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

GLOBAL GAW STATION CAPE POINT SOUTH AFRICA OCTOBER 2015

Submitted to the World Meteorological Organization by

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The fifth system and performance audit by WCC-Empa[1] at the Global GAW station Cape Point was conducted from 20 - 26 October 2015 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). Monitoring and research activities at the Cape Point (CPT) global GAW station are coordinated by the South African Weather Service (SAWS).

Previous audits at the Cape Point GAW observatory were conducted in January 1997 (Herzog et al., 1997), in September 1998 (Herzog et al., 1998), in April 2002 (Zellweger et al., 2002) and in September 2006 (Zellweger et al., 2006).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr. Simon Wyss	Empa Dübendorf, National Air Pollution Monitoring Network
Mr. Casper Labuschagne	SAWS, Senior Scientist
Dr. Nkanyiso Mbatha	SAWS, Senior Scientist
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Mr. Danie van der Spuy	SAWS, Station Technician
Ms. Thumeka Mkololo	SAWS, Junior Scientist

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

The report is distributed to the CPT station, the South African 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

The station is managed by the South African Weather Service. The offices of the station staff are located in Stellenbosch, and the station is usually visited on two days per week (normally Tuesday and Thursday). At the time of the audit, two positions for technical/scientific staff were vacant. The station management was handed over from Ernst-Günther Brunke, who retired in 2015, to Casper Labuschagne. In January 2017, a new station manager (Dr. Warren Joubert) was appointed. The responsibility for the financial and personnel management resides with the programme manager who is based at the SAWS headquarters in Pretoria.

Station Location and Access

The Cape Point station is located in a nature reserve at the southern end of the Cape Peninsula, South Africa. The monitoring station is exposed to the sea on top of a cliff 230 m a.s.l., about 60 km south from the city of Cape Town. Since the dominant wind direction is SE - S - SW, the station is subjected to maritime air from the South Atlantic most of the time. The station is accessible by road. Further information is available in the GAW Station Information System (GAWSIS, https://gawsis.meteoswiss.ch). No significant changes were made since the last audit by WCC-Empa.

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

Station Facilities

The Cape Point station comprises extensive laboratory space. Basic office, kitchen and sanitary facilities are available. Internet access is available but with a low bandwidth. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

Operation and Maintenance

The station is normally visited tice per week (Tuesday and Thursday). All instruments are closely monitored remotely. In case of instrument problems or failure, response time is usually within one day.

Measurement Programme

The CPT station comprises a very comprehensive measurement programme and covers different focal areas of the GAW programme. An overview on measured species is available from GAWSIS.

> **Recommendation 1 (**, important, ongoing)**
> *Since CPT features some of the longest continuous time series for many of the measured species in the Southern Hemisphere, continuation as well as expansion of the measurement programme at CPT is regarded of high importance.*

Air Inlet System

The air inlet systems were not changed since the last audit. Each instrument has its own air inlet system or inlet line. The design of these systems is adequate for its intended purpose.

Surface Ozone Measurements

Surface ozone measurements started in 1982 at the Cape Point site, and continuous time series are available since then.

Instrumentation. Currently three ozone analysers are used at the station for continuous surface ozone measurements at three different sampling altitudes (4m, 14m, and 30m above ground).

Standards. A TEI49i-PS ozone calibrator is available. The standard is traceable to the WMO/GAW reference trough calibration against NIST Standard Reference Photometer SRP#15 at WCC-Empa.

Intercomparison (Performance Audit). The ozone analysers at Cape Point were compared against the WCC-Empa travelling standard with traceability to a Standard Reference Photometer (SRP). The results of the comparison with respect to the Data Quality Objectives (DQOs) are summarised below. All three ozone analysers and the station calibrator were compared against the WCC-Empa ozone reference.

The data was acquired by both the WCC-Empa and the station data acquisition system. Data of the station DAQ was used for data evaluation, and the data was corrected by CPT staff using the correction function based on their calibrations and zero checks. The correction parameters are given in the following table.

Table 1. Zero offset and span coefficient used for the correction of the CPT ozone analysers. The unbiased values are obtained by subtraction of the zero offset from the instrument reading, followed by multiplying with the span factor.

	TEI 49i #1303156643	TEI 49C #71956-370	TEI 49i #13259053
Zero offset	1.05	-0.42	1.58
Span factor	0.9762	1.0400	1.6285

The following equations characterise the bias of the different instruments in their current states:

TEI 49i-PS #7088211231 (BKG -0.1 ppb, SPAN 1.019) – station calibrator:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OC] - 0.16 ppb) / 1.0039 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.59e-05 * $X_{O3}{}^2$) (1b)

TEI 49C #71956-370 (BKG +0.3 ppb, SPAN 1.000) – 30 m inlet:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.30 ppb) / 1.0123 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.34 ppb^2 + 2.59e-05 * $X_{O3}{}^2$) (1d)

TEI 49i #1303156643 (BKG 0.1 ppb, SPAN 1.047) – 4 m inlet:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.44 ppb) / 1.0081 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.38 ppb^2 + 2.67e-05 * $X_{O3}{}^2$) (1f)

TEI 49i #1327059053 (BKG -0.6 ppb, SPAN 0.6270) – 14 m inlet:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.47 ppb) / 0.9979 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.31 ppb^2 + 2.62e-05 * $X_{O3}{}^2$) (1h)

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

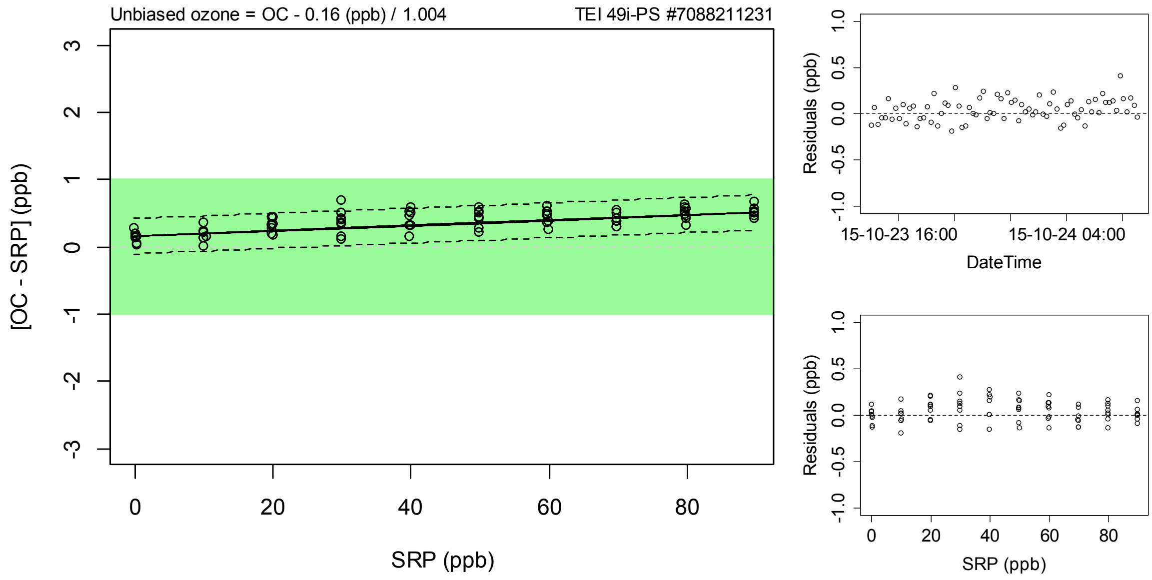

Figure 1. Left: Bias of the CPT ozone calibrator (TEI 49i-PS #7088211231) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the DQOs. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

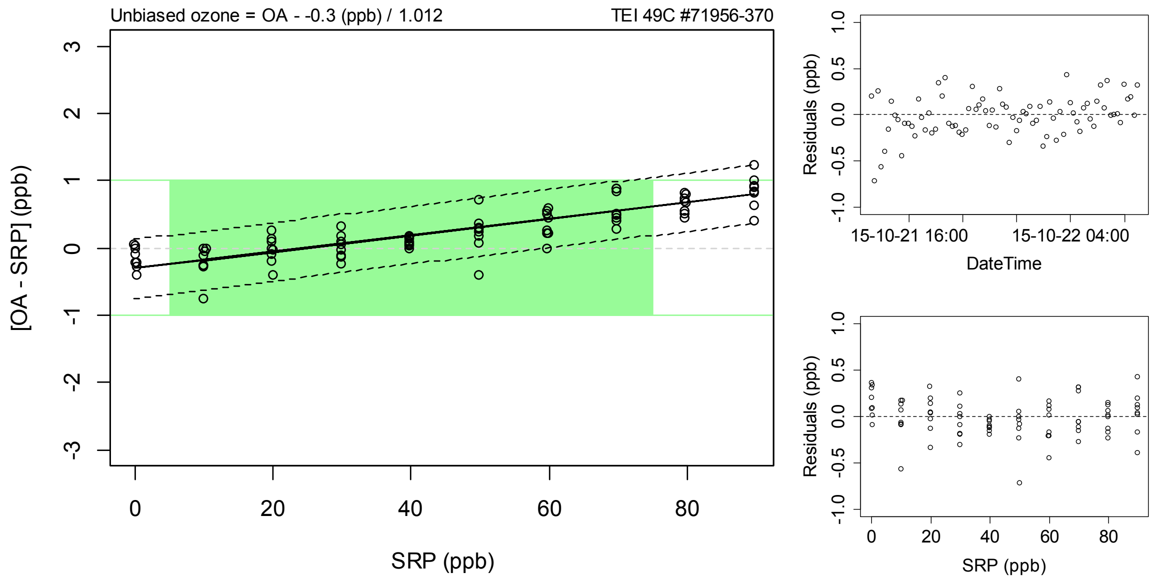

Figure 2. Same as Figure 1, for the TEI 49C #71956-370 station analyser.

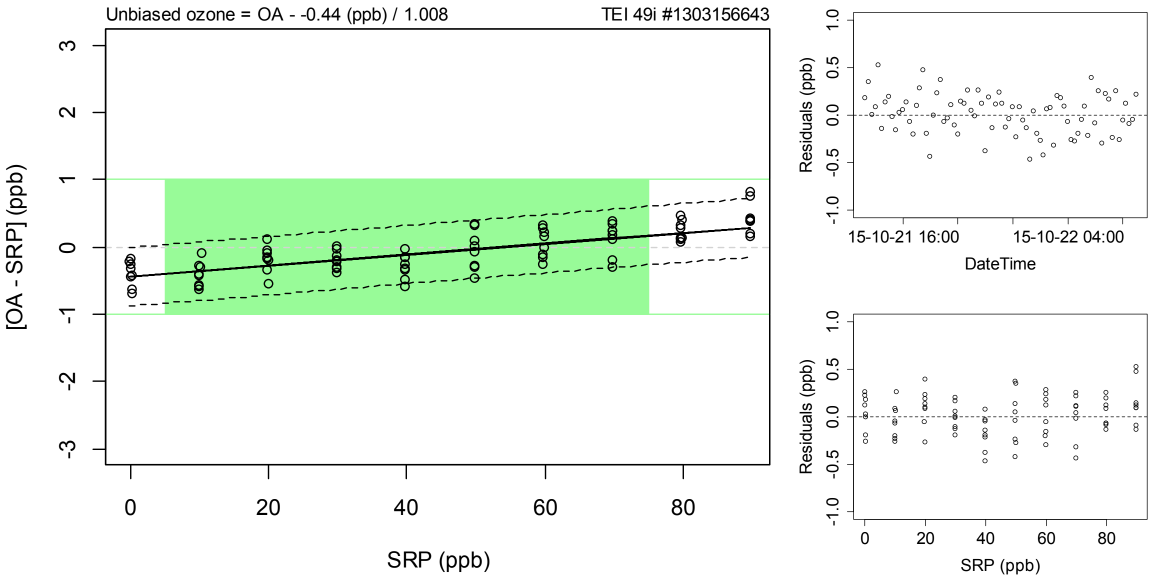

Figure 3. Same above, for the TEI 49i #1303156643 station analyser.

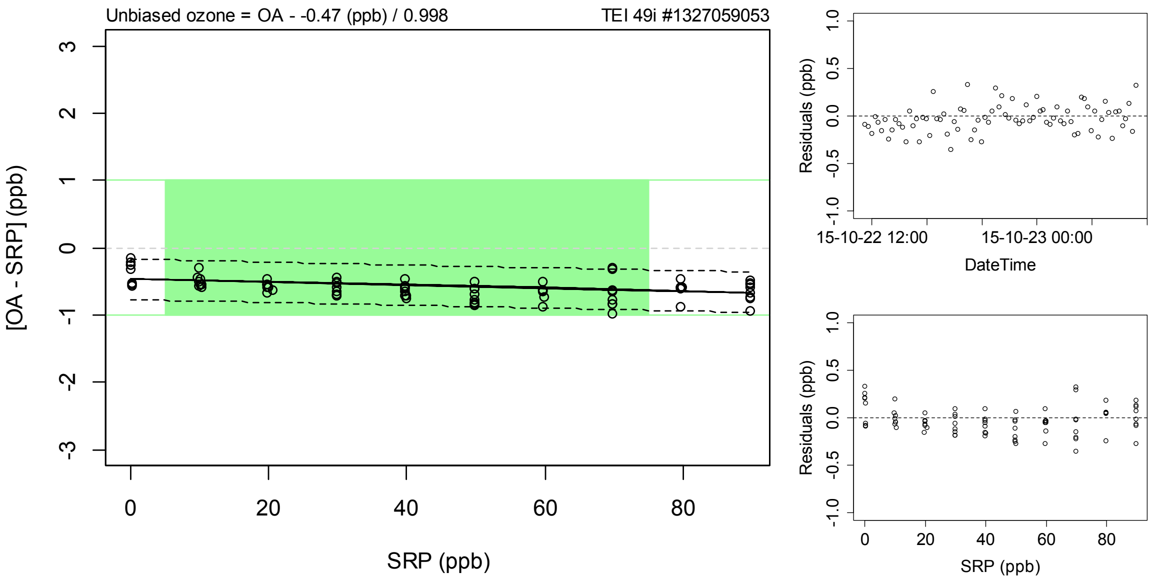

Figure 4. Same above, for the TEI 49i #1327059053 station analyser.

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

Good agreement between the WCC-Empa travelling instrument and the station instruments were found. However, the calibration factors in use require significant correction of the raw data. It should be considered to change these factors.

Recommendation 4 (, minor, 2017)**
The calibration settings of some of the instruments (especially TEI 49i #1327059053) were set in a way that requires large correction of the raw data. This has the disadvantage that the instrument display show different values and cannot directly be compared. It is recommended to adjust the calibration settings once based on a thorough calibration with the station calibrator After that, no further changes should be made.

In addition to the above comparison, the inlet filter holders were tested for ozone loss. No significant loss was observed at high ozone levels of 500 ppb. Therefore, the filter holders are adequate. However, a significant ozone loss (approx. 10%) was observed over the glass water traps. These traps were equipped with ¼ inch fittings on 6 mm outer diameter glass tubing, which resulted in significant leakage.

Recommendation 4 (*, critical, immediately)**
The water traps in the ozone inlet lines need to be removed until appropriate fittings are available. After re-installation, a leak check including the trap must be performed.

Carbon Monoxide Measurements

Carbon monoxide measurements at Cape Point were established in 1978, and continuous time series are available since then. The CPT CO data series is one of the longest in the Southern Hemisphere.

Instrumentation. Gas chromatography (RGA-3) (since 1978) and Cavity Ring Down Spectroscopy (CRDS) (Picarro G2302) (since 2012). The current instrumentation is adequate for CO measurement.

Standards. NOAA/ESRL laboratory standards and working standards (target and calibration gases) pressurised with CPT air using a RIX pump are available. At the time of the audit some of the laboratory standards were returned to NOAA for re-calibration. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT 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 5 and 10 with respect to the WMO/GAW compatibility goals (WMO, 2016):

RGA-3 #113087-003:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 0.7) / 0.9674 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (16.6 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

Picarro G2302 #835-CKADS2026:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 3.2) / 0.9970 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (2.4 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

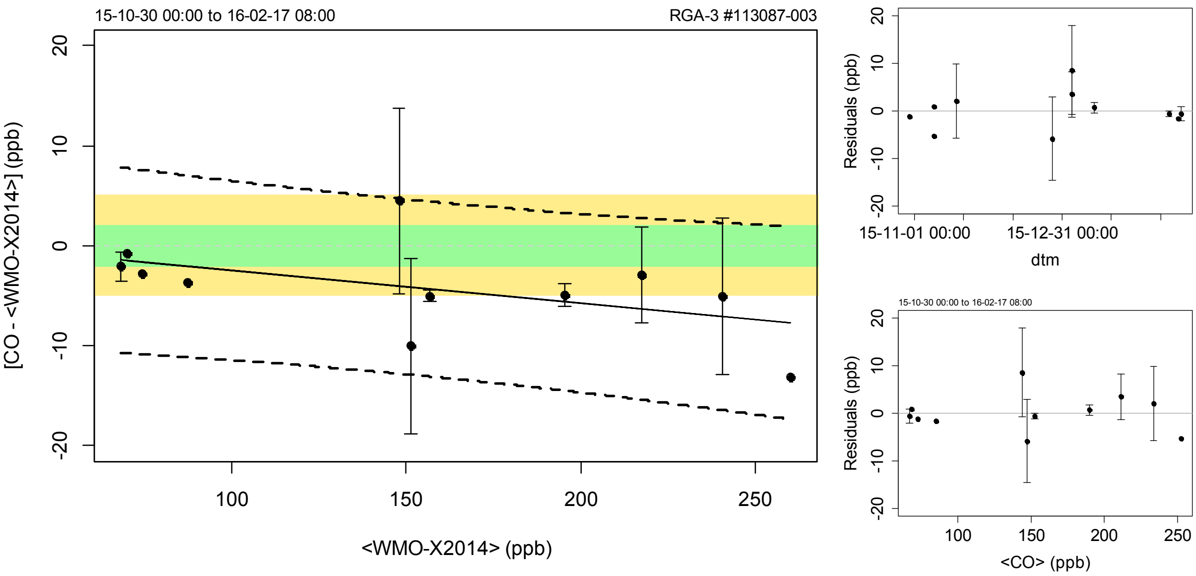

Figure 5. *Left: Bias of the CPT RGA-3 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. 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 CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

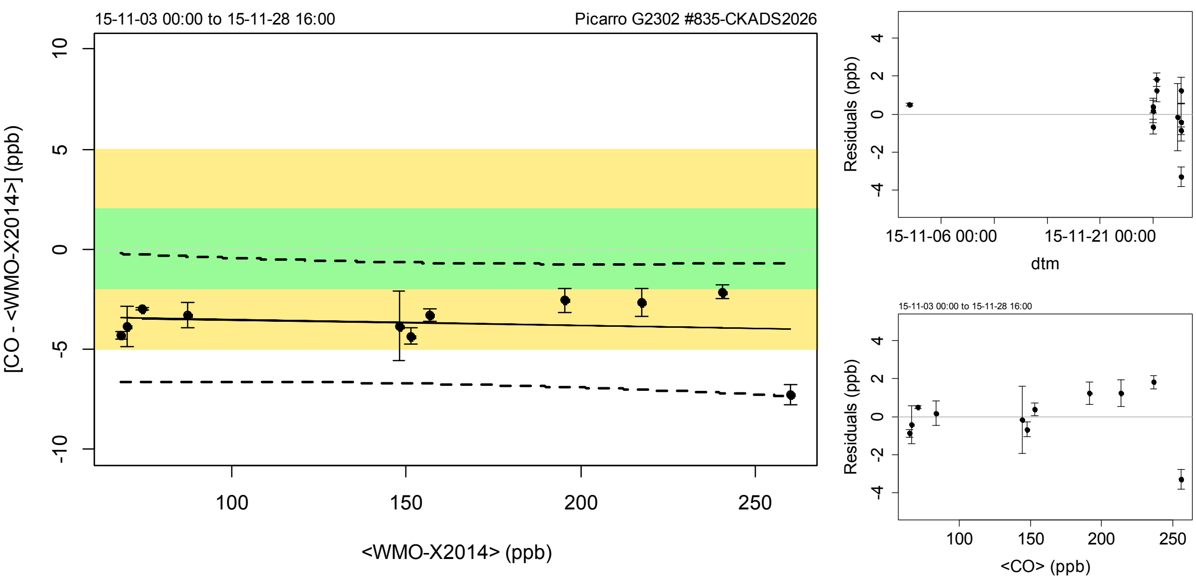

Figure 6. *Same as above, for the Picarro G2302 #835-CKADS2026.*

The results of the comparisons can be summarised as follows:

The comparison of the RGA-3 instrument confirmed the results obtained during the last WCC-Empa audit in 2011. Relatively good agreement within the WMO/GAW compatibility goals were found at low mole fractions relevant for the Southern Hemisphere background, but associated with large uncertainties. The Picarro G2302 instrument was measuring slightly lower compared to the WCC-Empa reference, which can be explained by calibration scale differences. CPT reported on the WMO-X2014 carbon monoxide scale, whereas WCC-Empa refers to WMO-X2014A.

