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

GLOBAL GAW STATION PUY DE DÔME FRANCE APRIL 2016

Submitted to the World Meteorological Organization by

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WCC-Empa Report 16/2

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CONTENTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit by WCC-Empa[1] at the Global GAW station Puy de Dôme was conducted from 11 - 14 April 2016 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). The measurements at the Puy de Dôme (PUY) GAW station are coordinated by the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-Sur-Yvette, and the Observatoire de Physique du Globe de Clermont-Ferrand (OPCG) of the University Blaise Pascal in Aubiere.

No previous audits have been conducted at the Puy de Dôme GAW station. The audit was conducted in parallel to an audit by the ICOS (Integrated Carbon Observing System) mobile laboratory. The results of the ICOS audit are available from on request from the PUY station.

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Michel Ramonet	LSCE, measurement leader greenhouse gases
Dr. Aurelie Colomb	OPCG, primary station contact; measurement leader greenhouse gases
Dr. Camille Yver	LSCE, scientist
Dr. Olivier Laurent	LSCE, scientist
Mr. Jean-Marc Pichon	OPCG, station engineer

This report summarises the assessment of the Puy de Dôme GAW station in general, as well as the surface ozone, carbon monoxide, methane and carbon dioxide measurements in particular.

The report is distributed to the involved institutes of the PUY station 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.

SYSTEM AUDIT

Station Management and Operation

GAW activities in France are made under the umbrella of the National Centre for Scientific Research (CNRS), a public organization under the responsibility of the French Ministry of Education and Research. The actual measurements are mainly carried out by two institutes; the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-Sur-Yvette, and the Observatoire de Physique du Globe de Clermont-Ferrand (OPCG) of the University Blaise Pascal in Aubiere. Details of the organisation are available from the corresponding websites and links therein.

OPGC: http://wwwobs.univ-bpclermont.fr/SO/mesures

LSCE: http://www.lsce.ipsl.fr

Station Location and Access

The Puy de Dôme Research Station (1465 m a.s.l), central France, is located on the western most mountain chain with predominately westerly winds. Puy de Dôme is the highest point of this mountain range which comprises 80 volcanoes aligned north to south on a 3 to 5 km wide strip of land, a little over 45 kilometres in length. The station is exposed to an oceanic climate. It is surrounded by a

[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.

protected area where agricultural fields and forests are predominant. The city of Clermont-Ferrand (150 000 inhabitants) is located 16 km east of the station at 396 m a.s.l. The PUY station is measuring a comprehensive set of gases and aerosol parameters, coupled with co-located RADAR, LIDAR and sun photometer measurements.

Further information about the PUY station is available from the GAW Station Information System (GAWSIS) (https://gawsis.meteoswiss.ch).

Station Facilities

Two laboratories are available for aerosol, greenhouse and reactive gases measurements. Gas cylinders are stored in a separate room. The station is further equipped with a living room and a kitchen, and two sleeping rooms with totally eight beds. The laboratories are air conditioned. Most of the available space is occupied by permanent measurements, but some additional space may be used for campaign based experiments. Due to its location it is an ideal platform for atmospheric research.

Measurement Programme

The PUY station comprises a very comprehensive measurement programme that covers all focal areas of the GAW programme. It further is part of national and international research programmes such as EMEP (European Monitoring and Evaluation Programme) and ICOS (Integrated Carbon Observing System). An overview on measured species is available from GAWSIS and the station web site (links above).

> **Recommendation 1 (**, minor, 2017)**
> *GAWSIS needs to be updated. The information is not up to date for some of the measured parameters.*

Data Submission

Data has only been partly submitted to the corresponding data centres. Surface O_3 (2008-2011), CO (2008-2011), CH_4 (2002-2015), and CO_2 (2010-2015) data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Slightly longer/different time series are available from the EBAS database for O_3 (2007-2014) and CO (2011-2013).

> **Recommendation 2 (**, important, 2017)**
> *It is recommended to submit data to the corresponding data centres at least in yearly intervals. Data of the reactive gases need to be submitted more regularly.*
>
> **Recommendation 3 (**, important, 2017)**
> *Submission of the entire ozone data series from 1999 – present to the newly established GAW World Data Centre for Reactive Gases (WDCRG) is encouraged.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG were reviewed. All reviewed data looks plausible, and no further action is required. Summary plots and a short description of the findings are presented in the Appendix.

Documentation

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

PERFORMANCE AUDIT

Surface Ozone Measurements

The surface ozone measurements at Puy de Dôme were established in 1999 and continuous time series are available since then.

Instrumentation. The station is equipped with two ozone analysers (TEI 49i and Environment SA 41 m). The Environment instrument is part of the local air quality monitoring network and not part of the GAW programme. The instrumentation is adequate for ozone measurements.

Data Acquisition. Custom made LabView based system. All available instrument parameters are recorded, and remote access/control is possible through Virtual Network Computing (VNC).

Standards. An ozone generator (Ansyco SYCOS KT-03M-FR) is available for span checks. This ozone generator is not suitable to performing calibrations of an ozone instrument.

> **Recommendation 3 (***, important, 2017)**
> *It is recommended to purchase an ozone calibrator to calibrate the PUY ozone instrument. The current ozone generator is not suitable for ozone calibrations.*

Air Inlet. The ozone inlet is mounted 2.4 m above the roof of the laboratory building and consists of a 7.4 m long PTFE tube with an inner diameter of 3.5 cm and flushed with a Busch Samos pump at a low rate of 1.3 m^3/h. The analyser is connected by 2 m ¼ inch PTFE tubing. A PFA filter holder equipped with Sartorius Stedim PTFE filters is used to protect the instrument from dust. The residence time is estimated to be approximately 6 seconds, which is appropriate for the measurement of ozone.

Intercomparison (Performance Audit). The GAW TEI49i ozone analyser of PUY was compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The calibration settings were adjusted after the first comparison, since the instrument has never been calibrated against an NIST traceable ozone reference. 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:

Initial comparison:

TEI 49i #0536415133 (BKG -0.5 ppb, COEF 1.053):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] – 1.20 ppb) / 0.9587 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.48 ppb^2 + 3.21e-05 * X_{O3}^2) (1b)

Final comparison after adjustment of calibration factors:

TEI 49C #429508925 (BKG +0.5 ppb, COEF 1.026):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.02 ppb) / 0.9977 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.32 ppb^2 + 2.72-05 * X_{O3}^2) (1d)

The result of the comparison is further illustrated in the figures below.

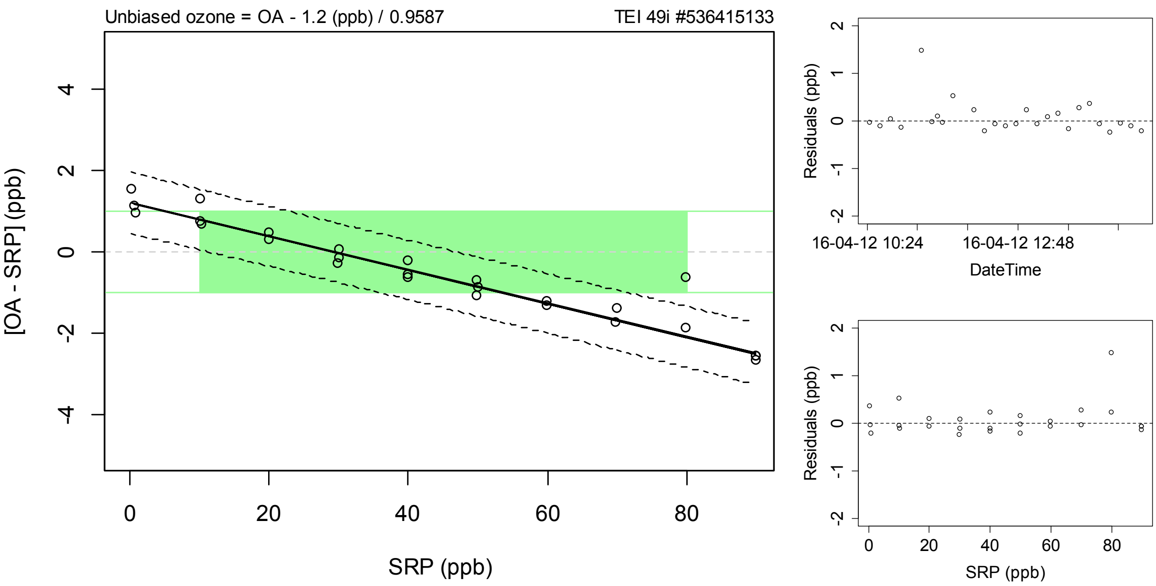

Figure 1. *Left: Bias of the PUY ozone analyser (TEI 49i #0536415133) with respect to the SRP as a function of mole fraction (initial comparison with unchanged calibration settings). Each point represents the average of the last 10 one-minute values at a given level. The green lines correspond to the DQOs, and the green area to the mole fraction range relevant for PUY. 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).*

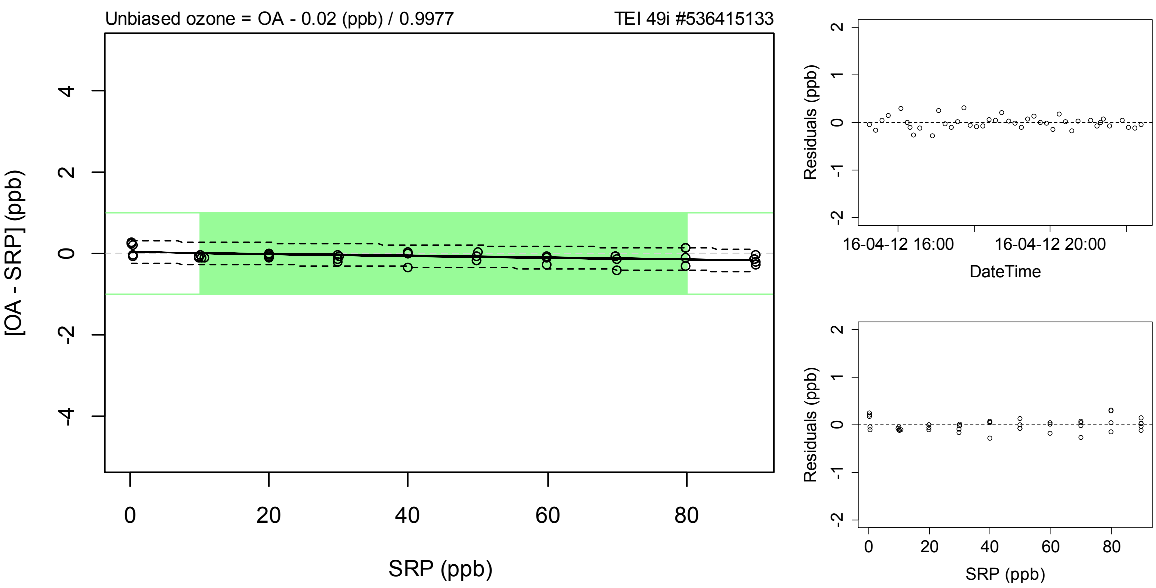

Figure 2. *Same as above after adjustment of the calibration settings.*

The results of the comparison can be summarised as follows:

After adjustment of the calibration settings, the TEI 49i #0536415133 ozone analyser was in good calibration and the bias is within the WMO/GAW DQOs for the relevant mole fraction range. It is strongly recommended to purchase an ozone calibrator for regular checks of the instrument calibration.

Recommendation 4 (, important, 2017)**
It is recommended to post-process and correct data acquired with the initial calibration settings according to the above equation (1a).

Carbon Monoxide Measurements

Carbon monoxide measurements at Puy de Dôme were established in 2008, and continuous time series are available since then.

Instrumentation. Puy de Dôme is equipped with a Picarro G2401 instrument based on Cavity Ring Down Spectroscopy (CRDS). Previously CO was also measured by Non-dispersive Infrared (NDIR) absorption technique. The current instrumentation is adequate for CO measurement.

Data Acquisition. Picarro integrated, Python based system.

Standards. Four calibration standards from the ICOS programme with traceability to the WMO/GAW reference scale are available at PUY. In addition, two target tanks are available. A list of the available standards is given in the Appendix

Air Inlet. The inlet for Greenhouse Gases (GHG) is located at a height of 3 m above the roof of the laboratory building and is made of 10 m 3/8 inch Synflex 1300 tuning, and two cryo traps (5 and -50°C) are used for sample drying. Four different filters (140, 40, 7 and 2 µm) are used to protect the system from particles. The residence time is estimated to be 5 min. The inlet system is adequate concerning location and materials.

> **Recommendation 5 (*, minor, 2017)**
> *The residence time in the GHG inlet system is relatively long. It has to be made sure that this is accounted for in the data evaluation.*

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PUY 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 with respect to the WMO GAW DQOs (WMO, 2014):

Picarro G2401 #2021-CFKADS-2161:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 0.1) / 1.0008 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.5 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

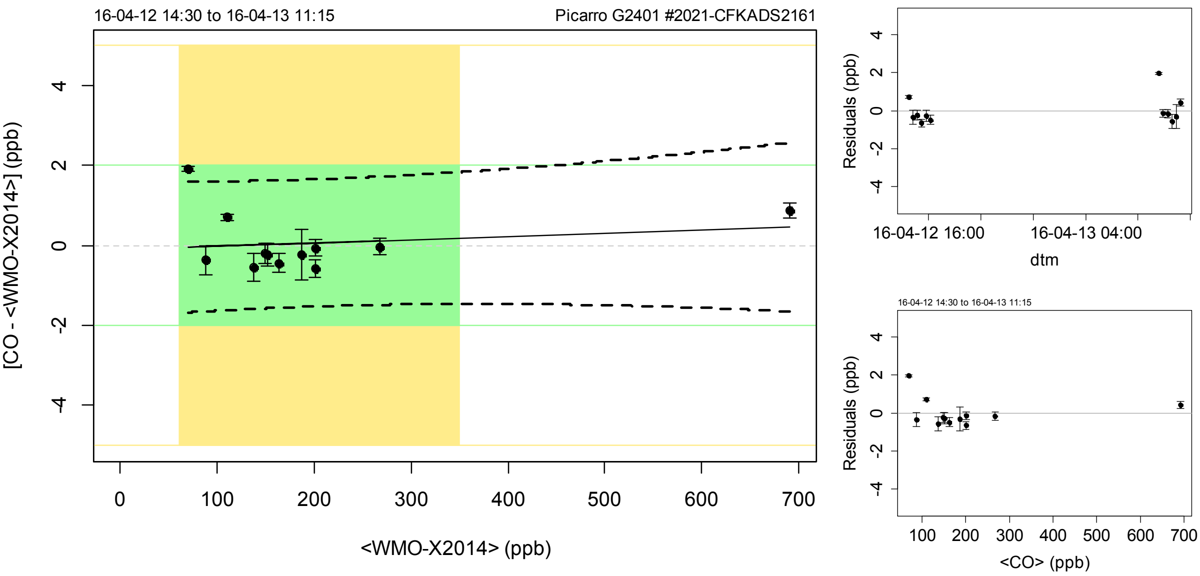

Figure 3. *Left: Bias of the PUY Picarro G2401 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for PUY. 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 comparisons can be summarised as follows:

The agreement of the Picarro G2401 analyser was well within the WMO/GAW compatibility goals of ±2 ppb over the entire relevant mole fraction range, which shows that the entire measurement set-up including calibration and data evaluation is fully appropriate.

Methane Measurements

Measurements of methane at PUY commenced in 2001, and data series are available since then. Initially, only flask measurements were made. Since 2001, a pair of flasks has been sampled once a week and analysed by GC for CO_2, CH_4, N_2O and SF_6 mole fractions and by a mass spectrometer for $\delta\,^{13}C$ and $\delta\,^{18}O$ in CO_2. In 2010, an Agilent HP-6890N with an FID detector was installed for semi-continuous of methane (Lopez et al., 2015), and since 2015, a Picarro G2401 CRDS instrument is used. Since then, data of the CRDS instrument is considered for submission to the WMO/GAW data centre.

Instrumentation. Picarro G2401 instrument based on Cavity Ring Down Spectroscopy (CRDS). The current instrumentation is adequate for CH_4 measurement.

Data Acquisition. Picarro integrated, Python based system.

Standards. Four calibration standards from the ICOS programme with traceability to the WMO/GAW reference scale are available at PUY. In addition, two target tanks are available. A list of the available standards is given in the Appendix.

Air Inlet. Same as for CO.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PUY 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 4 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2401, #2021-CFKADS-2161:

Unbiased CH_4 mixing ratio:	X_{CH4} (ppb) = (CH_4 – 4.3 ppb) / 0.99768	(3a)
Remaining standard uncertainty:	u_{CH4} (ppb) = sqrt (0.1 ppb^2 + 1.30e-07 * X_{CH4}^2)	(3b)

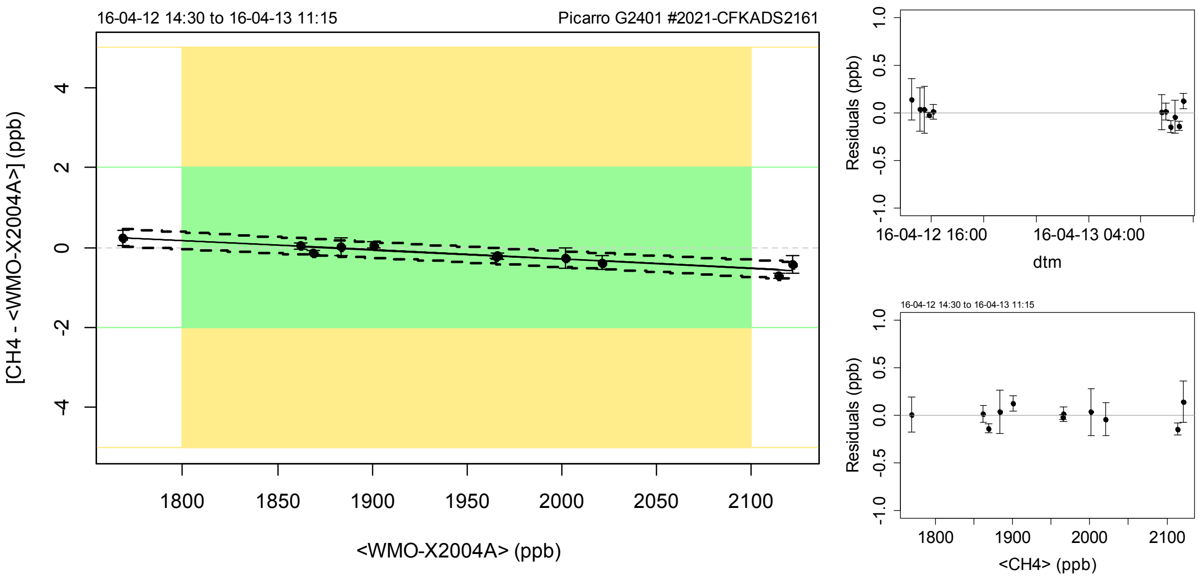

Figure 4. *Left: Bias of the PICARRO G2401 #2021-CFKADS-2161 methane instrument with respect to the WMO-X2004 CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 PUY. 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 ±2 ppb was found over the entire mole fraction range tested during the audit. These results show that the instrumentation is fully adequate and no further action is required.

Carbon Dioxide Measurements

The GHG observations at Puy de Dôme started in 2000 with continuous CO_2 measurements using a nondispersive infrared (NDIR) spectrometer. Since 2001, a pair of flasks has been sampled once a week and analysed by GC for CO_2, CH_4, N_2O and SF_6 mole fractions and by a mass spectrometer for $\delta\ ^{13}C$ and $\delta\ ^{18}O$ in CO_2. Since 2015, a Picarro G2401 CRDS instrument is used. Since then, data of the CRDS instrument is considered for submission to the WMO/GAW data centre.

Instrumentation. Picarro G2401 instrument based on Cavity Ring Down Spectroscopy (CRDS). The current instrumentation is adequate for CH_4 measurement.

Data Acquisition. Picarro integrated, Python based system.

Standards. Four calibration standards from the ICOS programme with traceability to the WMO/GAW reference scale are available at PUY. In addition, two target tanks are available. A list of the available standards is given in the Appendix.

Air Inlet. Same as for CO.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PUY 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 5 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2401, #2021-CFKADS-2161:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.74 ppm) / 0.99823 (4a)

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

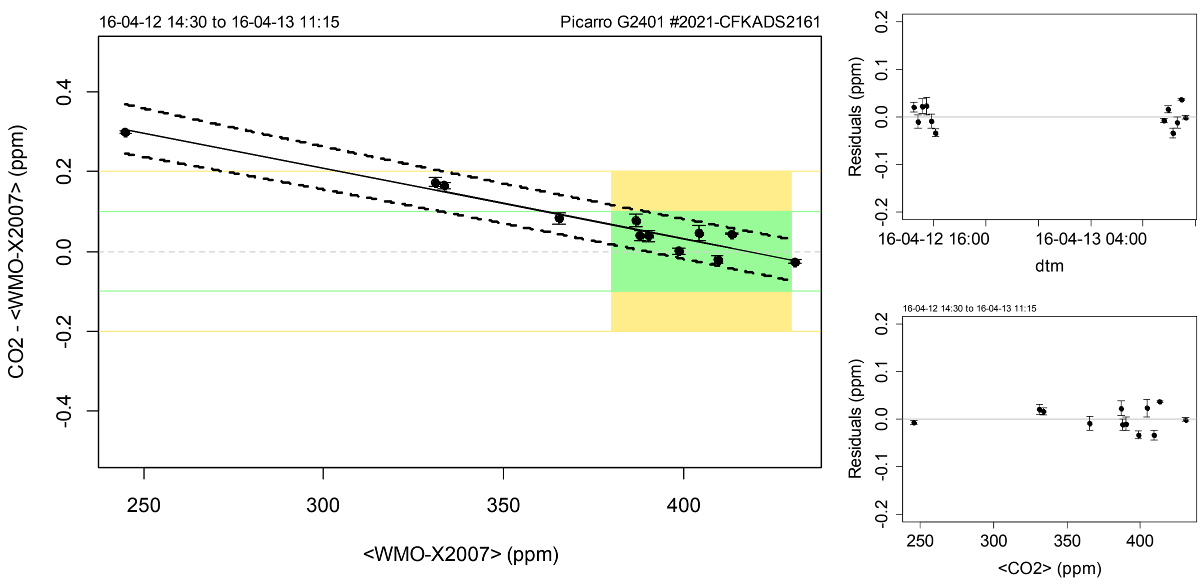

Figure 5. *Left: Bias of the PICARRO G2401 #2021-CFKADS-2161 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 PUY. 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 ±0.1 ppb was found in the relevant mole fraction range for the Picarro instrument. However, a significant positive bias was observed for lower mole fractions, which probably originates from the uncertainty of the standards used for calibration. It should be considered to implement a calibration scheme that covers a larger mole fraction range.

PUY PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the PUY 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 6 shows the bias vs. the slope of the performance audits audits made by WCC-Empa for O_3, CO, CH_4 and CO_2. 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 6 further highlights the results of the current audit (coloured dots), which are further discussed below.

Figure 6 (top left) 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, 54% of all ozone audits complied with this goal. The PUY results are shown in the same graph as couloured dots before (red) and after (blue) adjustment of the calibration settings. The result of the PUY ozone instrument with the new calibration settings meets the WMO/GAW compatibility goals in the range 0 – 100 ppb ozone. Data acqired with the initial calibration settings need to be corrected.

Figure 6 (top right) 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, 23% of all CO audits complied with the 2 ppb goal, 21% met the 5 ppb goal, and 56% were exceeding the WMO/GAW compatibility goal in the range of 30 – 300 ppb CO. The PUY performance audit result is shown in the same graph as a blue dot and fully complies with the WMO/GAW compatibility goal. Compared to other audits, the agreement is among the best.

Figure 6 (bottom left) 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, 58% of all CH_4 audits complied with the 2 ppb goal, 31% met the 5 ppb goal, and 11% were exceeding the WMO/GAW compatibility goal in the range of 1750 - 2100 ppb CH_4. The PUY performance audit result is shown in the same graph as a blue dot. The result of the PUY performance audit fully complies with the WMO/GAW compatibility goal.

Figure 6 (bottom right) 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, 26% of all CO_2 audits complied with the 0.1 ppm goal, 26% 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 PUY performance audit result is shown in the same graph as a blue dot. The result of the PUY performance audit complies with the WMO/GAW compatibility goal of 0.1 ppm over the entire range from 380 - 450 ppm CO_2.

The results of the ICOS audit (CO, CH_4 and CO_2) are shown as darkgreen dots in Figure 6. The WCC-Empa and ICOS performance audit results are not significantly different for CO and CH_4, but a slightly larger bias was observed between ICOS and the results of PUY and WCC-Empa for CO_2. This difference however was not observed in the comparison of ambient air between PUY and the ICOS mobile laboratory.

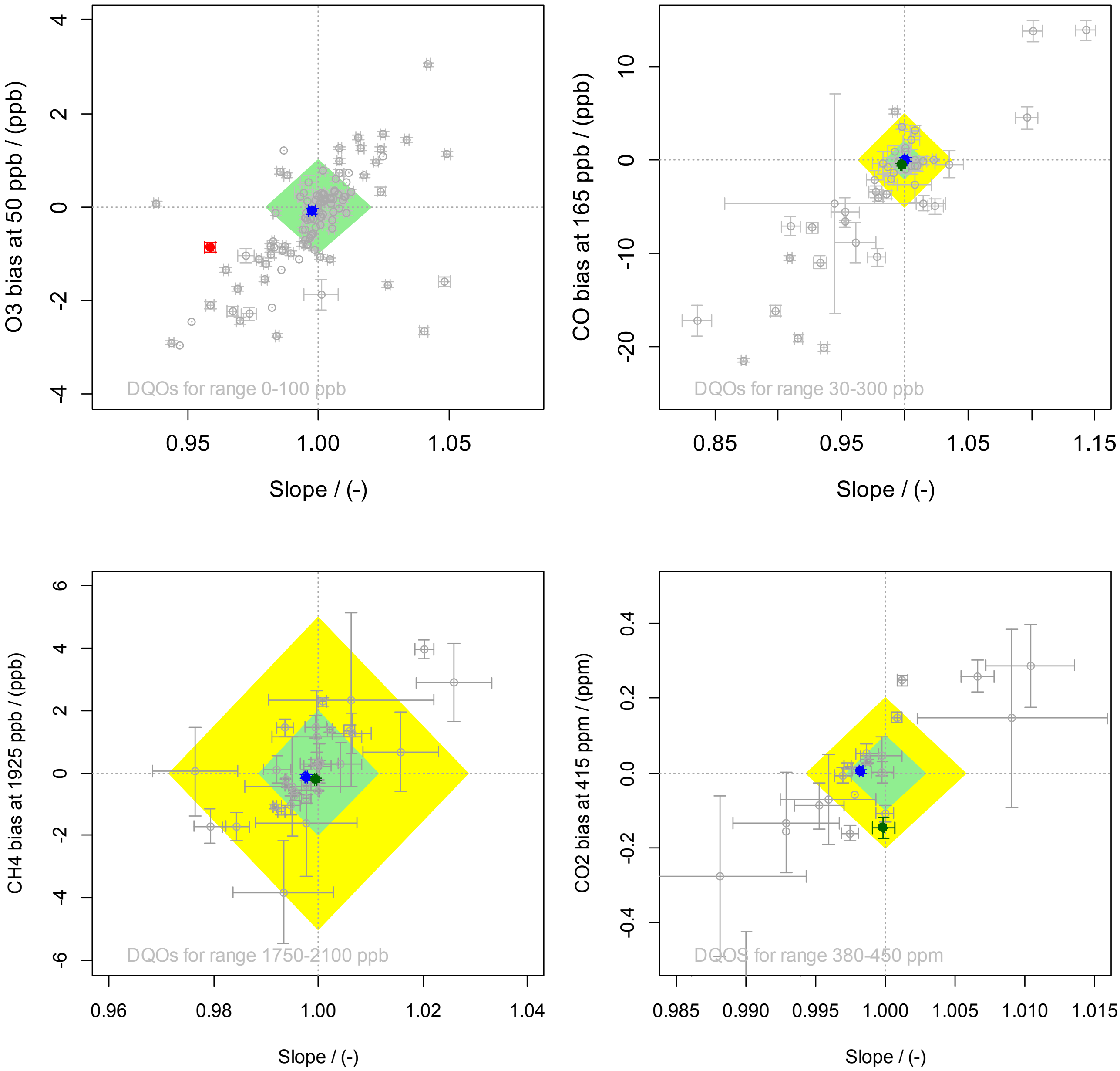

Figure 6. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to individual performance audits, while the coloured dots show PUY results (see text for further details). The coloured areas correspond to the WMO/GAW compatibility goals (green) and, if available, extended compatibility goals (yellow).*

PARALLEL MEASUREMENTS OF AMBIENT AIR

The audit included parallel measurements of CO_2, CH_4 and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401 SN # 1497-CFKADS2098). The TI was running from 11 April 2016 through 24 June 2016. The TI was sampling from a completely separate inlet line leading to the same air intake location as the PUY station inlet, and was also measuring using the same air intake as the PUY instrument during the last two weeks of the campaign starting from 7 June 2016. The air was not dried when using the independent inlet, while the PUY drying unit was used by the TI during the last two weeks. 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:

The temporal variation of CO was well captured by both the station instrument and the TI, which is illustrated in Figure 7 for the period when the TI measured humid air and in Figure 8 for the comparison of dry air. However, the two periods showed a significantly different bias, which was on average 1.40±0.87 ppb for the dry air comparison, and 5.85±0.94 ppb for the period when the TI sampled humid air. The corresponding deviation histograms are shown in Figure 9. These results indicate that the water vapour correction function of the TI was not working properly. This has been confirmed by the determination of the water vapour interference, which was up to 6 % depending on humidity after the instrument returned to the WCC-Empa laboratory. Therefore, only the period with dry air measurements should be considered, where the average bias was within the WMO/GAW compatibility goal of 2 ppb.

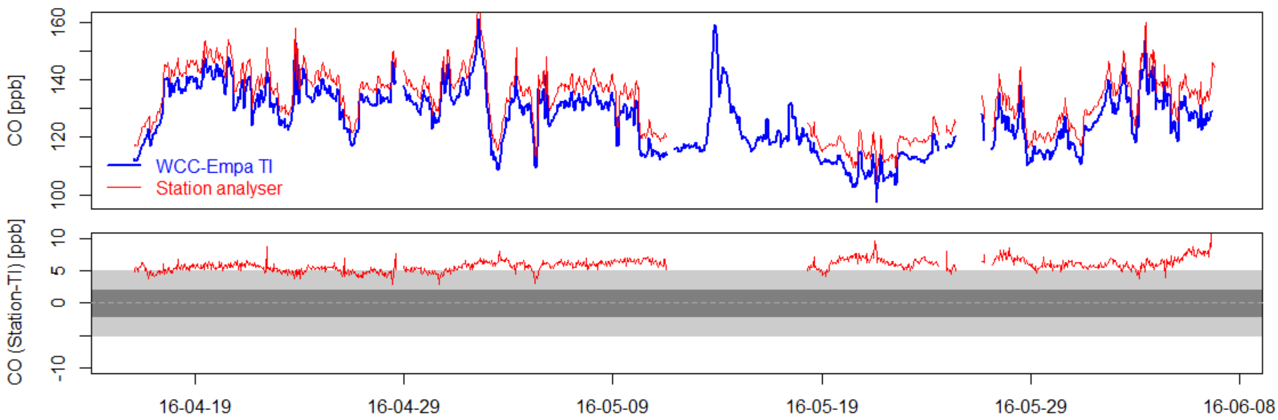

Figure 7. CO comparison at PUY between the WCC-Empa travelling instrument and the PUY Picarro G2401 for the period when the TI sampled humid air. Upper panel: CO time series (1 h data). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

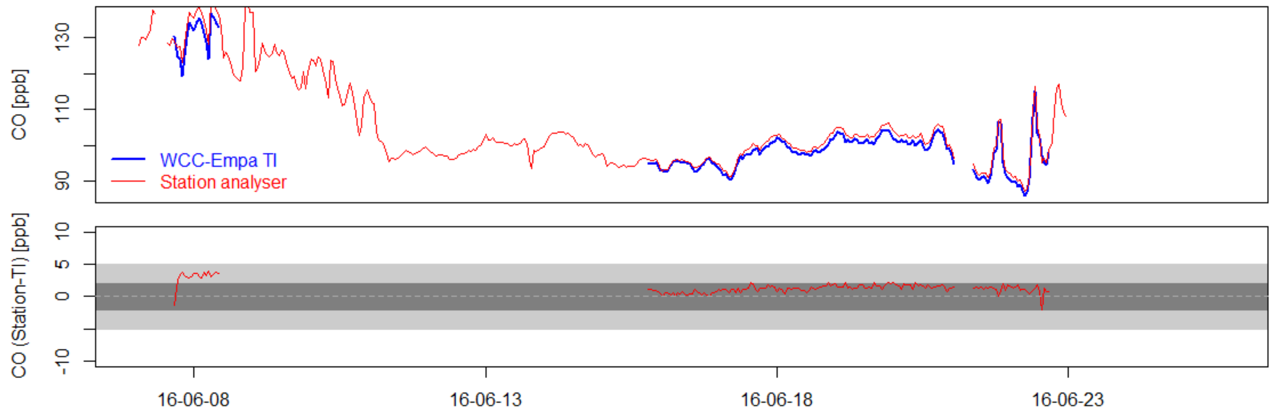

Figure 8. Same as above for the period when the TI was measuring dry air.

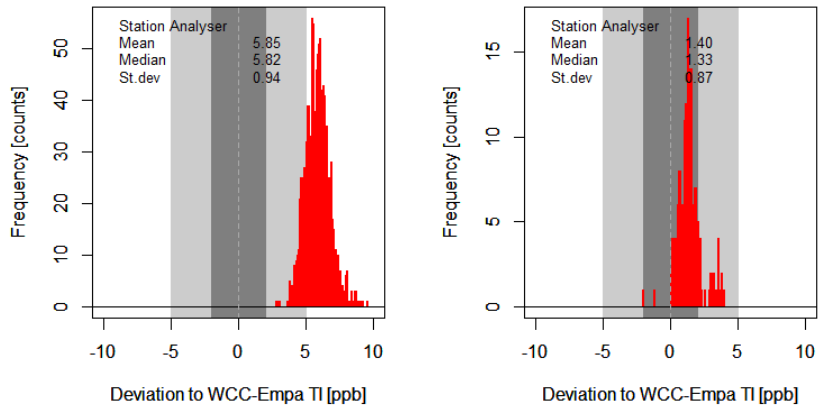

Figure 9. CO deviation histograms (1 h data, station analyser – TI) for the period with humid TI measurements (left) and for the period when the TI sampled dry air from the PUY inlet (right).

Methane:

Figure 10 shows the CH_4 comparison of the Picarro G2401 analyser with the WCC-Empa TI for the period when the TI sampled humid air. The temporal variation was well captured by both instruments, and the average bias was with -0.20±0.99 ppb within the WMO/GAW compatibility goal of 2 ppb. A similar bias of 0.24±0.77 ppb was found for the period when the TI measured dry air, as shown in Figure 11. The corresponding deviation histograms for both periods are shown in Figure 12.

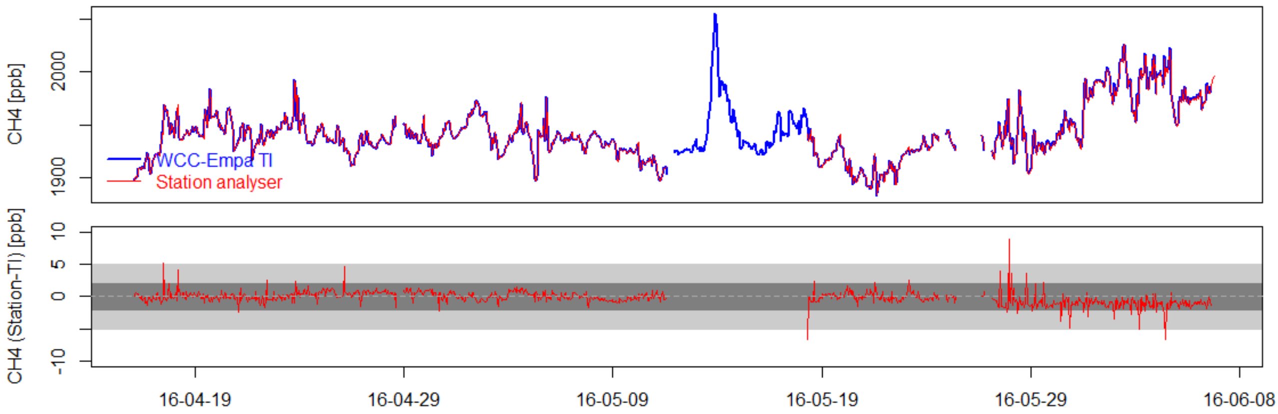

Figure 10. CH_4 comparison at PUY between the WCC-Empa travelling instrument and the PUY Picarro G2401 for the period when the TI sampled humid air. Upper panel: CH_4 time series (1 h data). Lower panel: CH_4 bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

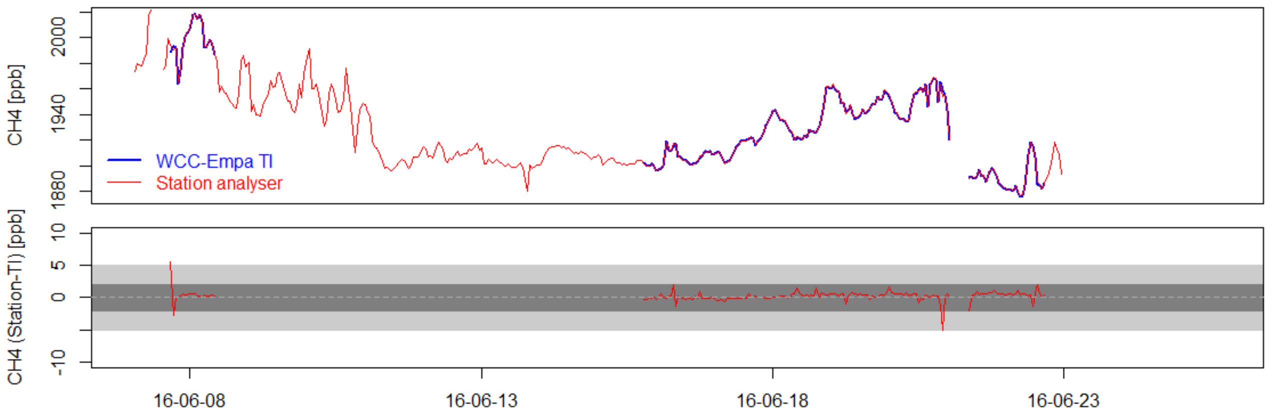

Figure 11. Same as above for the period when the TI was measuring dry air.

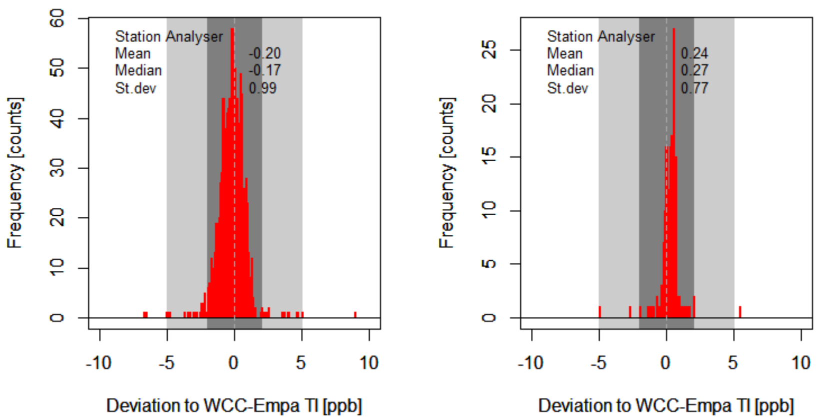

Figure 12. CH_4 deviation histograms (1 h data, station analyser – TI) for the period with humid TI measurements (left) and for the period when the TI sampled dry air from the PUY inlet (right).

Carbon dioxide:

Figure 13 shows the CO_2 comparison of the Picarro G2401 analyser with the WCC-Empa TI (1 h data) for the period when the TI sampled humid air from the separate inlet system. It can be seen that the temporal variation was well captured by both instruments, and the average bias of 0.06±0.16 ppm was within the WMO/GAW compatibility goal of 0.1 ppm. This is very similar to the average bias of 0.08±0.15 ppm which was found for the period when the TI was measuring dry air, as shown in Figure 14. The corresponding deviation histograms for both periods are shown in Figure 15.

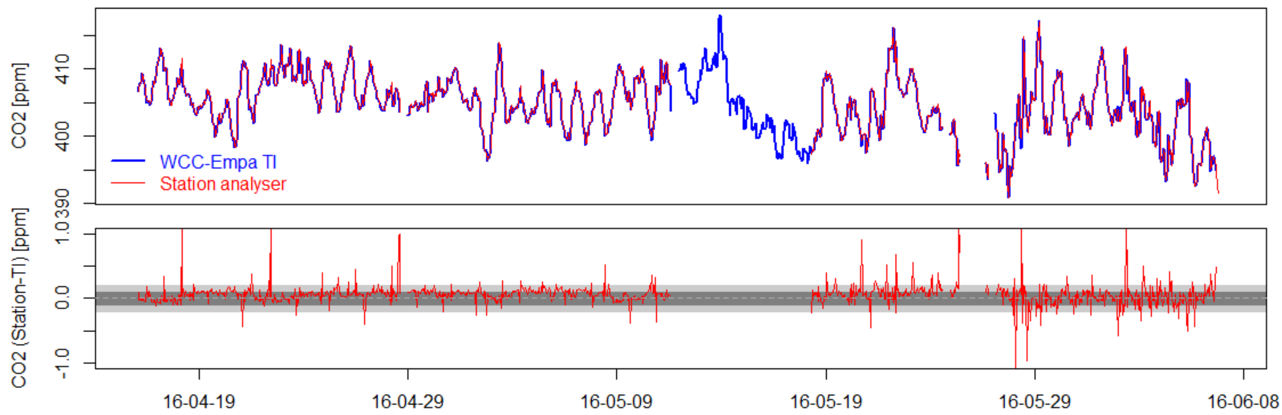

Figure 13. CO_2 comparison at PUY between the WCC-Empa travelling instrument and the PUY Picarro G2401 for the period when the TI was measuring humid air. Upper panel: CO_2 time series (1 h data). Lower panel: CO_2 bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

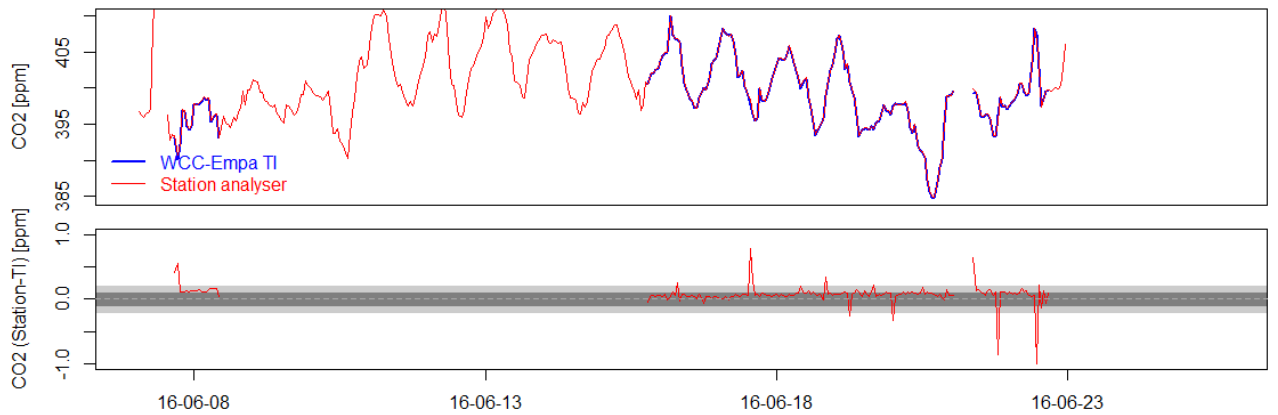

Figure 14. Same as above for the period when the TI was measuring dry air.

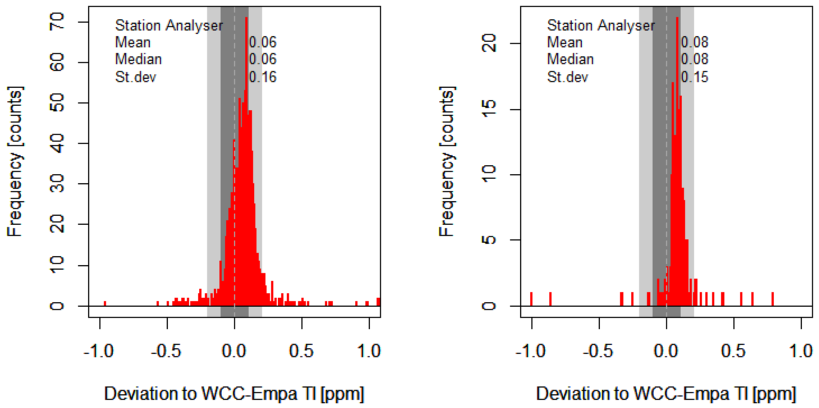

Figure 15. CO_2 deviation histograms (1 h data, station analyser – TI) for the period with humid TI measurements (left) and for the period when the TI sampled dry air from the PUY inlet (right).

Discussion of the ambient air comparison results

The ambient air comparison confirmed the results of the performance audit. The agreement between the PUY analyser and the WCC-Empa travelling instrument was within the WMO/GAW compatibility goals for all parameters except for CO when the TI was measuring humid air. However, this was most likely due to issues related to the correction of the water vapour interference of the WCC TI, and only data of dry period should be considered for CO.

CONCLUSIONS

The Global GAW station Puy de Dôme is situated at an important location for the GAW programme and has a comprehensive measurement programme, which makes the available data an important contribution to GAW.

All assessed parameters were of high data quality and met the WMO/GAW 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 initial	O_3 final	CO	CH_4	CO_2
Performance audit with TS	(✓)	✓	✓	✓	✓
Ambient air comparison	NA	NA	✓#	✓	✓

NA no ambient air comparison was made for ozone

\# Period with dry air measurements only, due to water vapour interference in the TI.

The results are in good agreement with the audit of the ICOS mobile laboratory, which was made at the same time as the WCC-Empa audit. The results of the ICOS audit are available on request from the PUY station.

The continuation of the Puy de Dôme measurement series is highly recommended and 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 PUY DE DÔME GAW STATION

System Audit Aspect	Adequacy[#]	Comment
Station Access	(5)	Year round access by train/car.
Facilities		
Laboratory and office space	(4)	Adequate but limited space for additional 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	(5)	Well-coordinated between different partners, clear responsibilities
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(4)	Adequate inlets for all parameters but long residence times for GHG
Instrumentation		
Ozone	(5)	Adequate instrumentation
$CO/CO_2/CH_4$ (Picarro G2401)	(5)	Adequate instrumentation
Standards		
Ozone	(1)	Only ozone generator for checks, no transfer standard available
CO, CO_2, CH_4	(4)	Link to CCL trough ICOS
Data Management		
Data acquisition	(5)	Adequate systems
Data processing	(5)	Adequate procedures
Data submission	(3)	Data partly submitted, submission frequency needs to be improved

[#]0: inadequate thru 5: adequate.

Dübendorf, July 2017

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WCC-Empa	QA/SAC Switzerland	Head of Department

APPENDIX

Data Review

The following figures show summary plots of PUY data accessed on 13 January 2017 from WDCGG (all parameters) and EBAS (only O_3 and CO). The plots show time series of hourly data, frequency distribution, and diurnal and seasonal variation.

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

Ozone:

- A few high values at the beginning of the time series were not flagged as invalid. These data points are only found at WDCGG, but not in EBAS.
- Otherwise, the data looks plausible showing a weak maximum in spring/early summer.

Carbon monoxide:

- Data set looks generally sound.
- Seasonal cycle is well captured.

Methane:

- Data set looks generally sound, both for flask and the continuous data set.
- Seasonal cycle looks plausible.

Carbon dioxide:

- Data set looks generally sound, both for flask and the continuous data set.
- Seasonal cycle looks plausible.

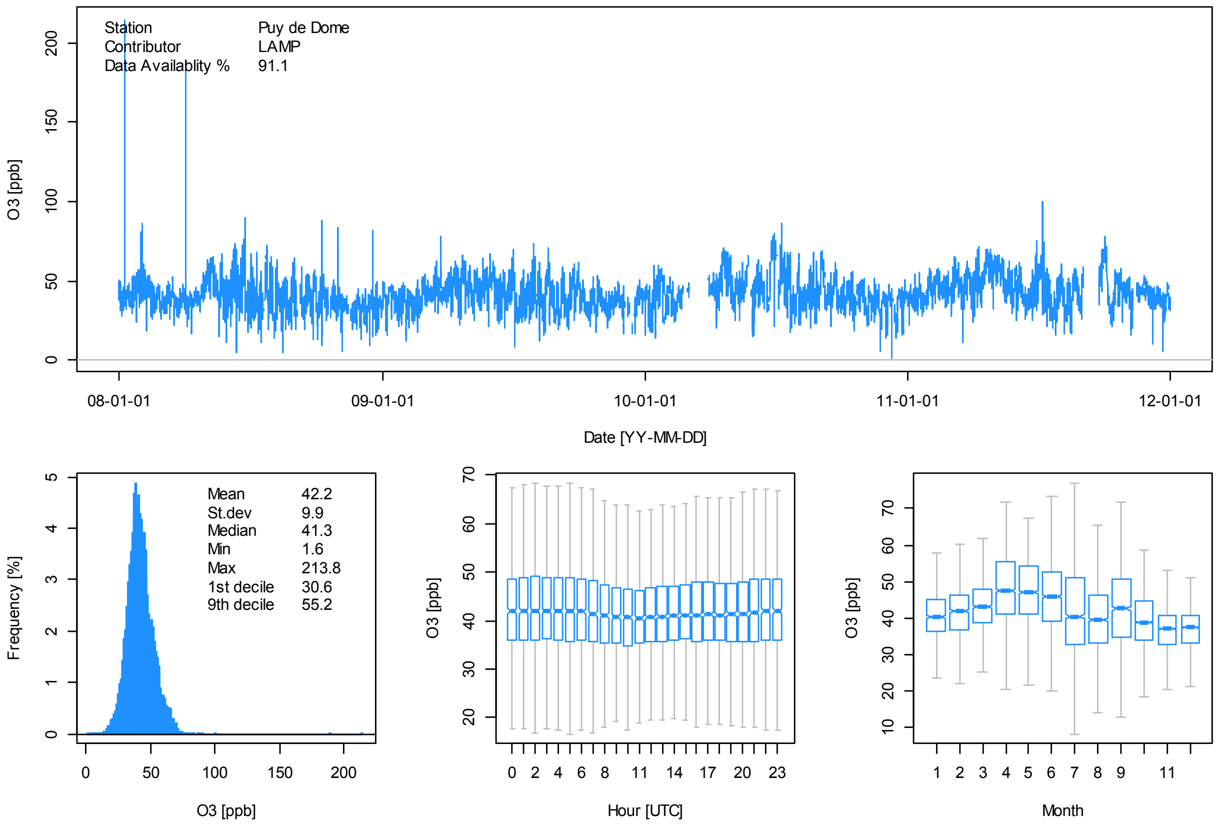

Figure 16. *Ozone data accessed from WDCGG. Top: Time series, 1-h data. Bottom: Left: Frequency distribution. Middle and right: Diurnal and seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

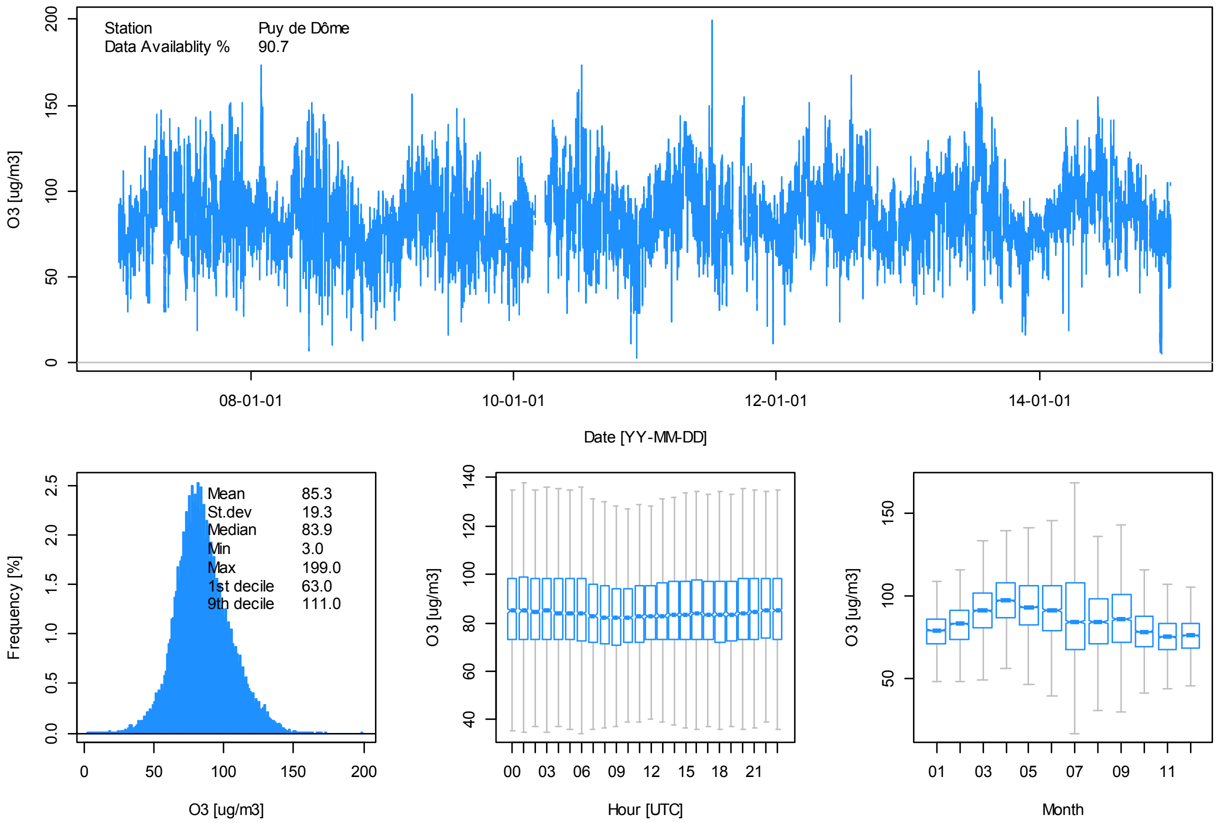

Figure 17. *Same as above for O_3 downloaded from EBAS.*

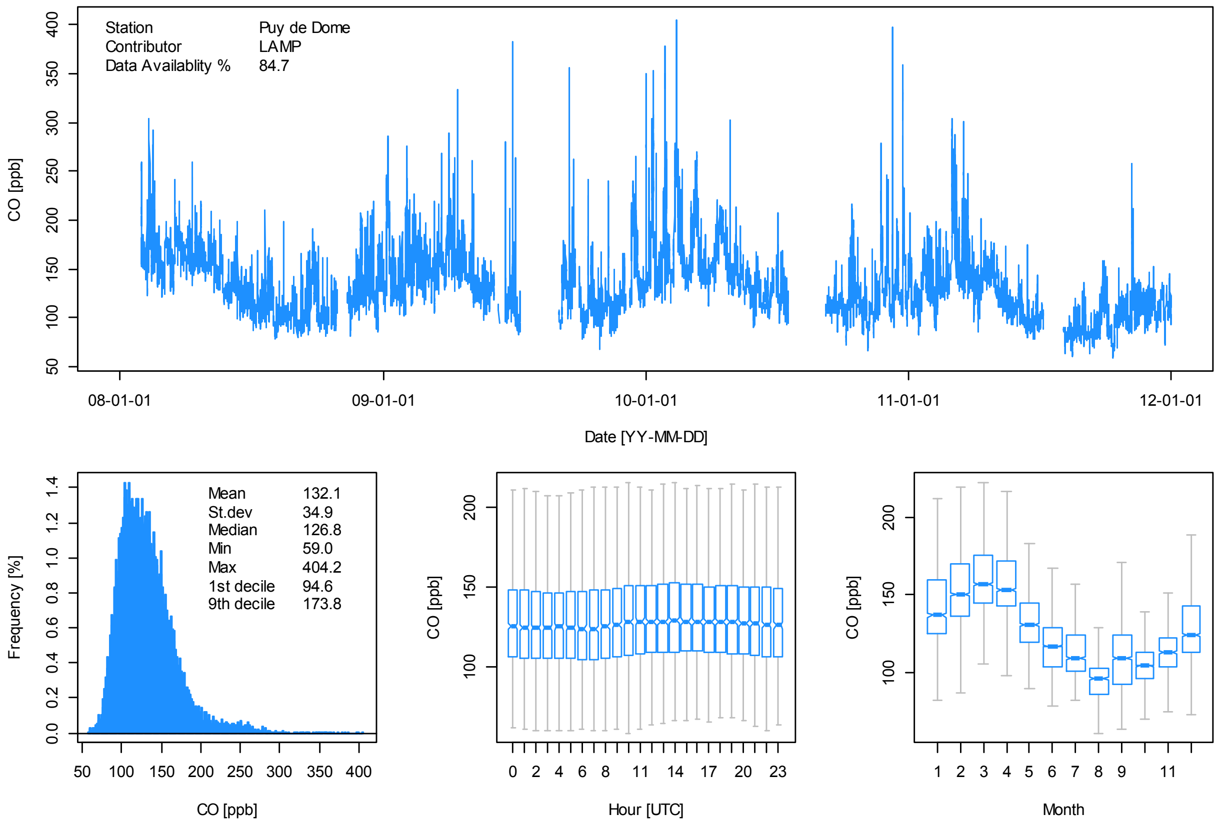

Figure 18. *CO data accessed from WDCGG. Top: Time series, 1-h data. Bottom: Left: Frequency distribution. Middle and right: Diurnal and seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

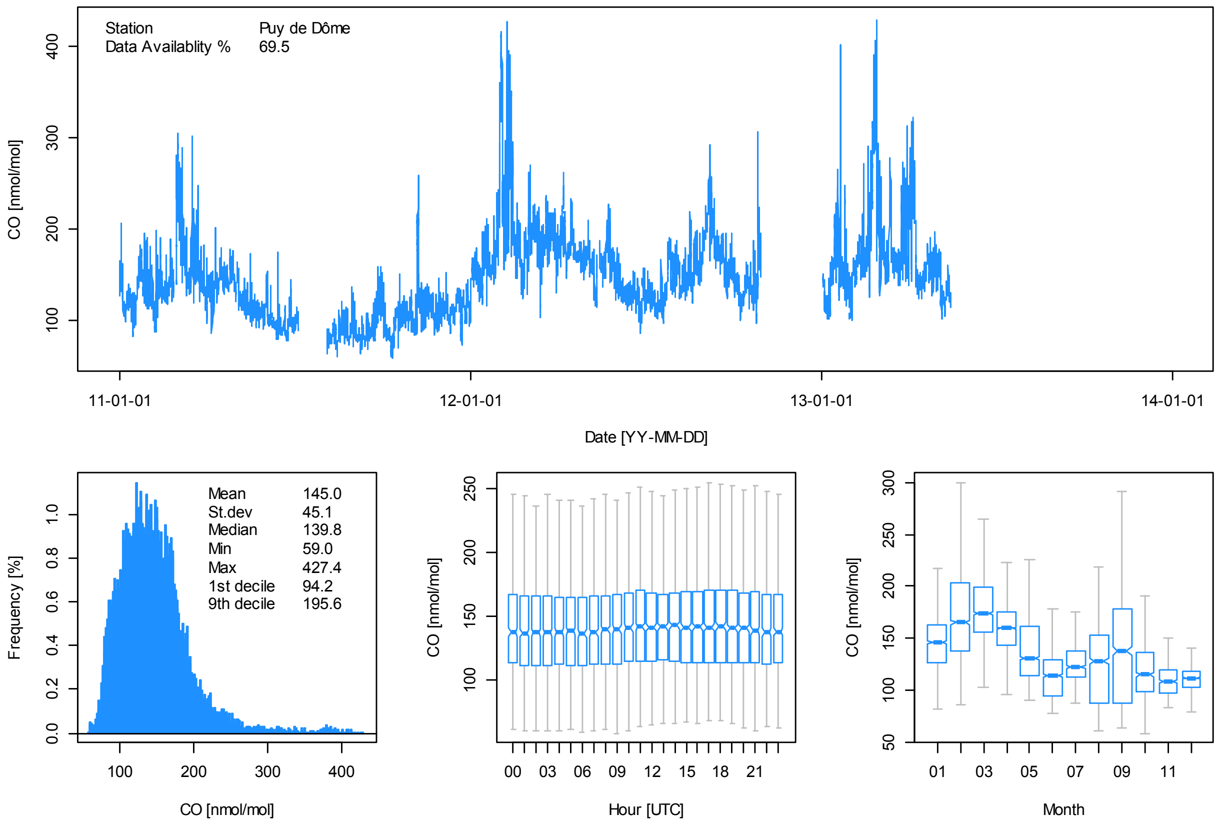

Figure 19. *Same as above for CO downloaded from EBAS.*

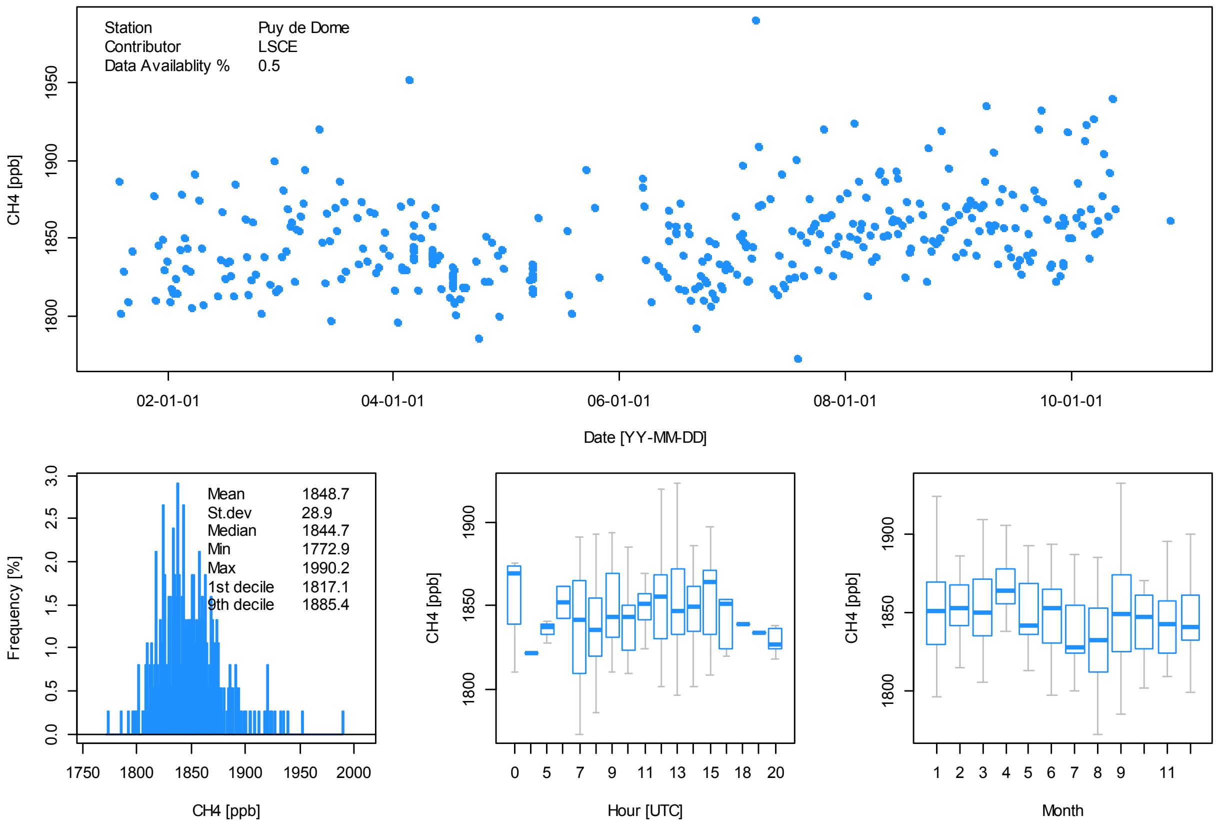

Figure 20. *CH_4 data accessed from WDCGG. Top: Time series, 1-h data. Bottom: Left: Frequency distribution. Middle and right: Diurnal and seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

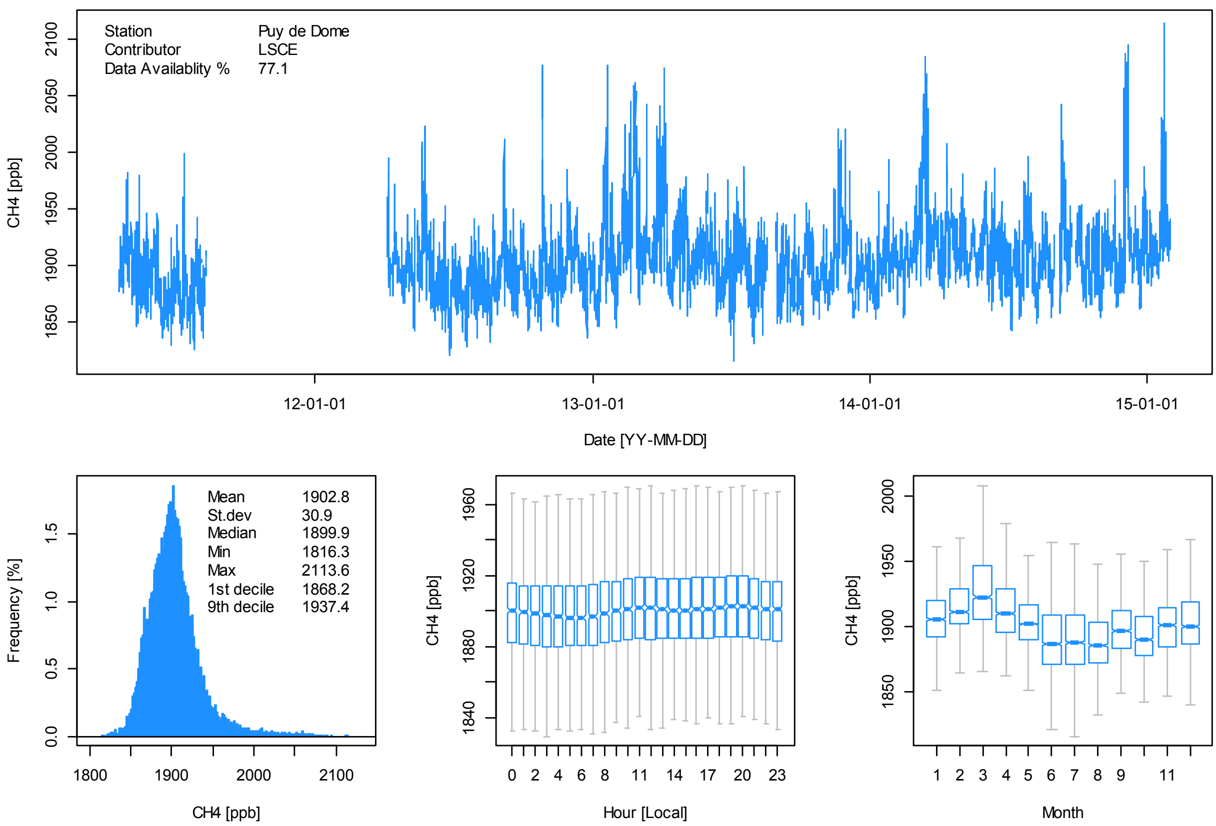

Figure 21. *Same as above for CH_4 CRDS measurements (since 2011).*

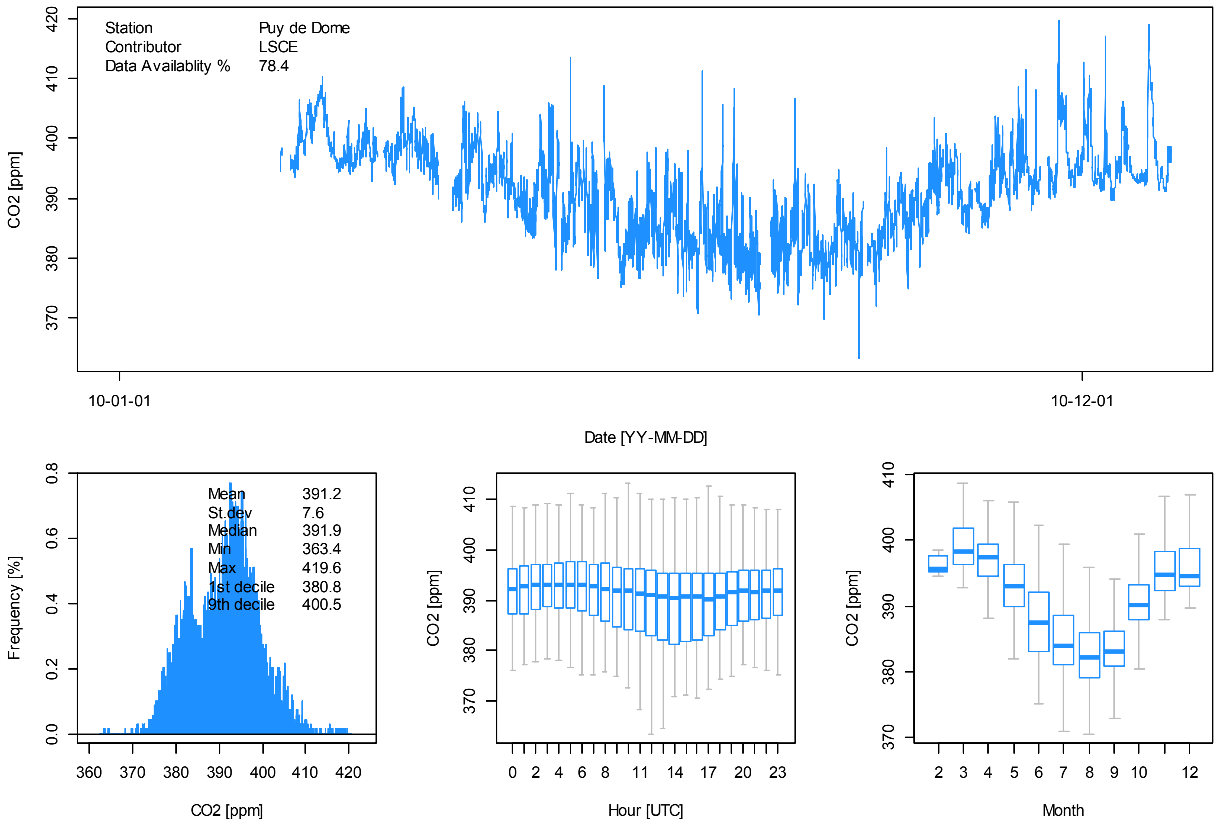

Figure 22. *Same as above for CO_2 NDIR measurements (only data available for 2010).*

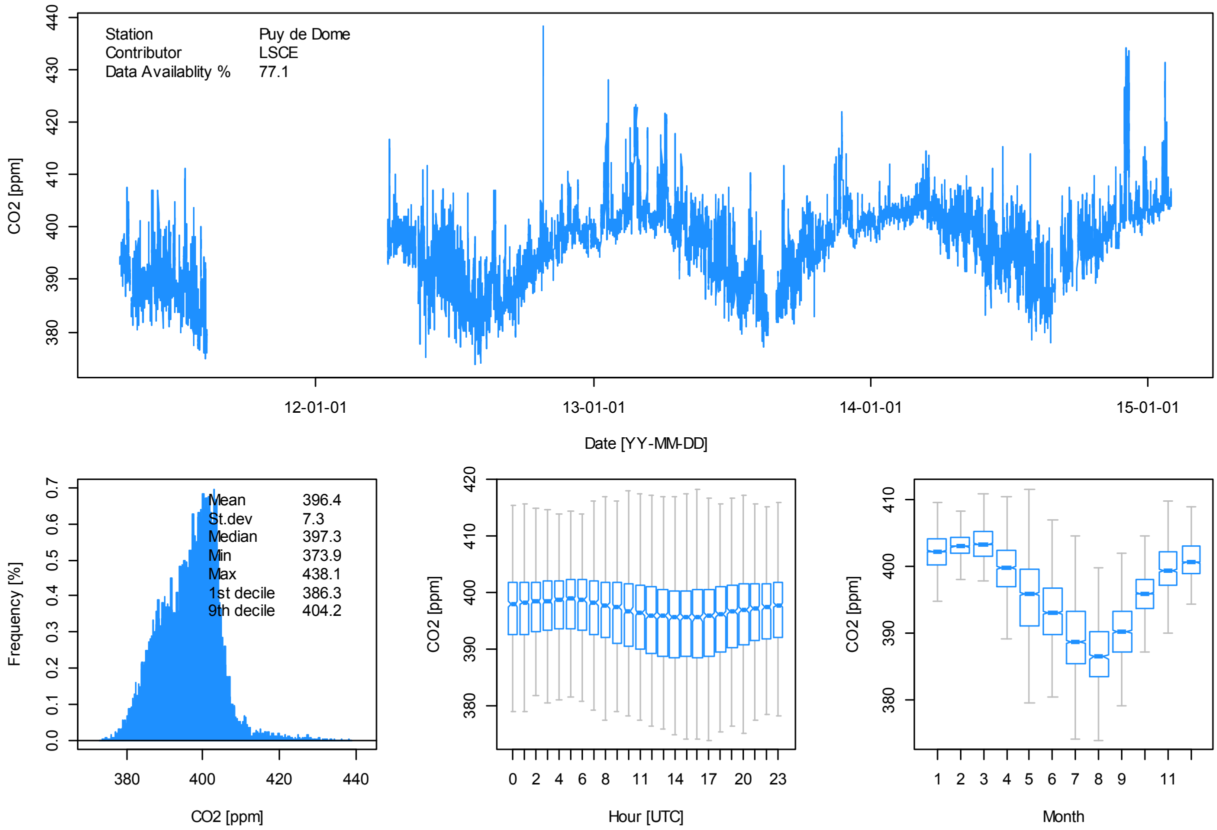

Figure 23. *Same as above for CO_2 CRDS measurements (data available since 2011).*

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 90 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 -01, COEF 1.008
Pressure readings (hPa)	Ambient 847.8; TS 848.2 (no adjustments were made)
Main station analyser (OA)	
Model, S/N	TEI 49i #0536415133
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -1.1 ppb, COEF 0.976 (initial settings) BKG 0.0 ppb, COEF 1.016 (after adjustment)
Pressure readings (hPa)	Ambient 847.8; OA 849.9 (no adjustments were made)

Results

Each ozone level was applied for 10 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 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 (Figure and Equations).

Table 3. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the PUY ozone analyser (OA) TEI 49i #0536415133 (initial calibration settings) 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 (%)
2016-04-12 10:26	1	0	0.64	1.76	0.17	0.44	1.12	NA
2016-04-12 10:36	1	30	30.03	29.79	0.18	0.22	-0.24	-0.8
2016-04-12 10:46	1	60	60.01	58.63	0.13	0.19	-1.38	-2.3
2016-04-12 10:56	1	90	90.04	87.16	0.04	0.30	-2.88	-3.2
2016-04-12 11:16	1	80	80.08	79.24	1.39	3.37	-0.84	-1.0
2016-04-12 11:26	1	50	50.04	49.03	0.30	0.49	-1.01	-2.0
2016-04-12 11:31	1	20	20.03	20.43	0.23	0.22	0.40	2.0

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-04-12 11:36	1	70	70.00	68.09	0.11	0.45	-1.91	-2.7
2016-04-12 11:46	1	10	10.11	11.38	0.40	0.24	1.27	12.6
2016-04-12 12:06	1	40	40.00	39.68	0.14	0.26	-0.32	-0.8
2016-04-12 12:16	2	0	0.74	1.70	0.13	0.13	0.96	NA
2016-04-12 12:26	2	90	90.03	87.22	0.13	0.44	-2.81	-3.1
2016-04-12 12:36	2	10	10.36	10.99	0.29	0.26	0.63	6.1
2016-04-12 12:46	2	60	59.99	58.49	0.16	0.28	-1.50	-2.5
2016-04-12 12:56	2	80	80.02	77.94	0.04	0.24	-2.08	-2.6
2016-04-12 13:06	2	20	20.05	20.30	0.12	0.35	0.25	1.2
2016-04-12 13:16	2	30	30.03	30.00	0.14	0.31	-0.03	-0.1
2016-04-12 13:26	2	50	50.01	49.16	0.05	0.33	-0.85	-1.7
2016-04-12 13:36	2	40	40.01	39.29	0.22	0.37	-0.72	-1.8
2016-04-12 13:46	2	70	70.02	68.44	0.12	0.46	-1.58	-2.3
2016-04-12 13:56	3	0	0.27	1.80	0.12	0.15	1.53	NA
2016-04-12 14:06	3	90	90.00	87.19	0.09	0.40	-2.81	-3.1
2016-04-12 14:16	3	30	30.01	29.66	0.06	0.16	-0.35	-1.2
2016-04-12 14:26	3	10	10.03	10.74	0.09	0.18	0.71	7.1
2016-04-12 14:36	3	40	40.06	39.38	0.08	0.25	-0.68	-1.7
2016-04-12 14:46	3	50	50.00	48.80	0.10	0.50	-1.20	-2.4

Table 4. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the PUY ozone analyser (OA) TEI 49i #0536415133 (after adjustment of calibration settings) 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 (%)
2016-04-12 15:14	1	0	0.45	0.41	0.18	0.13	-0.04	-8.9
2016-04-12 15:24	1	30	29.98	29.68	0.08	0.16	-0.30	-1.0
2016-04-12 15:34	1	60	60.00	59.76	0.10	0.37	-0.24	-0.4
2016-04-12 15:44	1	90	90.00	89.73	0.04	0.50	-0.27	-0.3
2016-04-12 16:04	1	80	80.00	79.92	0.10	0.34	-0.08	-0.1
2016-04-12 16:14	1	50	50.00	49.78	0.08	0.18	-0.22	-0.4
2016-04-12 16:19	1	20	20.02	19.83	0.15	0.26	-0.19	-0.9
2016-04-12 16:24	1	70	70.08	69.49	0.18	0.33	-0.59	-0.8
2016-04-12 16:34	1	10	10.24	10.07	0.30	0.31	-0.17	-1.7
2016-04-12 16:54	1	40	39.99	39.53	0.16	0.24	-0.46	-1.2
2016-04-12 17:04	2	0	0.25	0.50	0.16	0.13	0.25	NA
2016-04-12 17:14	2	90	90.00	89.55	0.13	0.34	-0.45	-0.5
2016-04-12 17:24	2	10	10.00	9.86	0.24	0.07	-0.14	-1.4
2016-04-12 17:34	2	60	60.02	59.76	0.13	0.22	-0.26	-0.4
2016-04-12 17:44	2	80	80.00	79.93	0.12	0.16	-0.07	-0.1
2016-04-12 17:54	2	20	20.01	19.87	0.09	0.25	-0.14	-0.7
2016-04-12 18:04	2	30	29.94	29.72	0.08	0.32	-0.22	-0.7
2016-04-12 18:14	2	50	50.00	49.70	0.17	0.28	-0.30	-0.6
2016-04-12 18:24	2	40	39.99	39.87	0.27	0.42	-0.12	-0.3
2016-04-12 18:34	2	70	69.98	69.70	0.12	0.25	-0.28	-0.4
2016-04-12 18:44	3	0	0.24	0.45	0.20	0.14	0.21	NA

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-04-12 18:54	3	90	89.98	89.60	0.08	0.21	-0.38	-0.4
2016-04-12 19:04	3	30	30.04	29.89	0.02	0.13	-0.15	-0.5
2016-04-12 19:14	3	10	10.69	10.55	0.37	0.35	-0.14	-1.3
2016-04-12 19:24	3	40	39.96	39.86	0.05	0.10	-0.10	-0.3
2016-04-12 19:34	3	50	50.04	49.94	0.13	0.28	-0.10	-0.2
2016-04-12 19:44	3	20	19.96	19.88	0.13	0.13	-0.08	-0.4
2016-04-12 19:54	3	70	70.01	69.67	0.05	0.21	-0.34	-0.5
2016-04-12 20:04	3	80	80.01	79.50	0.08	0.20	-0.51	-0.6
2016-04-12 20:14	4	0	0.38	0.57	0.16	0.19	0.19	NA
2016-04-12 20:24	4	30	30.01	29.90	0.17	0.47	-0.11	-0.4
2016-04-12 20:34	4	60	59.99	59.54	0.07	0.25	-0.45	-0.8
2016-04-12 20:44	4	90	89.96	89.58	0.07	0.43	-0.38	-0.4
2016-04-12 21:04	4	80	79.99	79.66	0.09	0.18	-0.33	-0.4
2016-04-12 21:14	4	50	49.97	49.66	0.14	0.28	-0.31	-0.6
2016-04-12 21:19	4	20	19.97	19.88	0.16	0.23	-0.09	-0.5
2016-04-12 21:24	4	70	70.00	69.75	0.09	0.23	-0.25	-0.4
2016-04-12 21:34	4	10	9.87	9.77	0.18	0.24	-0.10	-1.0
2016-04-12 21:54	4	40	39.96	39.83	0.15	0.24	-0.13	-0.3
2016-04-12 22:04	5	0	0.42	0.32	0.10	0.18	-0.10	NA
2016-04-12 22:14	5	90	90.01	89.48	0.07	0.18	-0.53	-0.6
2016-04-12 22:24	5	10	10.08	10.00	0.48	0.36	-0.08	-0.8

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 5 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 PUY data acquisition system. The standards used for the calibration of the PUY analyser are shown in Table 6.

Table 5. Experimental details of PUY 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 14.	
Main Station Analyser PUY (AL)	
Model, S/N	Picarro G2401 #2021-CFKADS-2161
Principle	CRDS
Drying system	Cryo trap (-50°C)
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports

Table 6. CO Standards available at PUY.

Cylinder ID	Manufacturer	Use	CO (ppb)	Scale
D337577	ICOS-FCL	Calibration	56.36	WMO-CO-X2014A
D337578	ICOS-FCL	Calibration	103.30	WMO-CO-X2014A
D337579	ICOS-FCL	Calibration	201.82	WMO-CO-X2014A
D337580	ICOS-FCL	Calibration	302.21	WMO-CO-X2014A
D337581	ICOS-FCL	Target	198.85	WMO-CO-X2014A
D337582	ICOS-FCL	Target	252.41	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 7. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2021-CFKADS-2161 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 (%)
(16-04-12 16:10:00)	150819_FF17309	163.4	0.4	162.9	0.2	3	-0.4	-0.3
(16-04-13 10:15:00)	120723_FA02789	267.5	0.1	267.5	0.2	3	0.0	0.0
(16-04-13 10:35:00)	120803_FA02769	137.8	0.1	137.2	0.4	3	-0.5	-0.4
(16-04-12 14:30:00)	100212_FF31496	109.9	0.1	110.6	0.1	3	0.7	0.7
(16-04-12 15:10:00)	130819_FB03870	149.4	0.2	149.2	0.3	3	-0.2	-0.1
(16-04-13 09:35:00)	080820_FA02785	69.9	0.2	71.8	0.1	3	1.9	2.8
(16-04-12 15:50:00)	140515_FB03377	151.6	0.3	151.4	0.3	3	-0.2	-0.2
(16-04-13 10:55:00)	140515_FA02783	187.0	0.2	186.7	0.6	3	-0.2	-0.1
(16-04-13 09:55:00)	120719_FA02770	201.0	0.1	200.9	0.2	3	-0.1	0.0
(16-04-12 14:50:00)	130905_FB03383	87.6	0.1	87.3	0.4	3	-0.4	-0.4
(16-04-12 15:30:00)	140514_FB03910	200.7	0.1	200.2	0.2	3	-0.6	-0.3
(16-04-13 11:15:00)	150601_FA02466	691.3	0.2	692.2	0.2	3	0.9	0.1

Methane Measurements

The comparison involved repeated challenges of the PUY instruments with randomised CH_4 and CO_2 levels and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 14 below.

Details of the experimental setup during the comparison of the transfer standards and the station analyser are shown in Table 5 above. The data used for the evaluation was recorded by the station data acquisition system. The standards used for the calibration of the PUY analyser are shown in Table 8.

Table 8. CH_4 Standards available at PUY.

Cylinder ID	Manufacturer	Use	CH_4 (ppb)	Scale
D337577	ICOS-FCL	Calibration	1816.29	WMO-CO-X2004A
D337578	ICOS-FCL	Calibration	1907.81	WMO-CO-X2004A
D337579	ICOS-FCL	Calibration	2098.72	WMO-CO-X2004A
D337580	ICOS-FCL	Calibration	2299.17	WMO-CO-X2004A
D337581	ICOS-FCL	Target	1999.32	WMO-CO-X2004A
D337582	ICOS-FCL	Target	2199.06	WMO-CO-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 9. CH_4 aggregates computed from single analysis (1-min mean and standard deviation) for each level during the comparison of the Picarro G2401 #2021-CFKADS-2161 (AL) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sd AL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-04-12 16:10:00)	150819_FF17309	1966.07	0.17	1965.87	0.08	3	-0.20	-0.01
(16-04-13 10:15:00)	120723_FA02789	2114.79	0.02	2114.09	0.06	3	-0.70	-0.03
(16-04-13 10:35:00)	120803_FA02769	2021.21	0.05	2020.83	0.17	3	-0.38	-0.02
(16-04-12 14:30:00)	100212_FF31496	2122.03	0.04	2121.60	0.22	3	-0.43	-0.02
(16-04-12 15:10:00)	130819_FB03870	1883.62	0.10	1883.64	0.23	3	0.02	0.00
(16-04-13 09:35:00)	140515_FB03377	1768.67	0.10	1768.92	0.18	3	0.25	0.01
(16-04-12 15:50:00)	140515_FA02783	1965.37	0.06	1965.14	0.03	3	-0.23	-0.01
(16-04-13 10:55:00)	120719_FA02770	1869.09	0.17	1868.97	0.05	3	-0.12	-0.01
(16-04-13 09:55:00)	130905_FB03383	1862.11	0.07	1862.15	0.09	3	0.04	0.00
(16-04-12 15:30:00)	140514_FB03910	2002.10	0.10	2001.84	0.25	3	-0.26	-0.01
(16-04-13 11:15:00)	150601_FA02466	1900.72	0.05	1900.78	0.08	3	0.06	0.00
(16-04-12 16:10:00)	150819_FF17309	1966.07	0.17	1965.87	0.08	3	-0.20	-0.01

Carbon Dioxide Comparison

The comparison involved repeated challenges of the PUY instruments with randomised CO_2 levels and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 14 below.

Details of the experimental setup during the comparison of the transfer standards and the station analyser are shown in Table 5 above. The data used for the evaluation was recorded by the station data acquisition system. The standards used for the calibration of the PUY analyser are shown in Table 8.

Table 10. CO_2 Standards available at PUY.

Cylinder ID	Manufacturer	Use	CO_2 (ppb)	Scale
D337577	ICOS-FCL	Calibration	379.63	WMO-CO-X2007
D337578	ICOS-FCL	Calibration	409.78	WMO-CO-X2007
D337579	ICOS-FCL	Calibration	439.45	WMO-CO-X2007
D337580	ICOS-FCL	Calibration	471.56	WMO-CO-X2007
D337581	ICOS-FCL	Target	389.98	WMO-CO-X2007
D337582	ICOS-FCL	Target	460.61	WMO-CO-X2007

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. CO_2 aggregates computed from single analysis (1-min mean and standard deviation) for each level during the comparison of the Picarro G2401 #2021-CFKADS-2161 (AL) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sd AL (ppm)	N	OA-AL (ppm)	OA-AL (%)
(16-04-12 16:10:00)	150819_FF17309	398.61	0.04	398.61	0.01	3	0.00	0.00
(16-04-13 10:15:00)	120723_FA02789	409.37	0.04	409.35	0.01	3	-0.02	0.00
(16-04-13 10:35:00)	120803_FA02769	387.96	0.03	388.00	0.01	3	0.04	0.01
(16-04-12 14:30:00)	100212_FF31496	331.03	0.03	331.20	0.01	3	0.17	0.05
(16-04-12 15:10:00)	130819_FB03870	386.82	0.04	386.90	0.02	3	0.08	0.02
(16-04-13 09:35:00)	080820_FA02785	245.05	0.02	245.35	0.00	3	0.30	0.12
(16-04-12 15:50:00)	140515_FB03377	365.45	0.03	365.53	0.01	3	0.08	0.02
(16-04-13 10:55:00)	140515_FA02783	413.30	0.07	413.34	0.00	3	0.04	0.01
(16-04-13 09:55:00)	120719_FA02770	333.59	0.02	333.75	0.01	3	0.17	0.05
(16-04-12 14:50:00)	130905_FB03383	390.28	0.03	390.32	0.01	3	0.04	0.01
(16-04-12 15:30:00)	140514_FB03910	404.30	0.05	404.35	0.02	3	0.05	0.01
(16-04-13 11:15:00)	150601_FA02466	430.96	0.06	430.94	0.00	3	-0.02	0.00

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 -0.1, 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 12. 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)).

$$X_{TS}\text{ (ppb)} = ([TS] + 0.01\text{ ppb}) / 1.0025 \quad (6a)$$

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

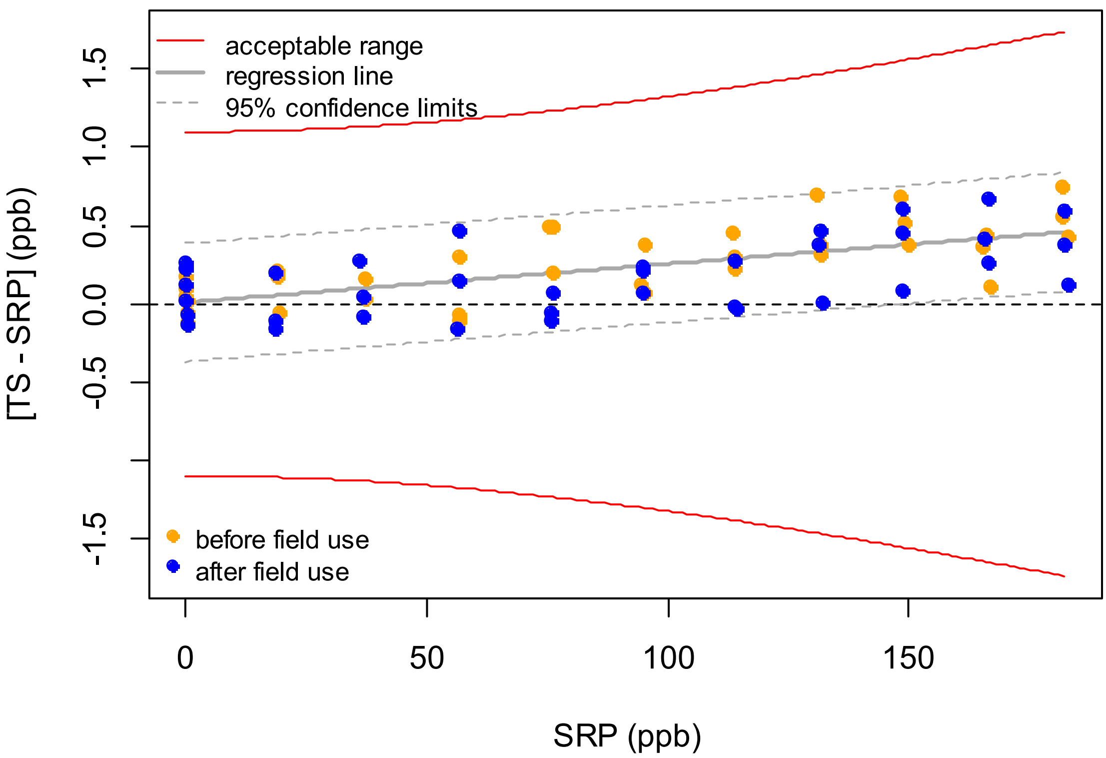

Figure 24. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 12. 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)
2016-03-22	1	0	-0.01	0.31	0.05	0.29
2016-03-22	1	95	95.27	0.21	95.66	0.16
2016-03-22	1	55	56.60	0.17	56.53	0.29
2016-03-22	1	150	149.11	0.39	149.63	0.35
2016-03-22	1	165	166.78	0.21	166.89	0.28
2016-03-22	1	75	75.88	0.26	76.38	0.12
2016-03-22	1	185	182.89	0.28	183.33	0.24
2016-03-22	1	20	19.17	0.13	19.11	0.23
2016-03-22	1	35	37.24	0.18	37.40	0.26
2016-03-22	1	130	131.72	0.23	132.04	0.49
2016-03-22	1	115	113.87	0.23	114.09	0.28
2016-03-22	1	0	0.09	0.23	-0.02	0.20
2016-03-22	2	0	0.21	0.43	0.23	0.18
2016-03-22	2	150	149.65	0.21	150.03	0.25
2016-03-22	2	165	166.10	0.22	166.54	0.07
2016-03-22	2	75	75.96	0.32	76.15	0.15
2016-03-22	2	55	56.41	0.15	56.31	0.29
2016-03-22	2	35	37.22	0.29	37.39	0.17
2016-03-22	2	180	181.96	0.21	182.51	0.28
2016-03-22	2	115	113.62	0.21	113.92	0.21
2016-03-22	2	95	95.03	0.32	95.11	0.22
2016-03-22	2	130	131.70	0.27	132.08	0.33
2016-03-22	2	20	18.95	0.22	19.13	0.23
2016-03-22	2	0	0.22	0.26	0.16	0.24
2016-03-22	3	0	-0.07	0.20	0.02	0.14
2016-03-22	3	55	56.40	0.22	56.70	0.17
2016-03-22	3	180	181.83	0.58	182.59	0.50
2016-03-22	3	115	113.33	0.34	113.80	0.24
2016-03-22	3	130	130.96	0.34	131.66	0.16
2016-03-22	3	35	37.10	0.32	37.13	0.28
2016-03-22	3	75	75.29	0.48	75.78	0.14
2016-03-22	3	20	18.97	0.40	19.18	0.24
2016-03-22	3	165	165.19	0.14	165.56	0.27
2016-03-22	3	150	148.19	0.22	148.87	0.26
2016-03-22	3	95	94.48	0.24	94.60	0.27
2016-03-22	3	0	-0.08	0.28	0.10	0.10
2016-07-04	4	0	-0.22	0.38	0.05	0.26
2016-07-04	4	55	56.31	0.33	56.15	0.17
2016-07-04	4	150	148.67	0.35	148.75	0.24
2016-07-04	4	95	94.82	0.64	95.03	0.11
2016-07-04	4	20	18.61	0.37	18.46	0.11
2016-07-04	4	115	113.86	0.38	114.13	0.18
2016-07-04	4	75	75.78	0.27	75.72	0.18
2016-07-04	4	35	36.08	0.34	36.37	0.18
2016-07-04	4	185	182.84	0.31	182.96	0.16
2016-07-04	4	130	132.15	0.46	132.16	0.30
2016-07-04	4	165	166.57	0.25	167.25	0.19
2016-07-04	4	0	-0.20	0.34	-0.18	0.21
2016-07-04	5	0	-0.14	0.37	-0.01	0.16
2016-07-04	5	150	148.78	0.21	149.23	0.20

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2016-07-04	5	165	166.47	0.32	166.73	0.25
2016-07-04	5	75	75.95	0.23	76.03	0.15
2016-07-04	5	95	94.86	0.20	95.09	0.11
2016-07-04	5	115	114.21	0.48	114.18	0.16
2016-07-04	5	130	131.59	0.41	132.05	0.16
2016-07-04	5	55	56.47	0.19	56.62	0.15
2016-07-04	5	180	182.23	0.17	182.82	0.27
2016-07-04	5	35	36.67	0.33	36.59	0.15
2016-07-04	5	20	18.52	0.24	18.72	0.19
2016-07-04	5	0	-0.16	0.35	0.06	0.26
2016-07-04	6	0	0.10	0.42	-0.04	0.20
2016-07-04	6	55	56.42	0.28	56.88	0.15
2016-07-04	6	130	131.27	0.26	131.65	0.19
2016-07-04	6	180	182.12	0.54	182.50	0.13
2016-07-04	6	150	148.45	0.22	149.06	0.23
2016-07-04	6	20	18.63	0.17	18.51	0.38
2016-07-04	6	75	75.80	0.32	75.69	0.14
2016-07-04	6	35	36.54	0.29	36.58	0.14
2016-07-04	6	95	94.66	0.22	94.74	0.15
2016-07-04	6	115	113.81	0.24	113.79	0.28
2016-07-04	6	165	165.60	0.37	166.02	0.14
2016-07-04	6	0	0.19	0.19	0.13	0.19

#the level is only indicative.

Greenhouse gases and carbon monoxide

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

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

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

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

Table 13 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 14, 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 13. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO	CH_4	N_2O	CO_2	CO	CH_4	N_2O	CO_2
	NOAA assigned values				WCC-Empa assigned values			
	(ppb)	(ppb)	(ppb)	(ppm)	(ppb)	(ppb)	(ppb)	(ppm)
CB099115	263.1	1986.6	334.08	448.48	262.7	1986.8	334.10	448.45
CC311856	103.8	1484.9	250.55	252.38	102.1	1483.8	252.14	250.56
CC311846	173.9	1804.8	317.32	377.90	172.8	1804.5	317.37	377.84

Table 14. 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)
080820_FA02785	69.87	0.21	1962.46	0.08	245.05	0.02	199.43	0.12
100212_FF31496	109.88	0.09	2122.03	0.04	331.03	0.03	298.71	0.04
130905_FB03383	87.64	0.14	1862.11	0.07	390.28	0.03	317.29	0.05
120719_FA02770	200.97	0.06	1869.09	0.17	333.59	0.02	335.38	0.03
120723_FA02789	267.51	0.11	2114.79	0.02	409.37	0.04	322.84	0.02
120803_FA02769	137.76	0.12	2021.21	0.05	387.96	0.03	346.45	0.02
130819_FB03870	149.38	0.18	1883.62	0.10	386.82	0.04	319.07	0.01
140514_FB03910	200.74	0.06	2002.10	0.10	404.30	0.05	328.47	0.03
140515_FA02783	186.96	0.15	1965.37	0.06	413.30	0.07	328.49	0.05
140515_FB03377	151.64	0.28	1768.67	0.10	365.45	0.03	317.57	0.01
150601_FA02466	691.31	0.21	1900.72	0.05	430.96	0.06	326.12	0.03
150819_FF17309	163.35	0.35	1966.07	0.17	398.61	0.04	329.12	0.02

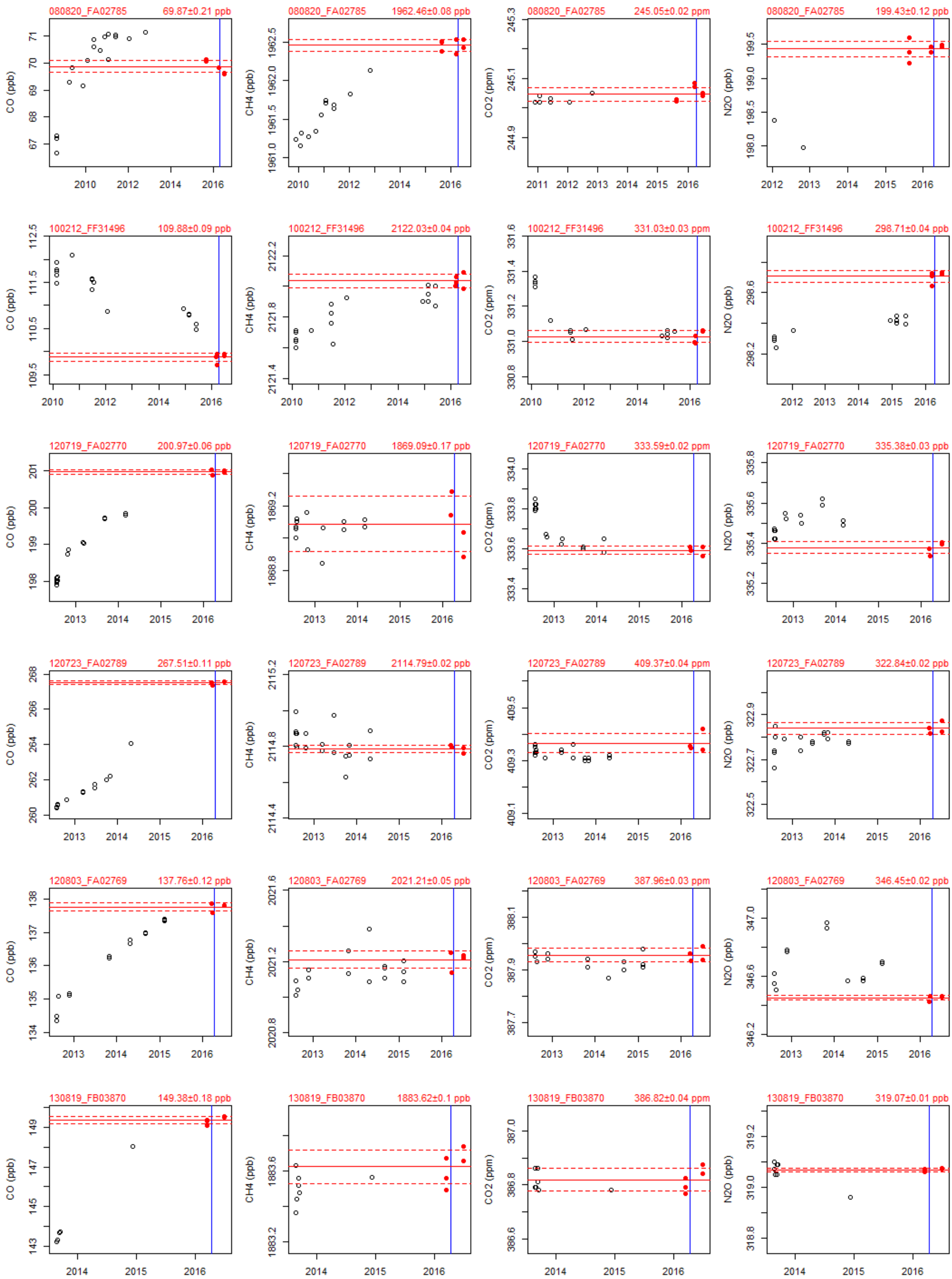

Figure 25. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

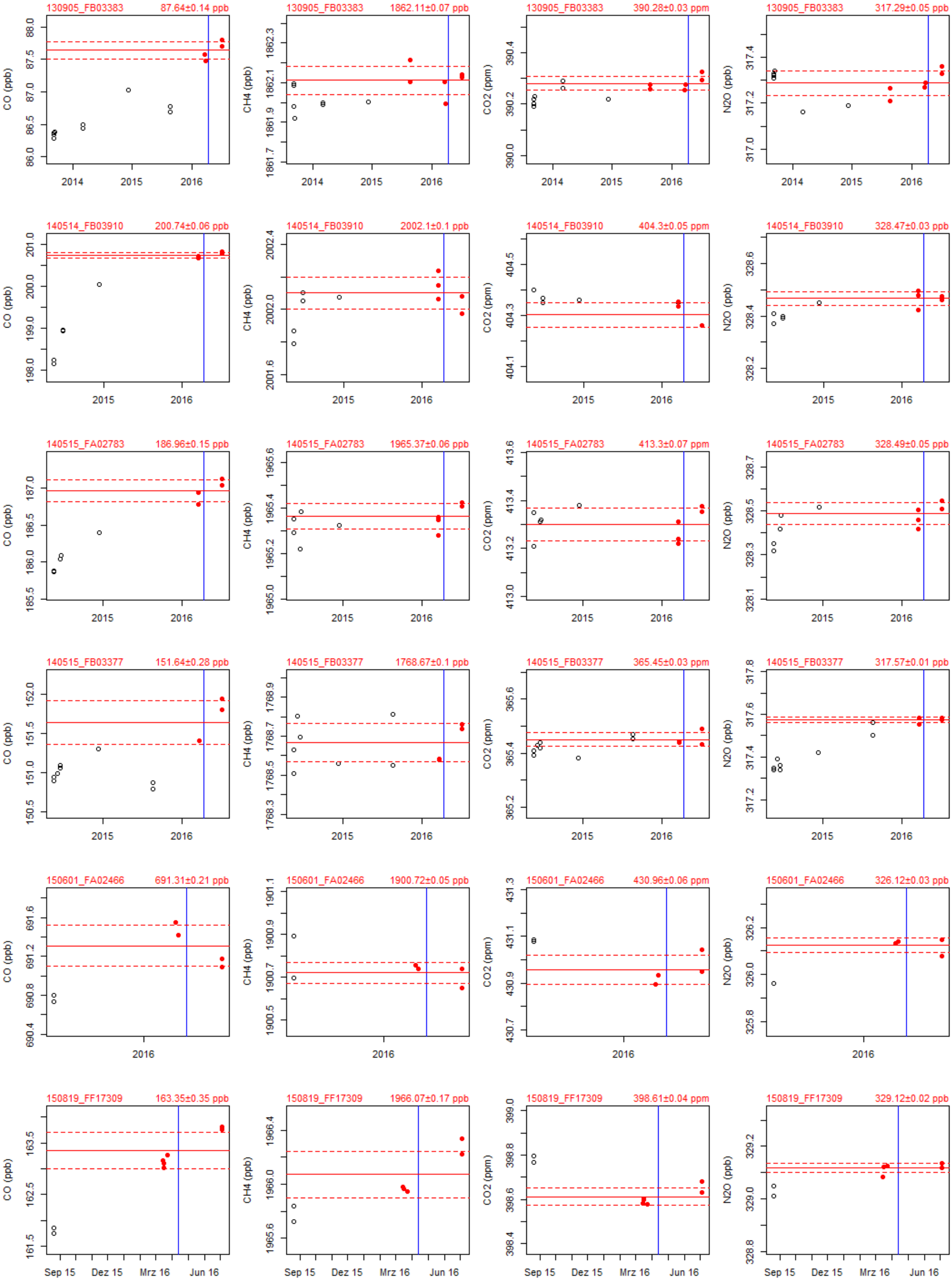

Figure 26. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. 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. 1 ppb for CH_4 and 0.07 ppm for CO_2. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements (except one outlier for CO_2).

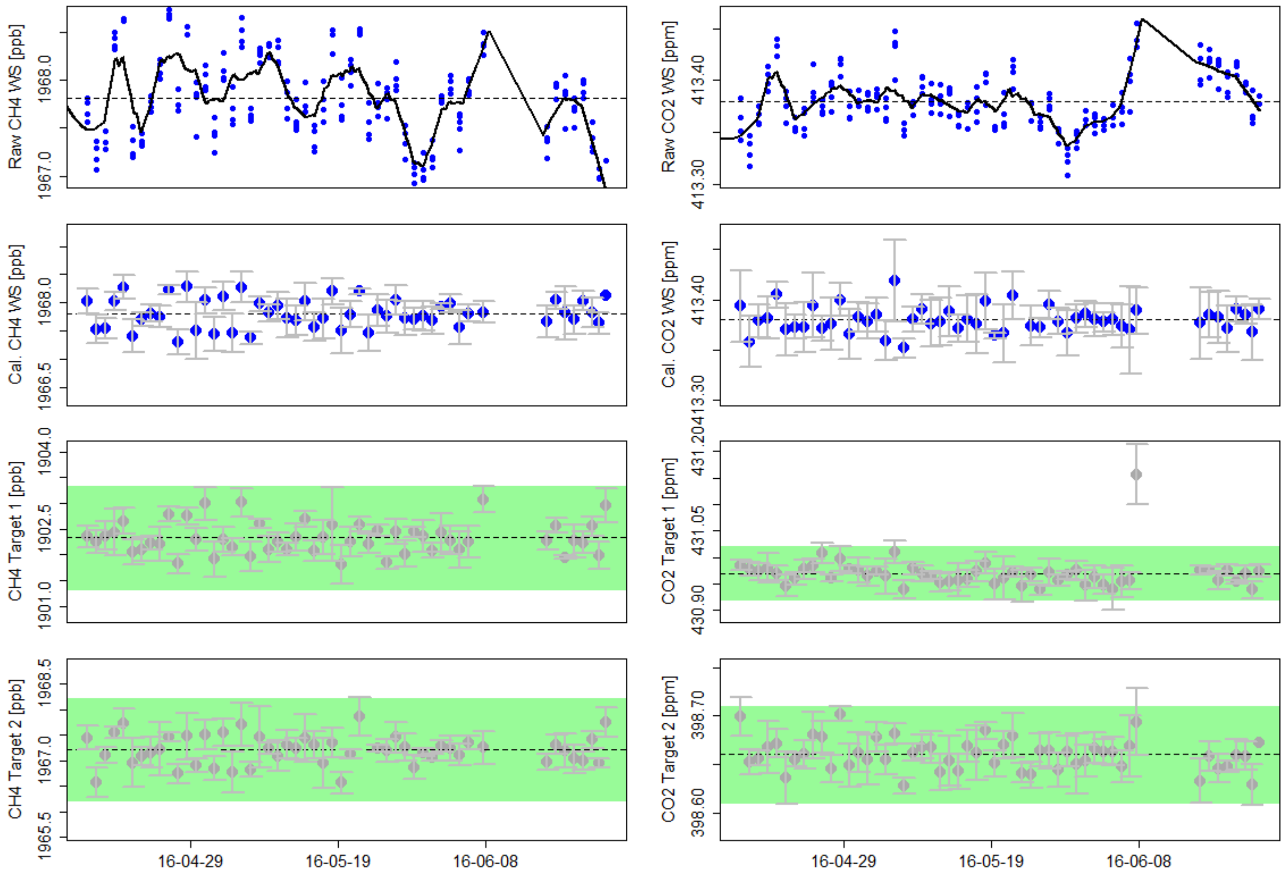

Figure 27. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1-min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower 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.

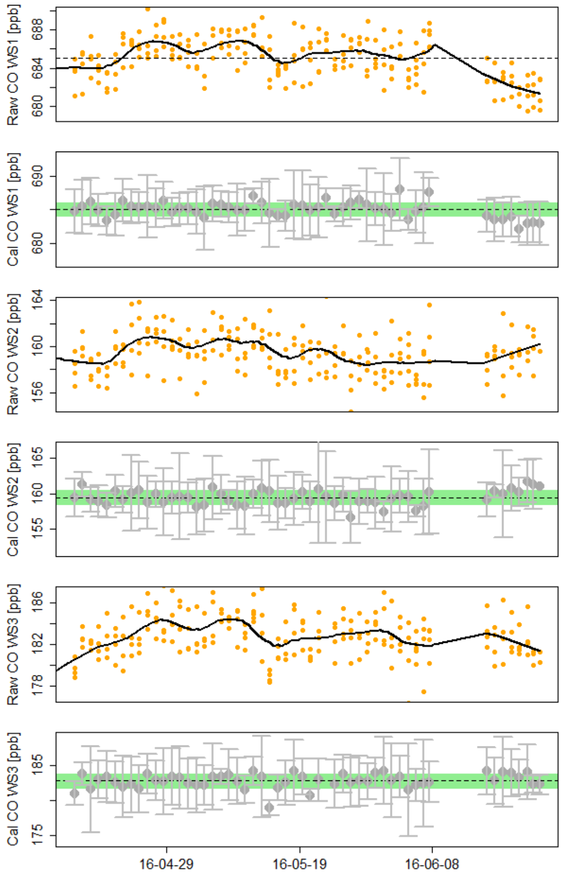

Figure 28. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1-min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

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LIST OF ABBREVIATIONS

a.s.l	above se level
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
ICOS-FCL	ICOS Flask and Calibration Laboratory
LS	Laboratory Standard
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
OPCG	Observatoire de Physique du Globe de Clermont-Ferrand
PUY	Puy de Dôme GAW Station
NA	Not Applicable
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
SOP	Standard Operating Procedure
TI	Travelling Instrument
TS	Traveling Standard
VNC	Virtual Network Computing
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization