (Agilent 6890N and 7890A) and Cavity Ring Down Spectroscopy (CRDS) (Picarro G2401) (since 2016). The current instrumentation is adequate for CH_4 measurement. At the time of the audit one of the GC systems had a problem, and the TS were only analysed on the Agilent 6890N.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at WLG. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from both the Picarro and the GC instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 80 m tower trough a 120 m long Synflex 1300 tube with an inner diameter of 10 mm. The flow rate in the sample line is 7 l/min, controlled by a KNF PM24385-022 pump. The overall residence time is approx. 80 s. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the WLG 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 6 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2016).

AGILENT 6890N #US10719008:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 2.2 ppb) / 0.99921 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.5 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

Picarro G2401 #2490-CFKADS2216:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 2.4 ppb) / 0.99914 (3c)

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

The result of the comparison can be summarised as follows:

The results of both the GC/FID system and the Picarro G2401 compare well and meet the WMO/GAW compatibility goals. The uncertainty of the Picarro instrument is considerably smaller compared to the GC/FID system. The results show that the instrumentation is fully adequate and no further action is required.

Recommendation 10 (*, minor, 2017)
Due to the better results it is recommended that the Picarro is considered as the main methane analyser.

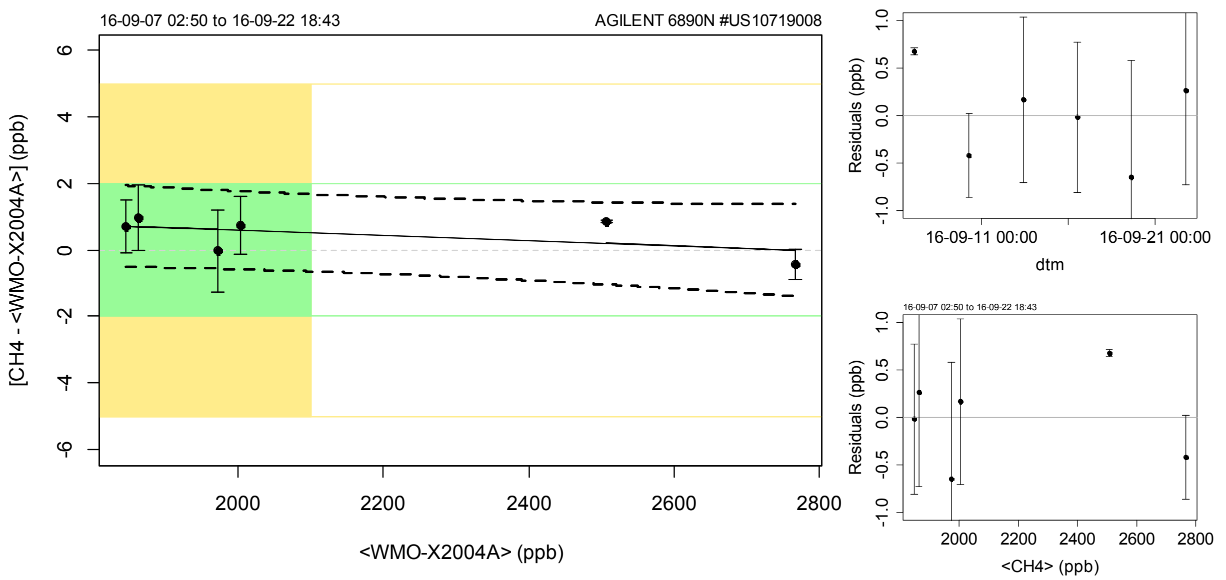

Figure 6. *Left: Bias of the* AGILENT 6890N #US10719008*methane instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 WLG. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

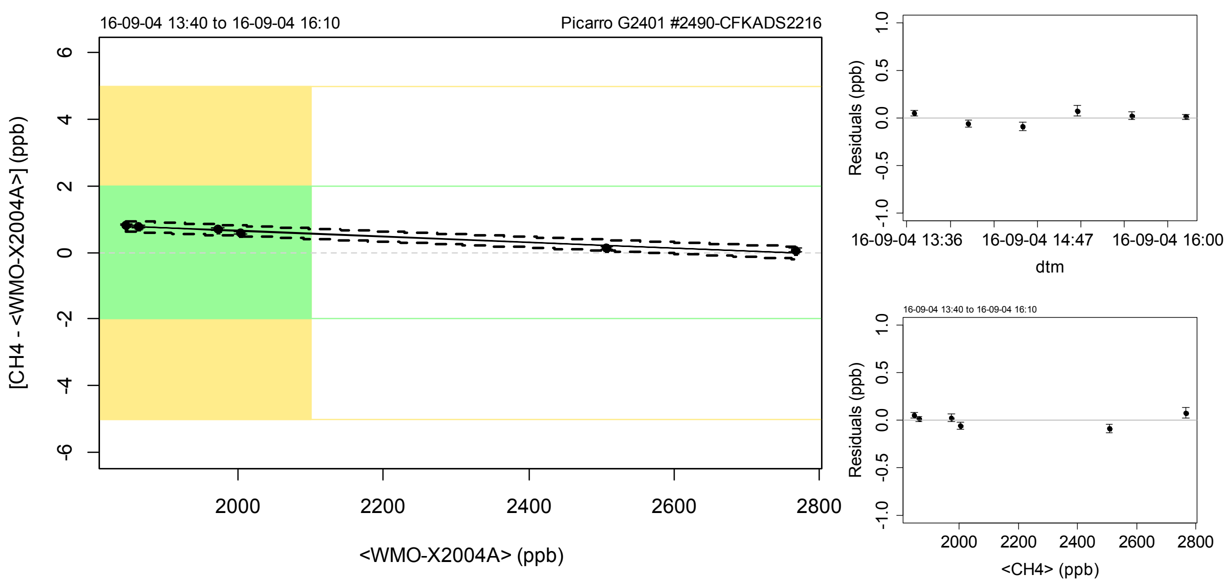

Figure 7. *Same as above, for the Picarro G2401 #2490-CFKADS2216.*

Carbon Dioxide Measurements

Continuous measurements of CO_2 at WLG started in 1994 using non-dispersive infrared (NDIR) absorption technique, and data is available since then. Since 2009 CO_2 measurements are made with Picarro CRDS instruments.

Instrumentation. Cavity Ring Down Spectroscopy (CRDS) (Picarro G2401) (since 2016). The current instrumentation is adequate for CO_2 measurement. Another Picarro instrument (G1302) was available since 2009. This instrument was decommissioned after replacement with the G2401.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at WLG. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from the Picarro instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 80 m tower trough a 120 m long Synflex 1300 tube with an inner diameter of 10 mm. The flow rate in the sample line is 7 l/min, controlled by a KNF PM24385-022 pump. The overall residence time is approx. 80 s. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the WLG 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 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2016).

Picarro G2401 #2490-CFKADS2216:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.66 ppm) / 0.99836 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.004 ppm^2 + 3.28e-08 * X_{CO2}^2) (4b)

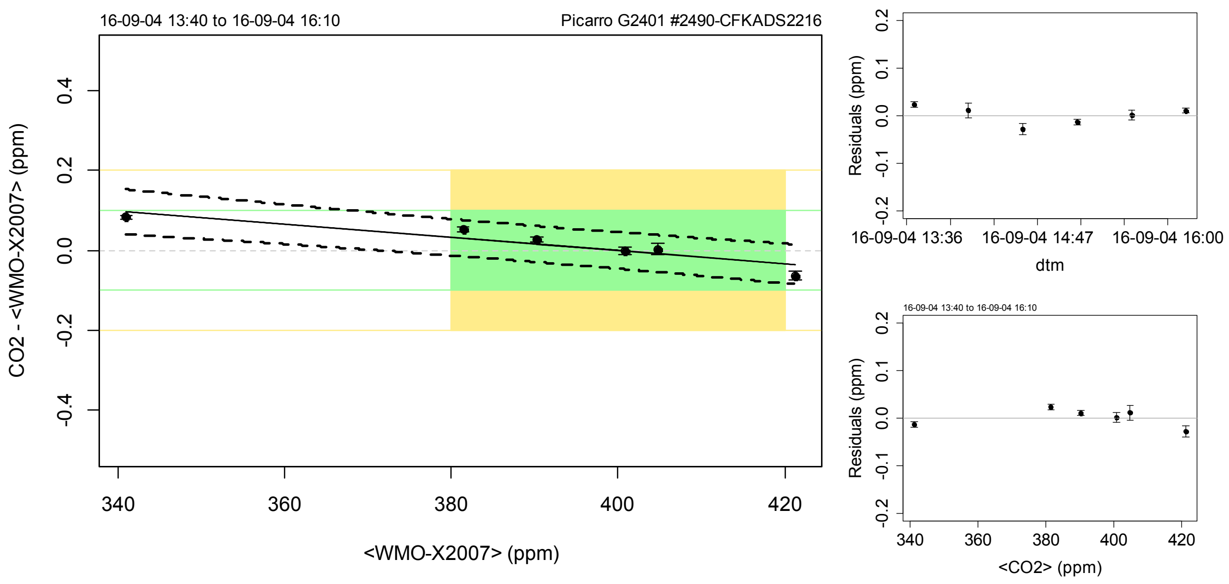

Figure 8. *Left: Bias of the PICARRO G2401 #2490-CFKADS2216 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 WLG. 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:

Agreement within the WMO/GAW compatibility goals of ±0.01 ppm was found over the entire tested CO_2 mole fraction range. The results show that the instrumentation and calibration strategy are fully adequate, and no further action is required.

Nitrous Oxide Measurements

Nitrous Oxide measurements at Mt. Waliguan were established in 2008, and continuous time series are available since then.

Instrumentation. Two gas chromatographs with Electron Capture Detector (ECD) (Agilent 6890N and 7890A). The current instrumentation is adequate for N_2O measurement. At the time of the audit one of the GC systems had a problem, and the TS were only analysed on the Agilent 6890N.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at WLG. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from the GC instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 80 m tower trough a 120 m long Synflex 1300 tube with an inner diameter of 10 mm. The flow rate in the sample line is 7 l/min, controlled by a KNF PM24385-022 pump. The overall residence time is approx. 80 s. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the WLG 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 9 with respect to the WMO GAW DQOs (WMO, 2016):

AGILENT 6890N #US10719008:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O - 11.86) / 0.96376 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.09 ppb^2 + 1.01e-07 * $X_{N2O}{}^2$) (5b)

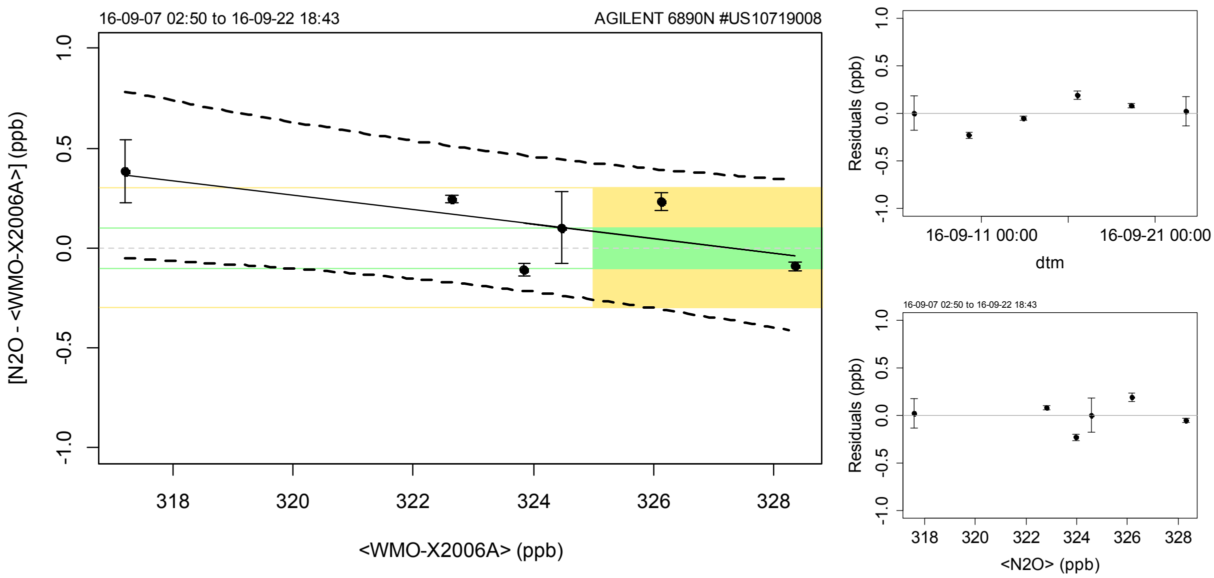

Figure 9. *Left: Bias of the WLG Agilent 6890N* US10719008 *nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual 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 WLG. 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 agreement of the GC/ECD system was within the extended WMO/GAW compatibility goals, and the measurement uncertainties were for most cylinders smaller than the WMO/GAW compatibility goal. Compared to other audits of GC/ECD system, this result is among the best, and reaching the WMO/GAW compatibility goal of 0.1 ppb remains challenging. The results show that the instrumentation and calibration strategy are fully adequate, and no further action is required.

WLG PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the WLG 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 were defined as observed the unpolluted air and given in the recommendation of the GGMT-2015 meeting (WMO, 2016) for the greenhouse gases and CO, and as 0 -100 ppb for surface ozone .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 10 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 11. 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 10 further highlights the results of the current audit (coloured dots), which are further discussed below.

Figure 10 (top left) shows the CO bias at 165 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2016. The green area shows the WMO/GAW compatibility goal of 2 ppb for the range from 30 - 300 ppb CO, and the yellow area represents the extended compatibility goal of 5 ppb. To date, 21% of all CO audits complied with the 2 ppb goal, 23% met the 5 ppb goal, and 56% were exceeding the WMO/GAW compatibility goal in the range of 30 – 300 ppb CO. The WLG performance audit results are shown in the same graph as a blue (Picarro G2401) and darkgreen (GC/FID) dot. The GC system was entirely within the extended WMO/GAW compatibility goal, while the Picarro was slightly exceeding the goal. Nevertheless, this is a good results compared other WCC-Empa CO audits.

Figure 10 (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 2016. The green area shows the WMO/GAW compatibility goal of 2 ppb for the range from 1750 - 2100 ppb CH_4, and the yellow area represents the extended compatibility goal of 5 ppb. To date, 59% of all CH_4 audits complied with the 2 ppb goal, 30% met the 5 ppb goal, and 11% were exceeding the WMO/GAW compatibility goal in the range of 1750 - 2100 ppb CH_4. The WLG performance audit results are shown in the same graph as a blue (Picarro G2401) and darkgreen (GC/FID) dot. The results of the WLG performance audit fully complies with the WMO/GAW compatibility goal for both instruments.

Figure 10 (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 2016. The green area shows the WMO/GAW compatibility goal of 0.1 ppm for the range from 380 - 450 ppm CO_2, and the yellow area represents the extended compatibility goal of 0.2 ppm. To date, 30% of all CO_2 audits complied with the 0.1 ppm goal, 22% met the 0.2 ppm goal, and 48 % were exceeding the WMO/GAW compatibility goal in the range of 380 - 450 ppm CO_2. The WLG performance audit result is shown in the same graph as a blue dot. The result of the WLG performance audit complies with the WMO/GAW compatibility goal of 0.1 ppm over the entire range from 380 - 450 ppm CO_2.

Figure 10 (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 2016. The green area shows the WMO/GAW compatibility goal of 0.1 ppb for the range from 325 - 335 ppb 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 33% met the 0.3 ppb goal, and 67 % were exceeding the WMO/GAW compatibility goal in the range of 325 - 335 ppb N_2O. The WLG performance audit result is shown in the same graph as a darkgreen dot. The result of the WLG performance audit complies with the extended WMO/GAW compatibility goal of 0.3 ppb over the entire range from 325 - 335 ppb N_2O.

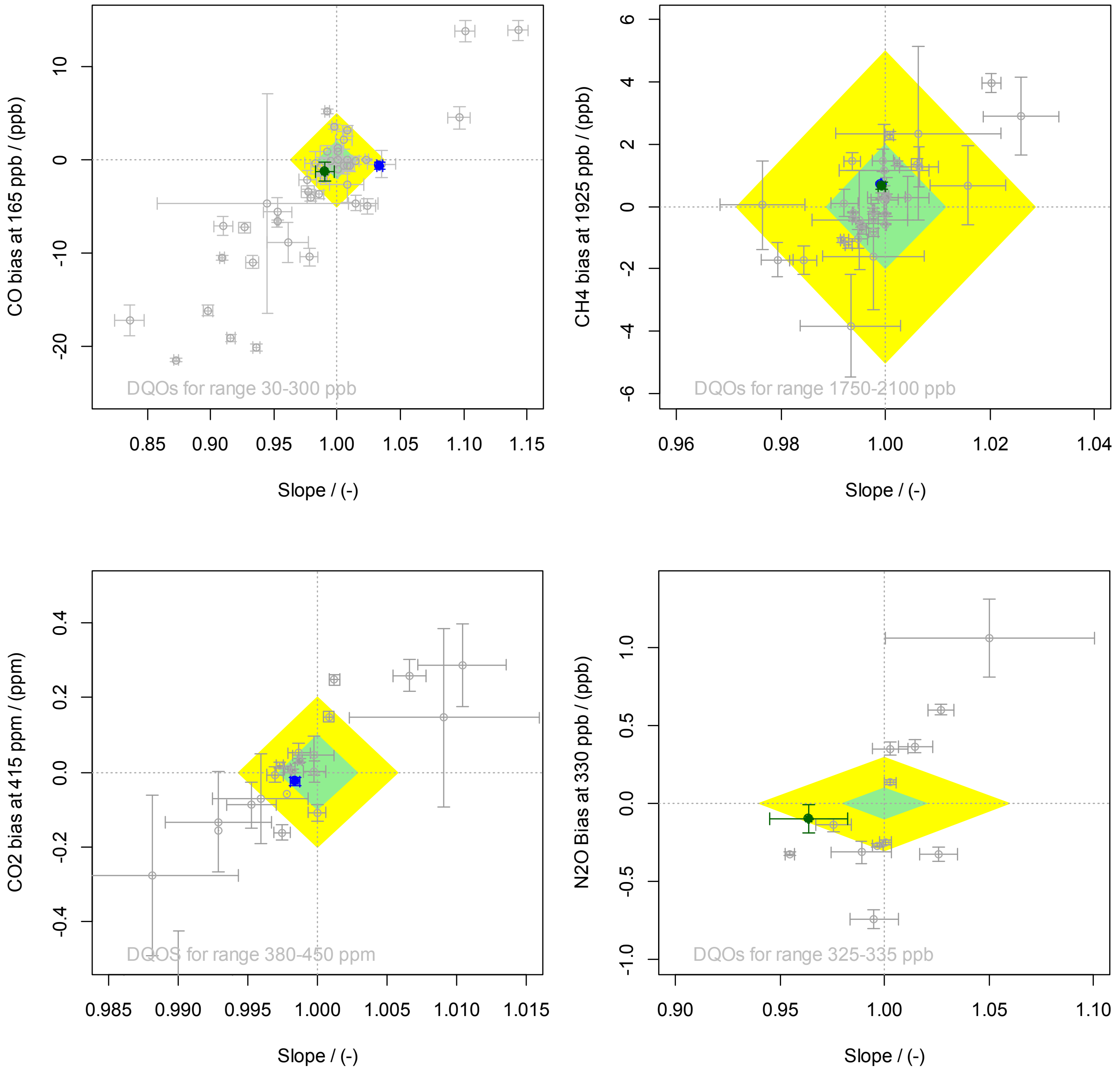

Figure 10. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to individual performance audits, while the coloured dots show WLG results (see text for further details). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

Figure 11 shows surface ozone audit results by WCC-Empa from 1996 until 2016. 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, 55% of all ozone audits complied with this goal. The WLG results are shown in the same graph as a red dot (ozone calibrator TEI 49i-PS) and blue dots (ozone analysers TEI 49i). The results of the WLG ozone calibrator and one of the analysers (TEI 49i#1031445279) meet the WMO/GAW compatibility goals in the range 0 – 100 ppb ozone, while the other analyser is exceeding the goal.

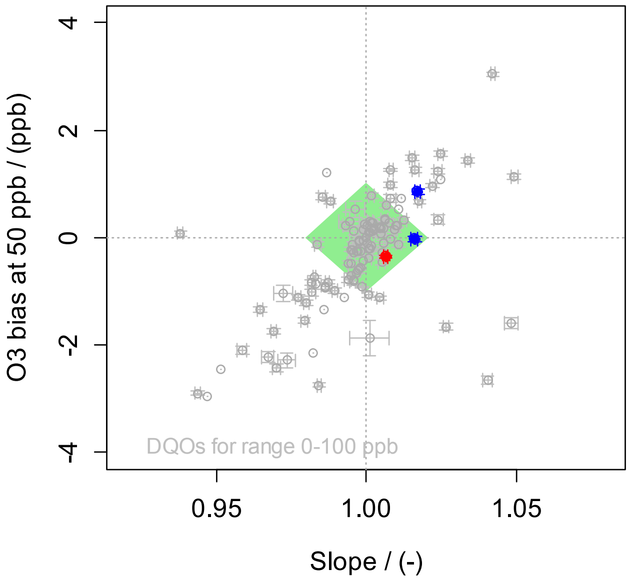

Figure 11. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to individual performance audits, while the coloured dots show WLG results (red: TEI 49i-PS, blue: TEI 49i). The green area corresponds to the WMO/GAW compatibility goal.*

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 # 617-CFKADS2001). The TI was running from 5 September 2016 through 11 October 2016. The TI was sampling from a completely separate inlet line leading to the same air intake location as the WLG station inlet. The air was not dried using the independent inlet, while the station analysers were measuring dry air. 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 12 shows the comparison of hourly CO data of the WLG Picarro G2401 instrument with the TI, and Figure 13 shows single injection of the WLG GC/FID system compared to 1 min TI data. The corresponding deviation histograms are shown in Figure 14. The station instruments were only partly working during the comparison campaign, which explains the different data coverage.

The median bias was within the WMO/GAW compatibility goal of 2 ppb for both the GC/FID and the Picarro G2401. However, both instruments measured during certain periods significantly lower CO mole fractions compared to the WCC-Empa TI. The fact that both WLG instruments were showing the same pattern in the bias is indicating either an issue with the WCC-Empa TI or the WLG inlet system. The reason however could not be identified.

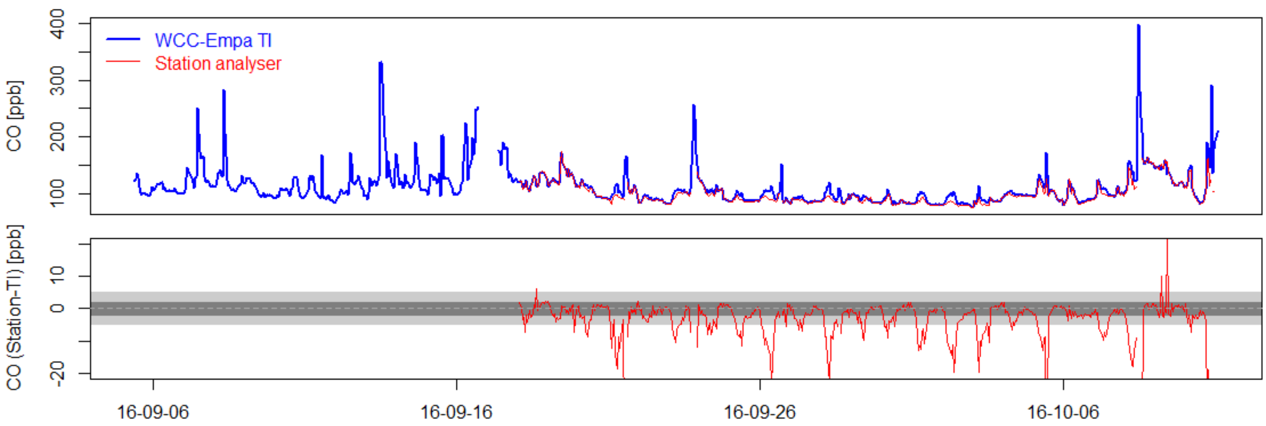

Figure 12. CO comparison at WLG between the WCC-Empa travelling instrument and the WLG Picarro G2401. Upper panel: CO time series (1 h data). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

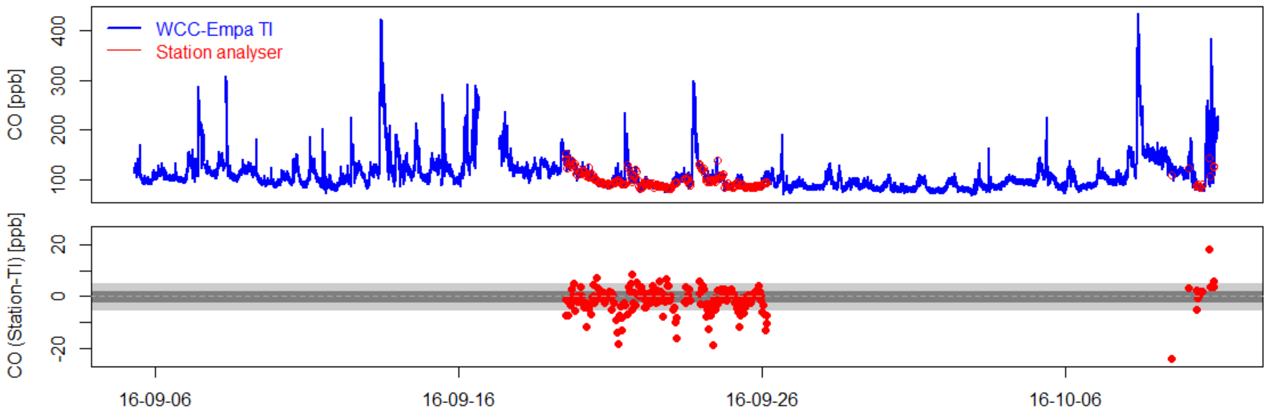

Figure 13. CO comparison at WLG between the WCC-Empa travelling instrument and the WLG GC/FID instrument. Upper panel: CO time series (1 min data). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

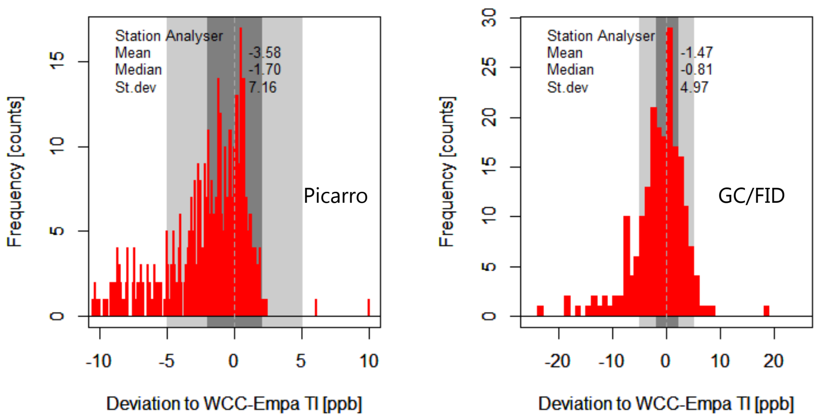

Figure 14. CO deviation histograms (1 h data, station analyser – TI) for the WLG Picarro G2401 (left) and for the WLG GC/FID instrument (1 min data, station analyser – TI) (right).

Methane:

Figure 15 shows the comparison of hourly CH_4 data of the WLG Picarro G2401 instrument with the TI, and Figure 16 shows single injection of the WLG GC/FID system compared to 1 min TI data. The corresponding deviation histograms are shown in Figure 17.

Good agreement was found between the WLG Picarro G2401 and the WCC-Empa TI, with a median bias of the WLG instrument of -0.17 ppb. This is well within the WMO/GAW compatibility goal of 2 ppb. The temporal variation was also well captured by both instruments.

The WLG GC/FID system showed poor agreement with the TI, and the WMO/GAW compatibility was not met for large parts of the comparison period. Furthermore, instrumental problems of the GC system reduced the amount of data for the comparison significantly.

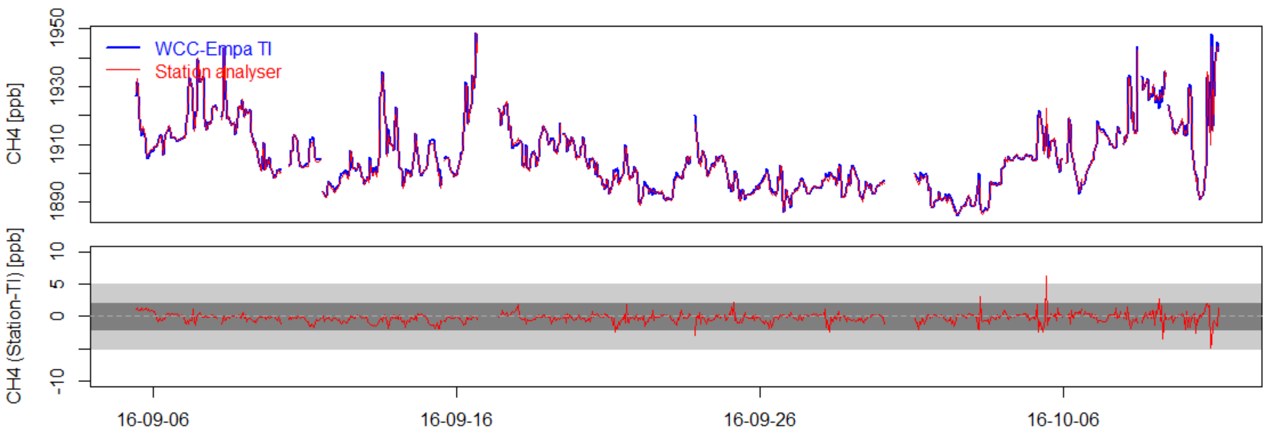

Figure 15. CH_4 comparison at WLG between the WCC-Empa travelling instrument and the WLG Picarro G2401. Upper panel: CH_4 time series (1 h data). Lower panel: CH_4 bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

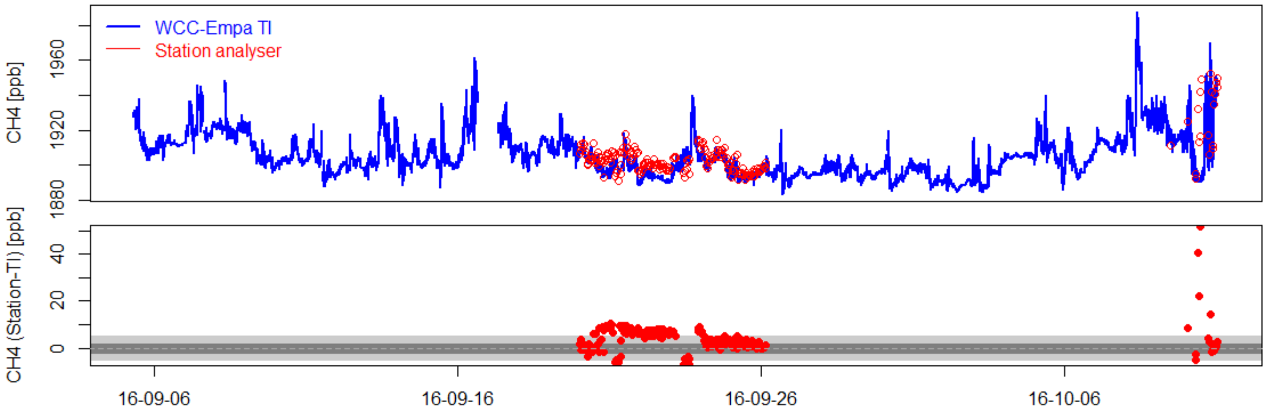

Figure 16. CH_4 comparison at WLG between the WCC-Empa travelling instrument and the WLG GC/FID instrument. Upper panel: CH_4 time series (1 min data). Lower panel: CH_4 bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

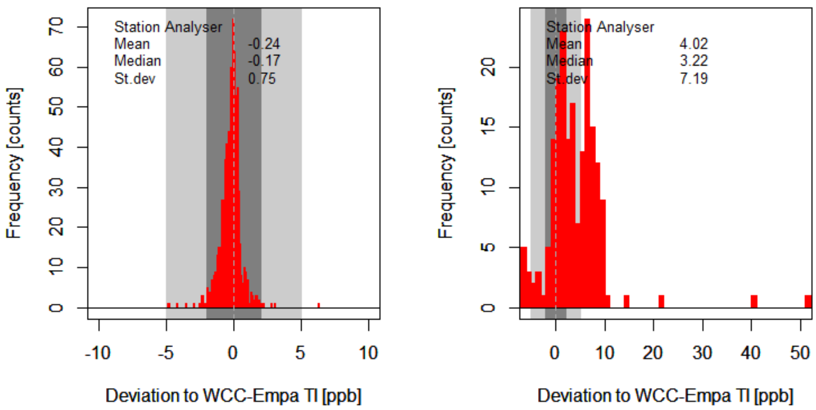

Figure 17. CH_4 deviation histograms (1 h data, station analyser – TI) for the WLG Picarro G2401 (left) and for the WLG GC/FID instrument (1 min data, station analyser – TI) (right).

Carbon dioxide:

Figure 18 shows the comparison of hourly CO_2 data of the WLG Picarro G2401 instrument with the TI. The corresponding deviation histogram is shown in Figure 19.

Overall, good agreement was found between the WLG Picarro G2401 and the WCC-Empa TI, with a median bias of the WLG instrument of +0.09 ppm. This is within the WMO/GAW compatibility goal of 0.1 ppm. The temporal variation was also well captured by both instruments. However, the bias was not constant over time and was for example significantly larger for the first few days of the comparison.

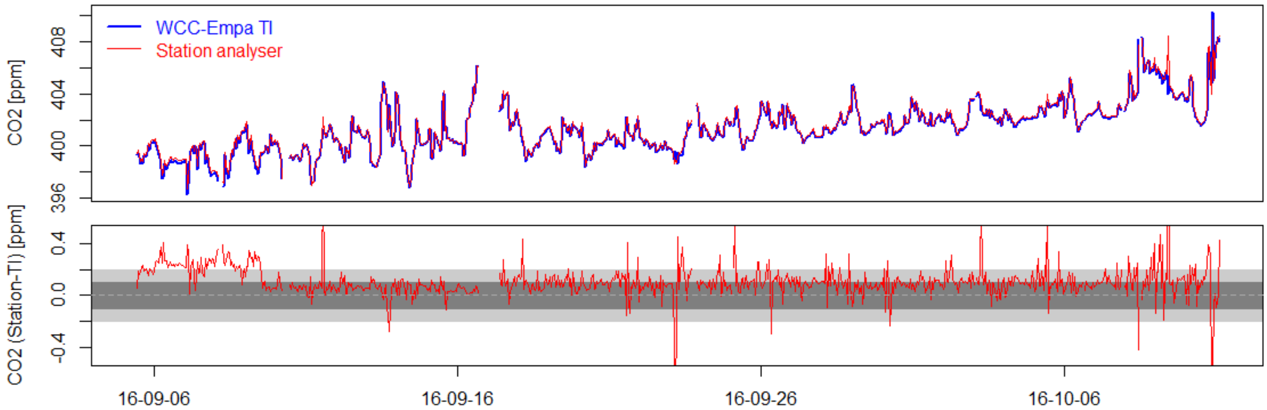

Figure 18. CO_2 comparison at WLG between the WCC-Empa travelling instrument and the WLG Picarro G2401. Upper panel: CO_2 time series (1 h data). Lower panel: CO_2 bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

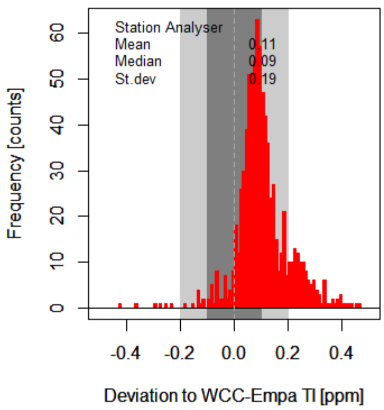

Figure 19. CO_2 deviation histograms (1 h data, WLG Picarro G2401 analyser – TI).

Discussion of the ambient air comparison results

The ambient air comparison largely 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 WLG Picarro analyser. However, the GC/FID had instrumental issues during the ambient air comparison campaign.

CONCLUSIONS

The Global GAW station Mt. Waliguan is situated at an important location for the GAW programme, which makes the available data a very significant contribution to GAW. Unfortunately, the available data series were only partly submitted to the WMO/GAW data centres. In order to fulfil the requirements of a global GAW station, data submission needs to be done on a timely manner by CMA.

All assessed parameters were of high data quality and met the WMO/GAW compatibility or extended compatibility goals in the relevant mole fraction range. Table 1 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals.

Table 1. 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	CO CRDS	CO GC	CH_4 CRDS	CH_4 GC	CO_2	N_2O
Performance audit with TS	✓ #	(✓)	(✓)	(✓)	✓	✓	(✓)
Ambient air comparison	NA	✓	✓	✓	✗	✓	NA

NA no ambient air comparison was made for ozone and nitrous oxide

Only WLG calibrator and one of the two analysers was within compatibility goal in the relevant mole fraction range.

The continuation of the Mt. Waliguan 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. However, the data must be freely available, and data submission needs to be initiated.

SUMMARY RANKING OF THE MT. WALIGUAN GAW STATION

System Audit Aspect	Adequacy#	Comment
Station Access	(5)	Year round access by car.
Facilities		
Laboratory and office space	(5)	Adequate with additional space for research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Adequate system
Power supply	(5)	Reliable with very few power cuts
General Management and Operation		
Organisation	(4)	Again well-coordinated between different partners, clear responsibilities
Competence of staff	(5)	Skilled staff
Air Inlet System	(5)	Adequate inlets for all parameters
Instrumentation		
Ozone	(5)	Adequate instrumentation
$CO/CO_2/CH_4$ (Picarro G2401)	(5)	Adequate instrumentation
$CO/CH_4/N_2O$ (GC system)	(5)	Adequate instrumentation
Standards		
Ozone	(5)	TEI 49i-PS
CO, CO_2, CH_4	(5)	Link to CCL with NOAA standards
Data Management		
Data acquisition	(5)	Adequate systems
Data processing	(5)	Adequate procedures
Data submission	(0)	Only a small part of the data has been submitted. Daily averaged data was submitted, which is insufficient.

#0: inadequate thru 5: adequate.

Dübendorf, July 2017

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APPENDIX

Data Review

The following figures show summary plots of WLG data accessed on 29 May 2017 from WDCGG (CO, CO_2 and O_3). Only daily data is available from WDCGG. However, higher resolution data is available and has been used in various scientific publications (Fang et al., 2014; Zhang et al., 2013; Zhang et al., 2011; Zhou et al., 2004) and assessments (e.g. the TOAR project, http://www.igacproject.org/activities/TOAR). The following plots show time series of daily data, frequency distribution, and seasonal variation. The data summary downloaded from the TOAR data base is shown in Figure 21.

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

Ozone:

- Data series looks plausible.
- Only daily data is available from WDCGG, which has been rounded to full ppb.
- Data accessed from the TOAR data base is in agreement with data from WDCGG.

Methane:

- Data set looks generally sound.
- A few periods however need further attention, e.g. the high mole fractions at the end of 2001, and the low mole fractions in spring 2007.

Carbon dioxide:

- Data set looks generally sound.
- Seasonal cycle and trend looks plausible.
- A few periods however need further attention, e.g. the low values after the pronounce drop in mole fractions in 2014.

Carbon monoxide and nitrous oxide:

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

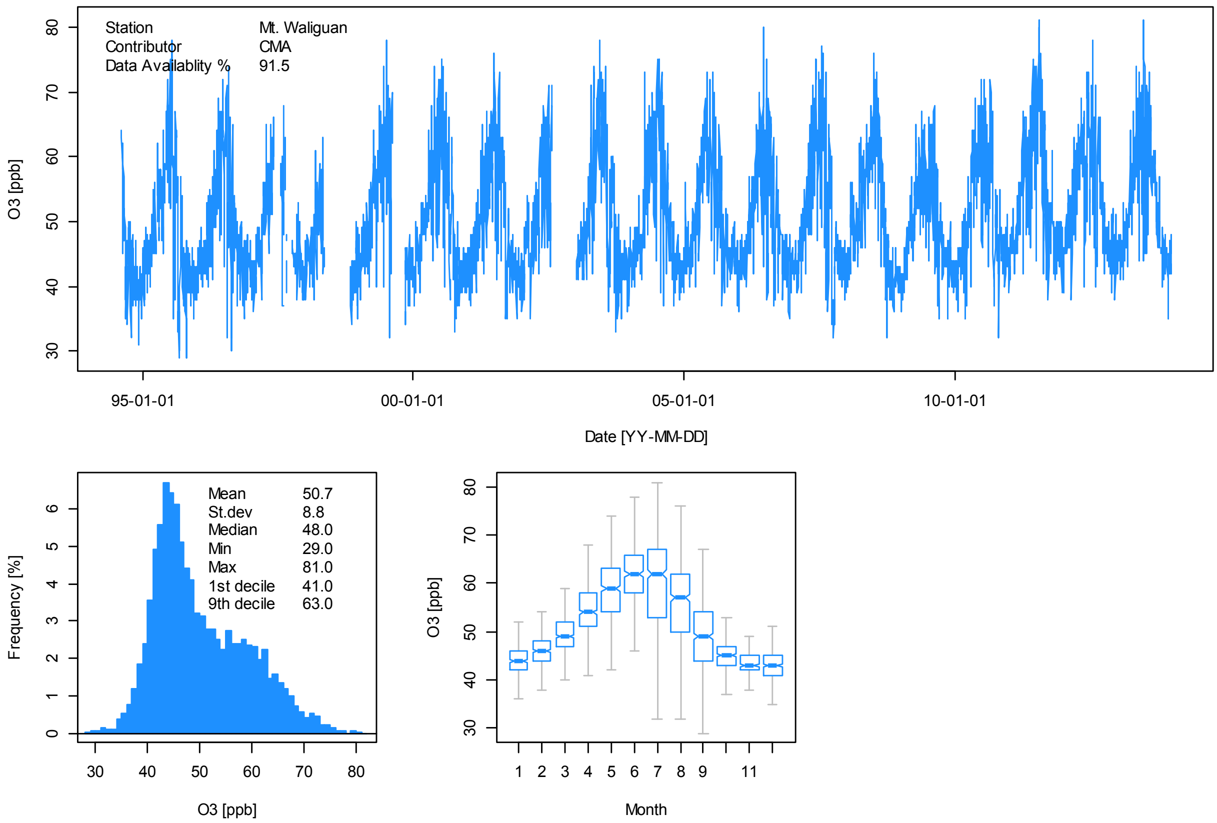

Figure 20. *Ozone data accessed from WDCGG. Top: Time series, daily averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

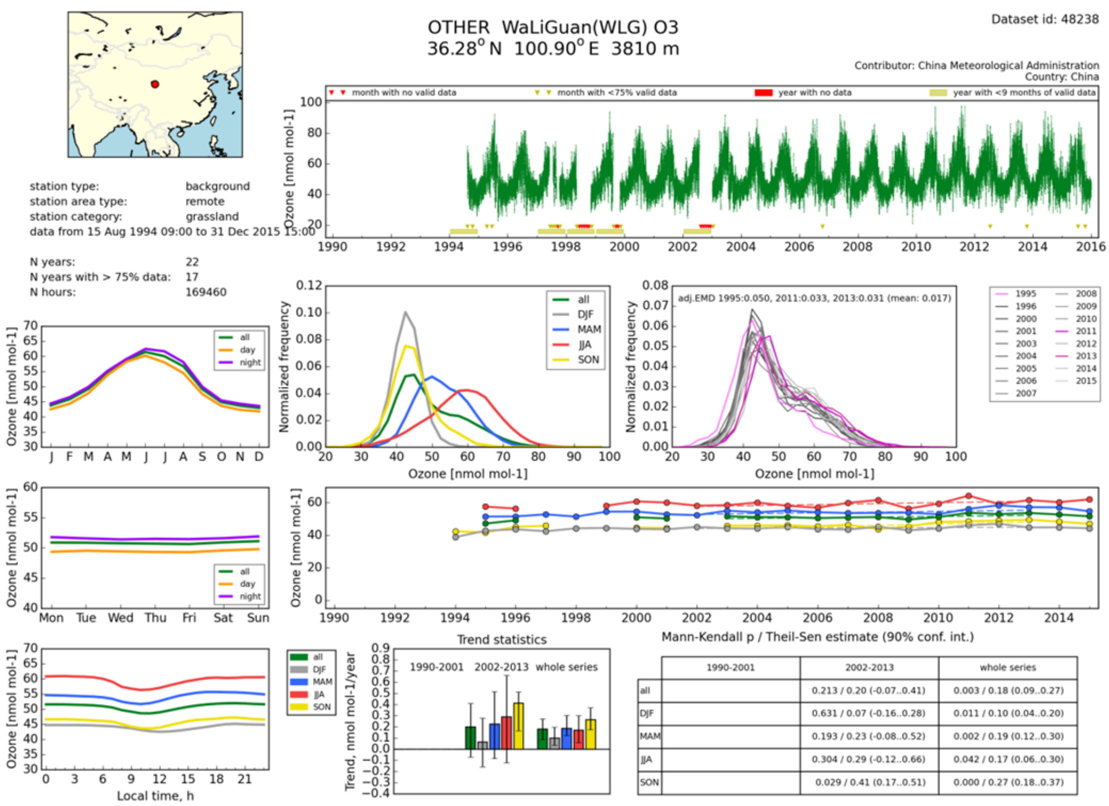

Figure 21. *Ozone data summary accessed from the TOAR webpage.*

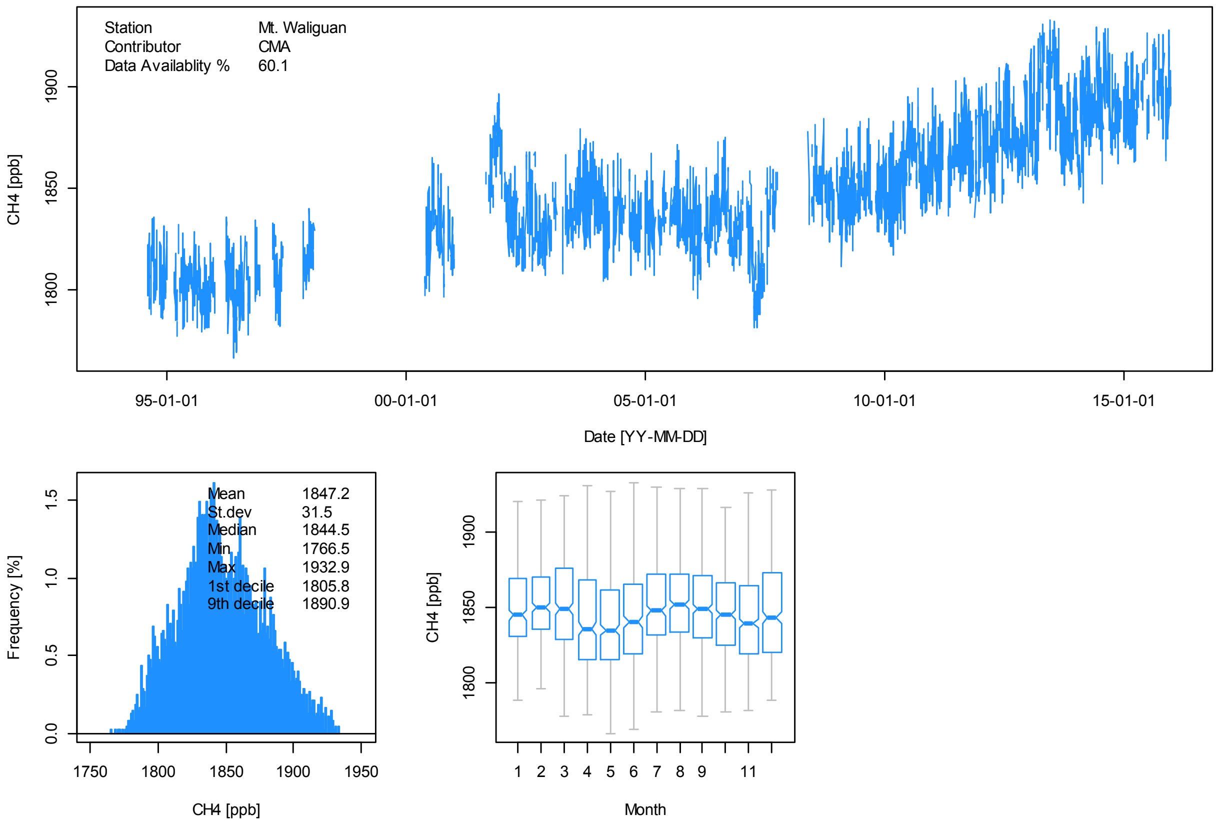

Figure 22. *CH_4 data accessed from WDCGG. Top: Time series, daily averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

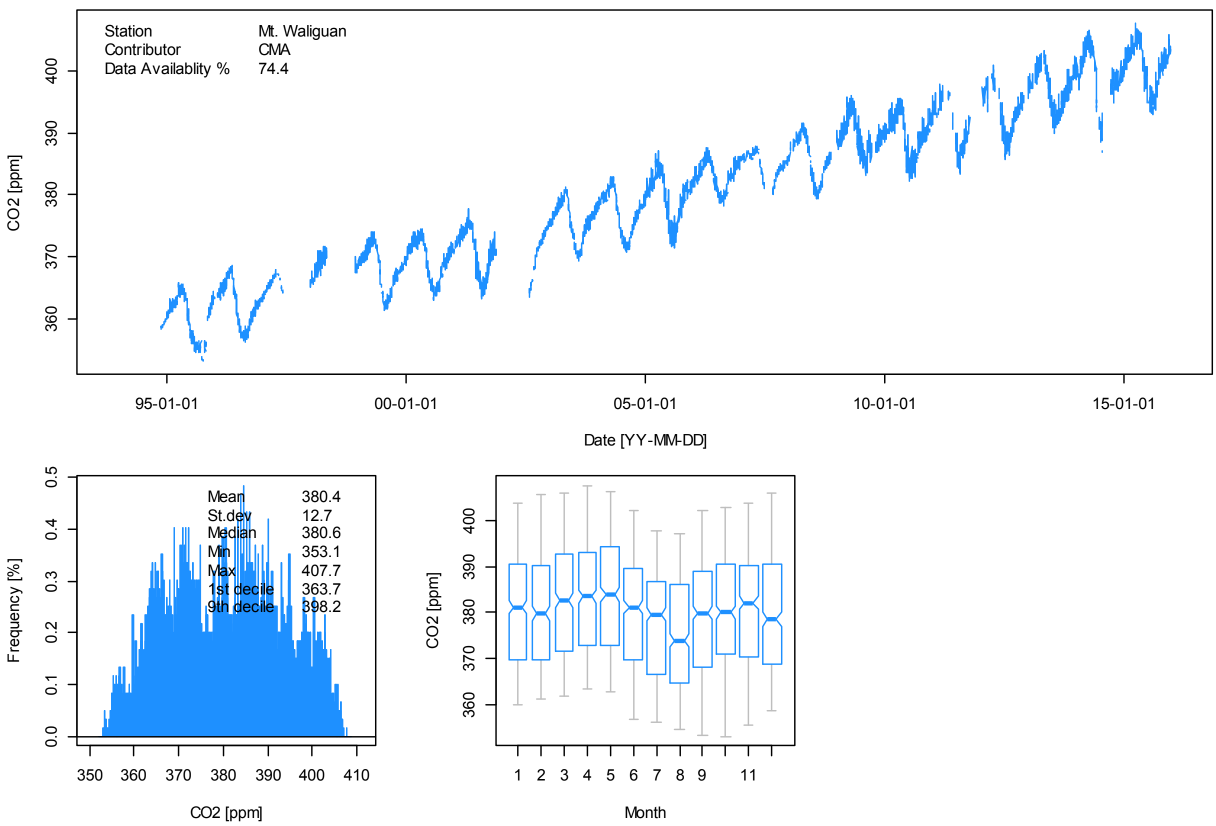

Figure 23. *Same as above for CO_2.*

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 (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 2 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 2. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
Settings	BKG -0.2, COEF 1.008
Pressure readings (hPa)	Ambient 640.0; TS 644.5 (adjustments to 640.0)
Station calibrator (OC)	
Model, S/N	TEI 49i-PS #1160770024
Principle	UV absorption
Range	0-1 ppm
Settings	BKG 0.0 ppb, COEF 1.035 (no adjustments were made)
Pressure readings (hPa)	Ambient 640.0; OC 652.8 (no adjustments were made)
Station analyser (OA)	
Model, S/N	TEI 49i # 1031445279
Principle	UV absorption
Range	0-1 ppm
Settings	BKG 0.4 ppb, COEF 1.054 (no adjustments were made)
Pressure readings (hPa)	Ambient 640.0; OC 649.4 (no adjustments were made)
Station analyser (OA)	
Model, S/N	TEI 49i #15500012
Principle	UV absorption
Range	0-1 ppm
Settings	BKG 0.0 ppb, COEF 1.010 (no adjustments were made)
Pressure readings (hPa)	Ambient 640.0; OC 641.3 (no adjustments were made)

Results

Each ozone level was applied for 15 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 2 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) and calibrator (OC) values.

The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary (Figures and Equations).

Table 3. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the WLG ozone calibrator (OC) TEI 49i-PS #1160770024 with the WCC-Empa travelling standard (TS).

Date - Time (UTC+8)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2016-09-04 06:18	1	40	39.99	39.60	0.12	0.19	-0.39	-1.0
2016-09-04 06:33	1	70	70.03	69.63	0.17	0.33	-0.40	-0.6
2016-09-04 06:48	1	90	90.02	89.55	0.18	0.29	-0.47	-0.5
2016-09-04 07:03	2	0	0.62	-0.25	0.41	0.12	-0.87	NA
2016-09-04 07:18	2	40	40.06	39.68	0.11	0.10	-0.38	-0.9
2016-09-04 07:33	2	10	10.16	9.27	0.14	0.31	-0.89	-8.8
2016-09-04 07:48	2	50	50.01	49.09	0.11	0.46	-0.92	-1.8
2016-09-04 08:03	2	60	59.96	59.14	0.15	0.41	-0.82	-1.4
2016-09-04 08:18	2	90	89.99	89.14	0.15	0.14	-0.85	-0.9
2016-09-04 08:33	2	20	20.09	19.42	0.27	0.23	-0.67	-3.3
2016-09-04 08:48	2	70	69.98	69.27	0.09	0.33	-0.71	-1.0
2016-09-04 09:03	2	30	30.02	29.26	0.12	0.14	-0.76	-2.5
2016-09-04 09:18	2	80	80.02	79.20	0.17	0.28	-0.82	-1.0
2016-09-04 09:33	3	0	0.57	-0.23	0.30	0.08	-0.80	NA
2016-09-04 09:48	3	50	49.96	49.36	0.17	0.24	-0.60	-1.2
2016-09-04 10:03	3	25	25.11	24.00	0.22	0.38	-1.11	-4.4
2016-09-04 10:18	3	100	99.99	99.54	0.13	0.06	-0.45	-0.5
2016-09-04 10:33	3	200	200.05	199.59	0.14	0.65	-0.46	-0.2
2016-09-04 10:48	3	150	150.00	149.50	0.13	0.62	-0.50	-0.3
2016-09-04 11:03	3	75	74.95	74.60	0.27	0.47	-0.35	-0.5
2016-09-04 11:18	3	175	174.99	174.59	0.12	0.25	-0.40	-0.2
2016-09-04 11:33	3	125	124.97	124.38	0.10	0.38	-0.59	-0.5
2016-09-04 11:48	4	0	0.41	-0.15	0.30	0.11	-0.56	NA
2016-09-04 12:03	4	30	30.03	29.18	0.21	0.29	-0.85	-2.8
2016-09-04 12:18	4	50	50.02	49.34	0.19	0.51	-0.68	-1.4
2016-09-04 12:48	4	10	10.34	9.65	0.59	0.19	-0.69	-6.7
2016-09-04 13:03	4	60	59.99	59.26	0.09	0.35	-0.73	-1.2
2016-09-04 13:18	4	20	19.91	18.97	0.19	0.32	-0.94	-4.7
2016-09-04 13:18	4	70	70.02	69.47	0.13	0.37	-0.55	-0.8
2016-09-04 13:33	4	80	80.04	79.21	0.15	0.45	-0.83	-1.0
2016-09-04 13:48	4	40	40.05	39.07	0.17	0.55	-0.98	-2.4
2016-09-04 14:18	4	90	89.98	89.64	0.17	0.32	-0.34	-0.4
2016-09-04 14:33	5	0	0.18	-0.12	0.18	0.16	-0.30	NA
2016-09-04 14:48	5	40	39.98	39.03	0.12	0.35	-0.95	-2.4
2016-09-04 15:03	5	10	10.52	10.15	0.55	0.41	-0.37	-3.5
2016-09-04 15:18	5	50	49.97	49.53	0.07	0.15	-0.44	-0.9
2016-09-04 15:33	5	60	59.99	59.33	0.14	0.26	-0.66	-1.1
2016-09-04 15:48	5	90	89.97	89.27	0.11	0.43	-0.70	-0.8
2016-09-04 16:03	5	20	20.10	19.17	0.10	0.17	-0.93	-4.6
2016-09-04 16:18	5	70	70.02	69.59	0.18	0.31	-0.43	-0.6
2016-09-04 16:33	5	30	30.00	29.00	0.18	0.22	-1.00	-3.3
2016-09-04 16:48	5	80	79.98	79.47	0.22	0.12	-0.51	-0.6

Date - Time (UTC+8)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2016-09-04 17:03	6	0	0.76	-0.20	0.35	0.10	-0.96	NA
2016-09-04 17:18	6	50	50.02	49.43	0.10	0.31	-0.59	-1.2
2016-09-04 17:33	6	25	24.93	24.29	0.41	0.58	-0.64	-2.6
2016-09-04 17:48	6	100	99.98	99.65	0.14	0.35	-0.33	-0.3
2016-09-04 18:03	6	200	199.99	199.67	0.08	0.32	-0.32	-0.2
2016-09-04 18:18	6	150	149.95	149.34	0.08	0.24	-0.61	-0.4
2016-09-04 18:33	6	75	75.04	74.61	0.21	0.31	-0.43	-0.6
2016-09-04 18:48	6	175	175.02	174.75	0.11	0.39	-0.27	-0.2
2016-09-04 19:03	6	125	124.96	124.62	0.09	0.33	-0.34	-0.3
2016-09-04 19:18	7	0	0.45	-0.25	0.21	0.19	-0.70	NA
2016-09-04 19:33	7	30	30.07	29.65	0.24	0.36	-0.42	-1.4
2016-09-04 19:48	7	50	50.05	49.17	0.18	0.27	-0.88	-1.8
2016-09-04 20:18	7	10	10.19	9.57	0.28	0.25	-0.62	-6.1
2016-09-04 20:33	7	60	59.96	59.12	0.21	0.43	-0.84	-1.4
2016-09-04 20:48	7	20	19.96	19.39	0.19	0.21	-0.57	-2.9
2016-09-04 20:48	7	70	70.01	69.54	0.11	0.32	-0.47	-0.7
2016-09-04 21:03	7	80	80.00	79.59	0.12	0.27	-0.41	-0.5
2016-09-04 21:18	7	40	40.01	39.02	0.30	0.42	-0.99	-2.5
2016-09-04 21:48	7	90	89.96	89.51	0.18	0.37	-0.45	-0.5
2016-09-04 22:03	8	0	0.29	-0.07	0.29	0.13	-0.36	NA
2016-09-04 22:18	8	40	39.96	39.31	0.29	0.30	-0.65	-1.6
2016-09-04 22:33	8	10	10.82	10.18	0.62	0.75	-0.64	-5.9
2016-09-04 22:48	8	50	50.01	49.28	0.04	0.19	-0.73	-1.5
2016-09-04 23:03	8	60	60.05	59.98	0.25	0.32	-0.07	-0.1
2016-09-04 23:18	8	90	90.01	89.66	0.10	0.32	-0.35	-0.4
2016-09-04 23:33	8	20	20.04	19.26	0.14	0.18	-0.78	-3.9
2016-09-04 23:48	8	70	70.00	69.45	0.06	0.22	-0.55	-0.8
2016-09-05 00:03	8	30	29.96	29.59	0.21	0.26	-0.37	-1.2
2016-09-05 00:18	8	80	80.02	79.70	0.09	0.31	-0.32	-0.4
2016-09-05 00:33	9	0	0.43	-0.09	0.49	0.06	-0.52	NA
2016-09-05 00:48	9	50	50.01	49.15	0.20	0.37	-0.86	-1.7
2016-09-05 01:03	9	25	24.90	24.40	0.25	0.50	-0.50	-2.0
2016-09-05 01:18	9	100	100.01	99.66	0.05	0.17	-0.35	-0.3
2016-09-05 01:33	9	200	199.98	200.10	0.15	0.27	0.12	0.1
2016-09-05 01:48	9	150	149.96	149.80	0.10	0.24	-0.16	-0.1
2016-09-05 02:03	9	75	74.98	74.31	0.16	0.63	-0.67	-0.9
2016-09-05 02:18	9	175	174.97	175.01	0.08	0.30	0.04	0.0
2016-09-05 02:33	9	125	125.02	124.77	0.12	0.23	-0.25	-0.2
2016-09-05 02:48	10	0	0.14	-0.27	0.33	0.19	-0.41	NA
2016-09-05 03:03	10	30	29.99	29.22	0.23	0.32	-0.77	-2.6
2016-09-05 03:18	10	50	50.02	49.32	0.10	0.24	-0.70	-1.4
2016-09-05 03:33	10	70	70.01	69.72	0.15	0.53	-0.29	-0.4
2016-09-05 03:48	10	10	10.04	9.35	0.24	0.18	-0.69	-6.9
2016-09-05 04:03	10	60	60.06	59.70	0.12	0.36	-0.36	-0.6
2016-09-05 04:18	10	20	20.25	19.40	0.59	0.57	-0.85	-4.2
2016-09-05 04:33	10	80	80.00	79.71	0.08	0.15	-0.29	-0.4

Table 4. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the WLG ozone analyser (OA) TEI 49i #1031445279 with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-03 10:35	1	0	1.27	0.10	0.46	0.19	-1.17	NA
2016-09-03 10:50	1	50	49.98	49.97	0.17	0.40	-0.01	0.0
2016-09-03 11:05	1	25	24.99	25.04	0.17	0.27	0.05	0.2
2016-09-03 11:20	1	100	100.05	100.58	0.18	0.30	0.53	0.5
2016-09-03 11:35	1	200	200.05	202.25	0.11	0.31	2.20	1.1
2016-09-03 11:50	1	150	150.03	150.99	0.13	0.84	0.96	0.6
2016-09-03 12:05	2	75	74.99	74.96	0.10	0.51	-0.03	0.0
2016-09-03 12:20	2	175	175.00	176.06	0.09	0.30	1.06	0.6
2016-09-03 12:35	2	125	124.97	125.91	0.13	0.63	0.94	0.8
2016-09-03 12:50	2	0	0.26	-0.19	0.27	0.24	-0.45	NA
2016-09-03 13:05	2	30	29.97	30.05	0.18	0.51	0.08	0.3
2016-09-03 13:20	2	50	50.02	49.87	0.12	0.41	-0.15	-0.3
2016-09-03 13:35	2	70	70.01	70.34	0.12	0.60	0.33	0.5
2016-09-03 13:50	2	10	10.03	9.20	0.24	0.11	-0.83	-8.3
2016-09-03 14:05	2	60	59.97	59.59	0.17	0.47	-0.38	-0.6
2016-09-03 14:20	2	20	19.91	19.45	0.18	0.42	-0.46	-2.3
2016-09-03 14:35	2	80	80.07	80.05	0.22	0.50	-0.02	0.0
2016-09-03 15:05	3	70	69.80	69.62	0.45	0.81	-0.18	-0.3
2016-09-03 15:20	3	40	40.05	39.62	0.18	0.90	-0.43	-1.1
2016-09-03 15:20	3	90	90.05	90.07	0.09	0.39	0.02	0.0
2016-09-03 15:35	3	0	1.10	-0.42	0.47	0.30	-1.52	NA
2016-09-03 16:05	3	10	10.40	9.97	0.32	0.41	-0.43	-4.1
2016-09-03 16:20	3	50	49.94	49.66	0.13	0.33	-0.28	-0.6
2016-09-03 16:35	4	60	60.06	60.06	0.14	0.17	0.00	0.0
2016-09-03 16:50	4	90	90.02	89.81	0.13	0.73	-0.21	-0.2
2016-09-03 17:05	4	20	19.96	19.14	0.22	0.39	-0.82	-4.1
2016-09-03 17:20	4	70	70.00	69.69	0.18	0.40	-0.31	-0.4
2016-09-03 17:35	4	30	30.00	29.78	0.33	0.47	-0.22	-0.7
2016-09-03 17:50	4	80	79.99	79.71	0.20	0.22	-0.28	-0.4
2016-09-03 18:05	4	0	0.47	-0.44	0.12	0.15	-0.91	NA
2016-09-03 18:20	4	50	49.97	49.67	0.10	0.43	-0.30	-0.6
2016-09-03 18:35	4	25	24.98	24.34	0.13	0.34	-0.64	-2.6
2016-09-03 18:50	4	100	99.94	100.40	0.07	0.57	0.46	0.5
2016-09-03 19:05	5	200	199.99	201.68	0.06	0.65	1.69	0.8
2016-09-03 19:20	5	150	150.05	150.98	0.09	0.36	0.93	0.6
2016-09-03 19:35	5	75	74.97	74.93	0.16	0.41	-0.04	-0.1
2016-09-03 19:50	5	175	175.04	175.81	0.09	0.64	0.77	0.4
2016-09-03 20:05	5	125	125.01	125.35	0.06	0.29	0.34	0.3
2016-09-03 20:20	5	0	0.30	-0.49	0.24	0.34	-0.79	NA
2016-09-03 20:35	6	30	30.03	29.13	0.34	0.80	-0.90	-3.0
2016-09-03 20:50	6	50	49.99	49.39	0.19	0.44	-0.60	-1.2
2016-09-03 21:20	6	10	10.23	8.98	0.22	0.30	-1.25	-12.2
2016-09-03 21:35	6	60	60.01	59.68	0.20	0.37	-0.33	-0.5
2016-09-03 21:50	6	20	20.02	19.19	0.21	0.25	-0.83	-4.1
2016-09-03 21:50	6	70	70.01	69.79	0.11	0.64	-0.22	-0.3

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-03 22:05	6	80	80.02	80.16	0.12	0.39	0.14	0.2
2016-09-03 22:20	6	40	39.98	40.07	0.16	0.37	0.09	0.2
2016-09-03 22:50	6	90	89.98	90.40	0.17	0.79	0.42	0.5
2016-09-03 23:05	6	0	0.28	-0.43	0.25	0.11	-0.71	NA
2016-09-03 23:20	7	40	39.98	39.53	0.18	0.56	-0.45	-1.1
2016-09-03 23:35	7	10	10.09	9.42	0.30	0.21	-0.67	-6.6
2016-09-03 23:50	7	50	50.04	49.64	0.06	0.49	-0.40	-0.8
2016-09-04 00:05	7	60	60.00	59.94	0.07	0.89	-0.06	-0.1
2016-09-04 00:20	7	90	90.02	90.44	0.12	0.97	0.42	0.5

Table 5. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the WLG ozone analyser (OA) TEI 49i #15500012 with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-04 06:18	1	40	39.99	40.81	0.12	0.17	0.82	2.1
2016-09-04 06:33	1	70	70.03	71.28	0.17	0.46	1.25	1.8
2016-09-04 06:48	1	90	90.02	91.45	0.18	0.37	1.43	1.6
2016-09-04 07:03	2	0	0.62	0.51	0.41	0.12	-0.11	NA
2016-09-04 07:18	2	40	40.06	41.08	0.11	0.33	1.02	2.5
2016-09-04 07:33	2	10	10.16	10.44	0.14	0.32	0.28	2.8
2016-09-04 07:48	2	50	50.01	50.60	0.11	0.59	0.59	1.2
2016-09-04 08:03	2	60	59.96	60.83	0.15	0.21	0.87	1.5
2016-09-04 08:18	2	90	89.99	91.29	0.15	0.50	1.30	1.4
2016-09-04 08:33	2	20	20.09	20.51	0.27	0.18	0.42	2.1
2016-09-04 08:48	2	70	69.98	71.11	0.09	0.26	1.13	1.6
2016-09-04 09:03	2	30	30.02	30.66	0.12	0.29	0.64	2.1
2016-09-04 09:18	2	80	80.02	81.16	0.17	0.31	1.14	1.4
2016-09-04 09:33	3	0	0.57	0.85	0.30	0.19	0.28	NA
2016-09-04 09:48	3	50	49.96	50.83	0.17	0.44	0.87	1.7
2016-09-04 10:03	3	25	25.11	25.24	0.22	0.32	0.13	0.5
2016-09-04 10:18	3	100	99.99	101.52	0.13	0.59	1.53	1.5
2016-09-04 10:33	3	200	200.05	202.73	0.14	0.61	2.68	1.3
2016-09-04 10:48	3	150	150.00	152.12	0.13	0.59	2.12	1.4
2016-09-04 11:03	3	75	74.95	75.94	0.27	0.48	0.99	1.3
2016-09-04 11:18	3	175	174.99	177.31	0.12	0.46	2.32	1.3
2016-09-04 11:33	3	125	124.97	126.48	0.10	0.43	1.51	1.2
2016-09-04 11:48	4	0	0.41	0.30	0.30	0.25	-0.11	NA
2016-09-04 12:03	4	30	30.03	30.32	0.21	0.28	0.29	1.0
2016-09-04 12:18	4	50	50.02	50.26	0.19	0.60	0.24	0.5
2016-09-04 12:48	4	10	10.34	10.54	0.59	0.25	0.20	1.9
2016-09-04 13:03	4	60	59.99	60.82	0.09	0.54	0.83	1.4
2016-09-04 13:18	4	20	19.91	19.79	0.19	0.43	-0.12	-0.6
2016-09-04 13:18	4	70	70.02	70.79	0.13	0.44	0.77	1.1
2016-09-04 13:33	4	80	80.04	80.95	0.15	0.70	0.91	1.1
2016-09-04 13:48	4	40	40.05	40.33	0.17	0.56	0.28	0.7

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-04 14:18	4	90	89.98	91.13	0.17	0.36	1.15	1.3
2016-09-04 14:33	5	0	0.18	0.24	0.18	0.20	0.06	NA
2016-09-04 14:48	5	40	39.98	40.14	0.12	0.23	0.16	0.4
2016-09-04 15:03	5	10	10.52	10.91	0.55	0.54	0.39	3.7
2016-09-04 15:18	5	50	49.97	50.86	0.07	0.31	0.89	1.8
2016-09-04 15:33	5	60	59.99	60.76	0.14	0.22	0.77	1.3
2016-09-04 15:48	5	90	89.97	90.67	0.11	0.46	0.70	0.8
2016-09-04 16:03	5	20	20.10	20.13	0.10	0.30	0.03	0.1
2016-09-04 16:18	5	70	70.02	70.84	0.18	0.46	0.82	1.2
2016-09-04 16:33	5	30	30.00	30.23	0.18	0.14	0.23	0.8
2016-09-04 16:48	5	80	79.98	81.46	0.22	0.53	1.48	1.9
2016-09-04 17:03	6	0	0.76	0.32	0.35	0.26	-0.44	NA
2016-09-04 17:18	6	50	50.02	50.62	0.10	0.22	0.60	1.2
2016-09-04 17:33	6	25	24.93	25.23	0.41	0.57	0.30	1.2
2016-09-04 17:48	6	100	99.98	101.13	0.14	0.31	1.15	1.2
2016-09-04 18:03	6	200	199.99	202.21	0.08	0.44	2.22	1.1
2016-09-04 18:18	6	150	149.95	151.55	0.08	0.35	1.60	1.1
2016-09-04 18:33	6	75	75.04	76.00	0.21	0.39	0.96	1.3
2016-09-04 18:48	6	175	175.02	177.09	0.11	0.44	2.07	1.2
2016-09-04 19:03	6	125	124.96	126.43	0.09	0.43	1.47	1.2
2016-09-04 19:18	7	0	0.45	0.33	0.21	0.21	-0.12	NA
2016-09-04 19:33	7	30	30.07	30.37	0.24	0.62	0.30	1.0
2016-09-04 19:48	7	50	50.05	50.57	0.18	0.32	0.52	1.0
2016-09-04 20:18	7	10	10.19	10.04	0.28	0.46	-0.15	-1.5
2016-09-04 20:33	7	60	59.96	60.28	0.21	0.43	0.32	0.5
2016-09-04 20:48	7	20	19.96	20.36	0.19	0.21	0.40	2.0
2016-09-04 20:48	7	70	70.01	70.88	0.11	0.49	0.87	1.2
2016-09-04 21:03	7	80	80.00	80.88	0.12	0.54	0.88	1.1
2016-09-04 21:18	7	40	40.01	40.09	0.30	0.47	0.08	0.2
2016-09-04 21:48	7	90	89.96	91.14	0.18	0.51	1.18	1.3
2016-09-04 22:03	8	0	0.29	0.29	0.29	0.14	0.00	NA
2016-09-04 22:18	8	40	39.96	40.24	0.29	0.36	0.28	0.7
2016-09-04 22:33	8	10	10.82	10.72	0.62	0.66	-0.10	-0.9
2016-09-04 22:48	8	50	50.01	50.30	0.04	0.18	0.29	0.6
2016-09-04 23:03	8	60	60.05	61.13	0.25	0.39	1.08	1.8
2016-09-04 23:18	8	90	90.01	90.76	0.10	0.29	0.75	0.8
2016-09-04 23:33	8	20	20.04	20.22	0.14	0.25	0.18	0.9
2016-09-04 23:48	8	70	70.00	70.63	0.06	0.27	0.63	0.9
2016-09-05 00:03	8	30	29.96	30.17	0.21	0.39	0.21	0.7
2016-09-05 00:18	8	80	80.02	81.27	0.09	0.21	1.25	1.6
2016-09-05 00:33	9	0	0.43	0.22	0.49	0.16	-0.21	NA
2016-09-05 00:48	9	50	50.01	50.17	0.20	0.53	0.16	0.3
2016-09-05 01:03	9	25	24.90	25.24	0.25	0.58	0.34	1.4
2016-09-05 01:18	9	100	100.01	101.16	0.05	0.37	1.15	1.1
2016-09-05 01:33	9	200	199.98	202.77	0.15	0.18	2.79	1.4
2016-09-05 01:48	9	150	149.96	152.16	0.10	0.37	2.20	1.5
2016-09-05 02:48	10	0	0.14	0.18	0.33	0.13	0.04	NA
2016-09-05 03:03	10	30	29.99	30.08	0.23	0.25	0.09	0.3

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-05 03:18	10	50	50.02	50.43	0.10	0.26	0.41	0.8
2016-09-05 03:33	10	70	70.01	71.14	0.15	0.39	1.13	1.6
2016-09-05 03:48	10	10	10.04	10.15	0.24	0.62	0.11	1.1
2016-09-05 04:03	10	60	60.06	60.72	0.12	0.47	0.66	1.1
2016-09-05 04:18	10	20	20.25	20.28	0.59	0.73	0.03	0.1
2016-09-05 04:33	10	80	80.00	81.38	0.08	0.25	1.38	1.7

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 WLG data acquisition system. The standards used for the calibration of the WLG analyser are shown in Table 7.

Table 6. Experimental details of WLG 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 19.	
Station Analyser WLG (AL)	
Model, S/N	Picarro G2401 #2490-CFKADS-2216
Principle	CRDS
Drying system	Nafion dryer followed by cryogenic trap (-50°C)
Station Analyser WLG (AL)	
Model, S/N	AGILENT 6890N #US10719008
Principle	GC/FID
Drying system	Nafion dryer followed by cryogenic trap (-50°C)
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports

Table 7. CO Standards available at WLG.

Cylinder ID	Manufacturer	Use	CO (ppb)	Scale
CB09602	Scott Marrin	WS (Picarro)	144.26	WMO-CO-X2014A
CB09181	Scott Marrin	WS (GC)	201.63	WMO-CO-X2014A
Target	Scott Marrin	target	164.89	WMO-CO-X2014A
CB10883	NOAA	LS	110.56	WMO-CO-X2014A
CB10823	NOAA	LS	128.8	WMO-CO-X2014A
CB11012	NOAA	LS	231.64	WMO-CO-X2014A
CB10846	NOAA	LS	419.78	WMO-CO-X2014A
CB11168	NOAA	LS	419.78	WMO-CO-X2014A
CB10851	NOAA	LS	505.84	WMO-CO-X2014A

Results

The results of the assessment are shown in the Executive Summary (figures and equations), 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 AGILENT 6890N #US10719008 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 (%)
(16-09-07 02:50:00)	160622_FA02474	236.8	0.4	235.3	1.4	3	-1.5	-0.6
(16-09-10 06:50:00)	110512_FB03348	131.0	0.1	129.0	0.2	3	-2.0	-1.5
(16-09-13 09:43:20)	140514_FB03904	203.2	0.2	200.7	0.4	3	-2.5	-1.3
(16-09-16 12:30:00)	140515_FB03384	157.2	0.2	156.2	1.4	3	-1.0	-0.6
(16-09-19 14:50:00)	140514_FB03918	184.4	0.4	183.7	1.6	3	-0.7	-0.4
(16-09-22 18:43:20)	130905_FB03383	87.6	0.2	87.8	1.6	3	0.1	0.2

Table 9. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2490-CFKADS2216 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 (%)
(16-09-04 13:40:00)	140515_FB03384	157.2	0.2	155.9	0.8	3	-1.3	-0.8
(16-09-04 14:10:00)	140514_FB03904	203.2	0.2	204.3	0.6	3	1.1	0.5
(16-09-04 14:40:00)	160622_FA02474	236.8	0.4	238.6	0.4	3	1.8	0.8
(16-09-04 15:10:00)	110512_FB03348	131.0	0.1	129.2	0.6	3	-1.8	-1.4
(16-09-04 15:40:00)	140514_FB03918	184.4	0.4	184.3	0.7	3	-0.1	-0.1
(16-09-04 16:10:00)	130905_FB03383	87.6	0.2	84.6	0.2	3	-3.0	-3.5

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.

Instrument details are identical to CO. The standards used for the calibration of the WLG analyser are shown in Table 10.

Table 10. CH_4 Standards available at WLG.

Cylinder ID	Manufacturer	Use	CH_4 (ppb)	Scale
CB09602	Scott Marrin	WS (Picarro)	1908.83	WMO-X2004A
CB09181	Scott Marrin	WS (GC)	1967.46	WMO-X2004A
Target	Scott Marrin	target	1859.58	WMO-X2004A
CB10883	NOAA	LS	1646.11	WMO-X2004A
CB10823	NOAA	LS	1799.91	WMO-X2004A
CB11012	NOAA	LS	2019.96	WMO-X2004A
CB10846	NOAA	LS	2179.18	WMO-X2004A
CB11168	NOAA	LS	2376.29	WMO-X2004A
CB10851	NOAA	LS	2579.00	WMO-X2004A

Results

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

Table 11. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the AGILENT 6890N #US10719008 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 (%)
(16-09-07 02:50:00)	160622_FA02474	2507.35	0.27	2508.22	0.04	3	0.87	0.03
(16-09-10 06:50:00)	110512_FB03348	2767.49	0.20	2767.06	0.44	3	-0.43	-0.02
(16-09-13 09:43:20)	140514_FB03904	2003.30	0.13	2004.06	0.87	3	0.76	0.04
(16-09-16 12:30:00)	140515_FB03384	1845.82	0.14	1846.52	0.79	3	0.70	0.04
(16-09-19 14:50:00)	140514_FB03918	1971.46	0.19	1971.43	1.22	3	-0.03	0.00
(16-09-22 18:43:20)	130905_FB03383	1862.01	0.13	1862.98	0.99	3	0.97	0.05

Table 12. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #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 (%)
(16-09-04 13:40:00)	140515_FB03384	1845.82	0.14	1846.66	0.03	3	0.84	0.05
(16-09-04 14:10:00)	140514_FB03904	2003.30	0.13	2003.89	0.04	3	0.59	0.03
(16-09-04 14:40:00)	160622_FA02474	2507.35	0.27	2507.48	0.04	3	0.13	0.01
(16-09-04 15:10:00)	110512_FB03348	2767.49	0.20	2767.56	0.06	3	0.07	0.00
(16-09-04 15:40:00)	140514_FB03918	1971.46	0.19	1972.16	0.04	3	0.70	0.04
(16-09-04 16:10:00)	130905_FB03383	1862.01	0.13	1862.80	0.03	3	0.79	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 G2401 described above is also used for CO_2 measurements. The standards used for the calibration of the WLG analyser are shown in Table 13.

Table 13. CO_2 Standards available at WLG.

Cylinder ID	Manufacturer	Use	CO_2 (ppb)	Scale
CB09602	Scott Marrin	WS	405.93	WMO-X2007A
Target	Scott Marrin	target	394.78	WMO-X2007A
CB10883	NOAA	LS	349.68	WMO-X2007A
CB10823	NOAA	LS	381.99	WMO-X2007A
CB11012	NOAA	LS	404.57	WMO-X2007A
CB10846	NOAA	LS	421.31	WMO-X2007A
CB11168	NOAA	LS	459.27	WMO-X2007A
CB10851	NOAA	LS	473.25	WMO-X2007A

Results

The results of the assessment are shown in the Executive Summary (figures and equations), 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 G2401 #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 (%)
(16-09-04 13:40:00)	140515_FB03384	381.44	0.05	381.49	0.01	3	0.05	0.01
(16-09-04 14:10:00)	140514_FB03904	404.79	0.08	404.79	0.02	3	0.00	0.00
(16-09-04 14:40:00)	160622_FA02474	421.29	0.03	421.23	0.01	3	-0.06	-0.01
(16-09-04 15:10:00)	110512_FB03348	341.02	0.03	341.10	0.01	3	0.08	0.02
(16-09-04 15:40:00)	140514_FB03918	400.82	0.03	400.82	0.01	3	0.00	0.00
(16-09-04 16:10:00)	130905_FB03383	390.27	0.04	390.30	0.01	3	0.03	0.01

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.

The GC system described above is equipped with an ECD detector, and this channel is used for N_2O measurements. The standards used for the calibration of the WLG analyser are shown in Table 15.

Table 15. N_2O Standards available at WLG.

Cylinder ID	Manufacturer	Use	N_2O (ppb)	Scale
CB09181	Scott Marrin	WS	328.07	WMO-X2006A
CB10883	NOAA	LS	289.02	WMO-X2006A
CB10823	NOAA	LS	315.59	WMO-X2006A
CB11012	NOAA	LS	329.05	WMO-X2006A
CB10846	NOAA	LS	332.98	WMO-X2006A
CB11168	NOAA	LS	338.8	WMO-X2006A
CB10851	NOAA	LS	340.62	WMO-X2006A

Results

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

Table 16. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the AGILENT 6890N #US10719008 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 (%)
(16-09-07 02:50:00)	160622_FA02474	324.47	0.14	324.57	0.18	3	0.10	0.03
(16-09-10 06:50:00)	110512_FB03348	323.85	0.10	323.74	0.03	3	-0.11	-0.03
(16-09-13 09:43:20)	140514_FB03904	328.36	0.10	328.27	0.02	3	-0.09	-0.03
(16-09-16 12:30:00)	140515_FB03384	326.13	0.07	326.36	0.05	3	0.23	0.07
(16-09-19 14:50:00)	140514_FB03918	322.64	0.12	322.89	0.02	3	0.25	0.08
(16-09-22 18:43:20)	130905_FB03383	317.21	0.17	317.59	0.16	3	0.38	0.12

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 49i-PS #0810-153, BKG -0.2, COEF 1.008

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 17. 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)).

$$X_{TS} \text{ (ppb)} = ([TS] - 0.04 \text{ ppb}) / 1.0038 \qquad (6a)$$

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

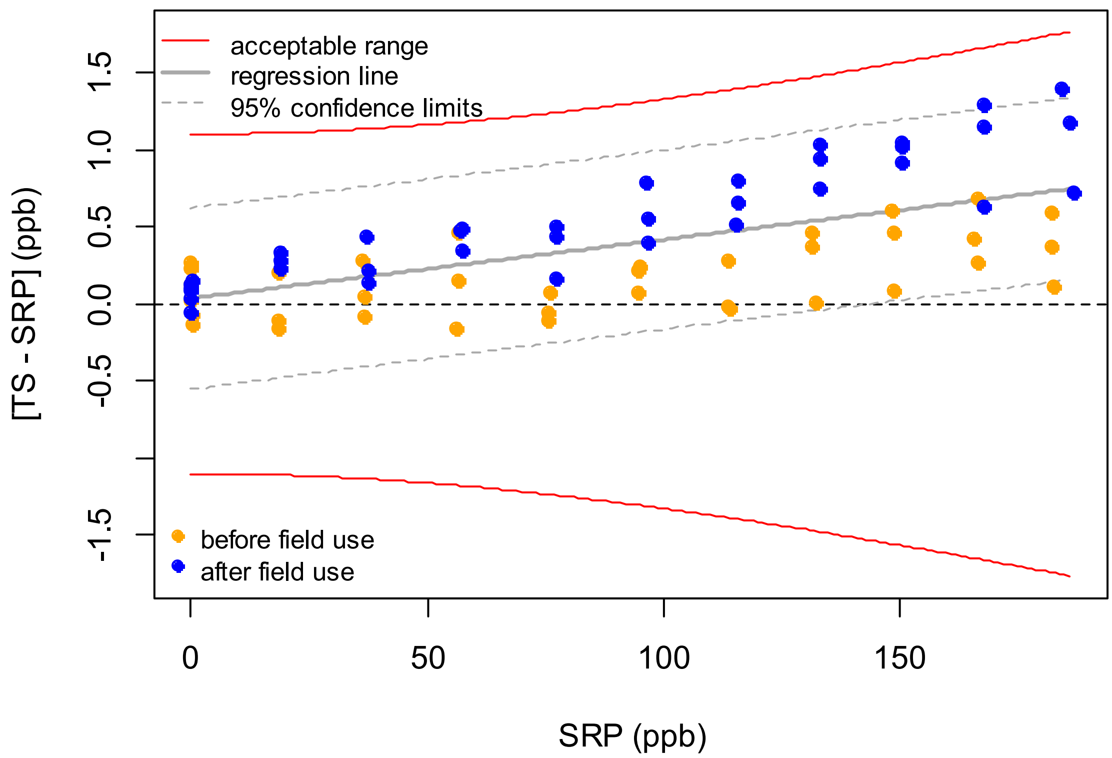

Figure 24. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 17. 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)
2016-07-04	1	0	-0.22	0.38	0.05	0.26
2016-07-04	1	55	56.31	0.33	56.15	0.17
2016-07-04	1	150	148.67	0.35	148.75	0.24
2016-07-04	1	95	94.82	0.64	95.03	0.11
2016-07-04	1	20	18.61	0.37	18.46	0.11
2016-07-04	1	115	113.86	0.38	114.13	0.18
2016-07-04	1	75	75.78	0.27	75.72	0.18
2016-07-04	1	35	36.08	0.34	36.37	0.18
2016-07-04	1	185	182.84	0.31	182.96	0.16
2016-07-04	1	130	132.15	0.46	132.16	0.30
2016-07-04	1	165	166.57	0.25	167.25	0.19
2016-07-04	1	0	-0.20	0.34	-0.18	0.21
2016-07-04	2	0	-0.14	0.37	-0.01	0.16
2016-07-04	2	150	148.78	0.21	149.23	0.20
2016-07-04	2	165	166.47	0.32	166.73	0.25
2016-07-04	2	75	75.95	0.23	76.03	0.15
2016-07-04	2	95	94.86	0.20	95.09	0.11
2016-07-04	2	115	114.21	0.48	114.18	0.16
2016-07-04	2	130	131.59	0.41	132.05	0.16
2016-07-04	2	55	56.47	0.19	56.62	0.15
2016-07-04	2	180	182.23	0.17	182.82	0.27
2016-07-04	2	35	36.67	0.33	36.59	0.15
2016-07-04	2	20	18.52	0.24	18.72	0.19
2016-07-04	2	0	-0.16	0.35	0.06	0.26
2016-07-04	3	0	0.10	0.42	-0.04	0.20
2016-07-04	3	55	56.42	0.28	56.88	0.15
2016-07-04	3	130	131.27	0.26	131.65	0.19
2016-07-04	3	180	182.12	0.54	182.50	0.13
2016-07-04	3	150	148.45	0.22	149.06	0.23
2016-07-04	3	20	18.63	0.17	18.51	0.38
2016-07-04	3	75	75.80	0.32	75.69	0.14
2016-07-04	3	35	36.54	0.29	36.58	0.14
2016-07-04	3	95	94.66	0.22	94.74	0.15
2016-07-04	3	115	113.81	0.24	113.79	0.28
2016-07-04	3	165	165.60	0.37	166.02	0.14
2016-07-04	3	0	0.19	0.19	0.13	0.19
2016-12-08	4	0	0.04	0.30	-0.02	0.36
2016-12-08	4	185	186.79	0.41	187.51	0.36
2016-12-08	4	170	168.03	0.39	169.31	0.14
2016-12-08	4	115	115.69	0.34	116.49	0.20
2016-12-08	4	35	37.35	0.33	37.49	0.11
2016-12-08	4	60	57.52	0.26	58.00	0.19
2016-12-08	4	135	133.26	0.42	134.29	0.17
2016-12-08	4	75	77.25	0.37	77.75	0.17
2016-12-08	4	95	96.63	0.29	97.03	0.17
2016-12-08	4	150	150.33	0.39	151.37	0.20
2016-12-08	4	20	18.84	0.25	19.17	0.14
2016-12-08	4	0	-0.03	0.25	0.06	0.18
2016-12-08	5	0	0.08	0.34	0.23	0.26
2016-12-08	5	185	186.15	0.34	187.32	0.32

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2016-12-08	5	55	57.35	0.35	57.69	0.07
2016-12-08	5	75	77.49	0.39	77.66	0.21
2016-12-08	5	135	133.32	0.44	134.07	0.15
2016-12-08	5	35	37.43	0.28	37.65	0.24
2016-12-08	5	150	150.44	0.32	151.35	0.22
2016-12-08	5	20	18.90	0.20	19.18	0.30
2016-12-08	5	170	167.91	0.22	169.05	0.32
2016-12-08	5	95	96.40	0.15	97.19	0.21
2016-12-08	5	115	115.58	0.25	116.09	0.33
2016-12-08	5	0	-0.03	0.30	0.07	0.17
2016-12-08	6	0	0.03	0.34	0.06	0.18
2016-12-08	6	95	96.92	0.20	97.48	0.15
2016-12-08	6	35	37.27	0.25	37.71	0.23
2016-12-08	6	150	150.53	0.29	151.55	0.18
2016-12-08	6	20	18.92	0.39	19.16	0.25
2016-12-08	6	135	133.23	0.30	134.17	0.30
2016-12-08	6	170	167.99	0.26	168.61	0.23
2016-12-08	6	185	184.27	0.34	185.66	0.29
2016-12-08	6	75	77.10	0.47	77.54	0.25
2016-12-08	6	55	56.97	0.42	57.45	0.25
2016-12-08	6	115	115.79	0.19	116.45	0.18
2016-12-08	6	0	-0.08	0.24	0.04	0.24

#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 18 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 19, 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 18. 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 19. 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)
110512_FB03348	130.98	0.12	2767.49	0.2	341.02	0.03	323.85	0.1
130905_FB03383	87.64	0.15	1862.01	0.13	390.27	0.04	317.21	0.17
140514_FB03904	203.19	0.22	2003.3	0.13	404.79	0.08	328.36	0.1
140514_FB03918	184.39	0.43	1971.46	0.19	400.82	0.03	322.64	0.12
140515_FB03384	157.15	0.21	1845.82	0.14	381.44	0.05	326.13	0.07
160622_FA02474	236.79	0.4	2507.35	0.27	421.29	0.03	324.47	0.14

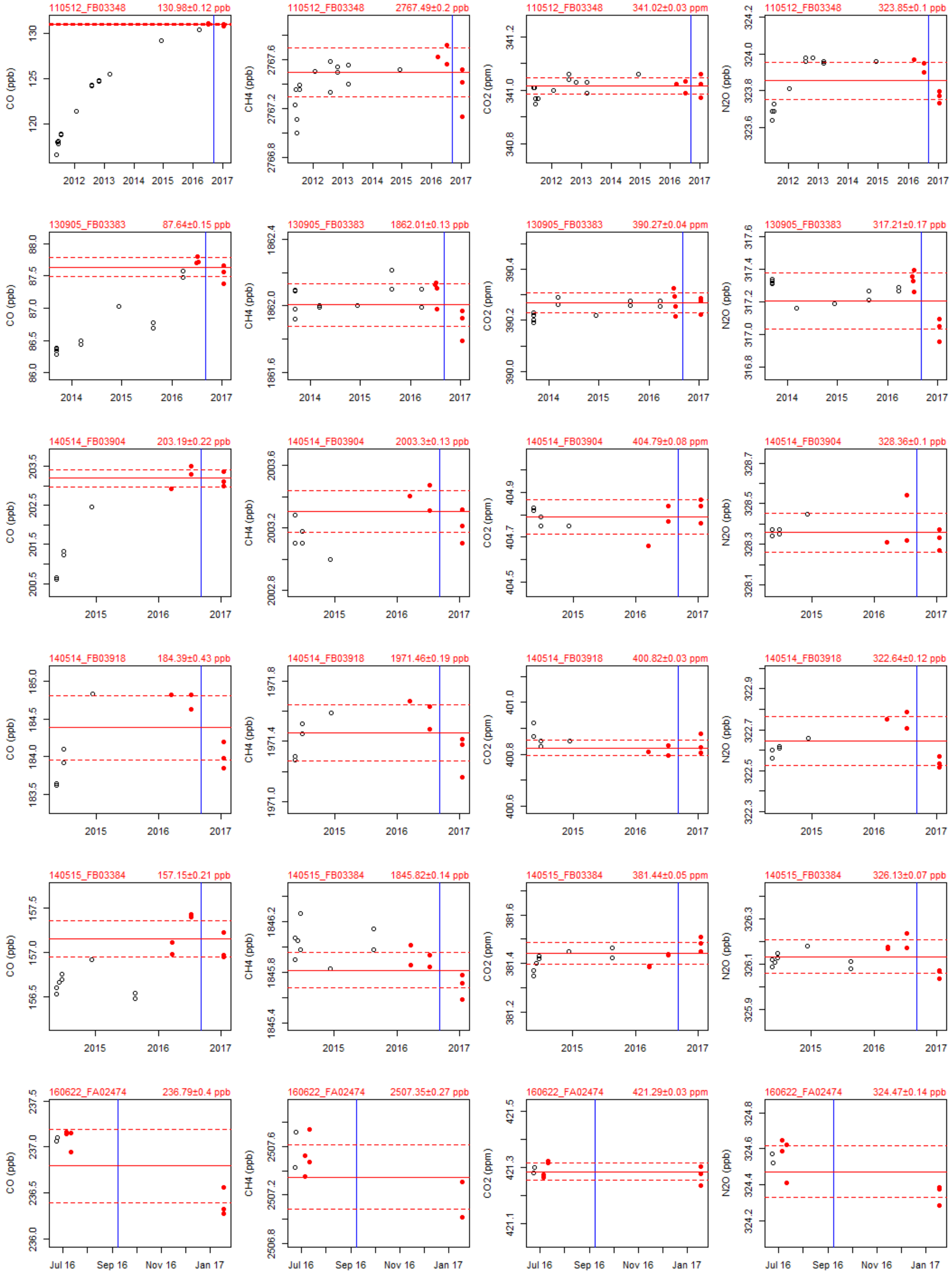

Figure 25. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. 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. 0.5 ppb for CH_4 and 0.05 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

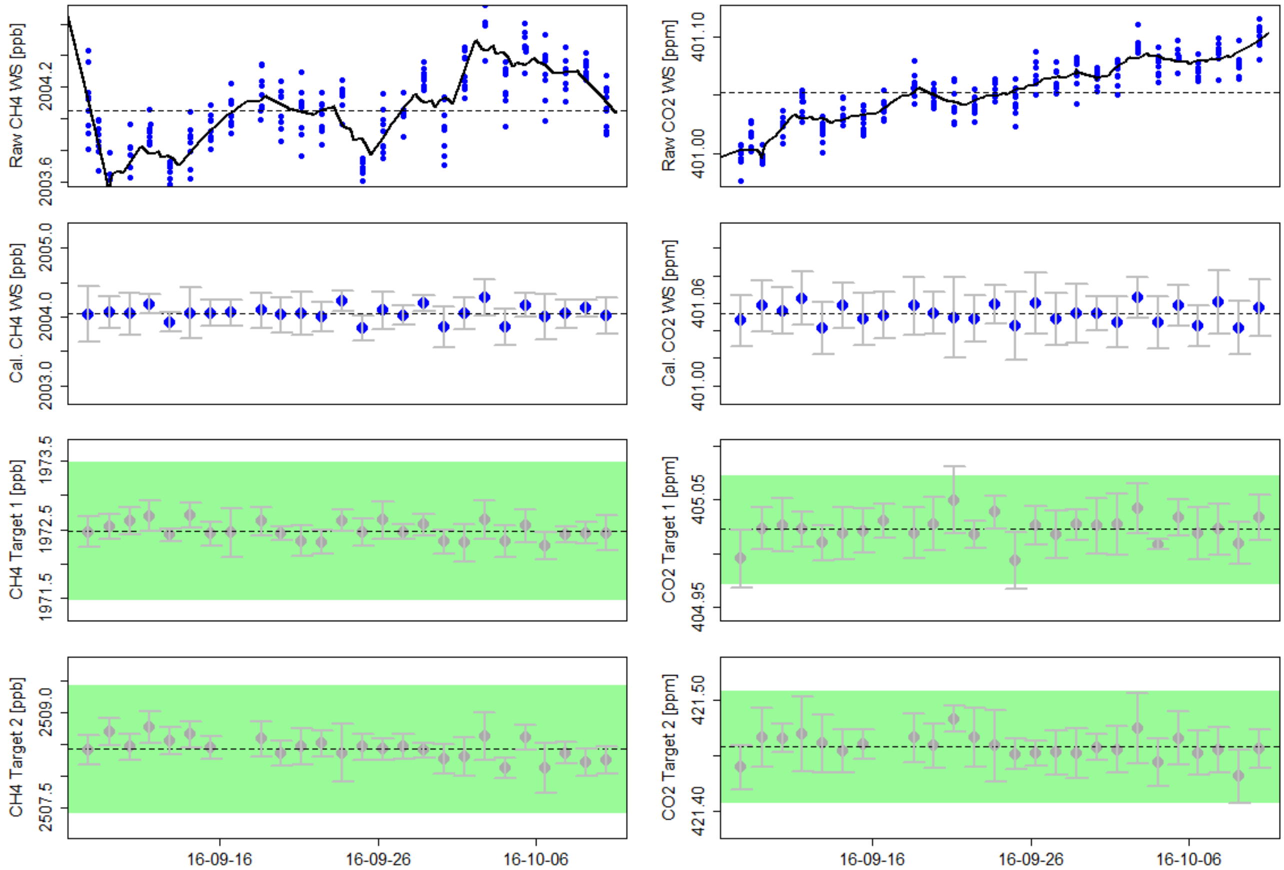

Figure 26. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1-min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower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

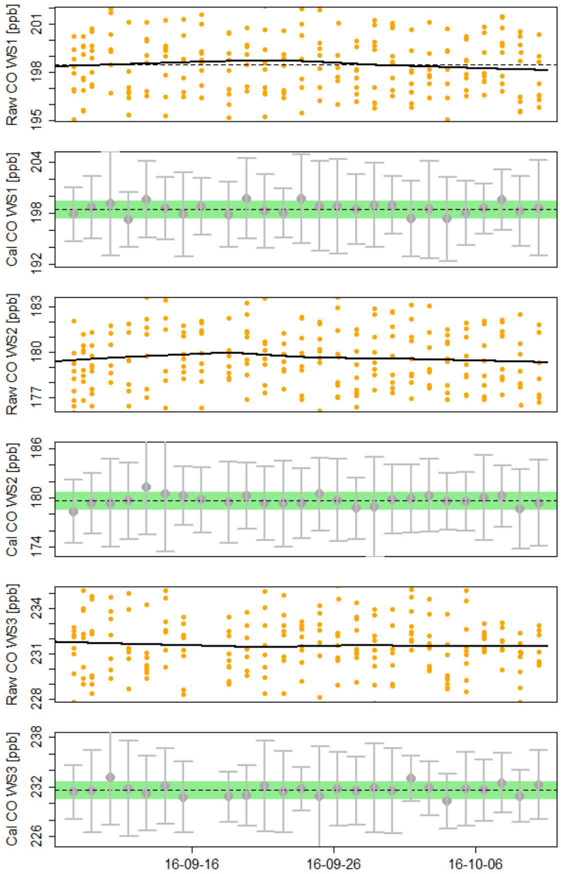

Figure 27. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1-min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels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

BKG	Background
CAMS	Chinese Academy for Meteorological Sciences
CAWAS	Centre for Atmosphere Watch and Services
CGAWBO	China Global Atmosphere Watch Baseline Observatory
COEF	Coefficient
CMA	China Meteorological Administration
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
LS	Laboratory Standard
NA	Not Applicable
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
QMB	Qinghai Meteorological Bureau
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
WLG	Mt. Waliguan GAW Station
WMO	World Meteorological Organization