Recommendation 4 (*, important, 2017)**
CPT CO data needs to be updated to the latest NOAA reference scale (WMO-X2014A) when revised values will become available for the standards under re-calibration.

Methane Measurements

Cape Point comprises one of the longest methane time series in the Southern Hemisphere with continuous measurements available since 1983.

Instrumentation. Varian CP-3800 GC/FID system (since 1983) and Cavity Ring Down Spectroscopy (CRDS) (Picarro G2301) (since 2012). The current instrumentation is adequate for CH_4 measurement.

Standards. NOAA/ESRL laboratory standards and working standards (target and calibration gases) pressurised with CPT air using a RIX pump are available at CPT. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT 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 7 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2016).

Varian CP-3800 #101605:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 1.6 ppb) / 0.99979 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (6.4 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

Picarro G2301 #923-CFADS2201:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 2.9 ppb) / 1.00221 (3c)

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

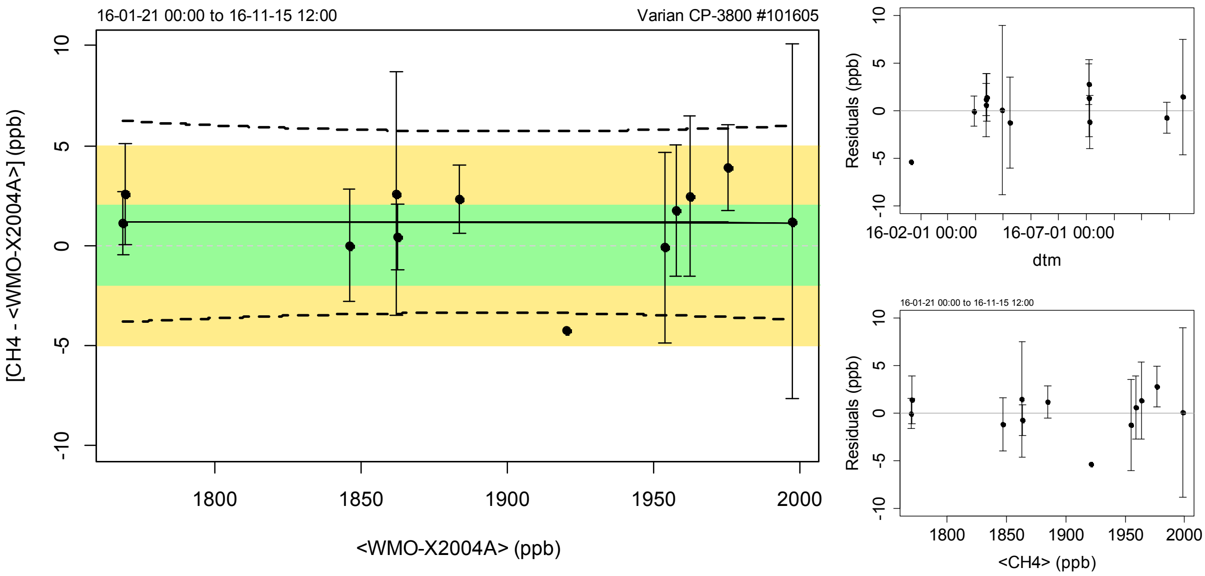

Figure 7. *Left: Bias of the Varian CP-3800 #101605 methane instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

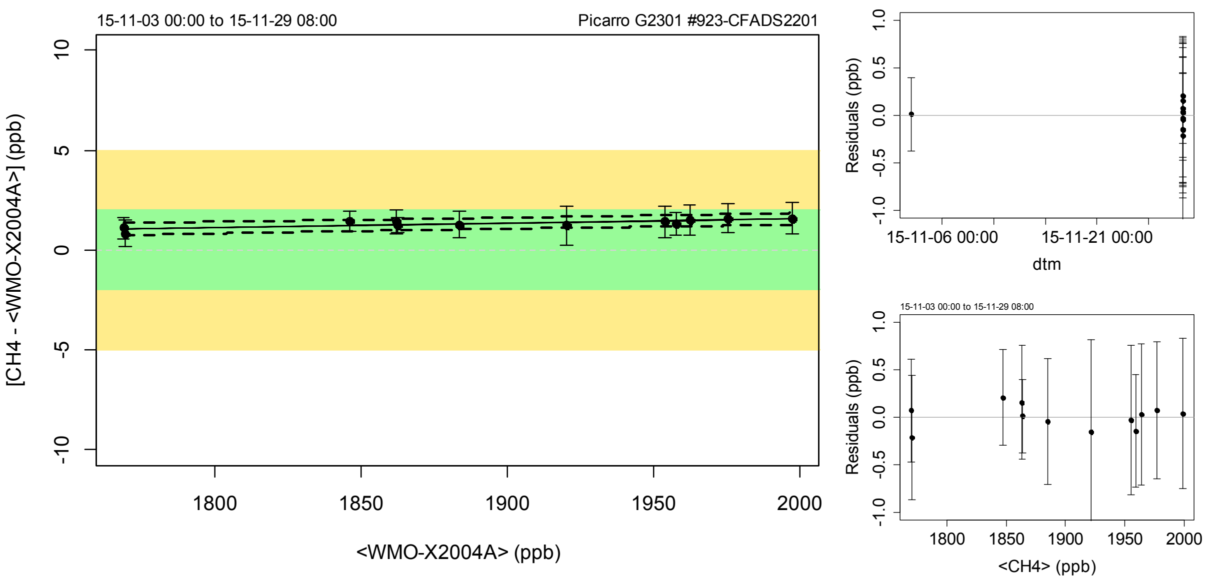

Figure 8. *Same as above, for the Picarro G2301 #923-CFADS2201.*

The result of the comparison can be summarised as follows:

The results of both the GC/FID system and the Picarro G2301 compare well and meet the WMO/GAW compatibility goals. The uncertainty of the Picarro instrument is considerably smaller compared to the GC/FID system. Thus, it is recommended that the data of the Picarro is considered as the main methane analyser. The results show that the instrumentation is fully adequate and no further action is required.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at CPT started in 1993 using non-dispersive infrared (NDIR) absorption technique, and data is available since then. Shortly after the last WCC-Empa audit in 2011 a Picarro CRDS instrument was installed.

Instrumentation. Cavity Ring Down Spectroscopy (CRDS) (Picarro G2302 and Picarro G2301) (since 2012). The current instrumentation is adequate for CO_2 measurement.

Standards. NOAA/ESRL laboratory standards and working standards (target and calibration gases) pressurised with CPT air using a RIX pump are available at CPT. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT 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 9 and 10 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2016).

Picarro G2302 #835-CKADS2026 (main station analyser):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.57 ppm) / 0.99869 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.008 ppm^2 + 3.28e-08 * X_{CO2}^2) (4b)

Picarro G2301 #923-CFADS2201 (backup instrument):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 1.01 ppm) / 0.99765 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.008 ppm^2 + 3.28e-08 * X_{CO2}^2) (4d)

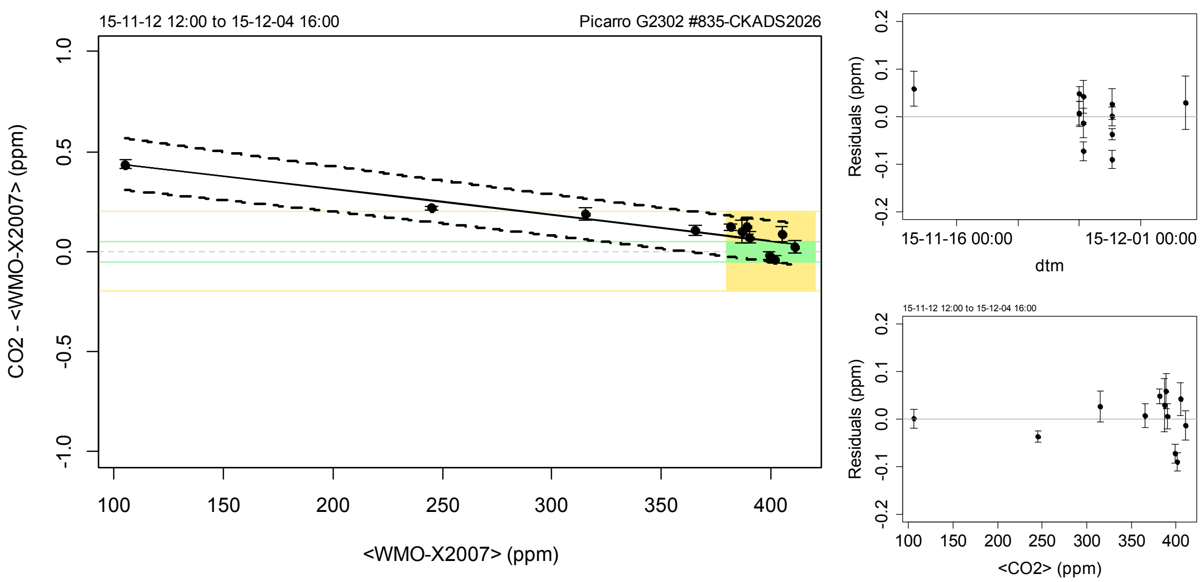

Figure 9. *Left: Bias of the PICARRO G2302 #835-CKADS2026 CO_2 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 CPT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

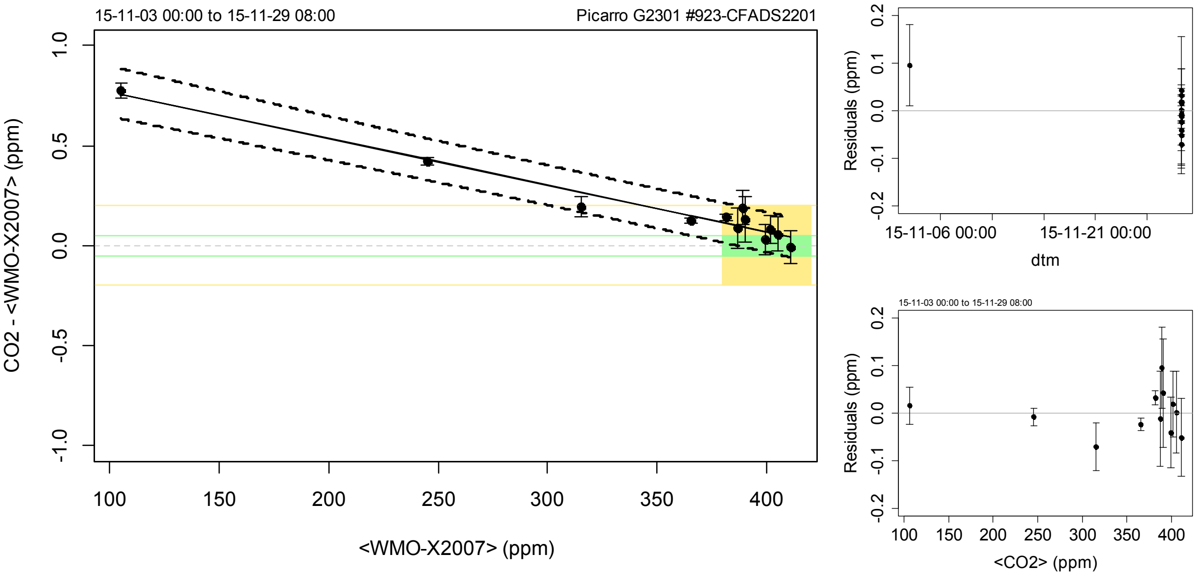

Figure 10. *Same as above for the Picarro G2301 #923-CFADS2201 instrument.*

The result of the comparison can be summarised as follows:

Agreement within the WMO/GAW compatibility goals for the Southern Hemisphere of ±0.05 ppm was found for mole fractions between approximately 400-420 ppm CO_2. Lower mole fractions were slightly overestimated, and higher CO_2 levels will most like be underestimated with the current instrument calibration. It should be considered to calibrate the zero offset of the instruments using CO_2 free air. This has to be done only once, since the calibration of these instruments remains usually stable over time.

Recommendation 4 (*, important, 2017)**
It is recommended to apply an instrument specific CO_2 offset in the user calibration option of the Picarro instruments using CO_2 free air. Afterwards, the zero calibration should be checked at least once per year and adjusted if needed.

Nitrous Oxide Measurements

Measurements of nitrous oxide commenced at CPT in 1983, making the CPT N_2O time series one of the longest in the Southern Hemisphere. Data is available since then with some interruptions related to instrumental problems.

Instrumentation. Gas chromatography with Electron Capture Detector (GC/ECD, Agilent 6890N US10649084).

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) pressurised with CPT air using a RIX pump are available at CPT. A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT 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 11 with respect to the WMO/GAW compatibility goals (WMO, 2016):

Agilent 6890N US10649084:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O + 16.08) / 1.05193 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (1.02 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

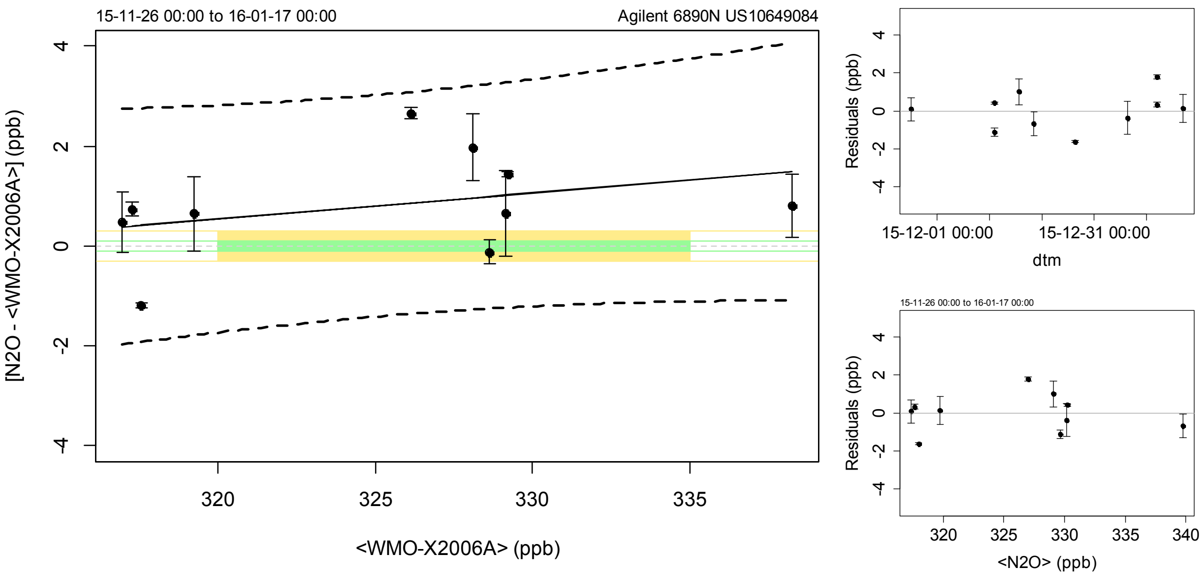

Figure 11. *Left: Bias of the CPT Agilent 6890N US10649084 nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 CPT. 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 did not comply with the WMO/GAW compatibility goals, and the associated measurement uncertainty was significantly too large for the type of instrument in use. The performance has been better in the past. The last audit by the WCC-N_2O (Scheel, 2012) showed deviations within the extended WMO/GAW compatibility goals of 0.3 ppb in the mole fraction range between 300 and 340 ppb N_2O. It needs to be explored if the current analytical system can be fixed.

Recommendation 2 (*, critical, 2017)**
The current analytical system shows poor repeatability and does not comply with the WMO/GAW compatibility goals. The cause of the malfunction needs to be identified and fixed if possible. Otherwise, instrument replacement should be considered.

Recommendation 5 (*, important, 2017)**
A system and performance audit by the WCC-N_2O is recommended.

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 22 October 2015 through 25 February 2016. The TI was using a completely separate inlet line leading to the same air intake location as the CPT station inlet. In addition, air was also sampled from the CPT inlet after the dryer. The TI was sampling using the following sequence: 1440 min ambient air from the independent WCC inlet (humid), 300 min ambient air from the CPT inlet after the dryer 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 WCC-Empa CRDS data. Details of the calibration of the TI are given in the Appendix. The following figures show the results of the ambient air comparisons.

Carbon Monoxide:

The CO comparison (1h data) between the WCC-Empa TI and the CPT Picarro G2302 analyser is shown in Figure 12. The comparison was characterised by two distinctly different periods. In the first half of the comparison until 24 December 2015 the agreement was reasonable, whereas the second half was characterised by a highly variable bias with CPT CO measurements tending to be low. The performance of the Picarro G2302 during this period was not good, and therefore we will focus our comparison on the first half, which is shown in Figure 13. During this period, the temporal variation was well captured by both instruments. A slight difference was observed between the two inlets, which is further illustrated in the histogram plots in Figures 14. The bias was about the same as for the travelling standard comparison (see Figure 10) when the TI was measuring from the same air inlet as CPT (dry air). It therefore is likely that the TI suffers from H_2O interference, resulting in a slight overestimation of the CO mole fraction when measuring humid air.

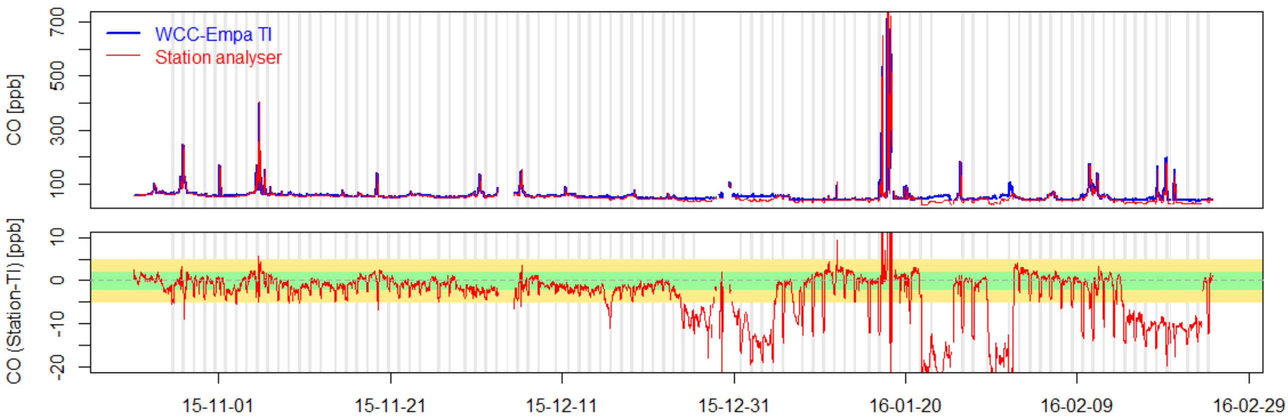

Figure 12. CO comparison at CPT between the WCC-Empa travelling instrument and the CPT Picarro G2302 analyser. Upper panel: CO time series (1 h data). Lower panel: CO bias of the station analyser vs time. The horizontal areas correspond to the WMO/GAW compatibility green) and extended compatibility (yellow) goals; vertical grey bars illustrate when different inlets were used (see text for details).

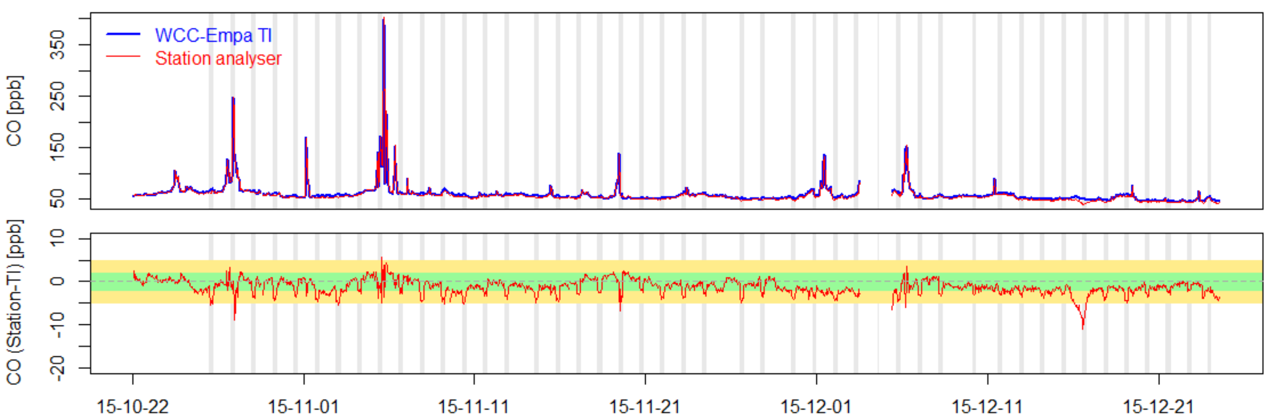

Figure 13. Same as above for the good period until 24 December 2015.

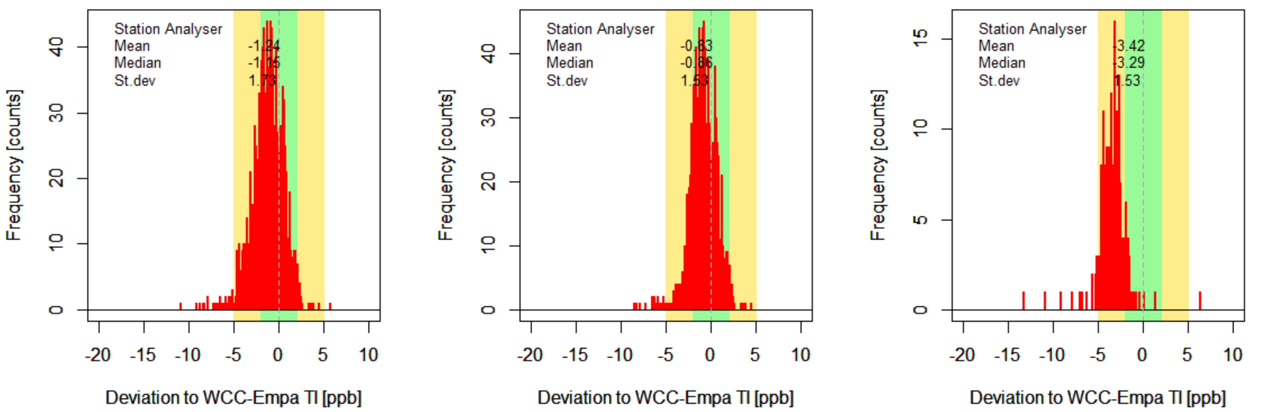

Figure 14. Deviation histograms (good period) for CO (Station analyser Picarro G2302– TI) for all data (left), for the period when the TI sampled from the independent inlet line (middle) and for the period when the TI sampled from CPT inlet (right).

Carbon dioxide:

Figure 15 shows the CO_2 comparison of the Picarro G2302 analyser with the WCC-Empa TI (1 h data). Only the period until 24 December 2015 was considered for the comparison, since there were instrumental issues with the CPT analyser after that time. It can be seen that the temporal variation was well captured by both instruments. The average bias was with -0.13 ppm exceeding the WMO/GAW extended compatibility goal of 0.1 ppm. In addition, a small difference was observed between the two inlets, which is illustrated by deviation histograms in Figure 16. It therefore cannot be excluded that a small fraction of CO_2 is lost in the CPT inlet and drying system.

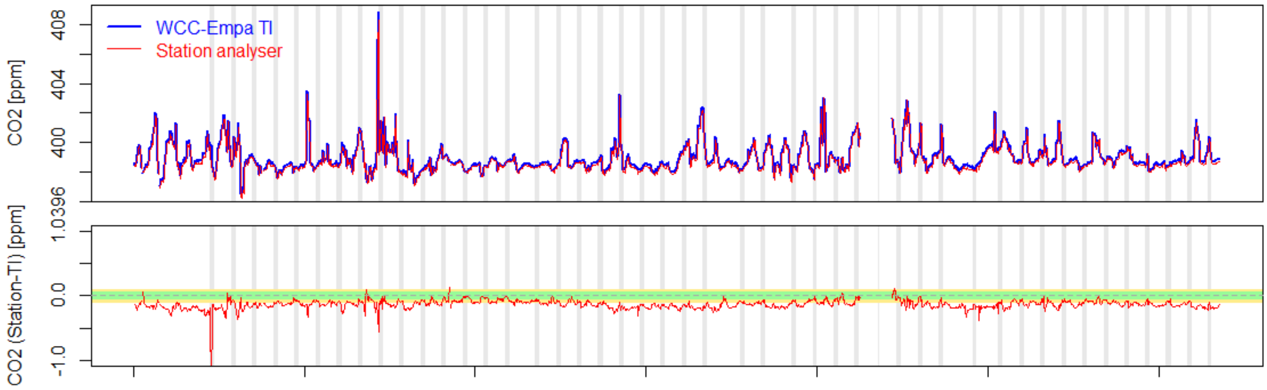

Figure 15. CO_2 comparison at CPT between the WCC-Empa travelling instrument and the CPT Picarro G2302. Upper panel: CO_2 time series (1 h data). Lower panel: CO_2 bias of the station analyser vs time. The horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals; vertical grey bars (left diagrams) illustrate when different inlets were used (see text for details).

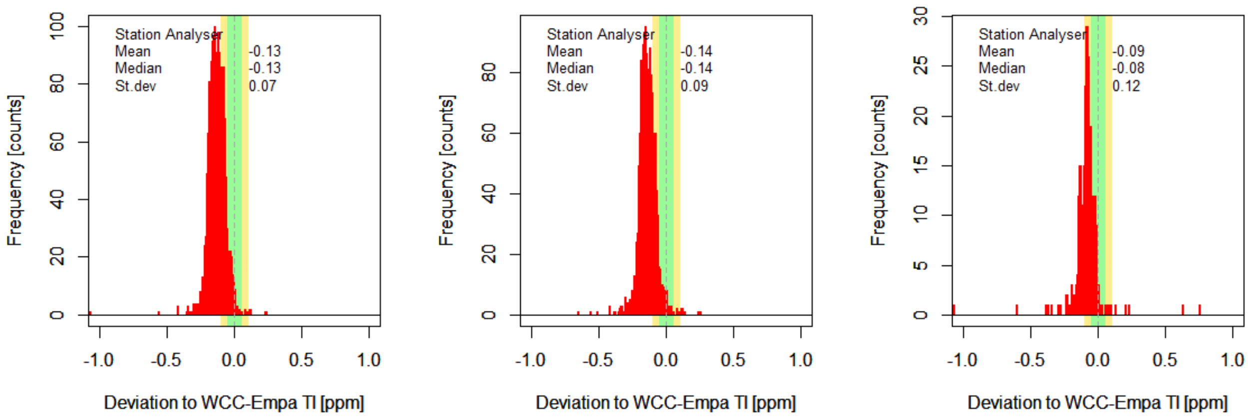

Figure 16. Deviation histograms (Station analyser – TI) for all data (left), for the period when the TI sampled from the independent inlet (middle) and for the period when the TI sampled from the CPT inlet (right).

Methane:

Figure 17 shows the CH_4 comparison of the Picarro G2301 analyser with the WCC-Empa TI. As for the other species, the temporal variation was well captured by both instruments, and the median bias was on average within the WMO/GAW compatibility goal of 2 ppb. The agreement was better during the first half of the comparison period. During the second half, prolonged episodes with CPT CH_4 values being significantly higher compared to the WCC TI occurred. A potential reason for this might be a temporary leak in the drying system. The CH_4 indoor mole fraction is significantly higher compared to ambient due to the use of CH_4 in Argon as a carrier gas of the GC/ECD system. Figure 18 shows deviation histograms (1 h data) of the bias for all data, for the period when the TI sampled from the independent inlet line, and for the period when the TI sampled from the CPT inlet. The few events with a strong positive bias can most likely be explained by leaks in the drying system.

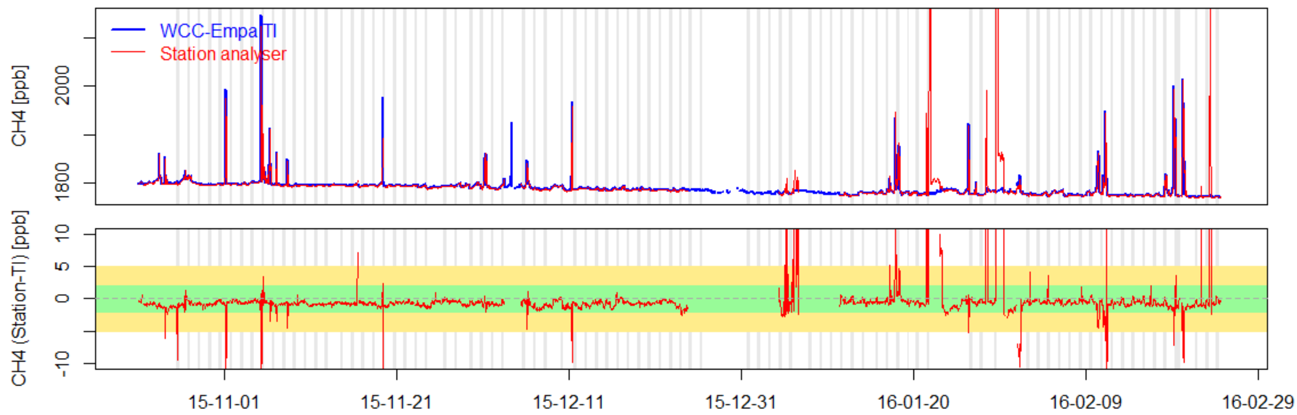

Figure 17. CH_4 comparison at CPT between the WCC-Empa travelling instrument and the CPT Picarro G2301. Upper panel: CH_4 time series (1 h data). Lower panel: CH_4 bias of the station analyser vs time. The horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals; vertical grey bars (left diagrams) illustrate when different inlets were used (see text for details).

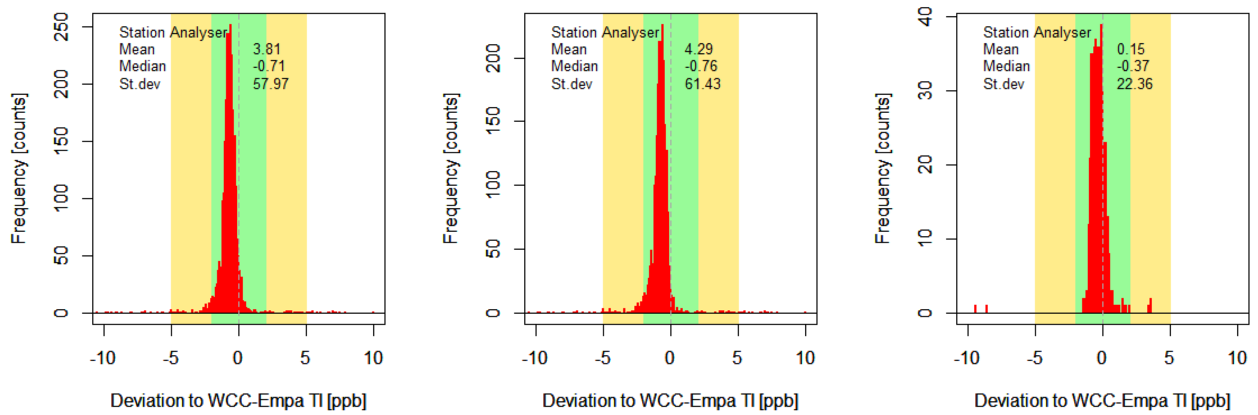

Figure 18. Deviation histograms (Station analyser – TI) for all data (left), for the period when the TI sampled from the independent inlet (middle) and for the period when the TI sampled from the CPT inlet (right).

Discussion of the ambient air comparison results

The ambient air comparison largely confirms the result of the performance audit using travelling standards. It was noticed that the second half of the comparison period showed larger discrepancies between the WCC TI and the station analysers. This was due to instrumental problems with one of the instruments (Picarro G2302), but also due to likely leakage in the CPT drying system.

Recommendation 3 (*, critical, ongoing)**
It must be made sure that no leakage occurs in the CPT drying system after the exchange of the water traps.
Recommendation 4 (, important, ongoing)**
If instrumental irregularities are observed, the reason must be timely analysed, and repair needs to be initiated. A budget must be available for handling unforeseen repair costs.

Data Acquisition and Management

GC instruments: All data is acquired using Datalys Azur Chromatography Data System Software (Version 2.0.4.). Data is archived on a monthly basis. Data can be accessed through the internet from the main office in Stellenbosch. Data validation is carried out at Stellenbosch.

Picarro instruments are using the integrated Python based data acquisition system.

Ozone: Testpoint data acquisition using ADAM 4017 D/A modules (Keithley) is used to acquire the analogue signals of the instruments. 1-minute and 30-minute averages are stored on the data acquisition computer. No additional instrument parameters are stored. Data back-ups are made weekly, and the data evaluation is made at the office in Stellenbosch.

> **Recommendation 5 (***, critical, 2017)**
> *The analogue data acquisition systems add additional uncertainty to the measurements. It is strongly recommended to replace these units by a solution that acquires the digital signal of the instrument, which also will allow the storage of ancillary instrument parameter.*

Documentation

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

Data Submission

Surface O_3 (1983-2014), CO (1979-2015), CH_4 (1983-2015), CO_2 (1993-2015, Empa) and N_2O (1994-2007) data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). The data has been submitted as filtered and unfiltered data sets.

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.

Conclusions

The Global GAW station Cape Point is situated at an important location for the GAW programme, which makes the available data a very significant contribution to GAW. The data series of CPT are among the longest in the Southern Hemisphere, and the station has one of the most comprehensive measurement programmes within the GAW network.

Significant improvements were made concerning the data quality compared to the last WCC-Empa audit in 2011. All assessed parameters met on average the WMO/GAW compatibility goals with the exception of CO and N_2O, where the goal was only partly reached. This remains challenging with the current instrumentation, but further optimisation should be feasible.

The continuation of the Cape Point measurement series is highly recommended and important for GAW. The large number of measured atmospheric constituents in combination with the high data quality and the long-term perspective are a significant contribution to GAW and the scientific community.

Summary Ranking of the Cape Point GAW Station

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access.
Facilities		
Laboratory and office space	(5)	Adequate, space available for research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(4)	Available but still temperature variations
Power supply	(5)	Reliable with few power cuts
General Management and Operation		
Organisation	(4)	More international scientific collaboration desirable
Competence of staff	(4)	Skilled staff, ongoing training remains important
Air Inlet System	(3)	Potential leakages in the drying system need attention
Instrumentation		
Ozone	(5)	Adequate instrumentation
CO_2/CH_4/CO (CRDS)	(5)	Adequate instrumentation
CO (RGA-3)	(4)	Adequate, calibration challenging
CH_4 (Varian GC)	(4)	No added value compared to CRDS
N_2O (Agilent GC)	(3)	Adequate, but instrumental issues
Standards		
Ozone	(5)	TEI 49i-PS traceable to SRP#15
CO, CO_2, CH_4, N_2O	(5)	NOAA standards / working standards available
Data Management		
Data acquisition	(3)	Analogue DAQ systems need to be replaced by digital solution
Data processing	(5)	Well established data validation procedures
Data submission	(4)	Timely submissions for all parameters except N_2O

#0: inadequate thru 5: adequate.

Dübendorf, March 2017

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WCC-Empa	QA/SAC Switzerland	Head of laboratory

APPENDIX

Data Review

The following figures show summary plots of CPT data accessed on 13 February 2017 from WDCGG. 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:

- Both filtered and unfiltered data set looks plausible, with values within the expected range.
- Seasonal cycle is well captured, and a less pronounced diurnal cycle with an afternoon maximum is observed.

Methane:

- Data set looks generally sound, both for filtered and unfiltered data.
- A few values of the filtered data set at the beginning of the period are probably not valid.
- Pollution events are largely absent in the early 90s, which seems unlikely.
- Frequency of pollution events significantly increased over time.
- Seasonal cycle and long-term trend look plausible.

Carbon monoxide:

- Data set looks generally sound, both for filtered and unfiltered data.
- Seasonal cycle is well captured.
- The early data contains some values which are extremely low and probably not valid.

Carbon dioxide:

- Data set looks generally sound, both for filtered and unfiltered data.
- The long-term trend is consistent with data from other stations.

Nitrous oxide:

- Data set looks generally sound, both for filtered and unfiltered data.
- The uncertainty of hourly values is most likely exceeding the WMO/GAW compatibility goal, which is consistent with the findings of this audit.

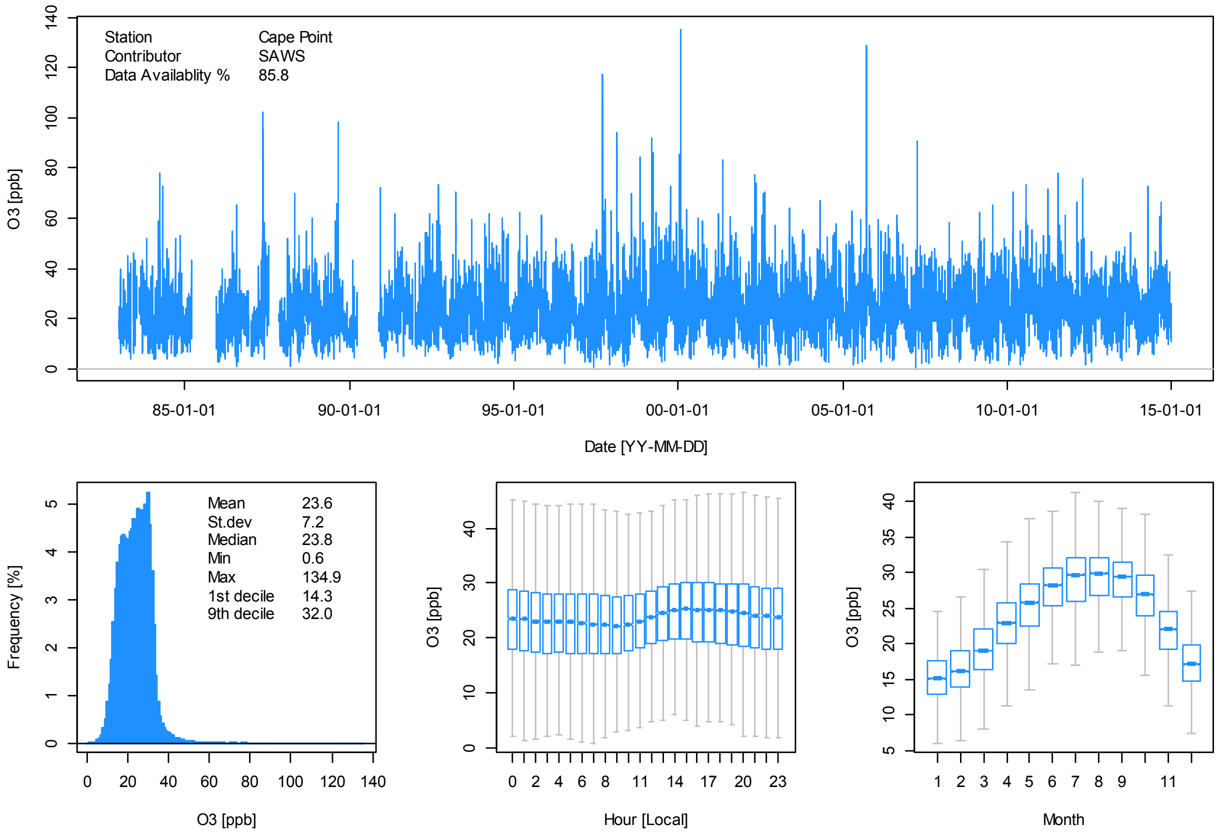

Figure 19. *Ozone data (unfiltered) accessed from WDCGG. Top: Time series, 1-h data. Bottom: Left: Frequency distribution. Middle and left: Diurnal and seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

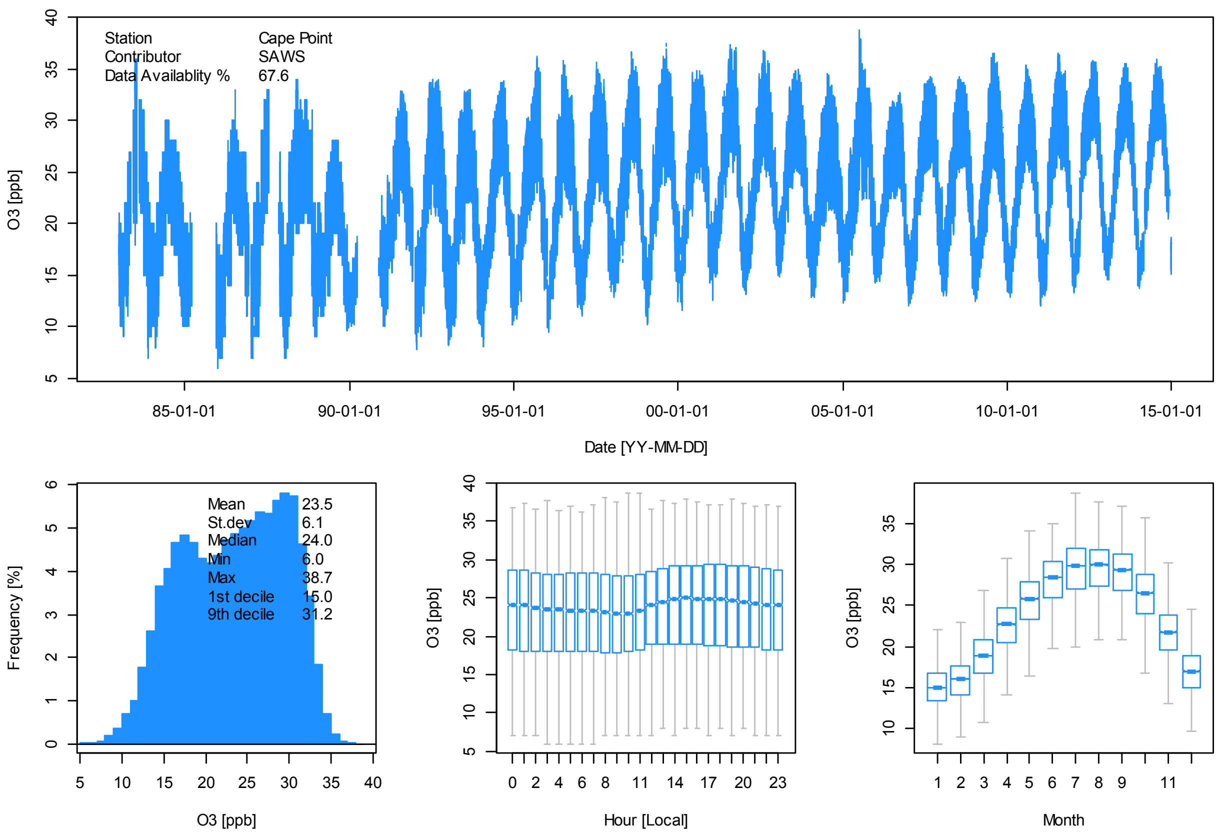

Figure 20. *Same as above for filtered ozone data.*

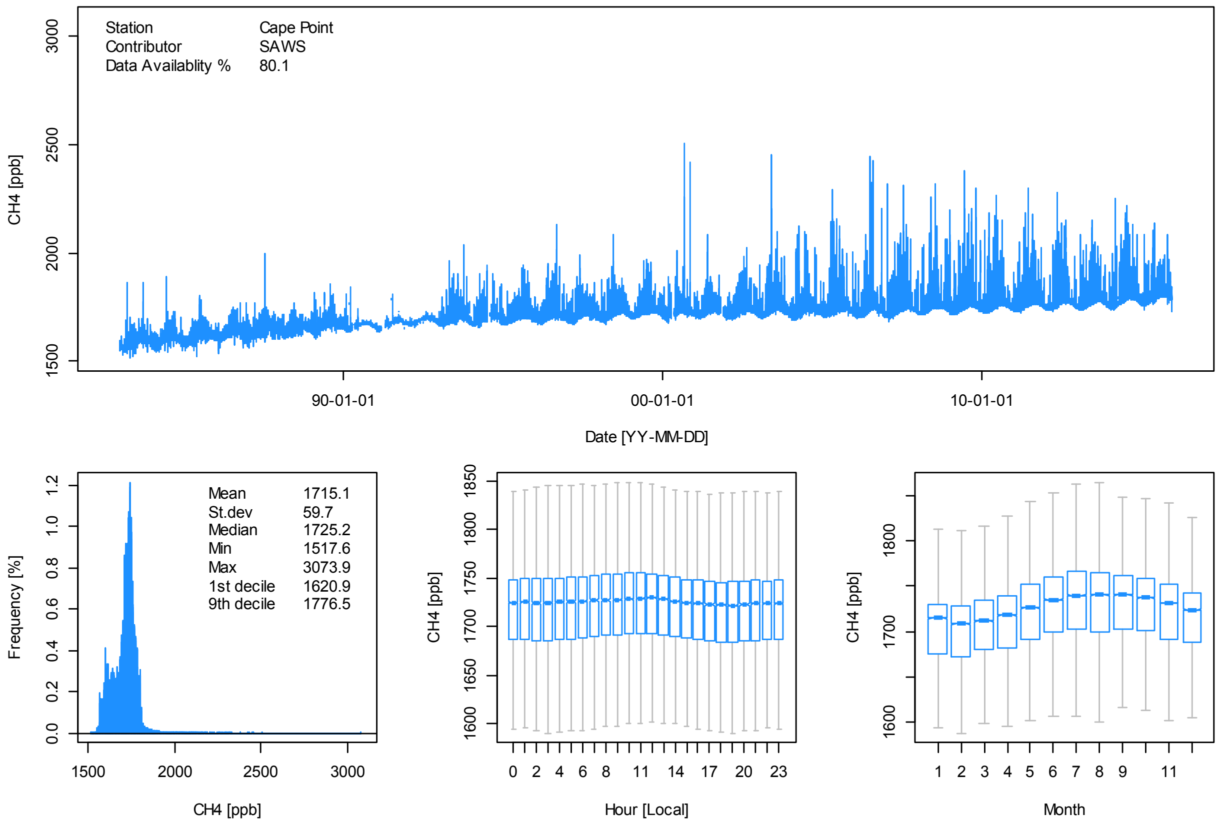

Figure 21. *Same as above for unfiltered CH_4 data.*

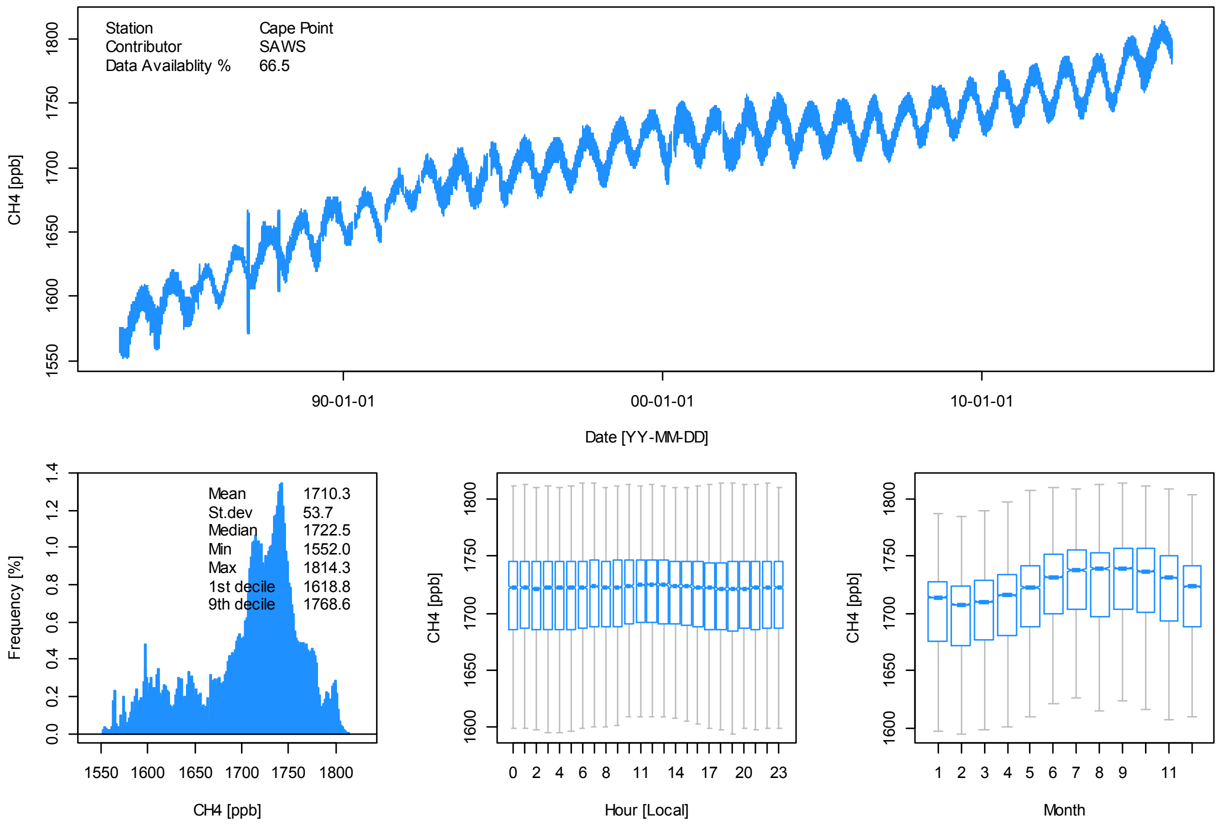

Figure 22. *Same as above for filtered CH_4 data.*

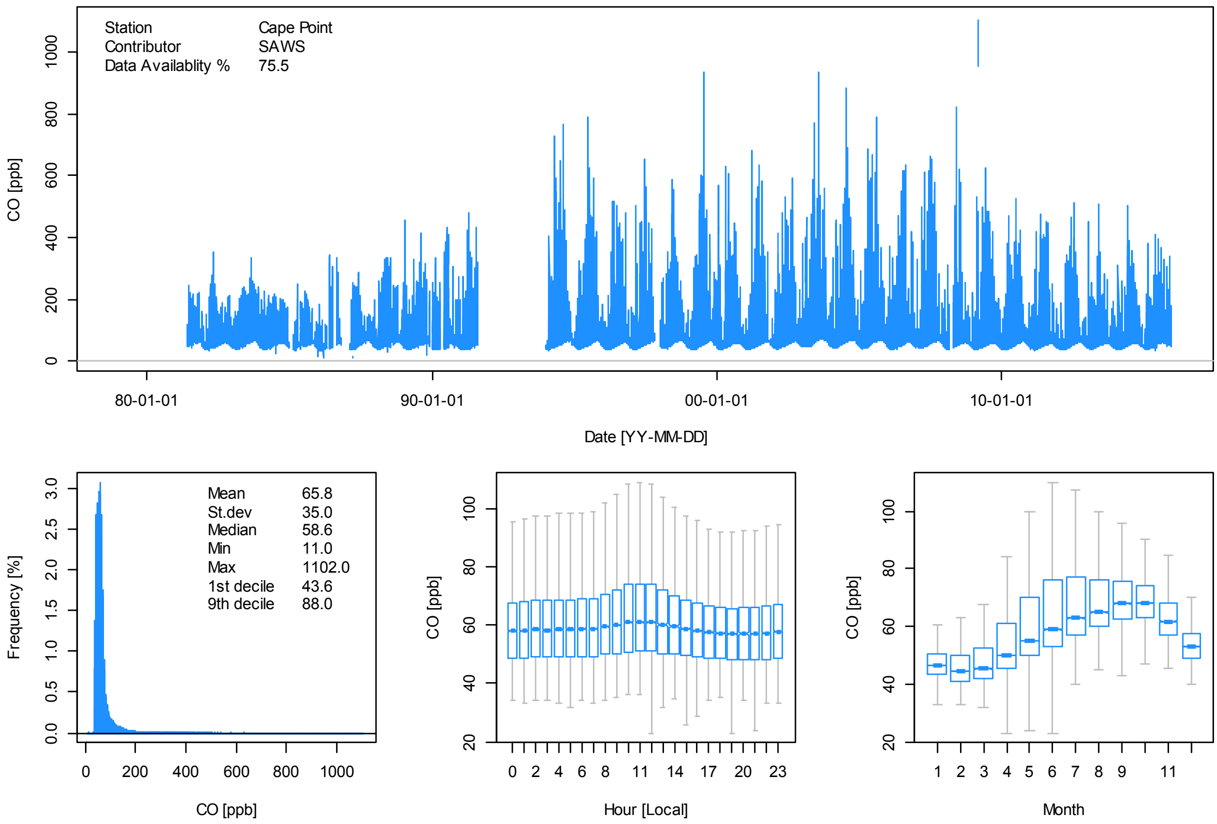

Figure 23. *Same as above for unfiltered CO data.*

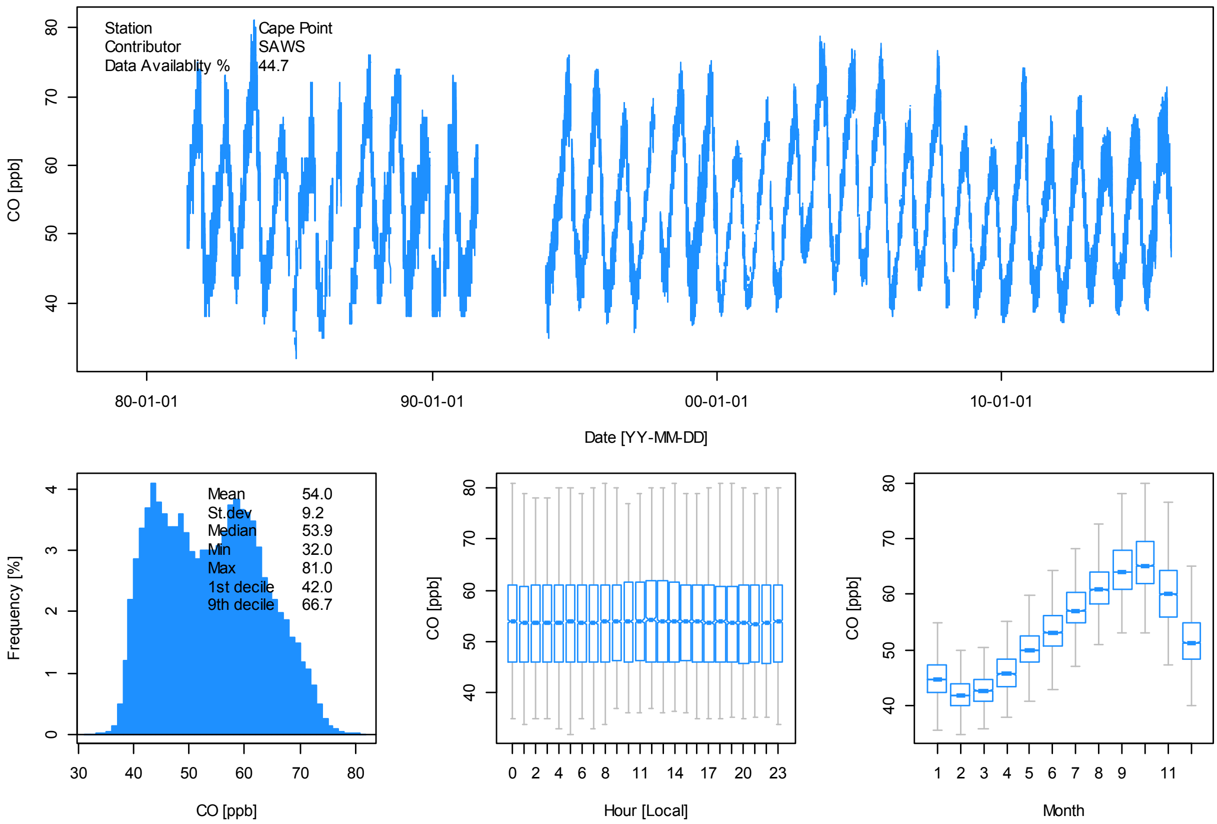

Figure 24. *Same as above for filtered CO data.*

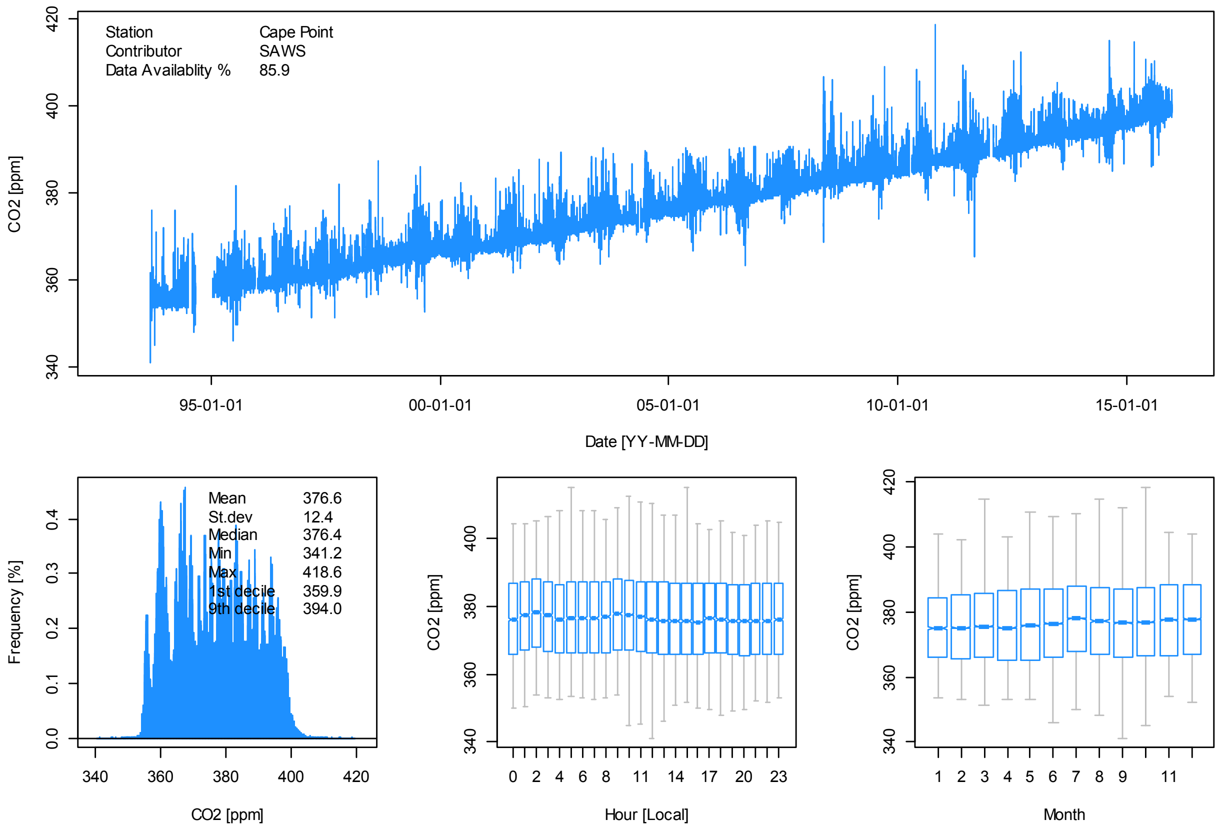

Figure 25. *Same as above for unfiltered CO_2 data.*

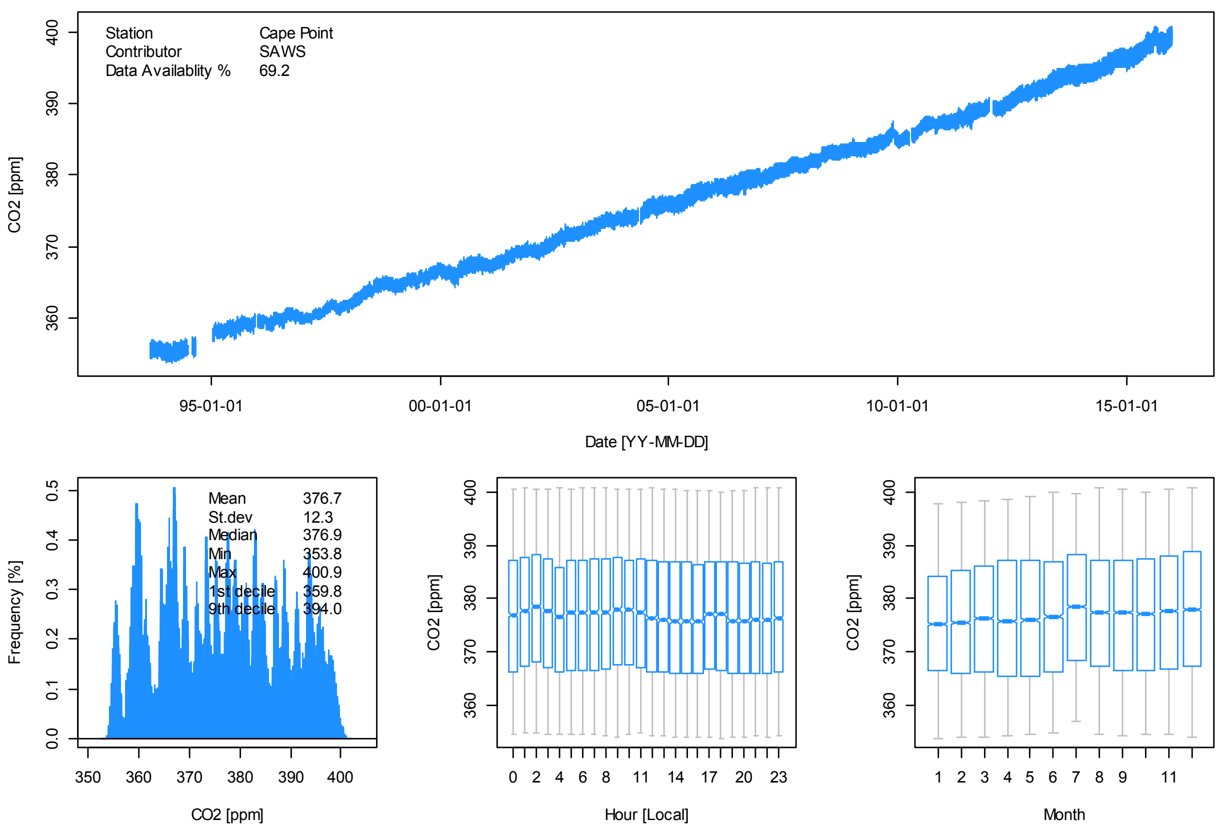

Figure 26. *Same as above for filtered CO_2 data.*

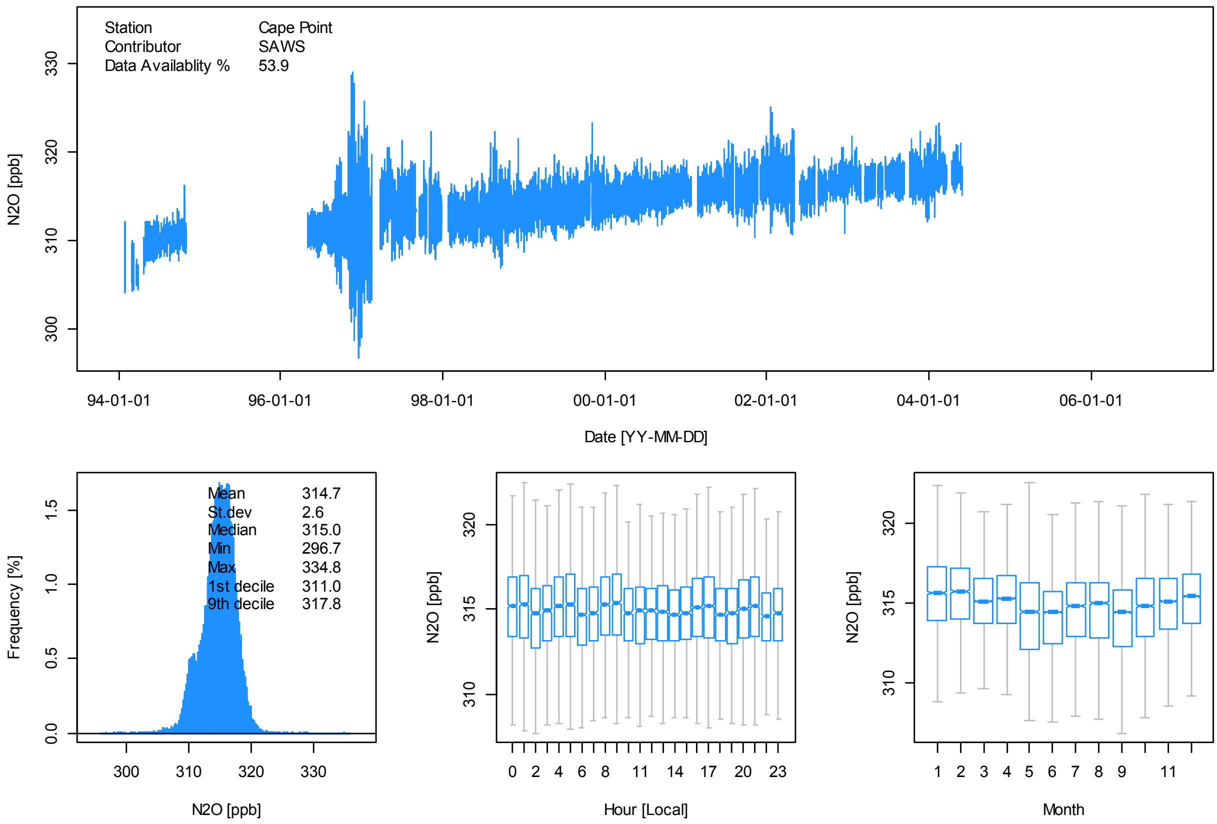

Figure 27. *Same as above for unfiltered* N_2O *data.*

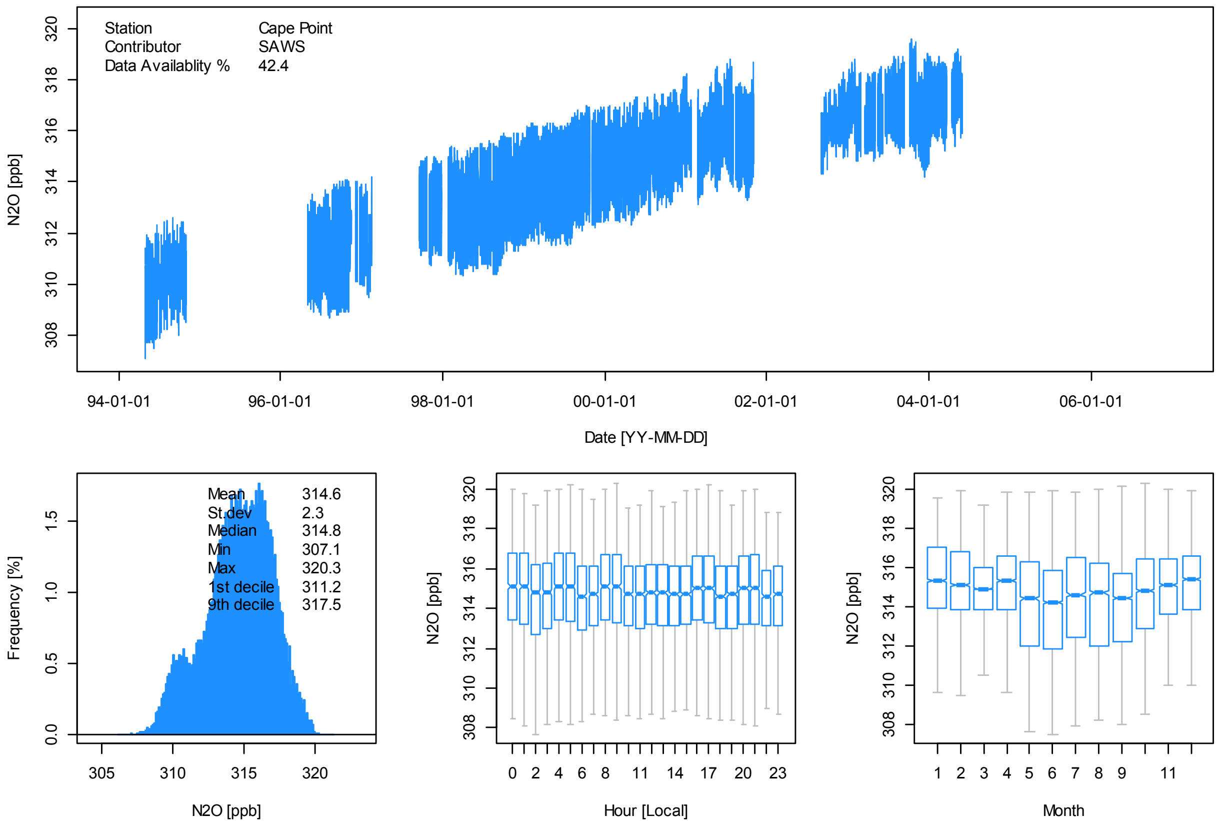

Figure 28. *Same as above for filtered* N_2O *data.*

Ozone Measurements

Comparison of the Ozone Analyser and Ozone Calibrator

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.

Setup and Connections

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. The data used for the evaluation was recorded by the WCC-Empa data acquisition system.

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. The results are valid for the calibration factors given in the Executive Summary. 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 2. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the CPT ozone calibrator (OC) TEI 49i-PS #7088211231 with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2015-10-23 14:03	1	0	0.30	0.23	0.15	0.04	-0.07	NA
2015-10-23 14:18	1	50	50.02	50.21	0.06	0.31	0.19	0.4
2015-10-23 14:33	1	30	30.05	30.03	0.06	0.09	-0.02	-0.1
2015-10-23 14:48	1	10	10.33	10.36	0.36	0.51	0.03	0.3
2015-10-23 15:03	1	90	90.02	90.15	0.12	0.16	0.13	0.1
2015-10-23 15:18	1	40	40.02	40.28	0.10	0.29	0.26	0.6
2015-10-23 15:33	1	20	20.04	20.06	0.12	0.17	0.02	0.1
2015-10-23 15:48	1	80	80.00	80.22	0.06	0.41	0.22	0.3
2015-10-23 16:03	1	70	70.00	70.10	0.16	0.19	0.10	0.1
2015-10-23 16:18	1	60	59.95	60.18	0.11	0.25	0.23	0.4
2015-10-23 16:33	2	0	0.25	0.19	0.19	0.12	-0.06	NA
2015-10-23 16:48	2	30	30.01	30.16	0.09	0.16	0.15	0.5
2015-10-23 17:03	2	50	49.98	50.18	0.12	0.34	0.20	0.4
2015-10-23 17:18	2	80	80.03	80.05	0.13	0.28	0.02	0.0
2015-10-23 17:33	2	10	10.01	10.02	0.06	0.07	0.01	0.1
2015-10-23 17:48	2	20	19.98	20.01	0.13	0.11	0.03	0.2
2015-10-23 18:03	2	60	60.00	60.21	0.09	0.16	0.21	0.4
2015-10-23 18:18	2	90	89.99	90.07	0.06	0.24	0.08	0.1
2015-10-23 18:33	2	40	39.93	40.26	0.05	0.16	0.33	0.8
2015-10-23 18:48	2	70	70.00	70.02	0.08	0.30	0.02	0.0
2015-10-23 19:03	3	0	0.18	0.24	0.10	0.08	0.06	NA
2015-10-23 19:18	3	20	20.02	20.22	0.08	0.15	0.20	1.0

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2015-10-23 19:33	3	50	49.96	50.16	0.09	0.09	0.20	0.4
2015-10-23 19:48	3	10	10.02	9.90	0.13	0.07	-0.12	-1.2
2015-10-23 20:03	3	40	40.02	40.41	0.15	0.49	0.39	1.0
2015-10-23 20:18	3	70	69.99	70.22	0.15	0.20	0.23	0.3
2015-10-23 20:33	3	30	30.06	29.99	0.14	0.08	-0.07	-0.2
2015-10-23 20:48	3	60	60.06	60.06	0.08	0.04	0.00	0.0
2015-10-23 21:03	3	90	89.98	90.22	0.12	0.30	0.24	0.3
2015-10-23 21:18	3	80	80.01	80.18	0.13	0.22	0.17	0.2
2015-10-23 21:33	4	0	0.28	0.32	0.18	0.10	0.04	NA
2015-10-23 21:48	4	50	50.00	50.28	0.12	0.22	0.28	0.6
2015-10-23 22:03	4	30	29.97	30.30	0.09	0.24	0.33	1.1
2015-10-23 22:18	4	10	10.00	10.01	0.17	0.25	0.01	0.1
2015-10-23 22:33	4	90	90.03	90.21	0.14	0.15	0.18	0.2
2015-10-23 22:48	4	40	39.93	40.04	0.15	0.17	0.11	0.3
2015-10-23 23:03	4	20	20.01	20.29	0.11	0.24	0.28	1.4
2015-10-23 23:18	4	80	79.99	80.31	0.10	0.30	0.32	0.4
2015-10-23 23:33	4	70	69.94	70.04	0.08	0.34	0.10	0.1
2015-10-23 23:48	4	60	60.00	60.36	0.16	0.42	0.36	0.6
2015-10-24 00:03	5	0	0.01	0.18	0.08	0.12	0.17	NA
2015-10-24 00:18	5	30	29.97	30.21	0.17	0.30	0.24	0.8
2015-10-24 00:33	5	50	49.99	50.03	0.11	0.08	0.04	0.1
2015-10-24 00:48	5	80	80.03	80.29	0.08	0.33	0.26	0.3
2015-10-24 01:03	5	10	10.05	10.13	0.12	0.12	0.08	0.8
2015-10-24 01:18	5	20	19.96	20.09	0.14	0.10	0.13	0.7
2015-10-24 01:33	5	60	60.02	60.14	0.17	0.37	0.12	0.2
2015-10-24 01:48	5	90	90.08	90.27	0.16	0.32	0.19	0.2
2015-10-24 02:03	5	40	40.07	40.37	0.42	0.46	0.30	0.7
2015-10-24 02:18	5	70	70.00	70.14	0.08	0.28	0.14	0.2
2015-10-24 02:33	6	0	0.22	0.25	0.17	0.14	0.03	NA
2015-10-24 02:48	6	20	20.06	20.25	0.19	0.17	0.19	0.9
2015-10-24 03:03	6	50	50.00	50.35	0.14	0.22	0.35	0.7
2015-10-24 03:18	6	10	10.12	10.23	0.36	0.29	0.11	1.1
2015-10-24 03:33	6	40	40.00	39.95	0.16	0.24	-0.05	-0.1
2015-10-24 03:48	6	70	70.02	70.04	0.06	0.15	0.02	0.0
2015-10-24 04:03	6	30	29.97	30.16	0.15	0.23	0.19	0.6
2015-10-24 04:18	6	60	59.99	60.25	0.09	0.28	0.26	0.4
2015-10-24 04:33	6	90	90.03	90.20	0.10	0.34	0.17	0.2
2015-10-24 04:48	6	80	80.02	80.13	0.06	0.09	0.11	0.1
2015-10-24 05:03	7	0	0.15	0.25	0.22	0.07	0.10	NA
2015-10-24 05:18	7	50	50.03	50.02	0.16	0.31	-0.01	0.0
2015-10-24 05:33	7	30	30.03	30.25	0.02	0.23	0.22	0.7
2015-10-24 05:48	7	10	10.04	10.12	0.09	0.14	0.08	0.8
2015-10-24 06:03	7	90	90.04	90.37	0.12	0.27	0.33	0.4
2015-10-24 06:18	7	40	40.03	40.15	0.16	0.27	0.12	0.3
2015-10-24 06:33	7	20	20.04	20.34	0.19	0.22	0.30	1.5
2015-10-24 06:48	7	80	79.95	80.23	0.07	0.24	0.28	0.4
2015-10-24 07:03	7	70	69.99	70.26	0.08	0.24	0.27	0.4
2015-10-24 07:18	7	60	59.94	60.21	0.14	0.37	0.27	0.5

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2015-10-24 07:33	8	0	0.15	0.24	0.19	0.11	0.09	NA
2015-10-24 07:48	8	30	30.00	30.50	0.12	0.47	0.50	1.7
2015-10-24 08:03	8	50	50.04	50.32	0.20	0.36	0.28	0.6
2015-10-24 08:18	8	80	79.97	80.15	0.28	0.34	0.18	0.2
2015-10-24 08:33	8	10	10.03	10.27	0.22	0.22	0.24	2.4
2015-10-24 08:48	8	20	20.01	20.18	0.31	0.22	0.17	0.8
2015-10-24 09:03	8	60	59.97	60.06	0.10	0.26	0.09	0.2

Table 3. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the backup ozone analyser (OA) TEI 49C #71956-370 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 (%)
2015-10-21 13:13	1	0	0.20	-0.01	0.14	0.55	-0.21	NA
2015-10-21 13:28	1	50	50.02	49.38	0.09	0.30	-0.64	-1.3
2015-10-21 13:43	1	30	30.06	30.20	0.12	0.89	0.14	0.5
2015-10-21 13:58	1	10	9.96	9.08	0.20	0.57	-0.88	-8.8
2015-10-21 14:13	1	90	90.00	90.07	0.05	0.35	0.07	0.1
2015-10-21 14:28	1	40	40.00	39.82	0.08	0.18	-0.18	-0.4
2015-10-21 14:43	1	20	19.98	19.91	0.15	0.39	-0.07	-0.4
2015-10-21 14:58	1	80	80.01	80.38	0.06	0.24	0.37	0.5
2015-10-21 15:13	1	70	70.02	70.24	0.08	0.13	0.22	0.3
2015-10-21 15:28	1	60	60.01	59.74	0.11	0.39	-0.27	-0.4
2015-10-21 15:43	2	0	0.23	-0.27	0.19	0.08	-0.50	NA
2015-10-21 15:58	2	30	29.98	29.77	0.13	0.17	-0.21	-0.7
2015-10-21 16:13	2	50	49.96	49.90	0.19	0.41	-0.06	-0.1
2015-10-21 16:28	2	80	80.00	80.13	0.10	0.45	0.13	0.2
2015-10-21 16:43	2	10	10.07	9.92	0.34	0.56	-0.15	-1.5
2015-10-21 16:58	2	20	20.01	19.77	0.13	0.15	-0.24	-1.2
2015-10-21 17:13	2	60	59.98	59.99	0.09	0.12	0.01	0.0
2015-10-21 17:28	2	90	90.04	90.53	0.12	0.23	0.49	0.5
2015-10-21 17:43	2	40	39.95	39.73	0.08	0.36	-0.22	-0.6
2015-10-21 17:58	2	70	69.96	70.08	0.12	0.32	0.12	0.2
2015-10-21 18:13	3	0	0.22	0.15	0.18	0.14	-0.07	NA
2015-10-21 18:28	3	20	20.00	19.98	0.11	0.20	-0.02	-0.1
2015-10-21 18:43	3	50	49.98	50.45	0.14	0.34	0.47	0.9
2015-10-21 18:58	3	10	10.03	9.62	0.22	0.20	-0.41	-4.1
2015-10-21 19:13	3	40	40.00	39.85	0.16	0.41	-0.15	-0.4
2015-10-21 19:28	3	70	70.05	70.20	0.07	0.16	0.15	0.2
2015-10-21 19:43	3	30	30.01	29.69	0.19	0.40	-0.32	-1.1
2015-10-21 19:58	3	60	59.96	59.92	0.13	0.61	-0.04	-0.1
2015-10-21 20:13	3	90	89.99	90.29	0.16	0.32	0.30	0.3
2015-10-21 20:28	3	80	79.94	80.37	0.07	0.27	0.43	0.5
2015-10-21 20:43	4	0	0.11	0.00	0.16	0.20	-0.11	NA
2015-10-21 20:58	4	50	49.99	50.13	0.15	0.30	0.14	0.3
2015-10-21 21:13	4	30	29.96	29.95	0.12	0.36	-0.01	0.0

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2015-10-21 21:28	4	10	10.50	10.36	0.64	1.17	-0.14	-1.3
2015-10-21 21:43	4	90	90.02	90.53	0.06	0.40	0.51	0.6
2015-10-21 21:58	4	40	39.99	39.86	0.09	0.18	-0.13	-0.3
2015-10-21 22:13	4	20	19.97	19.80	0.17	0.16	-0.17	-0.9
2015-10-21 22:28	4	80	79.98	80.21	0.13	0.32	0.23	0.3
2015-10-21 22:43	4	70	69.97	70.52	0.05	0.16	0.55	0.8
2015-10-21 22:58	4	60	59.99	60.28	0.03	0.27	0.29	0.5
2015-10-21 23:13	5	0	0.07	-0.26	0.26	0.32	-0.33	NA
2015-10-21 23:28	5	30	30.03	29.61	0.13	0.15	-0.42	-1.4
2015-10-21 23:43	5	50	49.99	50.03	0.21	0.36	0.04	0.1
2015-10-21 23:58	5	80	79.91	80.11	0.18	0.28	0.20	0.3
2015-10-22 00:13	5	10	10.03	9.65	0.20	0.31	-0.38	-3.8
2015-10-22 00:28	5	20	20.07	19.89	0.19	0.20	-0.18	-0.9
2015-10-22 00:43	5	60	60.04	60.22	0.10	0.29	0.18	0.3
2015-10-22 00:58	5	90	89.98	90.54	0.08	0.52	0.56	0.6
2015-10-22 01:13	5	40	40.01	39.89	0.11	0.36	-0.12	-0.3
2015-10-22 01:28	5	70	69.97	70.18	0.08	0.21	0.21	0.3
2015-10-22 01:43	6	0	0.26	-0.06	0.14	0.17	-0.32	NA
2015-10-22 01:58	6	20	20.04	19.48	0.14	0.22	-0.56	-2.8
2015-10-22 02:13	6	50	50.00	49.84	0.16	0.22	-0.16	-0.3
2015-10-22 02:28	6	10	10.16	9.98	0.43	0.54	-0.18	-1.8
2015-10-22 02:43	6	40	39.98	39.92	0.10	0.24	-0.06	-0.2
2015-10-22 02:58	6	70	70.01	70.01	0.08	0.35	0.00	0.0
2015-10-22 03:13	6	30	29.98	29.89	0.17	0.29	-0.09	-0.3
2015-10-22 03:28	6	60	60.03	59.99	0.11	0.33	-0.04	-0.1
2015-10-22 03:43	6	90	90.02	90.91	0.11	0.39	0.89	1.0
2015-10-22 03:58	6	80	80.03	80.53	0.09	0.37	0.50	0.6
2015-10-22 04:13	7	0	0.34	-0.05	0.10	0.14	-0.39	NA
2015-10-22 04:28	7	50	50.04	50.04	0.12	0.18	0.00	0.0
2015-10-22 04:43	7	30	30.00	29.69	0.10	0.17	-0.31	-1.0
2015-10-22 04:58	7	10	9.96	9.72	0.09	0.24	-0.24	-2.4
2015-10-22 05:13	7	90	90.01	90.61	0.08	0.47	0.60	0.7
2015-10-22 05:28	7	40	39.97	39.89	0.05	0.16	-0.08	-0.2
2015-10-22 05:43	7	20	19.99	19.64	0.08	0.30	-0.35	-1.8
2015-10-22 05:58	7	80	80.00	80.51	0.17	0.12	0.51	0.6
2015-10-22 06:13	7	70	69.94	70.53	0.06	0.15	0.59	0.8
2015-10-22 06:28	7	60	60.01	60.25	0.12	0.30	0.24	0.4
2015-10-22 06:43	8	0	0.01	-0.04	0.19	0.18	-0.05	NA
2015-10-22 06:58	8	30	30.03	29.91	0.16	0.20	-0.12	-0.4
2015-10-22 07:13	8	50	49.98	50.05	0.08	0.36	0.07	0.1
2015-10-22 07:28	8	80	79.97	80.35	0.08	0.40	0.38	0.5
2015-10-22 07:43	8	10	10.05	9.65	0.18	0.24	-0.40	-4.0
2015-10-22 07:58	8	20	19.86	19.97	0.13	0.25	0.11	0.6
2015-10-22 08:13	8	60	60.02	60.36	0.06	0.23	0.34	0.6
2015-10-22 08:28	8	90	90.01	90.67	0.10	0.13	0.66	0.7
2015-10-22 08:43	8	40	39.96	39.93	0.08	0.18	-0.03	-0.1
2015-10-22 08:58	8	70	69.97	70.55	0.07	0.43	0.58	0.8

Table 4. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the backup ozone analyser (OA) TEI 49i #1303156643 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 (%)
2015-10-21 13:13	1	0	0.20	-0.17	0.14	0.26	-0.37	NA
2015-10-21 13:28	1	50	50.02	50.10	0.09	0.42	0.08	0.2
2015-10-21 13:43	1	30	30.06	29.68	0.12	0.28	-0.38	-1.3
2015-10-21 13:58	1	10	9.96	9.55	0.20	0.51	-0.41	-4.1
2015-10-21 14:13	1	90	90.00	90.48	0.05	0.43	0.48	0.5
2015-10-21 14:28	1	40	40.00	39.53	0.08	0.20	-0.47	-1.2
2015-10-21 14:43	1	20	19.98	19.68	0.15	0.32	-0.30	-1.5
2015-10-21 14:58	1	80	80.01	80.10	0.06	0.37	0.09	0.1
2015-10-21 15:13	1	70	70.02	69.84	0.08	0.19	-0.18	-0.3
2015-10-21 15:28	1	60	60.01	59.64	0.11	0.29	-0.37	-0.6
2015-10-21 15:43	2	0	0.23	-0.29	0.19	0.20	-0.52	NA
2015-10-21 15:58	2	30	29.98	29.66	0.13	0.37	-0.32	-1.1
2015-10-21 16:13	2	50	49.96	49.82	0.19	0.43	-0.14	-0.3
2015-10-21 16:28	2	80	80.00	79.82	0.10	0.56	-0.18	-0.2
2015-10-21 16:43	2	10	10.07	9.37	0.34	0.57	-0.70	-7.0
2015-10-21 16:58	2	20	20.01	19.68	0.13	0.27	-0.33	-1.6
2015-10-21 17:13	2	60	59.98	60.04	0.09	0.43	0.06	0.1
2015-10-21 17:28	2	90	90.04	90.46	0.12	0.30	0.42	0.5
2015-10-21 17:43	2	40	39.95	39.42	0.08	0.45	-0.53	-1.3
2015-10-21 17:58	2	70	69.96	69.37	0.12	0.33	-0.59	-0.8
2015-10-21 18:13	3	0	0.22	-0.33	0.18	0.14	-0.55	NA
2015-10-21 18:28	3	20	20.00	19.79	0.11	0.28	-0.21	-1.0
2015-10-21 18:43	3	50	49.98	50.08	0.14	0.31	0.10	0.2
2015-10-21 18:58	3	10	10.03	9.47	0.22	0.30	-0.56	-5.6
2015-10-21 19:13	3	40	40.00	39.64	0.16	0.39	-0.36	-0.9
2015-10-21 19:28	3	70	70.05	69.99	0.07	0.49	-0.06	-0.1
2015-10-21 19:43	3	30	30.01	29.52	0.19	0.30	-0.49	-1.6
2015-10-21 19:58	3	60	59.96	59.54	0.13	0.66	-0.42	-0.7
2015-10-21 20:13	3	90	89.99	90.09	0.16	0.30	0.10	0.1
2015-10-21 20:28	3	80	79.94	79.96	0.07	0.65	0.02	0.0
2015-10-21 20:43	4	0	0.11	-0.18	0.16	0.22	-0.29	NA
2015-10-21 20:58	4	50	49.99	49.77	0.15	0.49	-0.22	-0.4
2015-10-21 21:13	4	30	29.96	29.57	0.12	0.59	-0.39	-1.3
2015-10-21 21:28	4	10	10.50	10.27	0.64	0.92	-0.23	-2.2
2015-10-21 21:43	4	90	90.02	90.09	0.06	0.42	0.07	0.1
2015-10-21 21:58	4	40	39.99	39.29	0.09	0.25	-0.70	-1.8
2015-10-21 22:13	4	20	19.97	19.72	0.17	0.20	-0.25	-1.3
2015-10-21 22:28	4	80	79.98	79.74	0.13	0.25	-0.24	-0.3
2015-10-21 22:43	4	70	69.97	69.93	0.05	0.38	-0.04	-0.1
2015-10-21 22:58	4	60	59.99	60.01	0.03	0.38	0.02	0.0
2015-10-21 23:13	5	0	0.07	-0.35	0.26	0.10	-0.42	NA
2015-10-21 23:28	5	30	30.03	29.52	0.13	0.63	-0.51	-1.7
2015-10-21 23:43	5	50	49.99	49.67	0.21	0.43	-0.32	-0.6
2015-10-21 23:58	5	80	79.91	79.89	0.18	0.37	-0.02	0.0
2015-10-22 00:13	5	10	10.03	9.31	0.20	0.24	-0.72	-7.2

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2015-10-22 00:28	5	20	20.07	19.72	0.19	0.34	-0.35	-1.7
2015-10-22 00:43	5	60	60.04	59.77	0.10	0.27	-0.27	-0.4
2015-10-22 00:58	5	90	89.98	89.80	0.08	0.32	-0.18	-0.2
2015-10-22 01:13	5	40	40.01	39.21	0.11	0.29	-0.80	-2.0
2015-10-22 01:28	5	70	69.97	69.86	0.08	0.24	-0.11	-0.2
2015-10-22 01:43	6	0	0.26	-0.48	0.14	0.38	-0.74	NA
2015-10-22 01:58	6	20	20.04	19.33	0.14	0.33	-0.71	-3.5
2015-10-22 02:13	6	50	50.00	49.30	0.16	0.23	-0.70	-1.4
2015-10-22 02:28	6	10	10.16	9.73	0.43	0.73	-0.43	-4.2
2015-10-22 02:43	6	40	39.98	39.74	0.10	0.35	-0.24	-0.6
2015-10-22 02:58	6	70	70.01	69.53	0.08	0.32	-0.48	-0.7
2015-10-22 03:13	6	30	29.98	29.80	0.17	0.40	-0.18	-0.6
2015-10-22 03:28	6	60	60.03	60.00	0.11	0.34	-0.03	0.0
2015-10-22 03:43	6	90	90.02	90.06	0.11	0.55	0.04	0.0
2015-10-22 03:58	6	80	80.03	79.86	0.09	0.25	-0.17	-0.2
2015-10-22 04:13	7	0	0.34	-0.47	0.10	0.42	-0.81	NA
2015-10-22 04:28	7	50	50.04	49.50	0.12	0.42	-0.54	-1.1
2015-10-22 04:43	7	30	30.00	29.42	0.10	0.25	-0.58	-1.9
2015-10-22 04:58	7	10	9.96	9.42	0.09	0.22	-0.54	-5.4
2015-10-22 05:13	7	90	90.01	90.06	0.08	0.35	0.05	0.1
2015-10-22 05:28	7	40	39.97	39.42	0.05	0.31	-0.55	-1.4
2015-10-22 05:43	7	20	19.99	19.95	0.08	0.23	-0.04	-0.2
2015-10-22 05:58	7	80	80.00	79.81	0.17	0.32	-0.19	-0.2
2015-10-22 06:13	7	70	69.94	70.04	0.06	0.50	0.10	0.1
2015-10-22 06:28	7	60	60.01	59.50	0.12	0.33	-0.51	-0.8
2015-10-22 06:43	8	0	0.01	-0.31	0.19	0.29	-0.32	NA
2015-10-22 06:58	8	30	30.03	29.82	0.16	0.27	-0.21	-0.7
2015-10-22 07:13	8	50	49.98	49.47	0.08	0.26	-0.51	-1.0
2015-10-22 07:28	8	80	79.97	80.12	0.08	0.28	0.15	0.2
2015-10-22 07:43	8	10	10.05	9.29	0.18	0.36	-0.76	-7.6
2015-10-22 07:58	8	20	19.86	19.37	0.13	0.42	-0.49	-2.5
2015-10-22 08:13	8	60	60.02	59.92	0.06	0.28	-0.10	-0.2
2015-10-22 08:28	8	90	90.01	89.88	0.10	0.34	-0.13	-0.1
2015-10-22 08:43	8	40	39.96	39.59	0.08	0.34	-0.37	-0.9
2015-10-22 08:58	8	70	69.97	70.03	0.07	0.51	0.06	0.1

Table 5. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the backup ozone analyser (OA) TEI 49i #1303156643 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 (%)
2015-10-22 11:28	1	0	0.28	-0.39	0.18	0.07	-0.67	NA
2015-10-22 11:43	1	50	50.02	49.09	0.20	0.25	-0.93	-1.9
2015-10-22 11:58	1	30	29.97	29.07	0.17	0.20	-0.90	-3.0
2015-10-22 12:13	1	10	10.00	9.36	0.23	0.27	-0.64	-6.4
2015-10-22 12:28	1	90	89.98	88.91	0.09	0.16	-1.07	-1.2

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2015-10-22 12:43	1	40	39.99	39.07	0.16	0.13	-0.92	-2.3
2015-10-22 12:58	1	20	19.99	19.29	0.20	0.20	-0.70	-3.5
2015-10-22 13:13	1	80	79.93	78.74	0.05	0.31	-1.19	-1.5
2015-10-22 13:28	1	70	70.02	68.97	0.10	0.20	-1.05	-1.5
2015-10-22 13:43	1	60	59.95	59.06	0.10	0.16	-0.89	-1.5
2015-10-22 13:58	2	0	0.28	-0.38	0.19	0.13	-0.66	NA
2015-10-22 14:13	2	30	30.09	29.25	0.11	0.15	-0.84	-2.8
2015-10-22 14:28	2	50	50.07	48.98	0.08	0.28	-1.09	-2.2
2015-10-22 14:43	2	80	79.99	79.09	0.19	0.22	-0.90	-1.1
2015-10-22 14:58	2	10	10.44	9.71	0.24	0.19	-0.73	-7.0
2015-10-22 15:13	2	20	19.98	19.28	0.08	0.16	-0.70	-3.5
2015-10-22 15:28	2	60	59.96	58.82	0.18	0.19	-1.14	-1.9
2015-10-22 15:43	2	90	89.98	88.96	0.10	0.31	-1.02	-1.1
2015-10-22 15:58	2	40	40.01	39.21	0.29	0.31	-0.80	-2.0
2015-10-22 16:13	2	70	69.97	68.85	0.10	0.33	-1.12	-1.6
2015-10-22 16:28	3	0	0.15	-0.17	0.08	0.09	-0.32	NA
2015-10-22 16:43	3	20	20.02	19.32	0.19	0.18	-0.70	-3.5
2015-10-22 16:58	3	50	50.00	49.15	0.06	0.26	-0.85	-1.7
2015-10-22 17:13	3	10	10.20	9.59	0.47	0.49	-0.61	-6.0
2015-10-22 17:28	3	40	40.04	39.08	0.08	0.13	-0.96	-2.4
2015-10-22 17:43	3	70	70.00	68.74	0.13	0.24	-1.26	-1.8
2015-10-22 17:58	3	30	29.99	29.21	0.29	0.23	-0.78	-2.6
2015-10-22 18:13	3	60	60.02	59.02	0.07	0.07	-1.00	-1.7
2015-10-22 18:28	3	90	89.96	89.03	0.07	0.34	-0.93	-1.0
2015-10-22 18:43	3	80	80.06	79.17	0.07	0.33	-0.89	-1.1
2015-10-22 18:58	4	0	0.05	-0.21	0.11	0.14	-0.26	NA
2015-10-22 19:13	4	50	50.00	48.94	0.09	0.28	-1.06	-2.1
2015-10-22 19:28	4	30	30.05	29.18	0.11	0.16	-0.87	-2.9
2015-10-22 19:43	4	10	10.27	9.59	0.45	0.30	-0.68	-6.6
2015-10-22 19:58	4	90	90.03	88.76	0.11	0.24	-1.27	-1.4
2015-10-22 20:13	4	40	39.96	39.18	0.17	0.22	-0.78	-2.0
2015-10-22 20:28	4	20	20.00	19.25	0.20	0.10	-0.75	-3.8
2015-10-22 20:43	4	80	80.03	79.13	0.13	0.32	-0.90	-1.1
2015-10-22 20:58	4	70	69.98	69.37	0.22	0.37	-0.61	-0.9
2015-10-22 21:13	4	60	59.94	59.17	0.09	0.39	-0.77	-1.3
2015-10-22 21:28	5	0	0.07	-0.30	0.21	0.09	-0.37	NA
2015-10-22 21:43	5	30	29.99	29.28	0.14	0.22	-0.71	-2.4
2015-10-22 21:58	5	50	49.92	49.09	0.06	0.29	-0.83	-1.7
2015-10-22 22:13	5	80	80.00	79.23	0.07	0.26	-0.77	-1.0
2015-10-22 22:28	5	10	10.38	9.70	0.35	0.49	-0.68	-6.6
2015-10-22 22:43	5	20	20.03	19.28	0.12	0.15	-0.75	-3.7
2015-10-22 22:58	5	60	59.98	59.07	0.09	0.22	-0.91	-1.5
2015-10-22 23:13	5	90	89.99	89.11	0.10	0.12	-0.88	-1.0
2015-10-22 23:28	5	40	39.99	39.17	0.09	0.13	-0.82	-2.1
2015-10-22 23:43	5	70	69.97	69.04	0.13	0.11	-0.93	-1.3
2015-10-22 23:58	6	0	0.10	-0.28	0.38	0.10	-0.38	NA
2015-10-23 00:13	6	20	19.94	19.32	0.11	0.10	-0.62	-3.1
2015-10-23 00:28	6	50	50.03	49.28	0.02	0.16	-0.75	-1.5

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2015-10-23 00:43	6	10	10.05	9.35	0.16	0.09	-0.70	-7.0
2015-10-23 00:58	6	40	40.00	39.14	0.11	0.13	-0.86	-2.1
2015-10-23 01:13	6	70	70.01	69.08	0.16	0.20	-0.93	-1.3
2015-10-23 01:28	6	30	29.94	29.32	0.10	0.25	-0.62	-2.1
2015-10-23 01:43	6	60	60.01	59.09	0.10	0.27	-0.92	-1.5
2015-10-23 01:58	6	90	89.99	88.90	0.04	0.22	-1.09	-1.2
2015-10-23 02:13	6	80	79.99	79.09	0.19	0.35	-0.90	-1.1
2015-10-23 02:28	7	0	0.29	-0.35	0.29	0.13	-0.64	NA
2015-10-23 02:43	7	50	49.97	48.96	0.12	0.16	-1.01	-2.0
2015-10-23 02:58	7	30	29.97	29.07	0.10	0.09	-0.90	-3.0
2015-10-23 03:13	7	10	9.96	9.53	0.23	0.16	-0.43	-4.3
2015-10-23 03:28	7	90	90.01	89.19	0.10	0.31	-0.82	-0.9
2015-10-23 03:43	7	40	40.02	39.34	0.07	0.14	-0.68	-1.7
2015-10-23 03:58	7	20	19.88	19.05	0.07	0.17	-0.83	-4.2
2015-10-23 04:13	7	80	80.04	79.14	0.13	0.29	-0.90	-1.1
2015-10-23 04:28	7	70	70.05	68.92	0.09	0.19	-1.13	-1.6
2015-10-23 04:43	7	60	59.99	59.09	0.03	0.17	-0.90	-1.5
2015-10-23 04:58	8	0	0.22	-0.21	0.19	0.15	-0.43	NA
2015-10-23 05:13	8	30	29.98	29.29	0.16	0.23	-0.69	-2.3
2015-10-23 05:28	8	50	49.97	48.93	0.15	0.30	-1.04	-2.1
2015-10-23 05:43	8	80	79.98	79.07	0.11	0.26	-0.91	-1.1
2015-10-23 05:58	8	10	9.93	9.35	0.17	0.21	-0.58	-5.8
2015-10-23 06:13	8	20	20.63	19.85	1.05	0.83	-0.78	-3.8
2015-10-23 06:28	8	60	59.99	59.10	0.04	0.10	-0.89	-1.5
2015-10-23 06:43	8	90	90.04	89.17	0.07	0.14	-0.87	-1.0
2015-10-23 06:58	8	40	40.07	39.15	0.19	0.31	-0.92	-2.3
2015-10-23 07:13	8	70	70.02	69.44	0.07	0.03	-0.58	-0.8

GHG and CO Measurements

Monitoring Set-up and Procedures

Standards

The NOAA standards currently available at CPT are listed below. Updated mole fraction values can be obtained from: http://www.esrl.noaa.gov/gmd/ccl/refgas.html. In addition, several other standards are available.

Table 6. GHG reference standards at CPT

Cylinder ID	Type	CO (ppb) WMO-X2014A	CH_4 (ppb) WMO- X2004A	CO_2 (ppm) WMO-X2007	Start of use	End of use
CA02907	NOAA	54.44	1730.50	353.23	1997	ongoing
CA02929	NOAA	79.26	1787.19	365.79	1997	ongoing
CA05050	NOAA	106.13	1806.20	382.53	2007	ongoing
CA05081	NOAA	58.84	1741.37	370.94	2007	ongoing
CA05712	NOAA	220.25	1901.68	395.72	2006	ongoing
CA05714	NOAA	61.80	1749.42	364.08	2004	ongoing
CA05715	NOAA	132.00	1857.37	388.90	2006	ongoing
CA05716	NOAA	91.41	1801.07	378.14	2006	ongoing
CA08110	NOAA	251.15	NA	410.36	2009	ongoing
CA08138	NOAA	47.14	NA	384.38	2009	ongoing
CB09797	NOAA	139.45	NA	399.95	2012	ongoing
CB09791	NOAA	53.61	NA	372.11	2012	ongoing
CB09770	NOAA	255.52	NA	453.18	2012	ongoing
CB09788	CSIRO	101.52	1769.13	384.82	2012	ongoing
CB09793	CSIRO	197.29	1768.83	430.49	2012	ongoing

Comparison of the GHG and Carbon Monoxide Analysers

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 Table 15 further below.

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 RGA-3 #113087-003 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 (%)
(15-12-27 00:00:00)	140515_FB03377	151.4	0.5	141.3	8.8	2.0	-10.1	-6.7
(16-02-16 00:00:00)	130905_FB03383	87.1	0.5	83.4	NA	1.0	-3.7	-4.3
(16-02-12 08:00:00)	140515_FB03384	156.8	0.3	151.7	0.6	3.0	-5.1	-3.2
(16-01-13 00:00:00)	140514_FB03894	195.4	0.1	190.5	1.1	3.0	-5.0	-2.5
(16-01-04 00:00:00)	140514_FB03911	217.5	1.0	214.6	4.8	2.0	-2.9	-1.3
(15-11-18 00:00:00)	140514_FB03930	240.7	0.6	235.6	7.9	2.0	-5.1	-2.1
(15-10-30 00:00:00)	130905_FB03358	74.2	0.1	71.3	NA	1.0	-2.9	-3.9

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-01-04 00:00:00)	130819_FB03887	147.9	0.6	152.4	9.3	2.0	4.5	3.0
(16-02-17 08:00:00)	110511_FB03382	68.2	1.3	66.1	1.5	3.0	-2.1	-3.1
(15-11-09 00:00:00)	130422_FA01469	260.2	0.1	247.1	NA	1.0	-13.1	-5.1
(15-11-09 00:00:00)	080820_FA02785	69.8	0.2	69.1	NA	1.0	-0.7	-1.1

Table 8. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2302 #835-CKADS2026 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 (%)
(15-11-26 00:00:00)	140515_FB03377	151.4	0.5	147.0	0.4	3.0	-4.4	-2.9
(15-11-26 00:00:00)	130905_FB03383	87.1	0.5	83.8	0.6	3.0	-3.3	-3.8
(15-11-26 00:00:00)	140515_FB03384	156.8	0.3	153.5	0.3	3.0	-3.3	-2.1
(15-11-26 08:00:00)	140514_FB03894	195.4	0.1	192.9	0.6	3.0	-2.6	-1.3
(15-11-28 16:00:00)	140514_FB03911	217.5	1.0	214.8	0.7	3.0	-2.7	-1.2
(15-11-26 08:00:00)	140514_FB03930	240.7	0.6	238.5	0.3	3.0	-2.2	-0.9
(15-11-03 00:00:00)	130905_FB03358	74.2	0.1	71.2	0.1	2.0	-3.0	-4.0
(15-11-28 08:00:00)	130819_FB03887	147.9	0.6	144.1	1.8	3.0	-3.9	-2.6
(15-11-28 16:00:00)	110511_FB03382	68.2	1.3	63.9	0.2	3.0	-4.3	-6.3
(15-11-28 16:00:00)	130422_FA01469	260.2	0.1	252.9	0.5	3.0	-7.3	-2.8
(15-11-28 16:00:00)	080820_FA02785	69.8	0.2	66.0	1.0	3.0	-3.9	-5.5

Table 9. CH_4 aggregates computed from single analysis (1-min mean and standard deviation) for each level during the comparison of the Varian CP-3800 #101605 (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(15-11-29 08:00:00)	140515_FB03377	1768.67	0.11	1769.80	1.57	3	1.13	0.06
(15-11-15 12:00:00)	130905_FB03383	1862.10	0.09	1864.70	6.08	2	2.60	0.14
(15-12-04 16:00:00)	140515_FB03384	1846.00	0.12	1846.00	2.80	3	0.00	0.00
(16-01-08 00:00:00)	140514_FB03894	1953.97	0.11	1953.88	4.77	3	-0.09	0.00
(15-12-12 16:00:00)	140514_FB03911	1957.70	0.15	1959.43	3.29	3	1.73	0.09
(15-12-03 16:00:00)	140514_FB03930	1975.50	0.16	1979.40	2.13	3	3.90	0.20
(15-10-28 12:00:00)	130905_FB03358	1862.53	0.11	1862.95	1.63	2	0.42	0.02
(15-12-12 16:00:00)	130819_FB03887	1883.69	0.18	1886.03	1.70	3	2.34	0.12
(15-12-13 16:00:00)	110511_FB03382	1769.28	0.12	1771.84	2.51	3	2.56	0.14
(15-12-30 08:00:00)	130422_FA01469	1997.57	0.13	1998.77	8.89	3	1.20	0.06
(15-12-04 00:00:00)	080820_FA02785	1962.46	0.08	1964.93	4.04	3	2.47	0.13
(15-10-26 00:00:00)	150601_FA02470	1920.37	0.11	1916.13	NA	1	-4.24	-0.20

Table 10. CH_4 aggregates computed from single analysis (1-min mean and standard deviation) for each level during the comparison of the Picarro G2301 #923-CFADS2201 (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(15-11-29 08:00:00)	140515_FB03377	1768.63	0.12	1769.75	0.54	3	1.12	0.06
(15-11-29 08:00:00)	130905_FB03383	1862.10	0.09	1863.51	0.60	3	1.41	0.08
(15-11-29 08:00:00)	140515_FB03384	1846.00	0.12	1847.43	0.50	3	1.43	0.08
(15-11-29 08:00:00)	140514_FB03894	1953.97	0.11	1955.40	0.79	3	1.43	0.07
(15-11-29 08:00:00)	140514_FB03911	1957.70	0.15	1959.02	0.59	3	1.32	0.07
(15-11-29 08:00:00)	140514_FB03930	1975.50	0.16	1977.08	0.72	3	1.58	0.08
(15-11-03 00:00:00)	130905_FB03358	1862.53	0.11	1863.80	0.39	2	1.27	0.07
(15-11-29 08:00:00)	130819_FB03887	1883.69	0.18	1884.95	0.66	3	1.26	0.07
(15-11-29 08:00:00)	110511_FB03382	1769.28	0.12	1770.11	0.65	3	0.83	0.05
(15-11-29 08:00:00)	130422_FA01469	1997.57	0.13	1999.16	0.79	3	1.59	0.08
(15-11-29 08:00:00)	080820_FA02785	1962.45	0.09	1963.95	0.74	3	1.50	0.08
(15-11-29 08:00:00)	150601_FA02470	1920.37	0.11	1921.60	0.97	3	1.23	0.06

Table 11. CO_2 aggregates computed from single analysis (1-min mean and standard deviation) for each level during the comparison of the Picarro G2302 #835-CKADS2026 (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(15-11-26 00:00:00)	140515_FB03377	365.45	0.01	365.55	0.03	3	0.10	0.03
(15-11-26 00:00:00)	130905_FB03383	390.27	0.01	390.34	0.03	3	0.07	0.02
(15-11-26 00:00:00)	140515_FB03384	381.42	0.04	381.54	0.02	3	0.12	0.03
(15-11-26 08:00:00)	140514_FB03894	410.99	0.02	411.01	0.03	3	0.02	0.00
(15-11-28 16:00:00)	140514_FB03911	401.64	0.02	401.60	0.02	3	-0.04	-0.01
(15-11-26 08:00:00)	140514_FB03930	404.95	0.04	405.04	0.04	3	0.09	0.02
(15-11-12 12:00:00)	130905_FB03358	389.03	0.02	389.15	0.04	2	0.12	0.03
(15-12-04 16:00:00)	130819_FB03887	386.84	0.01	386.94	0.06	3	0.10	0.03
(15-11-28 16:00:00)	110511_FB03382	315.18	0.02	315.37	0.03	3	0.19	0.06
(15-11-28 16:00:00)	130422_FA01469	105.33	0.05	105.77	0.02	3	0.44	0.42
(15-11-28 16:00:00)	080820_FA02785	245.05	0.02	245.27	0.01	3	0.22	0.09
(15-11-26 08:00:00)	150601_FA02470	399.14	0.06	399.12	0.02	3	-0.02	-0.01

Table 12. CO_2 aggregates computed from single analysis (1-min mean and standard deviation) for each level during the comparison of the Picarro G2301 #923-CFADS2201 (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(15-11-29 08:00:00)	140515_FB03377	365.45	0.01	365.57	0.01	3	0.12	0.03
(15-11-29 08:00:00)	130905_FB03383	390.27	0.01	390.40	0.11	3	0.13	0.03
(15-11-29 08:00:00)	140515_FB03384	381.42	0.04	381.56	0.02	3	0.14	0.04
(15-11-29 08:00:00)	140514_FB03894	410.99	0.02	410.98	0.08	3	-0.01	0.00
(15-11-29 08:00:00)	140514_FB03911	401.64	0.02	401.72	0.07	3	0.08	0.02
(15-11-29 08:00:00)	140514_FB03930	404.95	0.04	405.01	0.09	3	0.06	0.01
(15-11-03 00:00:00)	130905_FB03358	389.03	0.02	389.22	0.09	2	0.19	0.05
(15-11-29 08:00:00)	130819_FB03887	386.84	0.01	386.93	0.10	3	0.09	0.02
(15-11-29 08:00:00)	110511_FB03382	315.18	0.02	315.38	0.05	3	0.20	0.06
(15-11-29 08:00:00)	130422_FA01469	105.33	0.05	106.11	0.04	3	0.78	0.74
(15-11-29 08:00:00)	080820_FA02785	245.05	0.02	245.47	0.02	3	0.42	0.17
(15-11-29 08:00:00)	150601_FA02470	399.14	0.06	399.17	0.07	3	0.03	0.01

Table 13. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Agilent 6890N US10649084 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 (%)
(15-12-27 08:00:00)	140515_FB03377	317.56	0.03	316.36	0.04	3	-1.20	-0.38
(16-01-06 08:00:00)	140514_FB03894	329.15	0.05	329.80	0.85	3	0.65	0.20
(16-01-12 00:00:00)	140515_FB03384	326.13	0.05	328.78	0.11	2	2.65	0.81
(16-01-12 00:00:00)	130905_FB03383	317.26	0.03	317.99	0.14	2	0.73	0.23
(15-12-12 00:00:00)	140514_FB03930	328.64	0.03	328.51	0.23	2	-0.12	-0.04
(15-12-19 12:00:00)	130422_FA01469	338.27	0.03	339.07	0.62	4	0.80	0.24
(15-12-12 00:00:00)	150601_FA02470	329.21	0.09	330.64	0.04	2	1.43	0.43
(15-12-16 16:00:00)	140514_FB03911	328.10	0.07	330.07	0.67	3	1.97	0.60
(16-01-17 00:00:00)	130819_FB03887	319.24	0.04	319.88	0.74	3	0.64	0.20
(15-11-26 00:00:00)	130905_FB03358	316.96	0.11	317.44	0.60	2	0.48	0.15

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 14. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 29). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (ppb) = ([TS] - 0.11\ ppb) / 1.0025 \quad (6a)$$

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

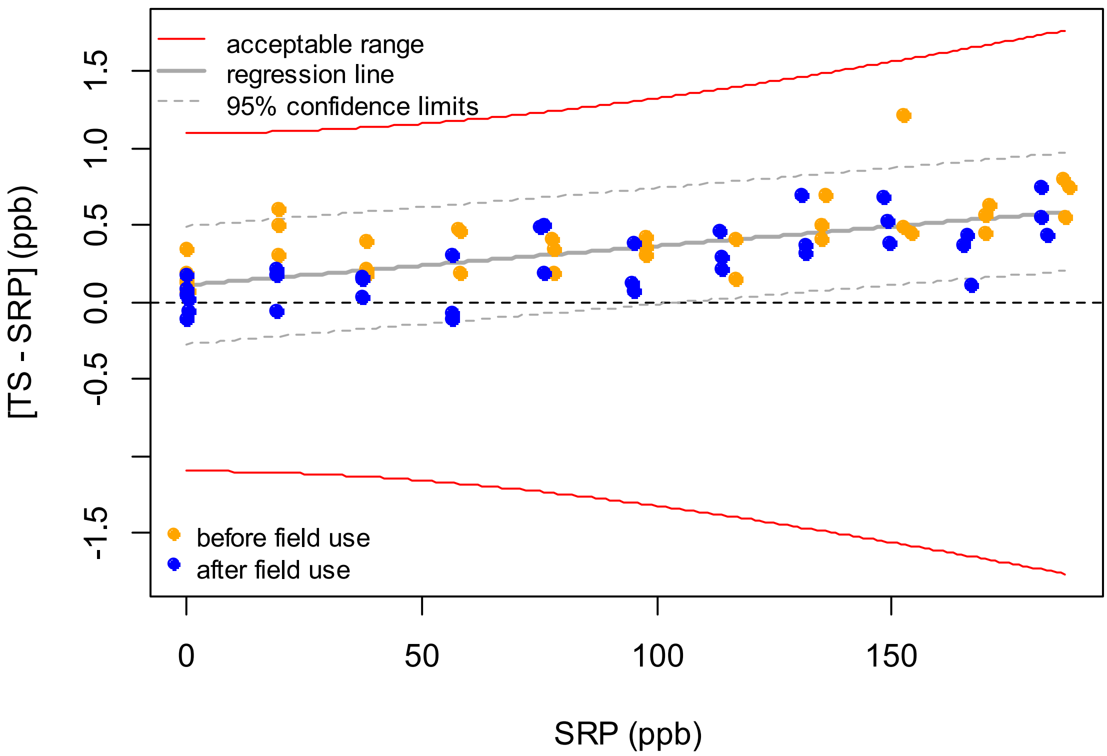

Figure 29. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 14. 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)
2015-09-07	1	0	-0.10	0.16	0.02	0.14
2015-09-07	1	155	154.24	0.30	154.69	0.16
2015-09-07	1	170	170.89	0.21	171.52	0.28
2015-09-07	1	80	78.00	0.21	78.35	0.34
2015-09-07	1	60	58.13	0.22	58.33	0.30
2015-09-07	1	40	38.28	0.24	38.50	0.23
2015-09-07	1	185	186.91	0.24	187.46	0.14
2015-09-07	1	115	116.87	0.21	117.28	0.24
2015-09-07	1	100	97.72	0.17	98.14	0.11
2015-09-07	1	135	135.17	0.24	135.67	0.17
2015-09-07	1	20	19.36	0.27	19.98	0.33
2015-09-07	1	0	-0.15	0.22	0.20	0.35
2015-09-07	2	0	0.09	0.25	0.23	0.27
2015-09-07	2	60	58.22	0.19	58.69	0.22
2015-09-07	2	190	187.62	0.41	188.37	0.21
2015-09-07	2	115	116.70	0.21	116.86	0.30
2015-09-07	2	135	135.18	0.28	135.59	0.20
2015-09-07	2	40	38.20	0.19	38.39	0.35
2015-09-07	2	80	77.81	0.39	78.23	0.23
2015-09-07	2	20	19.29	0.22	19.60	0.28
2015-09-07	2	170	170.01	0.42	170.58	0.36
2015-09-07	2	150	152.49	0.29	153.71	0.29
2015-09-07	2	95	97.48	0.34	97.84	0.15
2015-09-07	2	0	0.04	0.23	0.23	0.15
2015-09-07	3	0	0.13	0.28	0.21	0.32
2015-09-07	3	135	135.81	0.14	136.51	0.14
2015-09-07	3	80	77.89	0.21	78.09	0.33
2015-09-07	3	20	19.41	0.25	19.91	0.20
2015-09-07	3	185	186.38	0.22	187.18	0.34
2015-09-07	3	60	57.81	0.16	58.29	0.29
2015-09-07	3	115	116.79	0.28	116.95	0.40
2015-09-07	3	40	38.30	0.31	38.69	0.32
2015-09-07	3	170	170.06	0.26	170.52	0.23
2015-09-07	3	155	152.63	0.32	153.12	0.15
2015-09-07	3	100	97.57	0.21	97.89	0.18
2015-09-07	3	0	0.08	0.15	0.14	0.15
2016-03-22	4	0	-0.01	0.31	0.05	0.29
2016-03-22	4	95	95.27	0.21	95.66	0.16

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2016-03-22	4	55	56.60	0.17	56.53	0.29
2016-03-22	4	150	149.11	0.39	149.63	0.35
2016-03-22	4	165	166.78	0.21	166.89	0.28
2016-03-22	4	75	75.88	0.26	76.38	0.12
2016-03-22	4	185	182.89	0.28	183.33	0.24
2016-03-22	4	20	19.17	0.13	19.11	0.23
2016-03-22	4	35	37.24	0.18	37.40	0.26
2016-03-22	4	130	131.72	0.23	132.04	0.49
2016-03-22	4	115	113.87	0.23	114.09	0.28
2016-03-22	4	0	0.09	0.23	-0.02	0.20
2016-03-22	5	0	0.21	0.43	0.23	0.18
2016-03-22	5	150	149.65	0.21	150.03	0.25
2016-03-22	5	165	166.10	0.22	166.54	0.07
2016-03-22	5	75	75.96	0.32	76.15	0.15
2016-03-22	5	55	56.41	0.15	56.31	0.29
2016-03-22	5	35	37.22	0.29	37.39	0.17
2016-03-22	5	180	181.96	0.21	182.51	0.28
2016-03-22	5	115	113.62	0.21	113.92	0.21
2016-03-22	5	95	95.03	0.32	95.11	0.22
2016-03-22	5	130	131.70	0.27	132.08	0.33
2016-03-22	5	20	18.95	0.22	19.13	0.23
2016-03-22	5	0	0.22	0.26	0.16	0.24
2016-03-22	6	0	-0.07	0.20	0.02	0.14
2016-03-22	6	55	56.40	0.22	56.70	0.17
2016-03-22	6	180	181.83	0.58	182.59	0.50
2016-03-22	6	115	113.33	0.34	113.80	0.24
2016-03-22	6	130	130.96	0.34	131.66	0.16
2016-03-22	6	35	37.10	0.32	37.13	0.28
2016-03-22	6	75	75.29	0.48	75.78	0.14
2016-03-22	6	20	18.97	0.40	19.18	0.24
2016-03-22	6	165	165.19	0.14	165.56	0.27
2016-03-22	6	150	148.19	0.22	148.87	0.26
2016-03-22	6	95	94.48	0.24	94.60	0.27
2016-03-22	6	0	-0.08	0.28	0.10	0.10

#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).

WCC-Empa laboratory standards obtained from the CCL (NOAA standards CB11485, CB11499 and CC339478) were used for transferring the CCL calibration scales to the WCC-Empa TS (6 l aluminium cylinder containing a mixture of natural and synthetic air). The results including standard deviations of the WCC-Empa TS are listed in Table 15, and Figure 30 and 31shows 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 15. 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	69.84	0.21	1962.46	0.08	245.05	0.02	199.43	0.12
110511_FB03382	68.21	1.31	1769.28	0.12	315.18	0.02	311.59	0.08
130422_FA01469	260.23	0.05	1997.57	0.13	105.33	0.05	338.27	0.03
130819_FB03887	147.90	0.60	1883.69	0.18	386.84	0.01	319.24	0.04
130905_FB03358	74.16	0.10	1862.53	0.11	389.03	0.02	316.96	0.11
130905_FB03383	87.13	0.46	1862.10	0.09	390.27	0.01	317.26	0.03
140514_FB03894	195.43	0.06	1953.97	0.11	410.99	0.02	329.15	0.05
140514_FB03911	217.51	0.96	1957.70	0.15	401.64	0.02	328.10	0.07
140514_FB03930	240.65	0.57	1975.50	0.16	404.95	0.04	328.64	0.03
140515_FB03377	151.37	0.47	1768.67	0.11	365.45	0.02	317.56	0.03
140515_FB03384	156.78	0.31	1846.00	0.12	381.42	0.04	326.13	0.05
150601_FA02470	625.76	56.74	1920.37	0.11	399.14	0.06	329.21	0.09

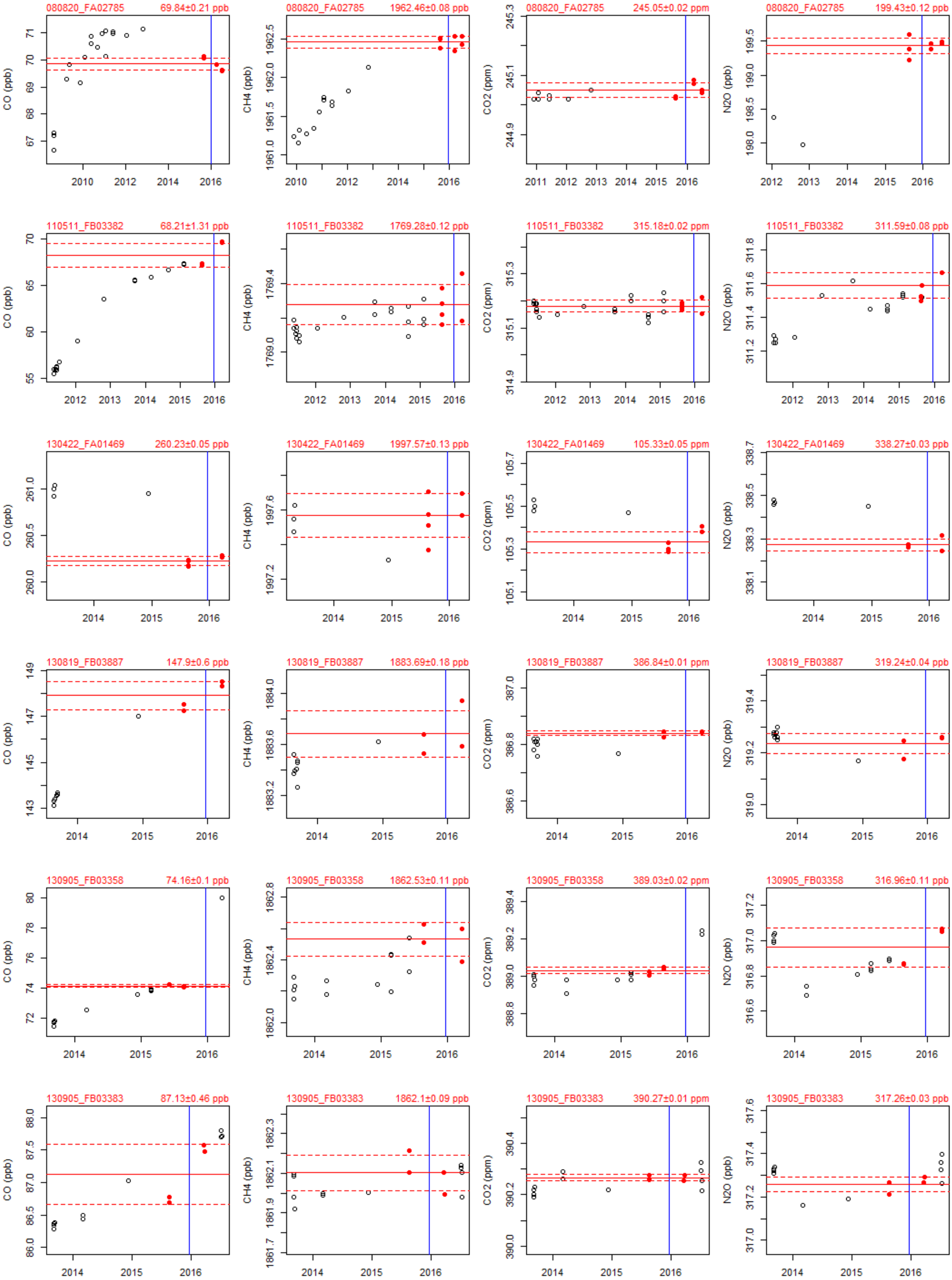

Figure 30. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

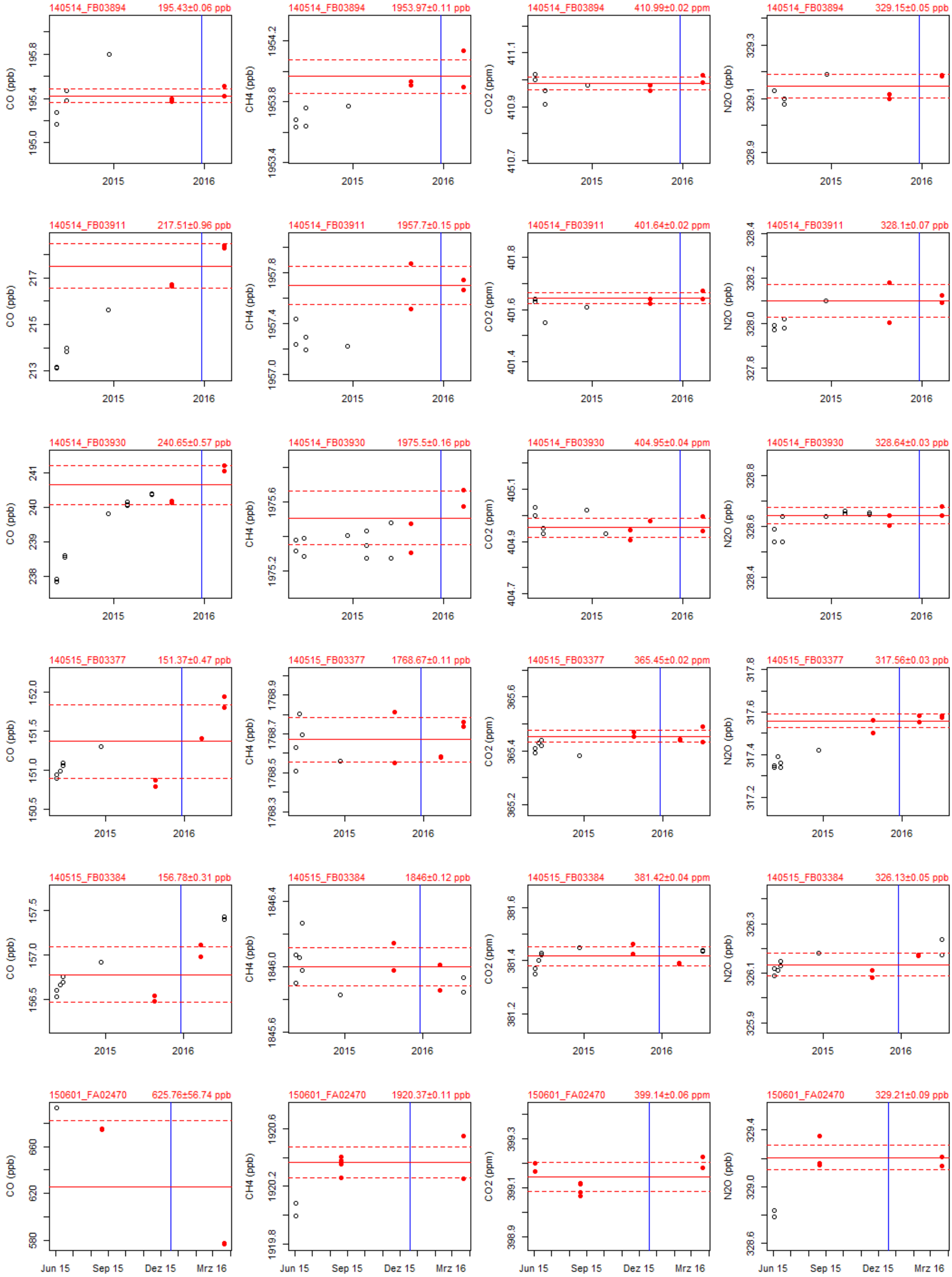

Figure 31. *Same as above for the remaining standards.*

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 1735 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 normally within half of the WMO/GAW compatibility goals for all measurements.

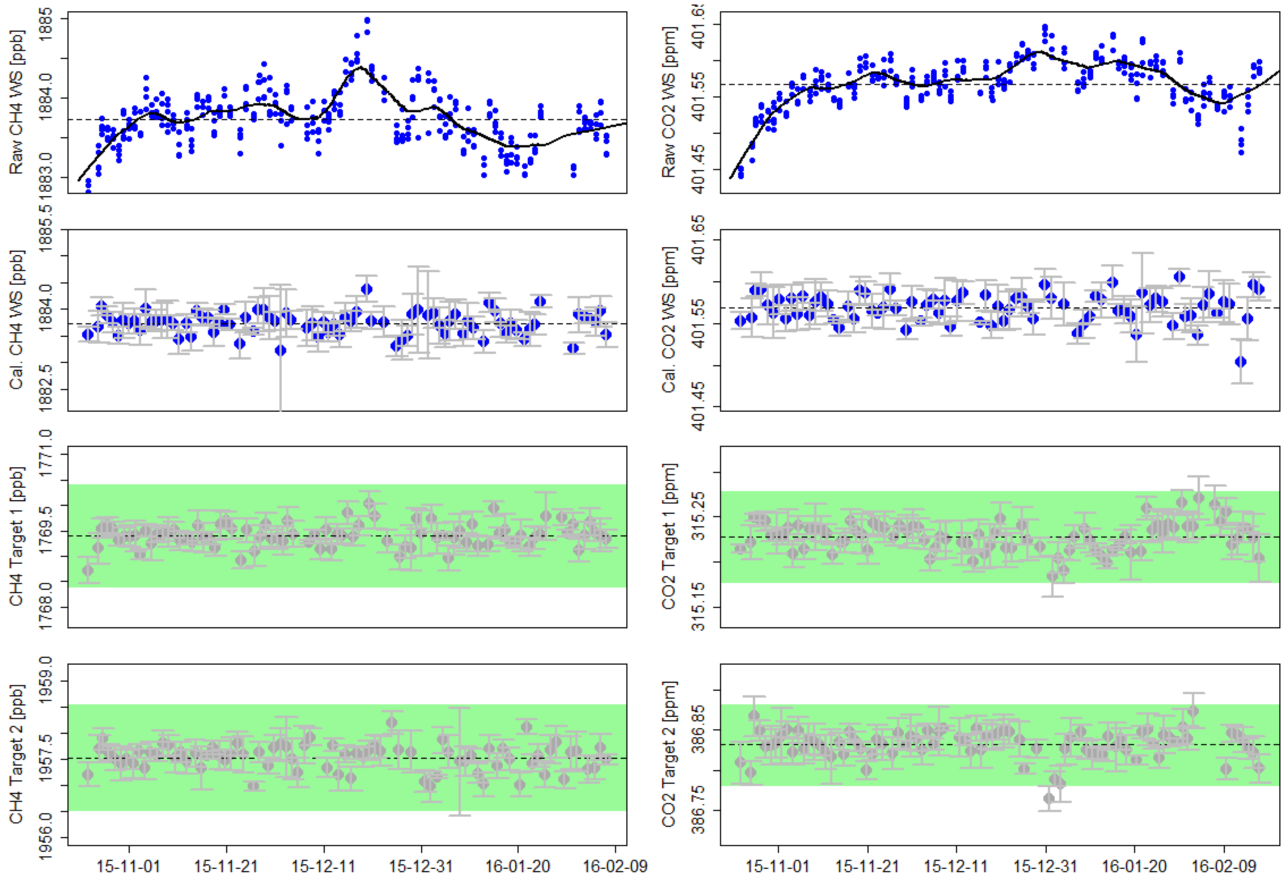

Figure 32. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1-min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 1735 min three WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

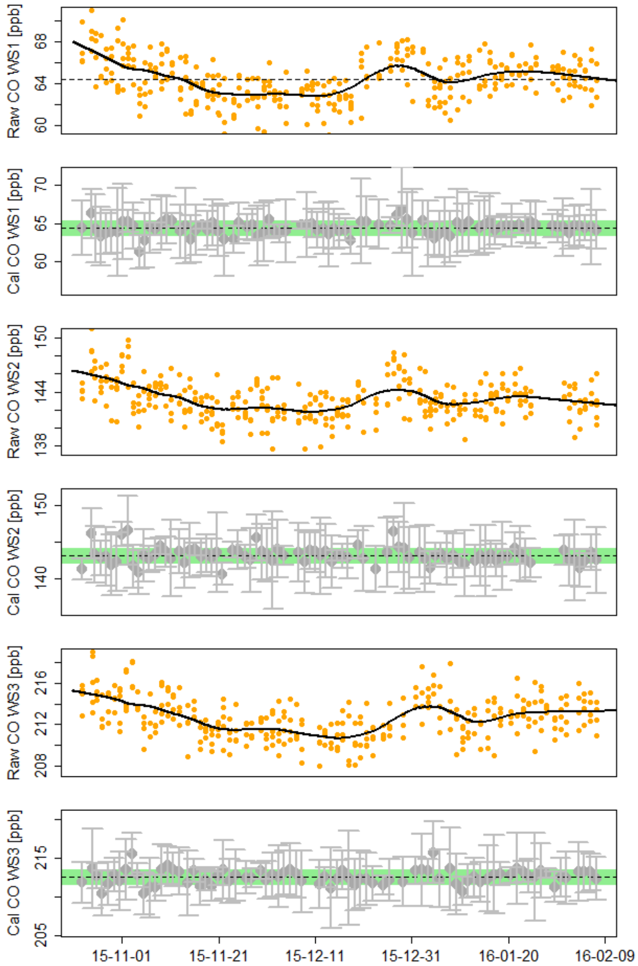

Figure 33. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1-min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels 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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Ozone Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4850°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2015-10-23/24
1.2	Auditor:	Christoph Zellweger, Simon A. Wyss
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Ms. Thumeka Mkololo, Mr. Danie van der Spuy
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i-PS #0810-153, BKG -0.1, COEF 1.008
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	[TS] = (1.0025±0.0006) • [SRP] + (0.11±0.06)
1.6	Ozone Calibrator [OC]	
1.6.1	Model:	TEI 49i-PS #7088211231
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = +-0.1; COEF = 1.019
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0039±0.0009) • [SRP] + (0.16±0.04)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OC] - 0.16 ppb) / 1.0039
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.30 ppb^2 + 2.59e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Ozone Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4850°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2015-10-23/24
1.2	Auditor:	Christoph Zellweger, Simon A. Wyss
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Ms. Thumeka Mkololo, Mr. Danie van der Spuy
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i-PS #0810-153, BKG -0.1, COEF 1.008
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	[TS] = (1.0025±0.0006) • [SRP] + (0.11±0.06)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #71956-370
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = +0.3; COEF = 1.000
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0123±0.0011) • [SRP] - (0.30±0.06)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.30 ppb) / 1.0123
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.34 ppb^2 + 2.59e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Ozone Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4850°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2015-10-21/22
1.2	Auditor:	Christoph Zellweger, Simon A. Wyss
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Ms. Thumeka Mkololo, Mr. Danie van der Spuy
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i-PS #0810-153, BKG -0.1, COEF 1.008
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	[TS] = (1.0025±0.0006) • [SRP] + (0.11±0.06)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #1303156643
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = +0.1; COEF = 1.047
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0081±0.0013) • [SRP] - (0.44±0.07)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.44 ppb) / 1.0081
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.38 ppb^2 + 2.67e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Ozone Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4850°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2015-10-22/23
1.2	Auditor:	Christoph Zellweger, Simon A. Wyss
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Ms. Thumeka Mkololo, Mr. Danie van der Spuy
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i-PS #0810-153, BKG -0.1, COEF 1.008
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	[TS] = (1.0025±0.0006) • [SRP] + (0.11±0.06)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #1303156643
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = -0.6; COEF = 0.6270
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9979±0.0009) • [SRP] - (0.47±0.05)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.47 ppb) / 0.9979
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.31 ppb^2 + 2.62e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Carbon Monoxide Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2015-10-22 – 2016-02-27
1.2	Auditor:	Dr. Christoph Zellweger
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-X2014A scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-X2014A scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	RGA-3 #113087-003
1.6.2	Range of calibration:	66 – 247 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9674±0.0188) · X_{CO} + (0.7±3.1)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 0.7) / 0.9674
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (16.6 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[CO]: Instrument readings; X: mixing ratios on the WMO-X2014A CO scale.

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Carbon Monoxide Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2015-10-22 – 2016-02-27
1.2	Auditor:	Dr. Christoph Zellweger
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-X2014A scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-X2014A scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro G2302 #835-CKADS2026
1.6.2	Range of calibration:	66 – 247 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9970±0.0065) • X_{CO} - (3.2±1.1)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 3.2) / 0.9970
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (2.4 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[CO]: Instrument readings; X: mixing ratios on the WMO-X2014A CO scale.

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Methane Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2015-10-22 – 2016-01-08
1.2	Auditor:	Christoph Zellweger
1.3	Staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (WMO-X2004A scale)
1.5	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	Varian CP-3800 #101605
1.6.2	Range of calibration:	1768 – 1976 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CH_4 = (0. 99979±0.00849) • X_{CH4} + (1.6±16.1) ppb
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 1.6ppb) / 0.99979
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (6.4 ppb^2 + 1.30e-07 * X_{CH4}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[CH_4]: Instrument readings; X: mixing ratios on the WMO-X2004A CH_4 scale.

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Methane Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2015-10-21 – 2016-01-21
1.2	Auditor:	Christoph Zellweger
1.3	Staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (WMO-X2004A scale)
1.5	CH_4 Transfer Standard [TS] standards	TS calibrated against the WCC-Empa laboratory
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro G2301 #923-CFADS2201
1.6.2	Range of calibration:	1863 – 2123 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CH_4 = (1.00221±0.00052) • X_{CH4} - (2.9±1.0) ppb
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 + 2.9 ppb) / 1.00221
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.1 ppb^2 + 1.30e-07 * $X_{CH4}{}^2$)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[CH_4]: Instrument readings; X: mixing ratios on the WMO-X2004A CH_4 scale.

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Carbon Dioxide Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2015-10-21 – 2016-01-21
1.2	Auditor:	Christoph Zellweger
1.3	Staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro G2302 #835-CKADS2026
1.6.2	Range of calibration:	105 – 411 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	CO_2 = (0. 99869±0.00016) • X_{CO2} +(0.57±0.06) ppm
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 – 0.57 ppm) / 0.99869
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.008 ppm^2 + 3.28e-08 * X_{CO2}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[CO_2]: Instrument readings; X: mixing ratios on the WMO-X2007 CO_2 scale.

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Carbon Dioxide Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2015-10-21 – 2016-01-21
1.2	Auditor:	Christoph Zellweger
1.3	Staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	G2301 #923-CFADS2201
1.6.2	Range of calibration:	105 – 411 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	CO_2 = (0. 99765±0.00016) • X_{CO2} +(1.01±0.06) ppm
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 – 1.01 ppm) / 0.99765
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.008 ppm^2 + 3.28e-08 * X_{CO2}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[CO_2]: Instrument readings; X: mixing ratios on the WMO-X2007 CO_2 scale.

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Nitrous Oxide Audit Executive Summary

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.3535°S, 18.4897°E (230 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2015-11-26 – 2016-01-27
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Mr. Casper Labuschagne, Dr. Nkanyiso Mbatha, Dr. Lynwill Martin, Mr. Danie van der Spuy
1.4	WCC-Empa N_2O Reference:	NOAA laboratory standards (WMO-X2006A scale)
1.5	N_2O Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2006A scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Agilent 6890N US10649084
1.6.2	Range of calibration:	317 – 338 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$N_2O = (1.05193 \pm 0.05010) \cdot X_{N2O} - (16.08 \pm 16.28)$
1.6.5	Unbiased N_2O mixing ratio (ppb) at start of audit:	X_{N2O} (ppb) = (N_2O + 16.08) / 1.05193
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{N2O} (ppb) = sqrt (1.08 ppb^2 + 1.01e-07 * X_{N2O}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased N_2O mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 15/4

[N_2O]: Instrument readings; X: mixing ratios on the WMO-X2006A N_2O scale.

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LIST OF ABBREVIATIONS

BKG	Background
COEF	Coefficient
CPT	Cape Point GAW Station
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
OA	Ozone Analyser
OC	Ozone Calibrator
SAWS	South African Weather Service
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization