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

GLOBAL GAW STATION CAPE GRIM AUSTRALIA NOVEMBER 2016

Submitted to the World Meteorological Organization by

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The third system and performance audit by WCC-Empa[1] at the global GAW station Cape Grim was conducted from 14 - 17 November 2016 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). Previous audits at the Cape Grim GAW station were made by WCC-Empa in 2002 and 2010 (Zellweger et al., 2002).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr Sam Cleland	BoM, Cape Grim, station manager
Mr Paul Krummel	CSIRO, lead scientist
Dr Ian Galbally	CSIRO, lead scientist
Ms Suzie Molloy	CSIRO, scientist
Dr Ray Langenfelds	CSIRO, lead scientist

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

The report is distributed to the Australian Bureau of Meteorology (BoM), the Cape Grim station manager, CSIRO Oceans and Atmosphere and the World Meteorological Organization in Geneva. The report will be posted on the internet (www.empa.ch/web/s503/wcc-empa).

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

Station Management and Operation

The Station's scientific research is jointly managed by the Bureau of Meteorology (BoM) and the GASLAB group of the Commonwealth Scientific and Industrial Research Organisation (CSIRO) - Oceans and Atmosphere. Other Australian and international research institutions contribute, in particular the University of Wollongong and the Australian Nuclear Science and Technology Organisation (ANSTO). CSIRO underwent re-organisation and restructuring over the past few years with significant cuts of staff and budget. As a consequence, the operation and maintenance of some activities were not always well organised, with a period of unclear assignments of responsibilities. The cuts further resulted in a significant loss of knowledge, since many very experienced scientists and technicians either left or needed to leave CSIRO. In the meantime, the situation has stabilised but available resources are critical. Cape Grim is staffed 5 days per week by BoM technical staff allowing quick response to most issues, and visited by scientists and CSIRO/ANSTO technical staff for regular maintenance. The station is also part of the Advanced Global Atmospheric Gases Experiment (AGAGE) programme.

Recommendation 1 (*, critical, ongoing)**
A clear commitment from CSIRO is needed concerning the long-term operation and support of the Cape Grim research station as well as the GASLAB facilities at CSIRO. This requires an adequate budget and a sufficient number of scientific and technical staff. Furthermore, long-term planning reliability is essential.

[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 Location and Access

The Cape Grim Baseline Air Pollution Station (40.6822°S, 144.6883°E, 94 m a.s.l.) is located on a cliff-top near the northern end of the west coast of Tasmania, overlooking the Southern Ocean. The building is on a small block surrounded by an additional 500 ha of grazing land known as the buffer zone. A small area within and next to the building is leased to a telecommunications company and its 74 m tower is used by the station. The buffer zone is surrounded by a 22,000 ha used mostly for dairy farming– a transition from early practice of mostly sheep and beef. From the station, the base-line sector where negligible local or regional influence on the observed trace gas concentrations is expected is 190-280 degrees. Winds from this sector occur about 35 % of the time.

Station Facilities

The Cape Grim (CGO) station comprises extensive laboratory and office space. Kitchen and sanitary facilities are available. Internet access is available with sufficient bandwidth. It is an ideal platform for continuous atmospheric research as well as for extensive measurement campaigns.

Measurement Programme

The CGO station comprises a comprehensive measurement programme that covers all focal areas of the GAW programme. The Atmospheric Research facility was established in 1976 to monitor and study global atmospheric composition.

An overview on measured species is available from GAWSIS (https://gawsis.meteoswiss.ch) and the station web site (http://www.bom.gov.au/inside/cgbaps/).

> **Recommendation 2 (***, important, ongoing)**
> *GAWSIS needs to be regularly updated. The last update was made in 2007 and does therefore not reflect the entire programme of Cape Grim. Furthermore, other important information such as station contacts need to be updated.*

Data Submission

Data has been submitted to the World Data Centre for Greenhouse Gases (WDCGG) by CSIRO for CO_2 (1976-2016) and surface ozone (1982-2014), and by AGAGE for CH_4, (1981-2016), CO (1993-2016) and N_2O (1978-2016). In addition, flask data for all species were submitted. Data shown in this report was accessed on 7 March 2018.

> **Recommendation 3 (***, important, ongoing)**
> *The Cape Grim time series are among the longest and most complete in the world, and most of it has been submitted to the corresponding data centres. Data submission is an obligation of all GAW stations. It is recommended to submit data to the corresponding data centres at least in yearly intervals.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG were reviewed. Summary plots and a short description of the findings are presented in the Appendix, while the recommendations based on the review are given below. In general, data is looking sound, but a few issues were identified.

> **Recommendation 4 (***, important, 2018)**
> *CO data submitted by AGAGE does not contain any valid data since the year 2000. The reason needs to be checked.*

Recommendation 5 (*, important, 2018)**
It was noticed that the time stamps of the submitted ozone time series were inconsistent. During some years, the hour ranges from 01:00 to 24:00, while others are from 00:00 to 23:00. Time stamps need to be coherent throughout the entire time series.

Documentation

During the current audit, only the documentation for the surface ozone measurements was reviewed. All information is entered in electronic and hand written log books. The instrument manuals are available at the site, and checklists are available. Standard Operating Procedures (SOPs) have been prepared by CSIRO. The reviewed information was very comprehensive and up-to-date.

Air Inlet System

The design of the air inlet systems has not been changed since the last audit by WCC-Empa. All systems are adequate, and no change is required.

Surface Ozone Measurements

The surface ozone measurements at CGO were established in 1983, and continuous time series are available since then.

Instrumentation. CGO is equipped with three ozone analysers (Thermo Scientific models 49C and 49i) and two ozone calibrators (Thermo Scientific models 49C-PS and 49i-PS). The instrumentation is fully adequate for ozone measurements.

Data Acquisition. A custom made data acquisition system is available, which also controls the automatic zero and span checks.

Intercomparison (Performance Audit). The CGO analysers and calibrators were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 90 ppb. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system, and no further corrections were applied. The following equations characterise the bias of the instruments:

Thermo Scientific 49C #78058-387 (BKG -0.9 ppb, SPAN 1.018):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 0.58 ppb) / 0.9614 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.73e-05 * X_{O3}^2) (1b)

Thermo Scientific 49i #0806127828 (BKG 0.1 ppb, SPAN 1.036):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.48 ppb) / 1.0143 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.36 ppb^2 + 2.46e-05 * X_{O3}^2) (1d)

Thermo Scientific 49i #CM16160046 (BKG -0.5 ppb, SPAN 0.984):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 0.28 ppb) / 0.9973 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.55e-05 * X_{O3}^2) (1f)

Thermo Scientific 49C-PS #78059-387 (BKG -0.6 ppb, SPAN 1.017):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.17 ppb) / 1.0152 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.36 ppb^2 + 2.46e-05 * X_{O3}^2) (1h)

Thermo Scientific 49i-PS #1315558104 (BKG 0.0 ppb, SPAN 1.035):

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.32 ppb) / 1.0443 (1i)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.24 ppb^2 + 2.32e-05 * $X_{O3}{}^2$) (1j)

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

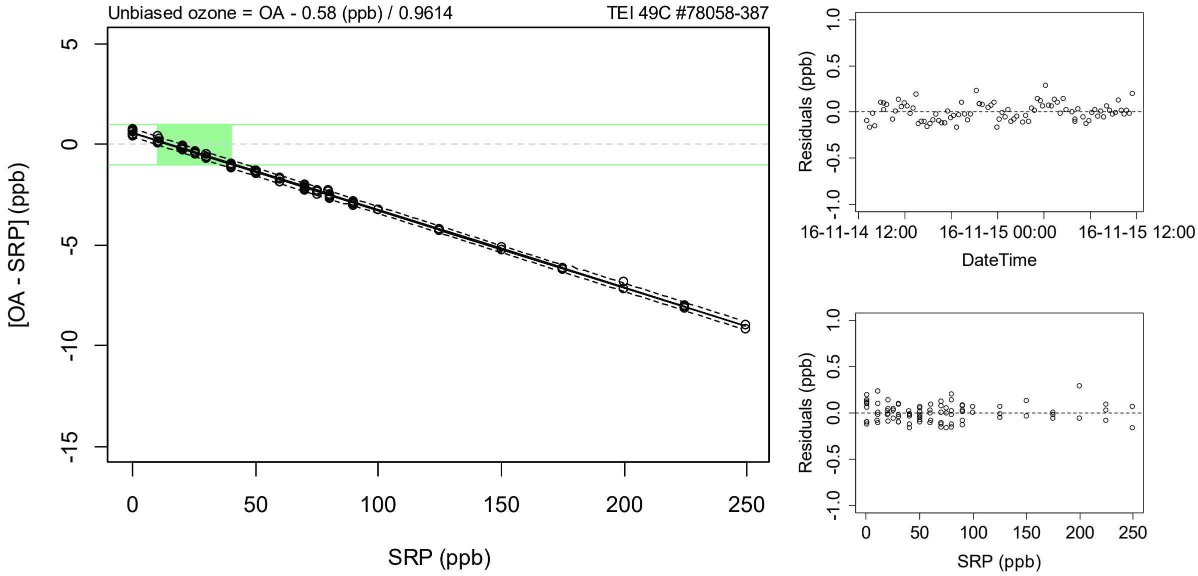

Figure 1. Left: Bias of the CGO ozone analyser (Thermo Scientific 49C #78058-387) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

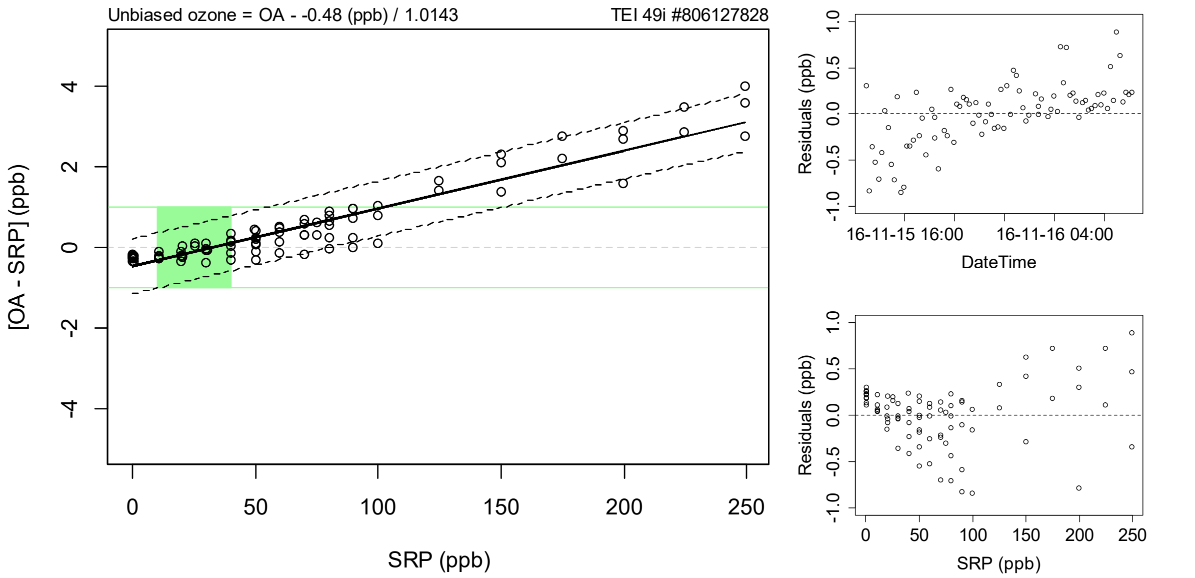

Figure 2. Same as above for the Thermo Scientific 49i #0806127828 ozone analyser.

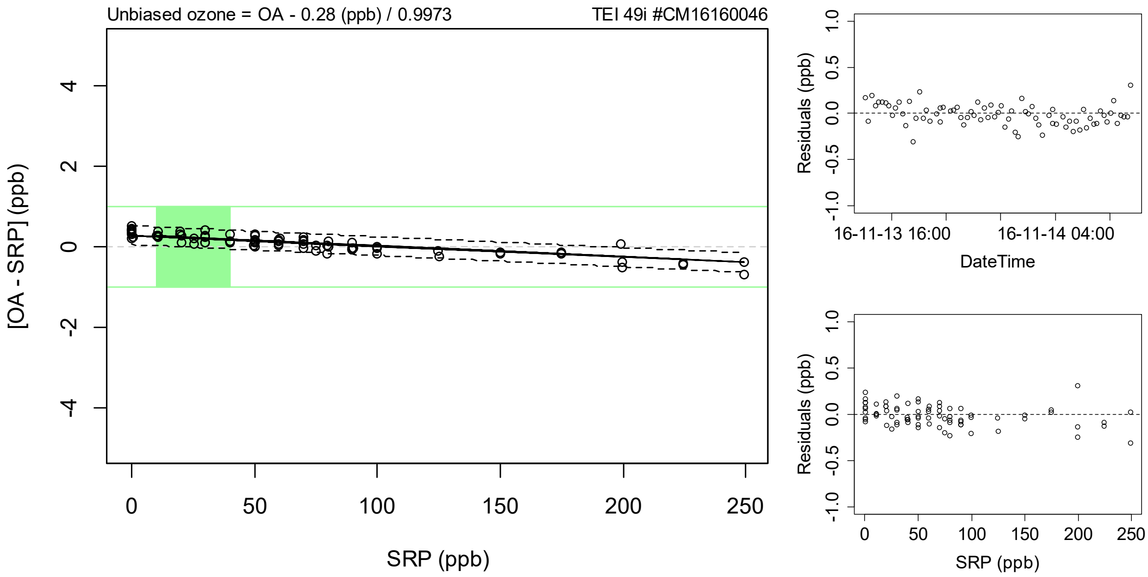

Figure 3. Same as above for the Thermo Scientific 49i #CM16160046 ozone analyser.

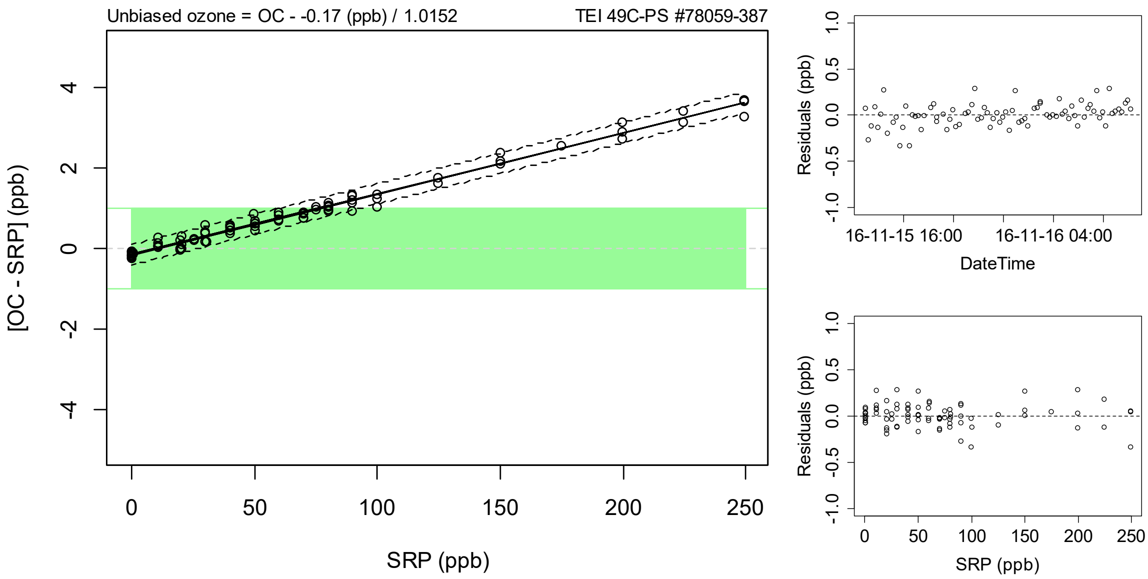

Figure 4. Same as above for the Thermo Scientific 49C-PS #78059-387 ozone calibrator.

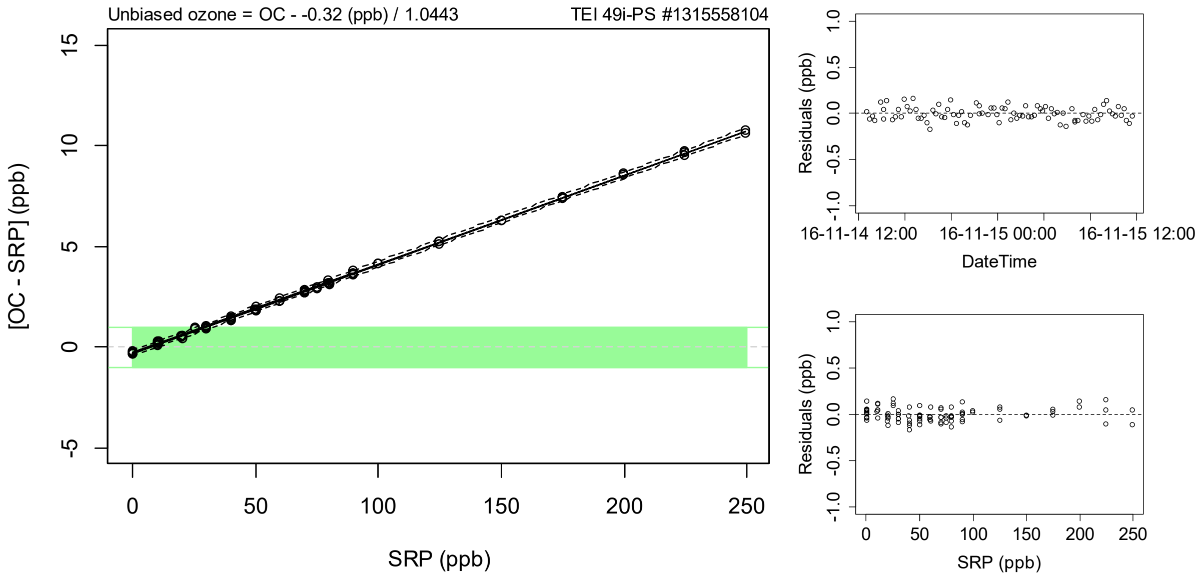

Figure 5. Same as above for the Thermo Scientific 49i-PS #1315558104 ozone calibrator.

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

The ozone mole fraction at Cape Grim shows relatively small variations compared to other station. The majority of the data is between 10 and 40 ppb. All ozone analysers agreed within 1 ppb over this range. However, significant differences were found between analysers:

- Thermo Scientific 49C #78058-387 was measuring low. It was noticed that the instrument has a potential leak in one of the solenoid valves.
- Thermo Scientific 49i #0806127828 was measuring higher compared to the WCC-Empa reference. This is expected due to the high span factor of 1.036 of the instrument.
- Thermo Scientific 49i #CM16160046: Good agreement over the entire tested range from 0 to 250 ppb ozone.

Both calibrators were also found in a good working condition; however, they both are reading higher compared to the WCC-Empa reference, which can be explained by the relatively high span factors.

The results of the calibrators were as follows:

- Thermo Scientific 49C-PS #78059-387 was measuring slightly higher compared to the WCC-Empa reference. Data of the instrument had to be filtered to remove invalid outliers. The instrument is not in a good working condition.
- Thermo Scientific 49i-PS #1315558104 was reading significantly higher compared to the WCC-Empa reference. This is expected due to the high span factor of 1.035.

Recommendation 6 (, important, 2018)**
The Thermo Scientific 49C #78058-387 ozone analyser and Thermo Scientific ozone calibrator 49C-PS #78059-387 have instrumental issues and should no longer be used.

Recommendation 7 (, important, 2018)**
It should be considered to change the calibration settings of the Thermo Scientific 49i-PS #1315558104 ozone calibrator, or otherwise, a correction must be applied.

Greenhouse Gases and Carbon Monoxide Measurements

The audit included comparison measurements of greenhouse gases and carbon monoxide. Cape Grim features one of the most extensive research programmes, and continuous data series are among the longest in the world. Therefore, continuation of the Cape Grim programme is of utmost importance for GAW. Comparisons were carried out both at Cape Grim and the laboratories of CSIRO in Aspendale. However, only one of the TS was measured for CO_2 and CH_4 on the CGO Picarro instrument. An overview of the instrumentation and the measurement programme can be found on the Cape Grim web site (http://www.bom.gov.au/inside/cgbaps/).

Intercomparison (Performance Audit). The comparison involved repeated challenges of the Aspendale and CGO instruments with randomised mole fraction levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated by figures showing the bias to the WMO GAW DQOs (WMO, 2014):

CSIRO GASLAB results:

Carbon monoxide, RGA-3 GC analyser:

Unbiased CO mixing ratio:	X_{CO} (ppb) = (CO – 2.02) / 0.9774	(2a)
Remaining standard uncertainty:	u_{CO} (ppb) = sqrt (0.3 ppb^2 + 1.01e-04 * X_{CO}^2)	(2b)

Methane, Carle GC/FID analyser:

Unbiased CH_4 mixing ratio:	X_{CH4} (ppb) = (CH_4 – 2.31 ppb) / 0.9989	(2c)
Remaining standard uncertainty:	u_{CH4} (ppb) = sqrt (1.43 ppb^2 + 1.30e-07 * X_{CH4}^2)	(2d)

Carbon dioxide, Carle GC/FID analyser:

Unbiased CO_2 mixing ratio:	X_{CO2} (ppm) = (CO_2 – 0.71 ppm) / 0.99823	(2e)
Remaining standard uncertainty:	u_{CO2} (ppm) = sqrt (0.008 ppm^2 + 3.28e-08 * X_{CO2}^2)	(2f)

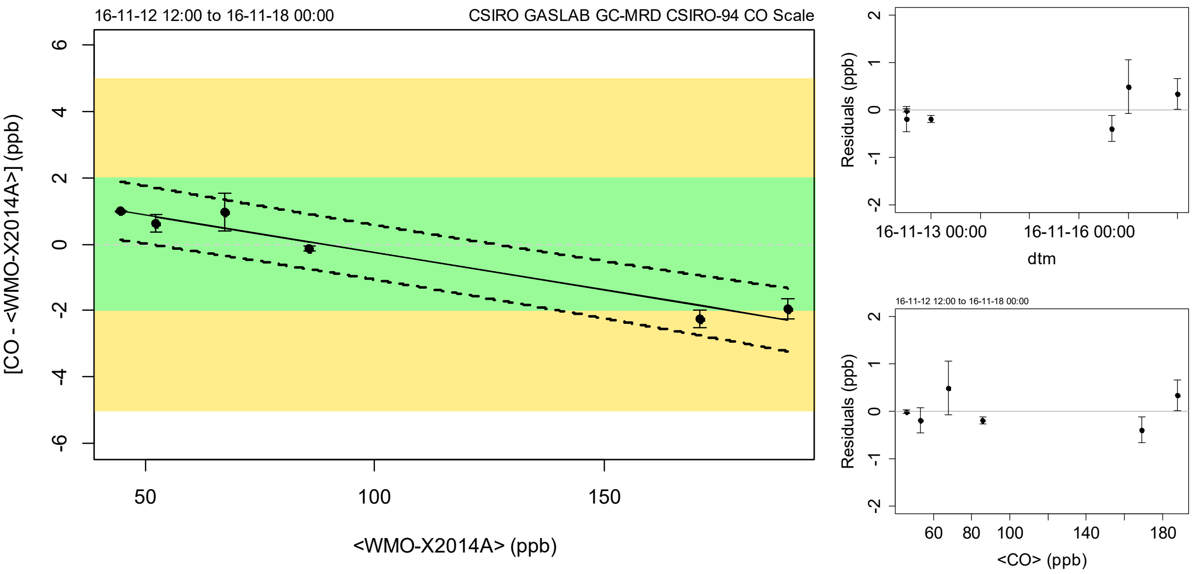

Figure 6. *Left: Bias of the CSIRO GASLAB carbon monoxide analysis with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow areas correspond to the WMO compatibility and extended compatibility goal. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Note that CSIRO measurements refer to the CSIRO-94 scale.*

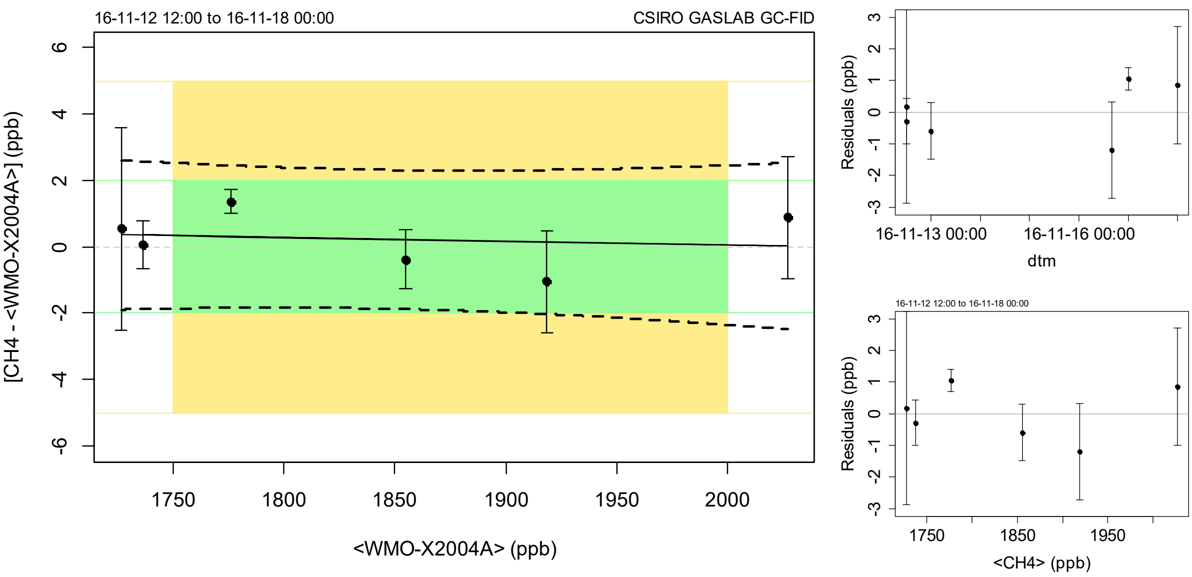

Figure 7. *Same as above, for the CSIRO GASLAB methane analyser with respect to the WMO-X2004A calibration scale.*

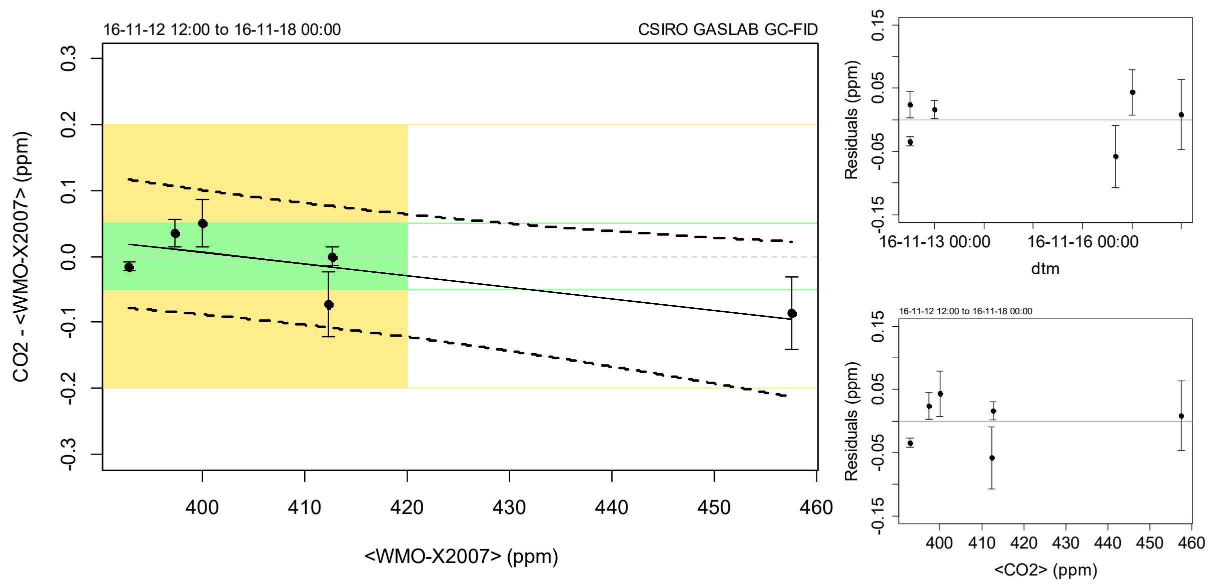

Figure 8. *Same as above, for the CSIRO GASLAB carbon dioxide analyser with respect to the WMO-X2004A calibration scale.*

CGO results:

Carbon monoxide, AGAGE GC/MRD analyser:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 2.56) / 1.0217 (2g)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.8 ppb^2 + 1.01e-04 * X_{CO}^2) (2h)

Methane, AGAGE GC/MRD analyser:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 + 7.90 ppb) / 1.0044 (2i)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.17 ppb^2 + 1.30e-07 * X_{CH4}^2) (2j)

Nitrous oxide, Carle GC/FID analyser:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 3.51 ppb) / 0.9908 (2k)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.014 ppb^2 + 1.01e-07 * X_{N2O}^2) (2l)

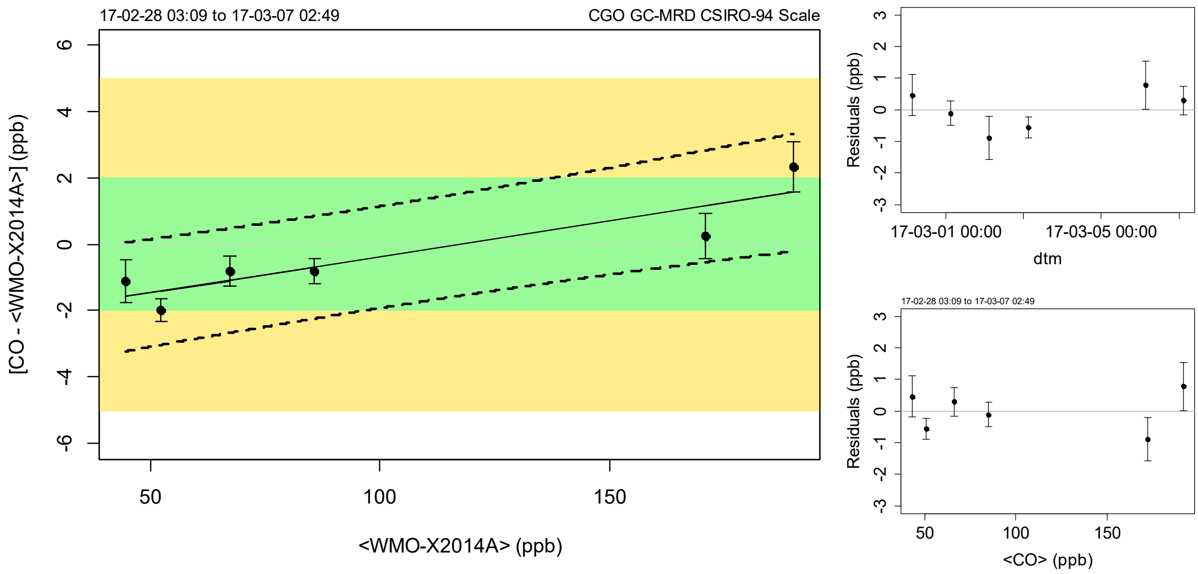

Figure 9. *Left: Bias of the CGO carbon monoxide analysis with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow areas correspond to the WMO compatibility and extended compatibility goal. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Note that CGO measurements refer to the CSIRO-94 scale.*

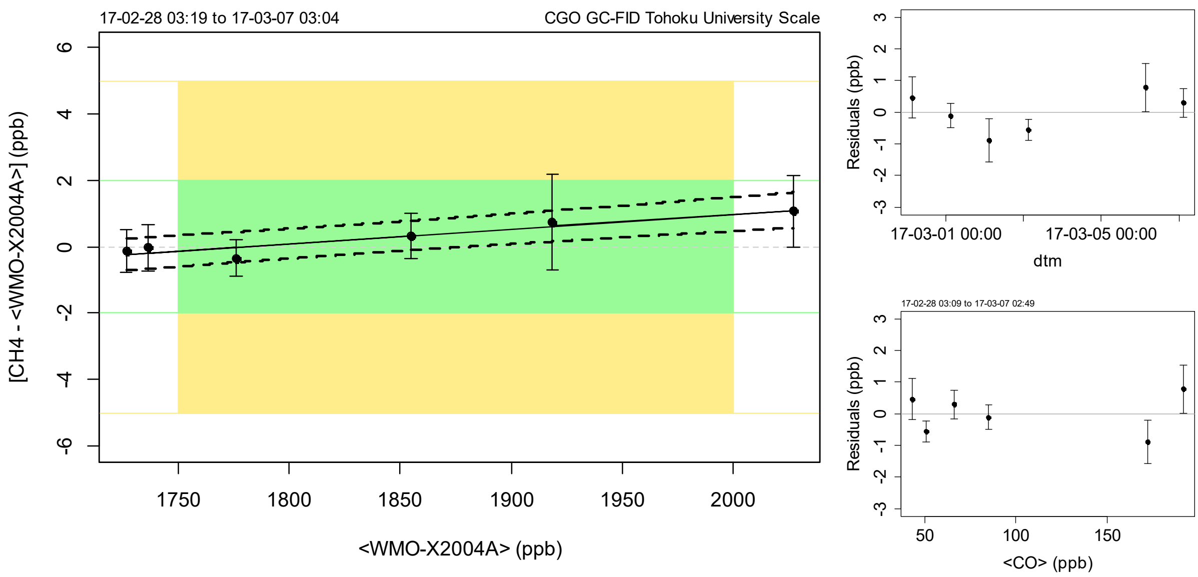

Figure 10. *Same as above, for the CGO GC/FID methane analyser with respect to the WMO-X2004A calibration scale. Note that CGO values refer to the Tohoku University scale.*

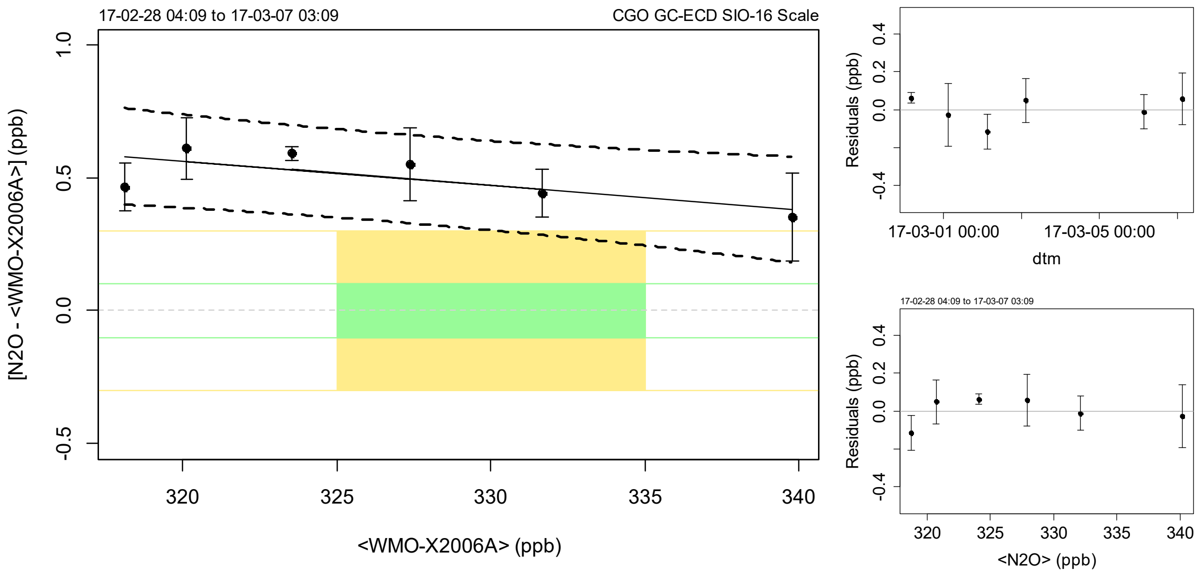

Figure 11. *Same as above, for the CGO nitrous oxide analyser with respect to the WMO-X2006A calibration scale. Note that CGO values refer to the SIO-16 scale.*

The results of the comparisons can be summarised as follows:

CSIRO GASLAB CO: Despite the fact that different calibration scales were used by WCC-Empa (WMO-X2014A) and CSIRO (CSIRO-94), the agreement was within the WMO/GAW compatibility goal in the most relevant mole fraction range below 150 ppb. A recent comparison between CSIRO and NOAA showed a difference of about 3%, with the CSIRO values being lower compared to NOAA. The current results show a slope of 0.9774, which is similar to what was found in the CSIRO/NOAA comparison. However, also an offset of 2 ppb was observed, which mostly compensates the difference in the relevant mole fraction range.

CSIRO GASLAB CH_4: Agreement not exceeding the WMO/GAW compatibility goal over the entire mole fraction range was found. Both CSIRO and WCC-Empa reported on the WMO-X2004A scale.

CSIRO GASLAB CO_2: On average, agreement within the WMO/GAW compatibility goal for the Southern Hemisphere of 0.05 ppm was found for values below 430 ppm. A slightly larger bias, but still within 0.1 ppm, was observed for higher values. Both CSIRO and WCC-Empa reported on the WMO-X2007A scale. The small remaining bias is most likely due to the uncertainty of the NOAA standards used by CSIRO and WCC-Empa.

N_2O was not measured at CSIRO.

CGO CO: CGO was also reporting on the CSIRO-94 calibration scale, and the agreement was within the WMO/GAW compatibility goal in the relevant mole fraction range. However, the offset and slope were in the opposite direction compared to the measurements of the same standards at CSIRO, which indicates non-perfect correction of the non-linearity either at CSIRO or CGO.

Recommendation 8 (, important, 2018)**
Re-assessment of the non-linearity of the CO/MRD instruments both at CSIRO and CGO is recommended.

CGO CH_4: Agreement not exceeding the WMO/GAW compatibility goal over the entire mole fraction range was found, despite the fact that CGO reported on the Tohoku University CH_4 scale. The small bias in the range of 0.5 to about 1 ppb can most likely be explained by the different scales (Dlugokencky et al., 2005).

CGO N_2O: Different calibration scales were used by CGO (SIO-16) and WCC-Empa (WMO-X2006A). The observed bias of the CGO measurements of about 0.5 ppb can most likely be explained by the different scales.

Recommendation 9 (, important, 2018)**
It is recommended to use the latest NOAA calibration scales for data which is submitted to GAW data centres.

CSIRO AND CGO PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the CGO and CSIRO GASLAB performance audits to other station audits made by WCC-Empa and WCC-N_2O. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2015 meeting (WMO, 2016) for CO_2, CH_4 and CO and refer to conditions usually found in unpolluted air masses. Using a fixed mole fraction range however might not be appropriate in the case of N_2O due to the significant upward trend in the atmosphere over the past decades. The range currently representing the unpolluted troposphere has been recently defined as 325-335 nmol/mol (WMO, 2016), which corresponds well to the mean global atmospheric N_2O amount fraction of 328.9 ± 0.1 nmol/mol observed in 2016 (WMO, 2017). A trend analysis showed an annual increase of about 0.8 nmol/mol per year over the last decade (Blunden and Arndt, 2017), which is in agreement with a fairly constant annual growth rate of 0.81 nmol/mol per year from 1977 until today determined by the National Oceanic and Atmospheric Administration (NOAA, 2018). Based on this, our analysis of N_2O audit results was made using a variable amount fraction range covering 10 nmol/mol with the centre being representative for the unpolluted troposphere for the year of the audit. For surface ozone the mole fraction range of 0 -100 ppb was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility goals in a certain mole fraction range. Figure 12 shows the bias vs. the slope of the performance audits made by WCC-Empa for CO, CH_4, CO_2 and N_2O, while the results for O_3 are shown in Figure 13. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current CGO and CSIRO audits are shown as coloured dots in Figure 12 and 13, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

It can be seen that the results were within the DQOs for CO_2, CH_4 and O_3, while CO was within the extended compatibility goal. CO was measured on a different calibration scale, which possibly explains the slightly larger deviation. N_2O measurements made at CGO were exceeding the compatibility goals. However, N_2O was also measured on a different calibration scale (SIO-16), which explains the observed difference.

Table 1. CSIRO and CGO performance audit results compared to other stations. The 4th and 5th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the columns 6-8 show the percentage of all WCC-Empa audits within these criteria since the year 2005 for CO, CH_4 and CO_2, and for all WCC-N_2O and WCC-Empa audits since 2002 for N_2O.

Compound	Range	Unit	CSIRO within DQO*/eDQO	CGO within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]	% of audits outside eDQOs
CO	30 - 300	ppb	✓# (orange)	✓# (orange)	21	47	53
CH_4	1750 - 2100	ppb	✓ (green)	✓# (green)	64	91	9
CO_2	380 - 450	ppm	✓ (green)	NA	33	56	44
N_2O	325 - 335	ppb	NA	✗# (red)	0	38	62
O_3	0 -100	ppb	NA	✓ (green)	61	NA	39

[1] Percentage of stations within the eDQO and DQO

* DQO of 0.1 ppm CO_2 (Northern Hemisphere) is used for performance comparison with other station audits

Different calibration scales

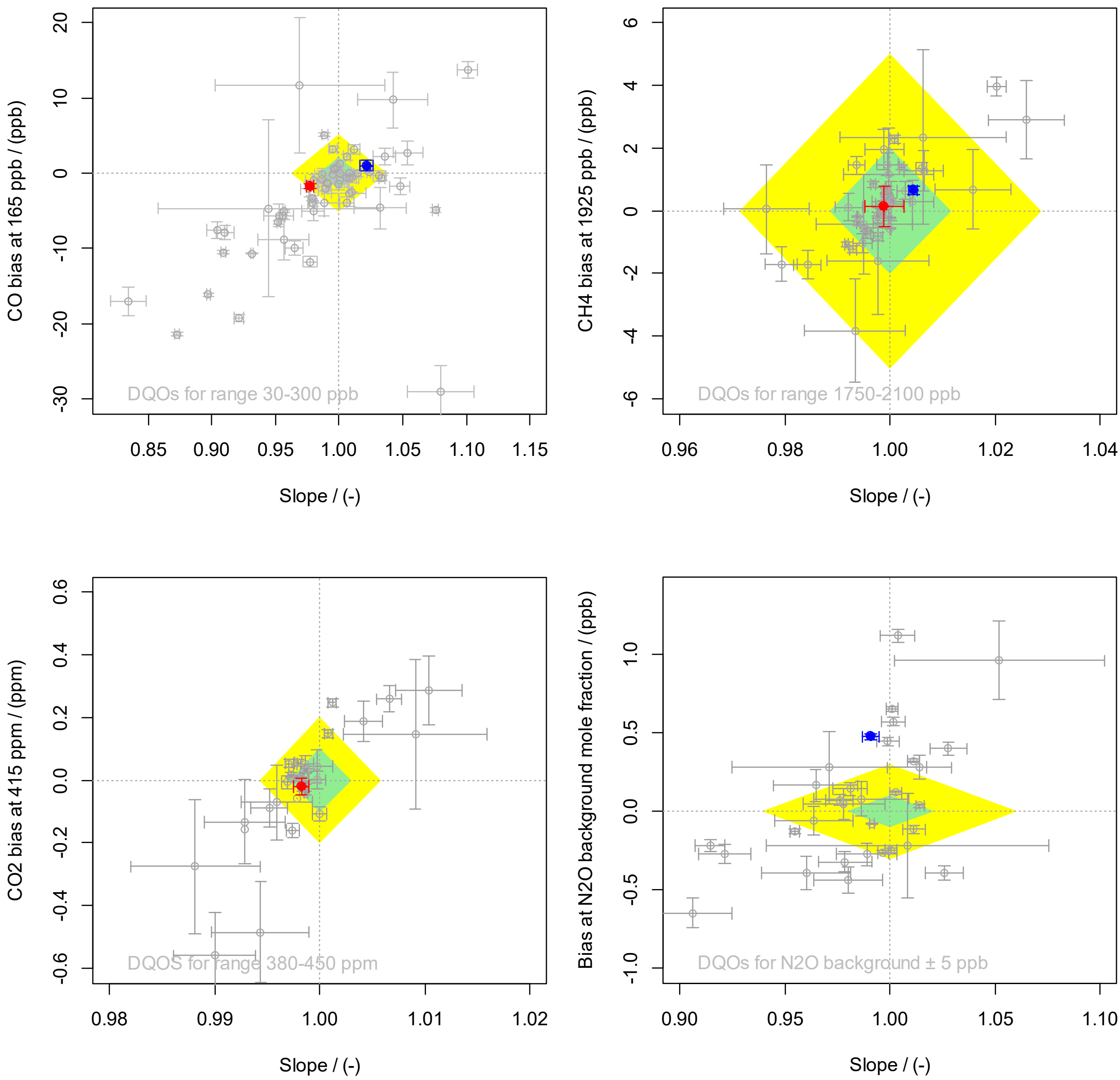

Figure 12. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa and WCC-N_2O. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show CGO and CSIRO GASLAB results (blue: CGO, red: CSIRO GASLAB). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

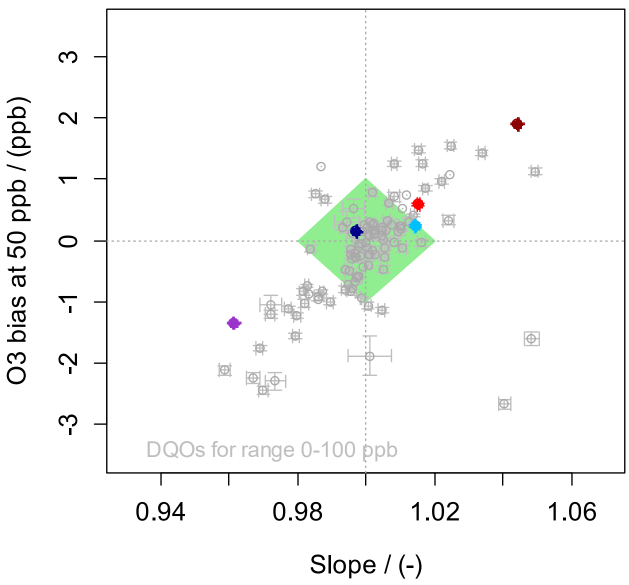

Figure 13. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the CGO results (dark blue: TEI 49i #CM16160046, light blue: TEI 49i #806127828, purple: TEI 49C #78058-387, red: TEI 49C-PS #78059-387TEI, dark red: TEI 49i-PS 1315558104). The green area corresponds to the WMO/GAW DQO for surface ozone.*

CONCLUSIONS

The global GAW station Cape Grim provides extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects, which makes it a very significant contribution to the GAW programme.

The facilities at CSIRO Aspendale hosts the GASLAB, which analyses flask samples and allows for efficient and central calibration of working standards.

Assessed measurements showed high data quality and mostly met the WMO/GAW compatibility goals or extended compatibility goals in the relevant mole fraction range. Table 2 summarises the results of the performance audit with respect to the WMO/GAW compatibility goals. Note that Table 2 refers only to the mole fractions relevant to CGO, whereas Table 1 further above covers a wider mole fraction range.

Table 2. Synthesis of the performance audit and ambient air comparison results. A tick mark indicates that the compatibility goal (green) or extended compatibility goal (orange) was met on average. A cross indicates results outside the compatibility goals.

Comparison	O_3	CO	CH_4	CO_2	N_2O
Performance audit with TS (CSIRO)	✓	✓	✓	✓	NA
Performance audit with TS (CGO)	NA	✓	✓	NA	✗

NA: No comparison was made

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

SUMMARY RANKING OF THE CAPE GRIM GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access by road.
Facilities		
Laboratory and office space	(5)	Adequate, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable with very few power cuts
General Management and Operation		
Organisation	(3)	Well-coordinated, but re-organisation caused problems
Competence of staff	(4)	Skilled staff, but knowledge loss due to reorganisation of CSIRO
Air Inlet System	(5)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
$CO/CH_4/CO_2/N_2O$	(5)	Fully adequate, not all systems were assessed during the current audit
Standards		
Ozone	(4)	Traceability to WMO reference only through WCC-Empa
CO, CO_2, CH_4, N_2O	(5)	NOAA and / or SIO traceable stand-ards and WS available
Data Management		
Data acquisition	(5)	Fully adequate system except for ozone with manual data download
Data processing	(5)	Highly skilled staff
Data submission	(4)	Data for all parameters have been submitted with acceptable delay

#0: inadequate thru 5: adequate.

Dübendorf, November 2018

Dr. C. Zellweger
WCC-Empa

Dr. M. Steinbacher
QA/SAC Switzerland

Dr. B. Buchmann
Head of Department

APPENDIX

Data Review

The following figures show summary plots of CGO data accessed on 7 March 2018 from WDCGG. Three different providers delivered data for parameters within the scope of WCC-Empa (CSIRO/BoM, AGAGE and NOAA). The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

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

CSIRO/BoM data:

Ozone:

- Data looks fully plausible with regard to all aspects (mole fraction range, seasonal variation, and trend).
- However, it was noticed that the time stamp is not coherent between different years. In some years, the hours range from 0 – 23, and in other years from 1 – 24.This needs to be corrected.

Carbon dioxide:

- Data looks fully plausible with regard to all aspects (mole fraction range, diurnal and seasonal variation, and trend).
- Non-baseline events are appropriately flagged.
- Data has been submitted as two data sets: baseline (clean air conditions) and all valid data.

AGAGE data:

Methane:

- Data looks fully plausible with regard to all aspects (mole fraction range, diurnal and seasonal variation, and trend).
- At the beginning (1980s, early 90s) of the measurements, data showed significantly higher noise most likely associated with higher measurement uncertainty at that time.
- Non-baseline events are appropriately flagged.
- Data has been submitted as two data sets: baseline (clean air conditions) and all valid data.

Carbon monoxide:

- Data looks fully plausible with regard to all aspects (mole fraction range, diurnal and seasonal variation, and trend).
- Non-baseline events are appropriately flagged.
- Data has been submitted as two data sets: baseline (clean air conditions) and all valid data.
- Since 2000, no data is available. All data points are set to NA. Needs to be checked.

Nitrous oxide:

- Data looks fully plausible with regard to all aspects (mole fraction range, diurnal and seasonal variation, and trend).
- At the beginning (1970s to mid-90s) of the measurements, data showed significantly higher noise most likely associated with higher measurement uncertainty at that time.
- Non-baseline events are appropriately flagged.
- Data has been submitted as two data sets: baseline (clean air conditions) and all valid data.

Flask data submitted by CSIRO:

CH_4, CO_2, CO and N_2O:

- Data looks fully plausible with regard to all aspects (mole fraction range, seasonal variation, and trend).

Flask data submitted by NOAA:

CH_4, CO_2, CO and N_2O:

- Data looks fully plausible with regard to all aspects (mole fraction range, seasonal variation, and trend).

Plots for data submitted by BoM/CSIRO:

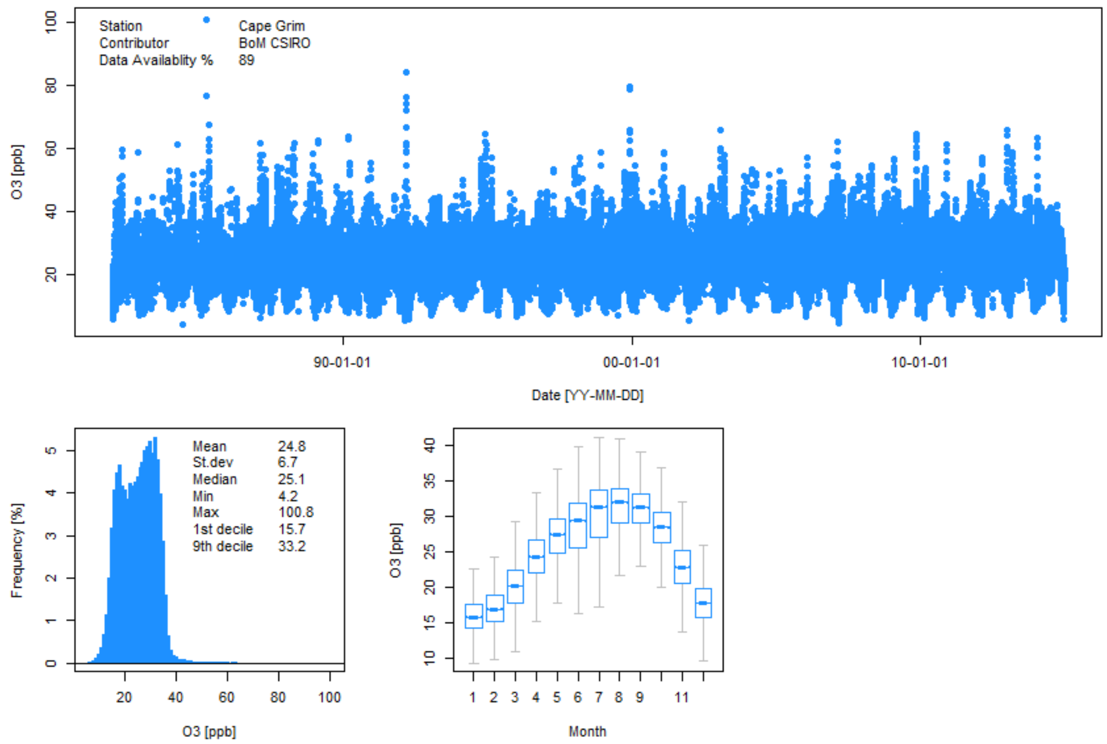

Figure 14. *O_3 data submitted by BoM/CSIRO accessed from WDCGG. Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

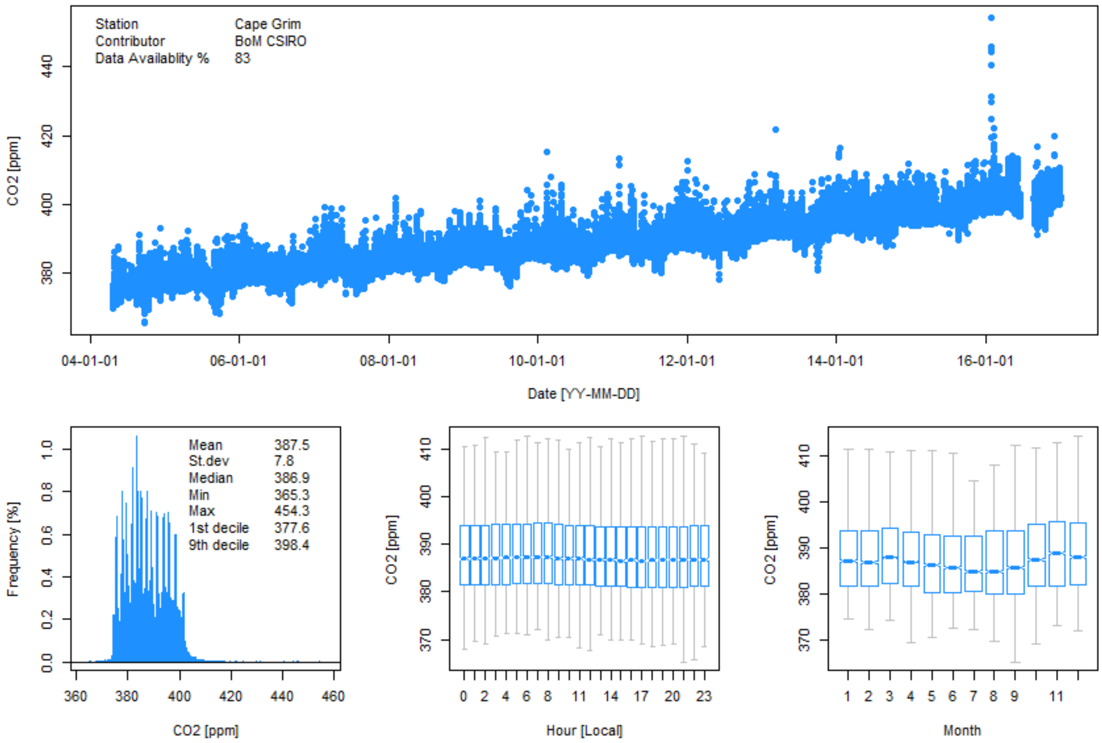

Figure 15. *CO_2 data submitted by BoM/CSIRO accessed from WDCGG. All data, including non-baseline episodes, is shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Middle: Diurnal variation. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

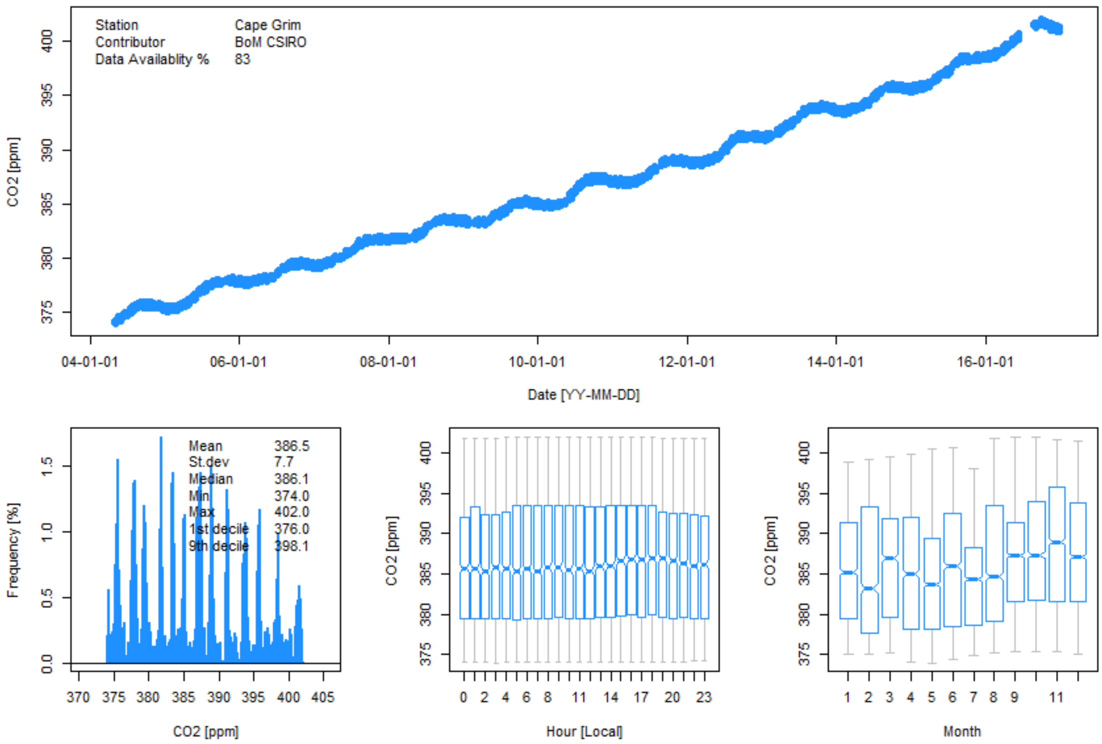

Figure 16. *Same as above, for baseline data only.*

Plots for data submitted by AGAGE:

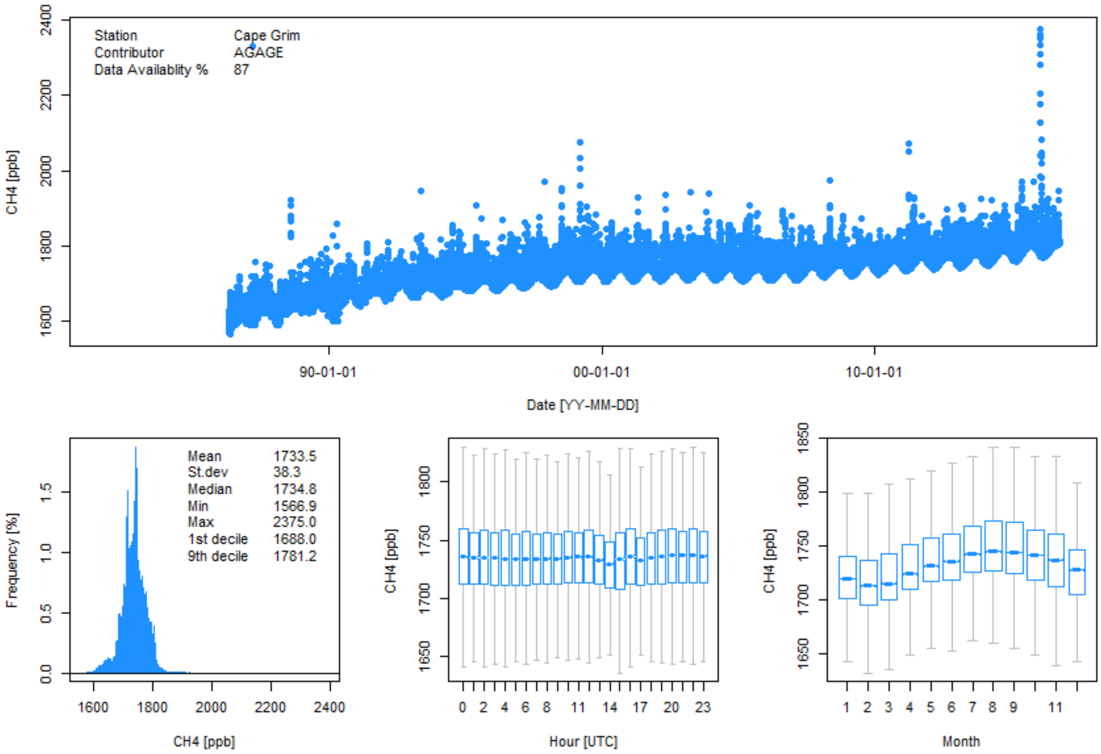

Figure 17. *CH_4 data submitted by AGAGE accessed from WDCGG. All data, including non-baseline episodes, is shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

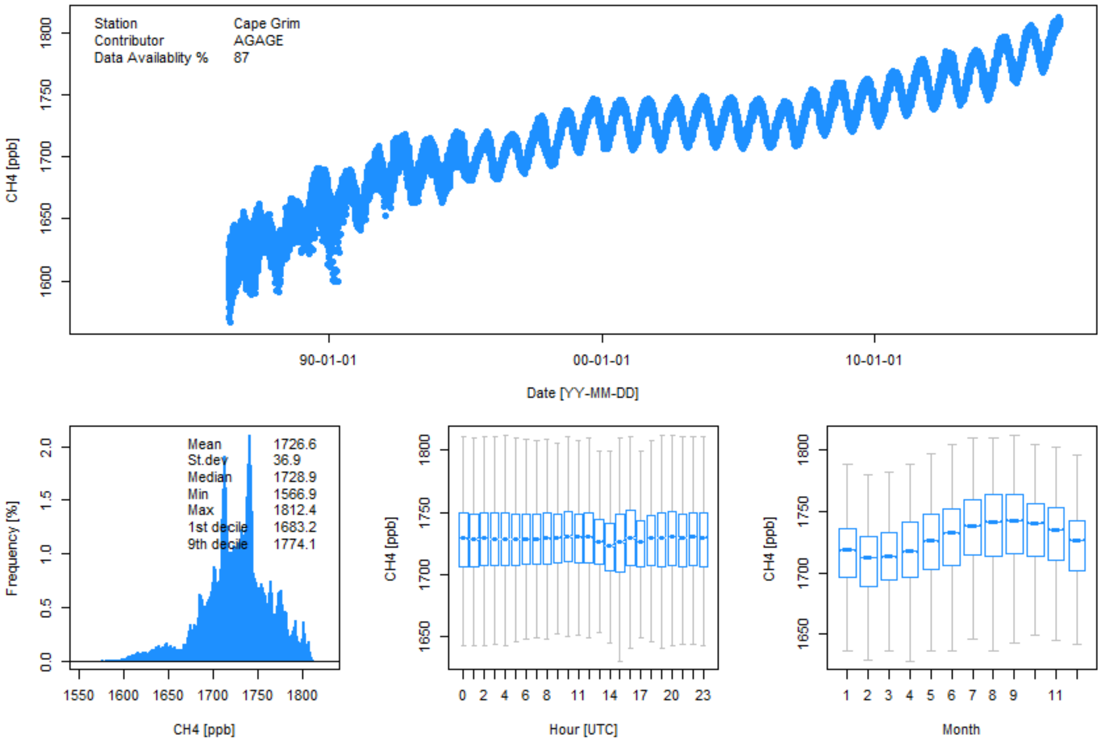

Figure 18. *Same as above, for baseline data only.*

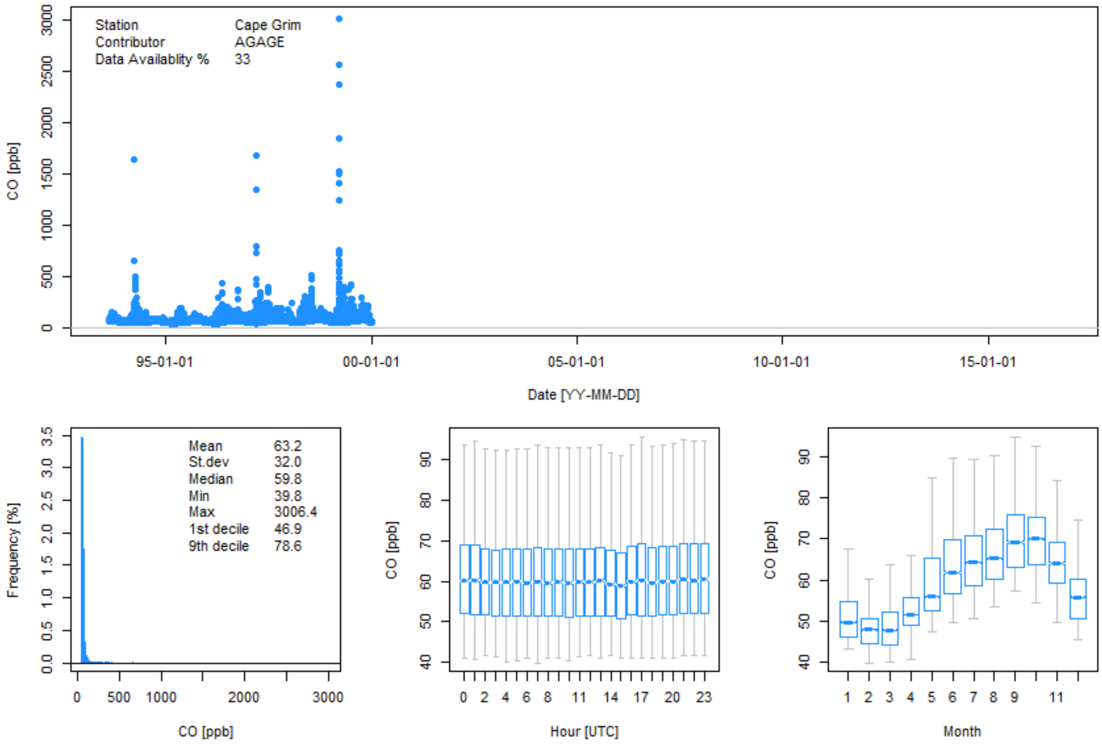

Figure 19. *CO data submitted by AGAGE accessed from WDCGG. All data, including non-baseline episodes, is shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Middle: Diurnal variation. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

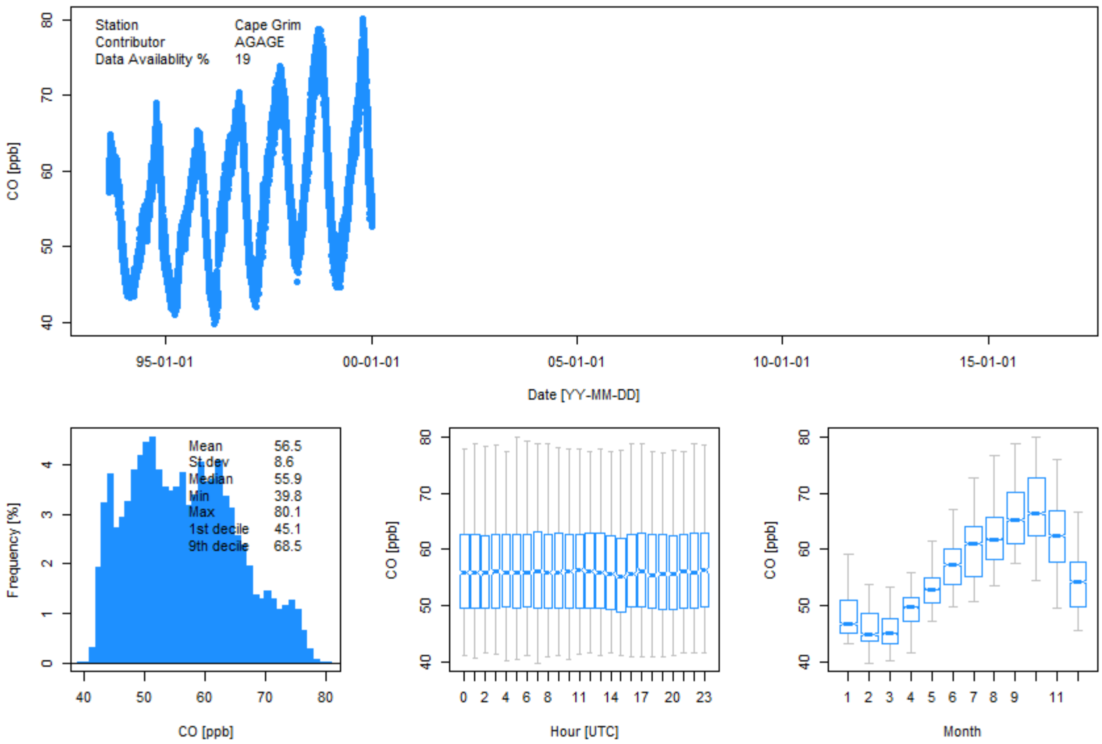

Figure 20. *Same as above, for baseline data only.*

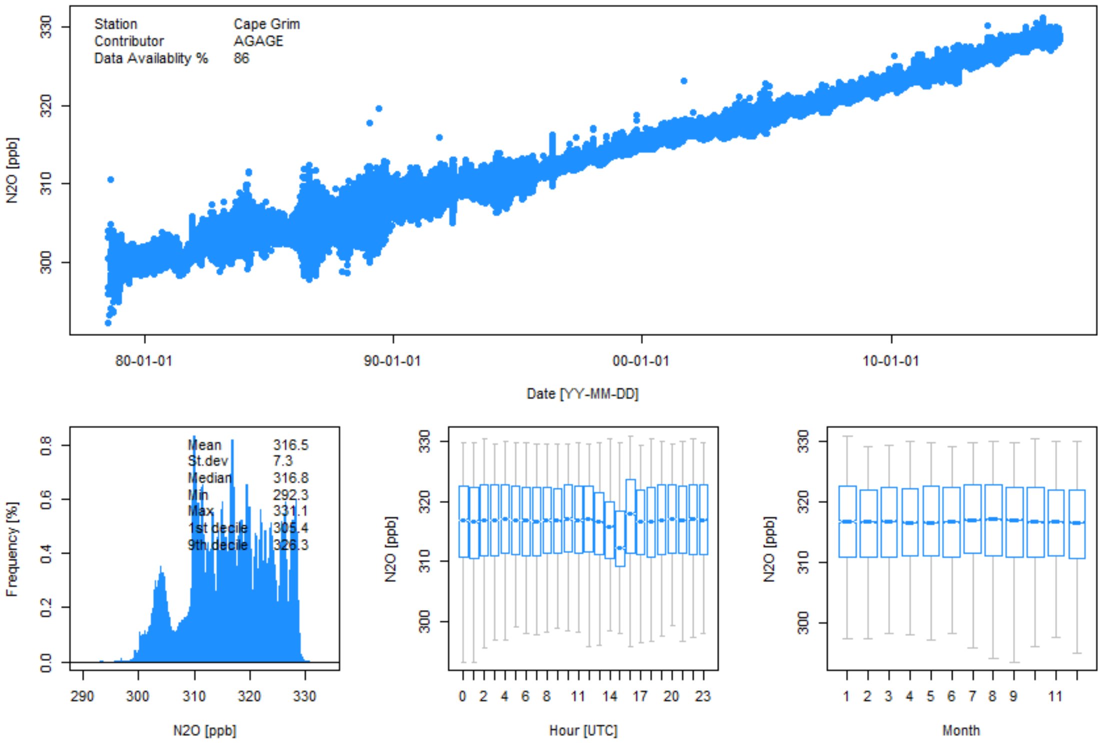

Figure 21. *N_2O data submitted by AGAGE accessed from WDCGG. All data, including non-baseline episodes, is shown. Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Middle: Diurnal variation. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

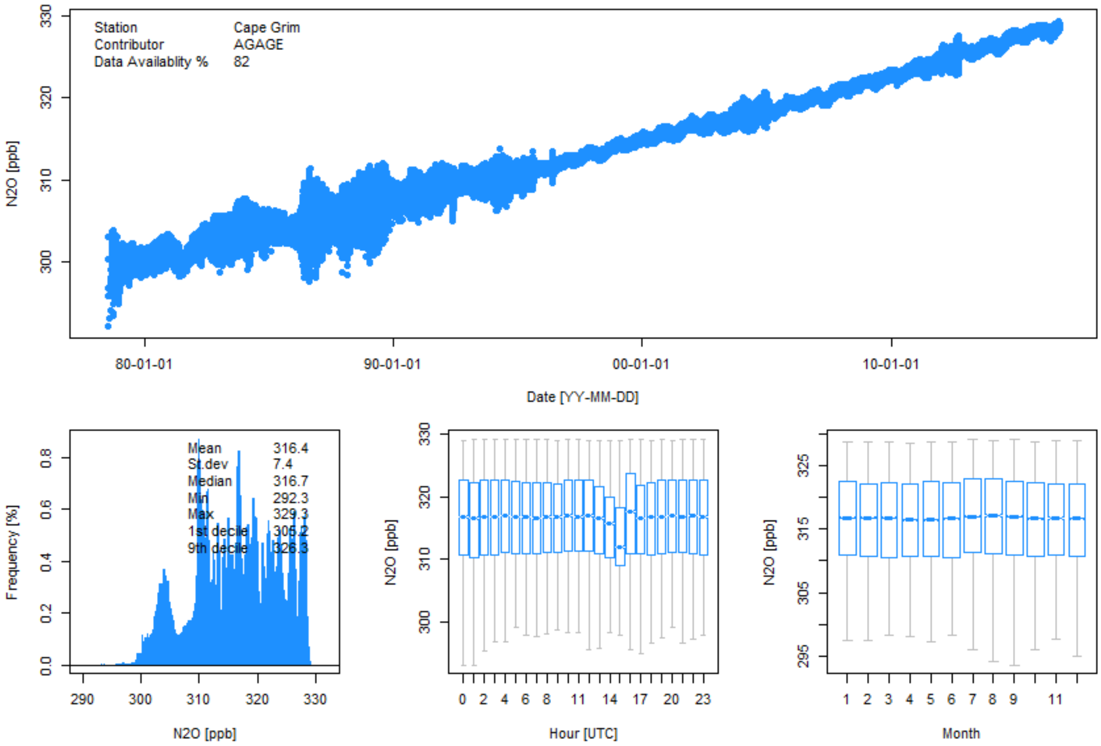

Figure 22. *Same as above, for baseline data only.*

Plots for data submitted by CSIRO:

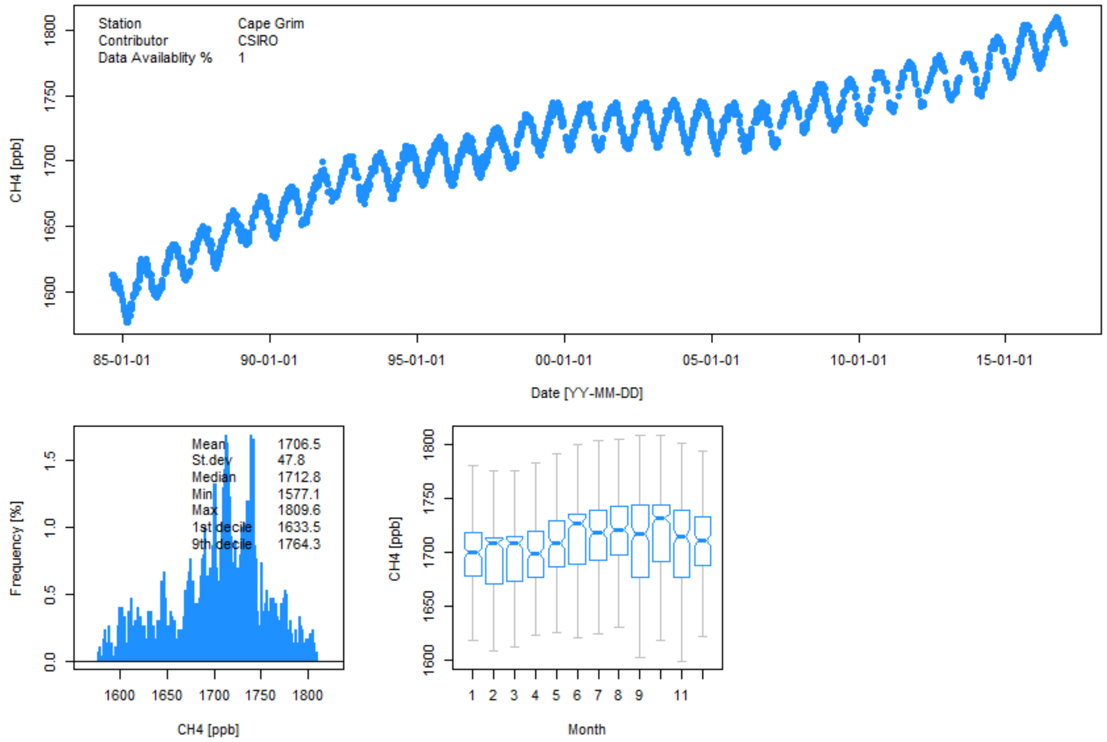

Figure 23. *CH_4 data submitted by CSIRO accessed from WDCGG. Only data for baseline conditions are shown Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

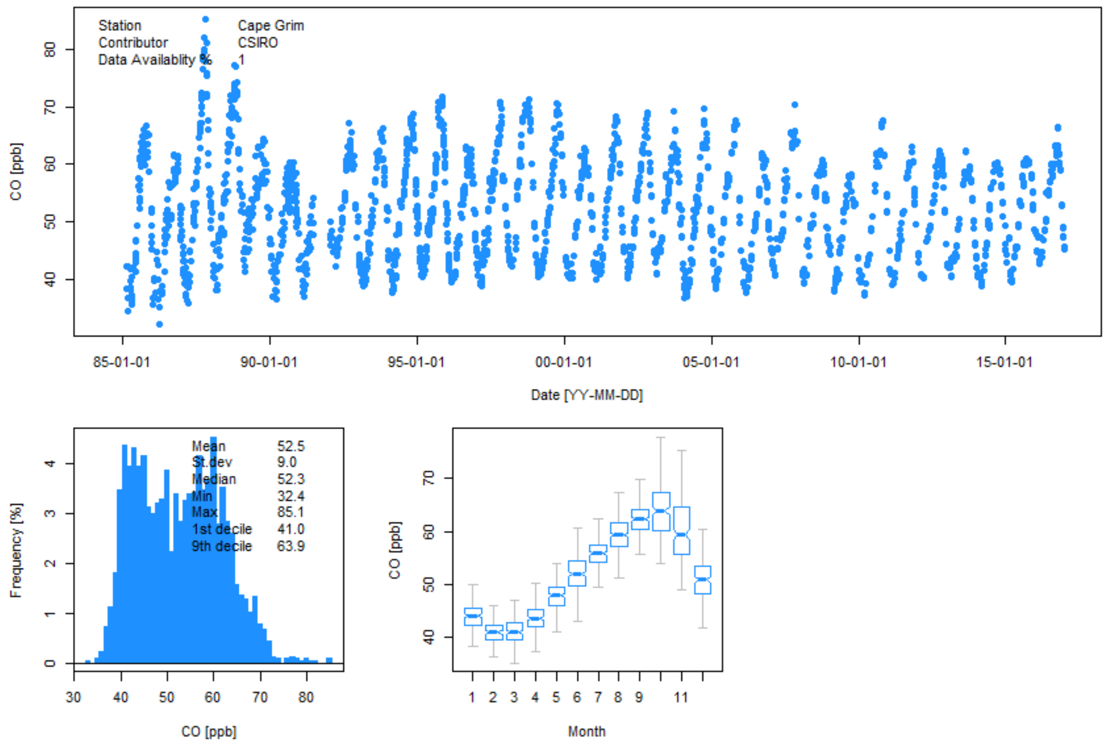

Figure 24. *Same as above for CO.*

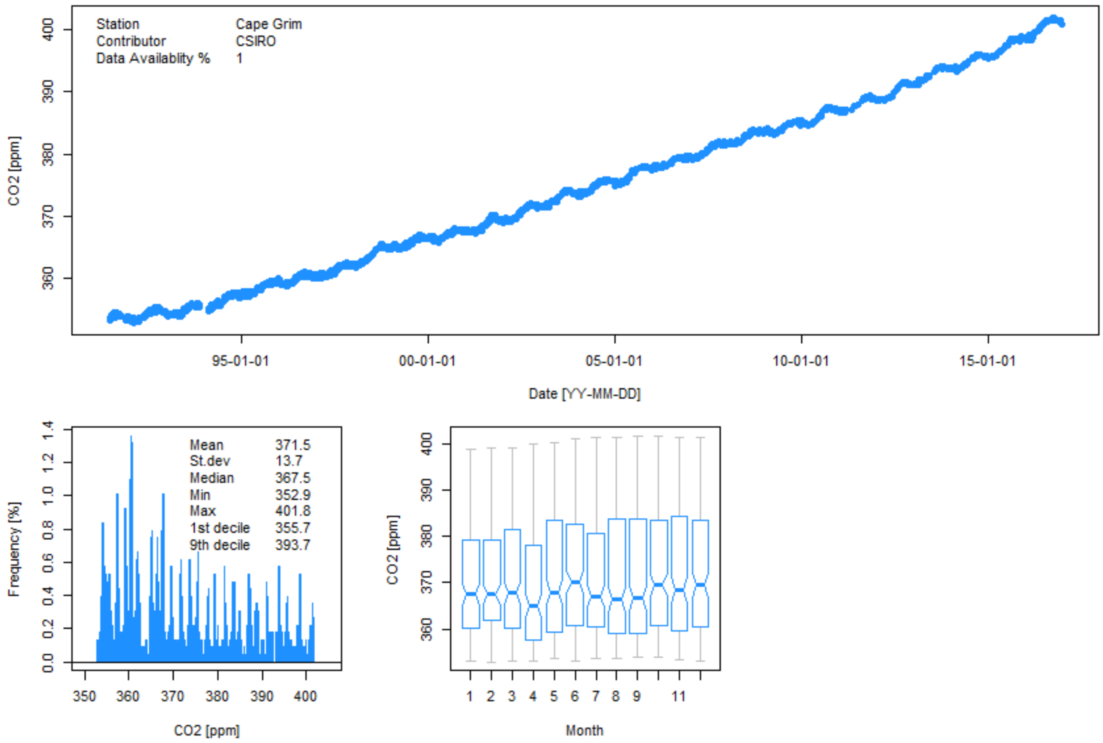

Figure 25. *Same as above for CO_2.*

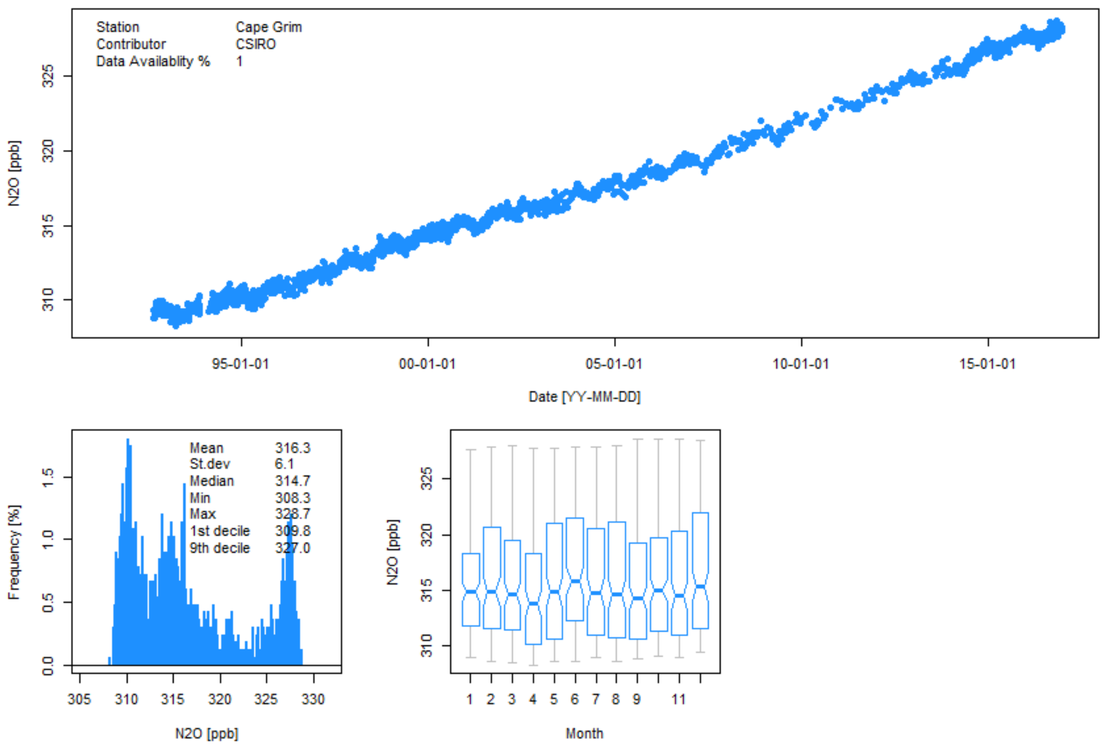

Figure 26. *Same as above for N_2O.*

Plots for data submitted by NOAA:

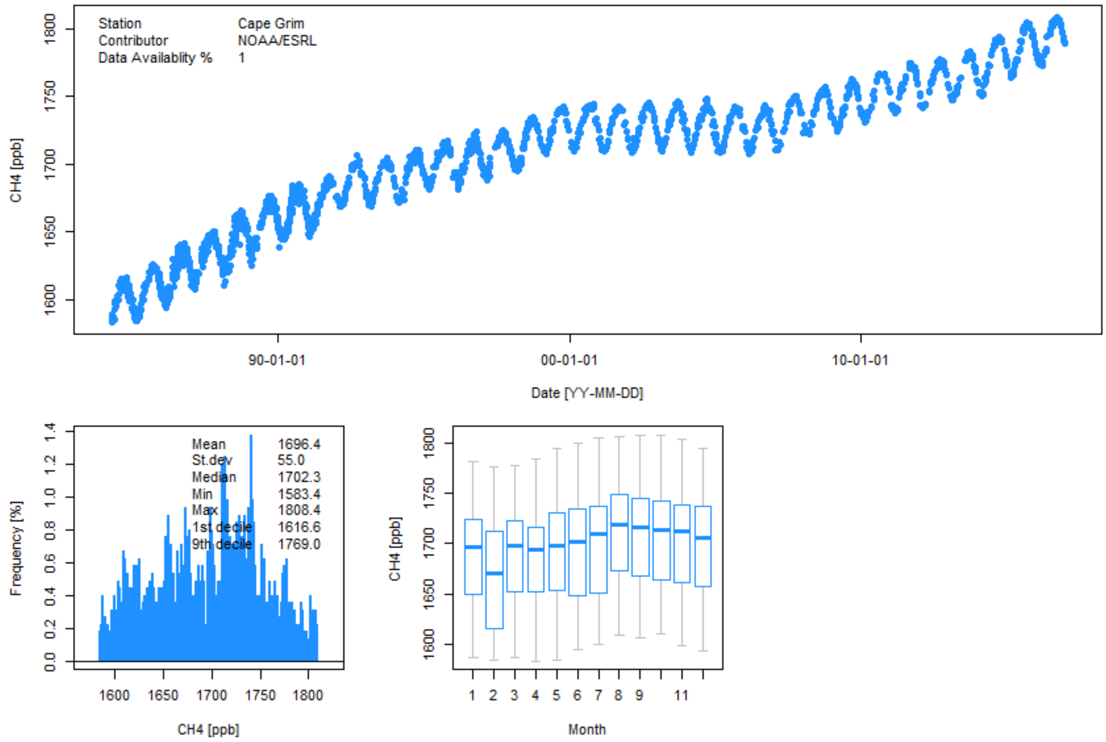

Figure 27. *CH_4 data submitted by NOAA accessed from WDCGG. Only data for baseline conditions are shown Top: Time series, hourly averages. Bottom: Left: Frequency distribution. Right: Seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

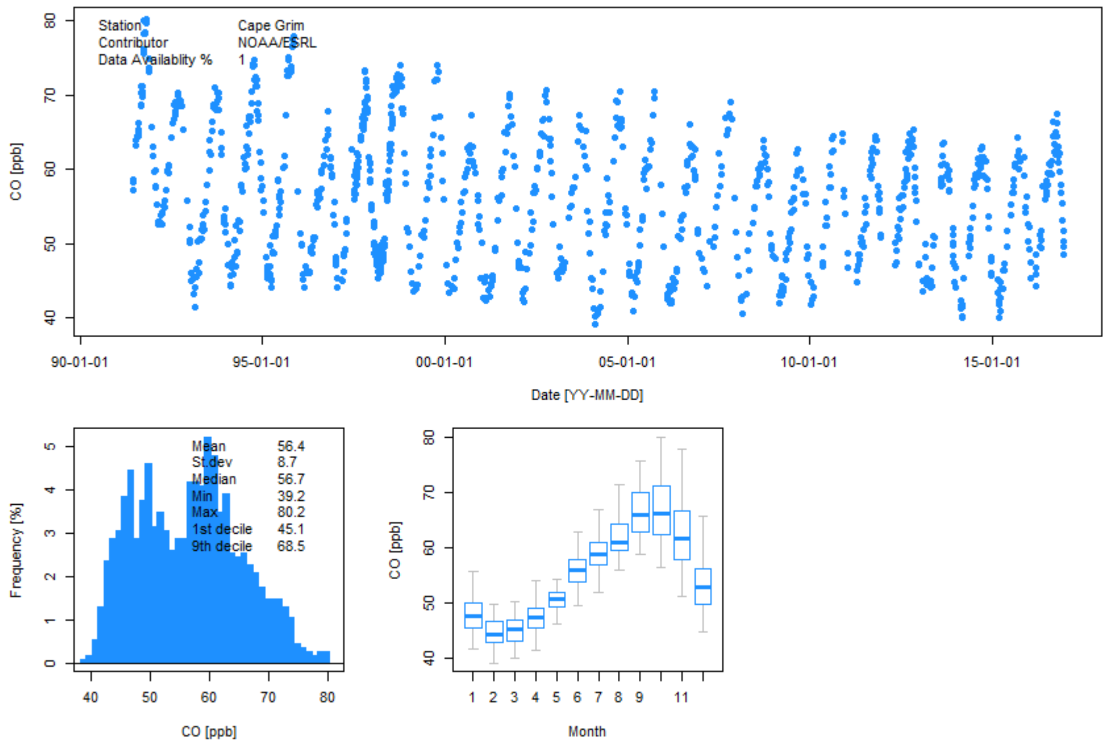

Figure 28. *Same as above for CO.*

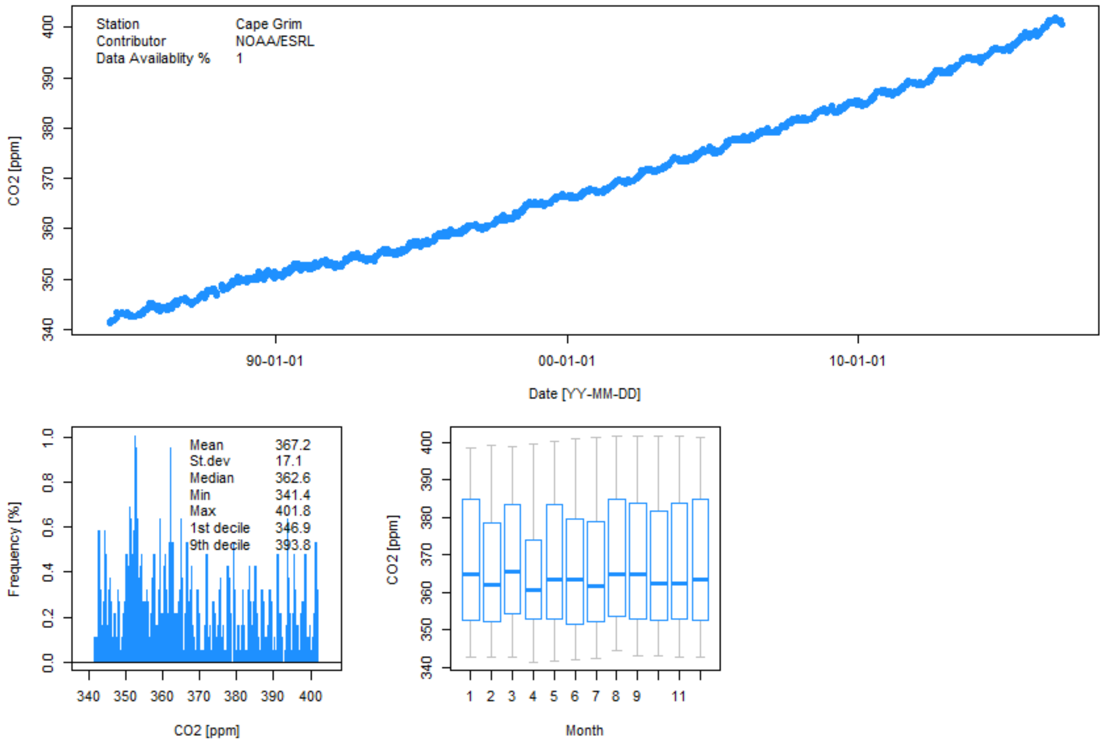

Figure 29. *Same as above for CO_2.*

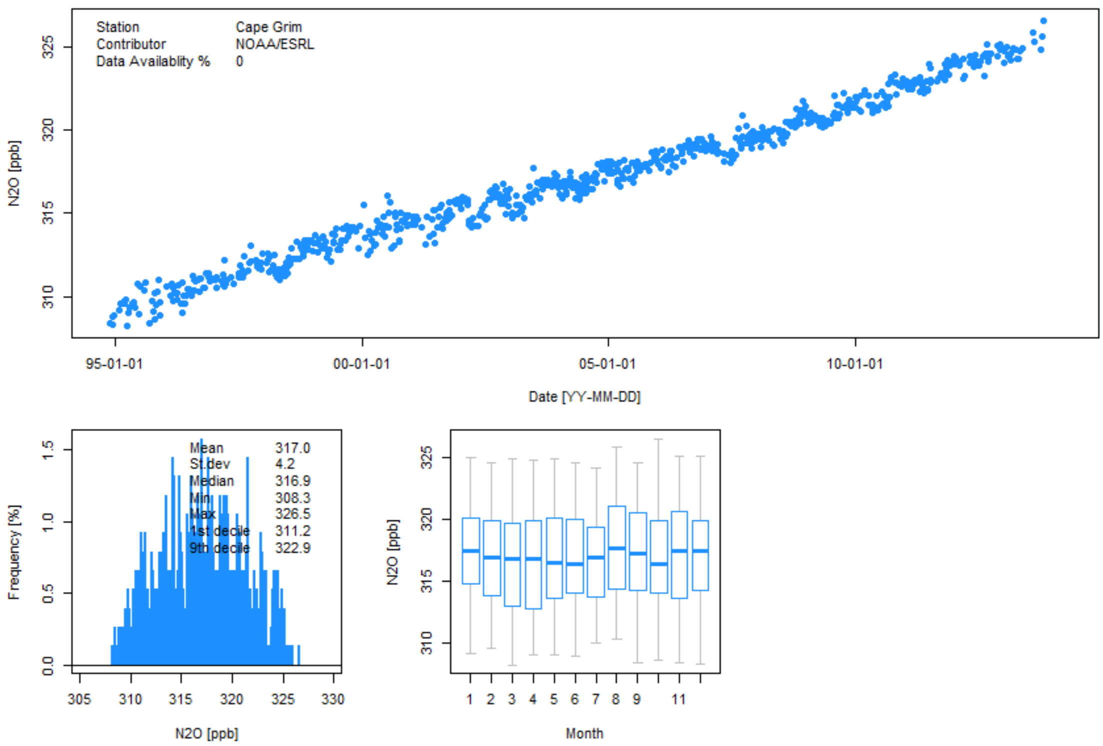

Figure 30. *Same as above for N_2O.*

Surface Ozone Comparisons

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

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. Zero air was generated using a custom built zero air generator (Nafion drier, activated charcoal, Purafil). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa data acquisition system.

Table 3. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49C-PS #54509-300 (WCC-Empa)
Settings	BKG -0.3, COEF 1.009
Pressure readings (hPa)	Ambient 982.6 TS 983.0, no adjustments were made
CGO Station analyser TECO3 (OA)	
Model, S/N	Thermo Scientific 49C #78058-387
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.9 ppb, COEF 1.018
Pressure readings (hPa)	No adjustment was made
CGO Station analyser TECO4(OA)	
Model, S/N	Thermo Scientific 49i #0806127828
Principle	UV absorption
Range	0-1 ppm
Settings	BKG 0.1 ppb, COEF 1.036
Pressure readings (hPa)	No adjustment was made
CGO Station analyser TECO6(OA)	
Model, S/N	Thermo Scientific 49i #CM16160046
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.5 ppb, COEF 0.984
Pressure readings (hPa)	No adjustment was made
CGO Station calibrator TC2 (OC)	
Model, S/N	Thermo Scientific 49C-PS #78059-387
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.6 ppb, COEF 1.017
Pressure readings (hPa)	No adjustment was made
CGO Station analyser TC3 (OC)	
Model, S/N	Thermo Scientific 49C #78058-387
Principle	UV absorption
Range	0-1 ppm
Settings	BKG 0.0 ppb, COEF 1.035
Pressure readings (hPa)	No adjustment was made

Results

Each ozone level was applied for 10 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

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

Table 4. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CGO ozone analyser (OA) Thermo Scientific 49C #78058-387 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-14 12:39	1	0	0.16	0.79	0.15	0.14	0.63	NA
2016-11-14 12:54	1	40	40.04	38.97	0.09	0.08	-1.07	-2.7
2016-11-14 13:09	1	20	20.12	20.01	0.06	0.06	-0.11	-0.5
2016-11-14 13:24	1	80	79.91	77.22	0.07	0.14	-2.69	-3.4
2016-11-14 13:54	1	10	10.37	10.78	0.20	0.16	0.41	4.0
2016-11-14 14:09	1	30	29.93	29.54	0.12	0.09	-0.39	-1.3
2016-11-14 14:09	1	60	59.97	58.27	0.12	0.10	-1.70	-2.8
2016-11-14 14:24	1	90	89.87	87.01	0.11	0.20	-2.86	-3.2
2016-11-14 14:54	1	50	50.09	48.70	0.04	0.08	-1.39	-2.8
2016-11-14 15:09	1	70	70.07	67.94	0.07	0.07	-2.13	-3.0
2016-11-14 15:24	2	0	0.15	1.01	0.08	0.11	0.86	NA
2016-11-14 15:39	2	75	75.08	72.79	0.07	0.07	-2.29	-3.1
2016-11-14 15:54	2	225	224.74	216.37	0.06	0.04	-8.37	-3.7
2016-11-14 16:09	2	125	124.94	120.63	0.02	0.09	-4.31	-3.4
2016-11-14 16:24	2	175	174.80	168.37	0.12	0.11	-6.43	-3.7
2016-11-14 16:39	2	25	25.21	24.95	0.05	0.09	-0.26	-1.0
2016-11-14 16:54	3	0	0.09	1.01	0.09	0.14	0.92	NA
2016-11-14 17:09	3	90	89.97	86.89	0.09	0.13	-3.08	-3.4
2016-11-14 17:24	3	30	30.11	29.51	0.11	0.10	-0.60	-2.0
2016-11-14 17:39	3	60	59.96	58.13	0.06	0.11	-1.83	-3.1
2016-11-14 17:54	3	70	69.99	67.71	0.09	0.03	-2.28	-3.3
2016-11-14 18:09	3	40	40.11	39.08	0.09	0.12	-1.03	-2.6
2016-11-14 18:24	3	10	10.21	10.44	0.11	0.14	0.23	2.3
2016-11-14 18:39	3	20	19.89	19.79	0.09	0.07	-0.10	-0.5
2016-11-14 18:54	3	50	49.91	48.50	0.12	0.12	-1.41	-2.8
2016-11-14 19:09	3	80	79.88	77.22	0.14	0.15	-2.66	-3.3
2016-11-14 19:24	4	0	0.19	0.79	0.09	0.10	0.60	NA
2016-11-14 19:39	4	100	99.87	96.53	0.11	0.18	-3.34	-3.3
2016-11-14 19:54	4	200	199.71	192.21	0.12	0.14	-7.50	-3.8
2016-11-14 20:09	4	50	50.09	48.73	0.07	0.12	-1.36	-2.7
2016-11-14 20:24	4	250	249.79	240.14	0.09	0.08	-9.65	-3.9
2016-11-14 20:39	4	150	149.95	144.52	0.12	0.07	-5.43	-3.6
2016-11-14 20:54	5	0	0.10	0.93	0.03	0.09	0.83	NA
2016-11-14 21:09	5	40	40.03	39.10	0.11	0.05	-0.93	-2.3
2016-11-14 21:24	5	20	20.06	19.89	0.08	0.14	-0.17	-0.8
2016-11-14 21:39	5	80	79.90	77.34	0.04	0.11	-2.56	-3.2

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-14 22:09	5	10	10.33	10.87	0.22	0.17	0.54	5.2
2016-11-14 22:24	5	30	29.95	29.55	0.12	0.08	-0.40	-1.3
2016-11-14 22:24	5	60	60.00	58.37	0.11	0.14	-1.63	-2.7
2016-11-14 22:39	5	90	89.91	87.05	0.09	0.14	-2.86	-3.2
2016-11-14 23:09	5	50	49.99	48.73	0.05	0.02	-1.26	-2.5
2016-11-14 23:24	5	70	70.03	67.97	0.08	0.13	-2.06	-2.9
2016-11-14 23:39	6	0	0.04	0.87	0.09	0.08	0.83	NA
2016-11-14 23:54	6	75	74.95	72.45	0.12	0.09	-2.50	-3.3
2016-11-15 00:09	6	225	224.74	216.19	0.06	0.11	-8.55	-3.8
2016-11-15 00:24	6	125	124.92	120.53	0.10	0.03	-4.39	-3.5
2016-11-15 00:39	6	175	174.84	168.37	0.06	0.13	-6.47	-3.7
2016-11-15 00:54	6	25	25.22	24.95	0.07	0.08	-0.27	-1.1
2016-11-15 01:09	7	0	0.14	0.77	0.08	0.07	0.63	NA
2016-11-15 01:24	7	90	89.96	86.93	0.04	0.07	-3.03	-3.4
2016-11-15 01:39	7	30	30.04	29.49	0.13	0.11	-0.55	-1.8
2016-11-15 02:09	7	70	69.95	67.71	0.08	0.13	-2.24	-3.2
2016-11-15 02:24	7	40	40.04	39.10	0.07	0.13	-0.94	-2.3
2016-11-15 02:39	7	10	10.30	10.50	0.11	0.21	0.20	1.9
2016-11-15 02:54	7	20	19.97	19.93	0.13	0.11	-0.04	-0.2
2016-11-15 03:09	7	50	49.90	48.60	0.07	0.11	-1.30	-2.6
2016-11-15 03:24	7	80	79.81	77.42	0.11	0.09	-2.39	-3.0
2016-11-15 03:39	8	0	0.16	1.01	0.07	0.17	0.85	NA
2016-11-15 03:54	8	100	99.94	96.65	0.02	0.09	-3.29	-3.3
2016-11-15 04:09	8	200	199.75	192.60	0.13	0.08	-7.15	-3.6
2016-11-15 04:24	8	50	50.04	48.80	0.05	0.16	-1.24	-2.5
2016-11-15 04:39	8	250	249.71	240.29	0.08	0.22	-9.42	-3.8
2016-11-15 04:54	8	150	150.04	144.77	0.14	0.22	-5.27	-3.5
2016-11-15 05:09	9	0	0.14	0.97	0.08	0.09	0.83	NA
2016-11-15 05:24	9	40	40.11	39.18	0.09	0.07	-0.93	-2.3
2016-11-15 05:39	9	20	20.15	20.20	0.13	0.07	0.05	0.2
2016-11-15 05:54	9	80	79.96	77.44	0.07	0.12	-2.52	-3.2
2016-11-15 06:24	9	10	10.38	10.69	0.14	0.18	0.31	3.0
2016-11-15 06:39	9	30	29.99	29.40	0.07	0.16	-0.59	-2.0
2016-11-15 06:39	9	60	60.05	58.25	0.11	0.15	-1.80	-3.0
2016-11-15 06:54	9	90	89.90	86.99	0.10	0.06	-2.91	-3.2
2016-11-15 07:24	9	50	50.03	48.67	0.07	0.14	-1.36	-2.7
2016-11-15 07:39	9	70	70.03	67.77	0.03	0.06	-2.26	-3.2
2016-11-15 07:54	10	0	0.15	0.78	0.14	0.05	0.63	NA
2016-11-15 08:09	10	75	74.96	72.62	0.09	0.14	-2.34	-3.1
2016-11-15 08:24	10	225	224.61	216.18	0.06	0.17	-8.43	-3.8
2016-11-15 08:39	10	125	124.98	120.55	0.09	0.08	-4.43	-3.5
2016-11-15 08:54	10	175	174.86	168.45	0.12	0.10	-6.41	-3.7
2016-11-15 09:09	10	25	25.26	24.90	0.07	0.11	-0.36	-1.4
2016-11-15 09:24	11	0	0.09	0.88	0.04	0.11	0.79	NA
2016-11-15 09:39	11	90	89.90	86.97	0.12	0.11	-2.93	-3.3
2016-11-15 09:54	11	30	30.04	29.52	0.13	0.12	-0.52	-1.7
2016-11-15 10:09	11	60	59.97	58.25	0.12	0.09	-1.72	-2.9
2016-11-15 10:24	11	70	69.90	67.90	0.06	0.07	-2.00	-2.9

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-15 10:39	11	40	39.96	39.08	0.06	0.04	-0.88	-2.2
2016-11-15 10:54	11	10	10.36	10.65	0.17	0.17	0.29	2.8
2016-11-15 11:09	11	20	19.92	19.86	0.05	0.17	-0.06	-0.3
2016-11-15 11:24	11	50	49.92	48.59	0.12	0.09	-1.33	-2.7
2016-11-15 11:39	11	80	79.80	77.47	0.30	0.38	-2.33	-2.9

Table 5. Same as above for the Thermo Scientific 49i #0806127828.

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-15 12:57	1	0	0.08	0.06	0.06	0.10	-0.02	NA
2016-11-15 13:12	1	90	89.84	89.76	0.08	0.03	-0.08	-0.1
2016-11-15 13:27	1	30	30.02	29.69	0.09	0.12	-0.33	-1.1
2016-11-15 13:42	1	60	59.96	59.82	0.07	0.11	-0.14	-0.2
2016-11-15 13:57	1	70	70.01	69.82	0.11	0.11	-0.19	-0.3
2016-11-15 14:12	1	40	40.05	39.79	0.03	0.13	-0.26	-0.6
2016-11-15 14:27	1	10	10.41	10.25	0.10	0.16	-0.16	-1.5
2016-11-15 14:42	1	20	19.90	19.66	0.09	0.15	-0.24	-1.2
2016-11-15 14:57	1	50	49.98	49.70	0.03	0.16	-0.28	-0.6
2016-11-15 15:12	1	80	79.86	79.78	0.08	0.14	-0.08	-0.1
2016-11-15 15:27	2	0	0.14	0.00	0.05	0.13	-0.14	NA
2016-11-15 15:42	2	100	100.00	100.02	0.07	0.12	0.02	0.0
2016-11-15 15:57	2	200	199.82	201.08	0.13	0.14	1.26	0.6
2016-11-15 16:12	2	50	50.12	50.04	0.11	0.10	-0.08	-0.2
2016-11-15 16:27	2	250	249.76	252.06	0.15	0.19	2.30	0.9
2016-11-15 16:42	2	150	149.92	151.09	0.09	0.13	1.17	0.8
2016-11-15 16:57	3	0	0.17	0.08	0.09	0.14	-0.09	NA
2016-11-15 17:12	3	40	40.02	39.94	0.09	0.09	-0.08	-0.2
2016-11-15 17:27	3	20	20.10	19.98	0.08	0.18	-0.12	-0.6
2016-11-15 17:42	3	80	79.97	80.15	0.18	0.10	0.18	0.2
2016-11-15 18:12	3	10	10.39	10.24	0.09	0.10	-0.15	-1.4
2016-11-15 18:27	3	60	60.02	60.15	0.10	0.15	0.13	0.2
2016-11-15 18:27	3	30	29.91	29.90	0.06	0.10	-0.01	0.0
2016-11-15 18:42	3	90	89.93	90.08	0.04	0.17	0.15	0.2
2016-11-15 19:12	3	50	49.98	50.06	0.04	0.12	0.08	0.2
2016-11-15 19:27	3	70	69.96	70.23	0.09	0.13	0.27	0.4
2016-11-15 19:42	4	0	0.14	0.08	0.05	0.08	-0.06	NA
2016-11-15 19:57	4	75	74.96	75.22	0.11	0.15	0.26	0.3
2016-11-15 20:12	4	225	224.68	227.13	0.14	0.13	2.45	1.1
2016-11-15 20:27	4	125	124.93	126.17	0.10	0.12	1.24	1.0
2016-11-15 20:42	4	175	174.86	176.79	0.14	0.20	1.93	1.1
2016-11-15 20:57	4	25	25.25	25.38	0.04	0.18	0.13	0.5
2016-11-15 21:12	5	0	0.18	-0.03	0.11	0.09	-0.21	NA
2016-11-15 21:27	5	90	89.92	90.56	0.15	0.16	0.64	0.7
2016-11-15 21:42	5	30	30.07	30.22	0.09	0.16	0.15	0.5
2016-11-15 21:57	5	60	59.92	60.30	0.12	0.13	0.38	0.6
2016-11-15 22:12	5	70	69.97	70.26	0.15	0.11	0.29	0.4

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-15 22:27	5	40	40.06	40.13	0.13	0.13	0.07	0.2
2016-11-15 22:42	5	10	10.37	10.28	0.14	0.13	-0.09	-0.9
2016-11-15 22:57	5	20	19.95	19.85	0.10	0.09	-0.10	-0.5
2016-11-15 23:12	5	50	49.93	50.04	0.08	0.10	0.11	0.2
2016-11-15 23:27	5	80	79.96	80.45	0.14	0.13	0.49	0.6
2016-11-15 23:42	6	0	0.17	0.11	0.16	0.12	-0.06	NA
2016-11-15 23:57	6	100	99.90	100.60	0.13	0.11	0.70	0.7
2016-11-16 00:12	6	200	199.72	202.07	0.03	0.19	2.35	1.2
2016-11-16 00:27	6	50	50.11	50.37	0.11	0.16	0.26	0.5
2016-11-16 00:42	6	250	249.69	252.80	0.13	0.18	3.11	1.2
2016-11-16 00:57	6	150	150.01	151.89	0.12	0.22	1.88	1.3
2016-11-16 01:12	7	0	0.20	0.13	0.07	0.08	-0.07	NA
2016-11-16 01:27	7	40	40.06	40.28	0.04	0.19	0.22	0.5
2016-11-16 01:42	7	20	20.14	19.98	0.05	0.09	-0.16	-0.8
2016-11-16 01:57	7	80	79.89	80.51	0.02	0.18	0.62	0.8
2016-11-16 02:27	7	10	10.36	10.38	0.17	0.10	0.02	0.2
2016-11-16 02:42	7	30	29.96	29.99	0.12	0.15	0.03	0.1
2016-11-16 02:42	7	60	59.99	60.46	0.06	0.12	0.47	0.8
2016-11-16 02:57	7	90	89.90	90.80	0.10	0.08	0.90	1.0
2016-11-16 03:27	7	50	50.05	50.29	0.08	0.13	0.24	0.5
2016-11-16 03:42	7	70	69.90	70.46	0.04	0.14	0.56	0.8
2016-11-16 03:57	8	0	0.22	0.09	0.08	0.13	-0.13	NA
2016-11-16 04:12	8	75	74.88	75.47	0.08	0.23	0.59	0.8
2016-11-16 04:27	8	225	224.67	227.75	0.13	0.11	3.08	1.4
2016-11-16 04:42	8	125	125.02	126.51	0.12	0.15	1.49	1.2
2016-11-16 04:57	8	175	174.90	177.38	0.09	0.08	2.48	1.4
2016-11-16 05:12	8	25	25.31	25.49	0.09	0.11	0.18	0.7
2016-11-16 05:27	9	0	0.16	0.07	0.08	0.11	-0.09	NA
2016-11-16 05:42	9	90	89.94	90.82	0.13	0.23	0.88	1.0
2016-11-16 05:57	9	30	30.14	30.13	0.07	0.18	-0.01	0.0
2016-11-16 06:12	9	60	59.99	60.50	0.08	0.16	0.51	0.9
2016-11-16 06:27	9	70	70.00	70.65	0.03	0.07	0.65	0.9
2016-11-16 06:42	9	40	40.13	40.33	0.05	0.10	0.20	0.5
2016-11-16 06:57	9	10	10.36	10.22	0.18	0.14	-0.14	-1.4
2016-11-16 07:12	9	20	19.93	19.93	0.07	0.09	0.00	0.0
2016-11-16 07:27	9	50	49.77	50.25	0.12	0.12	0.48	1.0
2016-11-16 07:42	9	80	79.86	80.58	0.13	0.14	0.72	0.9
2016-11-16 07:57	10	0	0.19	0.09	0.09	0.13	-0.10	NA
2016-11-16 08:12	10	100	99.94	100.87	0.16	0.24	0.93	0.9
2016-11-16 08:27	10	200	199.75	202.31	0.15	0.27	2.56	1.3
2016-11-16 08:42	10	50	50.08	50.50	0.09	0.07	0.42	0.8
2016-11-16 08:57	10	250	249.66	253.19	0.08	0.17	3.53	1.4
2016-11-16 09:12	10	150	149.99	152.07	0.06	0.25	2.08	1.4
2016-11-16 09:27	11	0	0.20	0.01	0.05	0.09	-0.19	NA
2016-11-16 09:42	11	40	39.99	40.37	0.05	0.05	0.38	1.0
2016-11-16 09:57	11	20	20.17	20.29	0.08	0.05	0.12	0.6
2016-11-16 10:10	11	80	79.88	80.73	0.10	0.09	0.85	1.1

Table 6. Same as above for the Thermo Scientific 49i #CM16160046.

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-13 14:03	1	0	0.16	0.76	0.08	0.12	0.60	NA
2016-11-13 14:18	1	90	90.36	90.25	0.26	0.10	-0.11	-0.1
2016-11-13 14:33	1	30	29.99	30.47	0.19	0.19	0.48	1.6
2016-11-13 14:48	1	60	60.20	60.41	0.11	0.15	0.21	0.3
2016-11-13 15:03	1	70	70.17	70.37	0.17	0.07	0.20	0.3
2016-11-13 15:18	1	40	40.17	40.52	0.09	0.06	0.35	0.9
2016-11-13 15:33	1	10	10.41	10.91	0.19	0.12	0.50	4.8
2016-11-13 15:48	1	20	19.85	20.27	0.11	0.19	0.42	2.1
2016-11-13 16:03	1	50	49.99	50.15	0.04	0.11	0.16	0.3
2016-11-13 16:18	1	80	79.97	80.05	0.13	0.12	0.08	0.1
2016-11-13 16:33	2	0	0.14	0.70	0.07	0.09	0.56	NA
2016-11-13 16:48	2	100	100.00	99.91	0.07	0.17	-0.09	-0.1
2016-11-13 17:03	2	200	199.81	199.07	0.12	0.19	-0.74	-0.4
2016-11-13 17:18	2	50	50.07	50.38	0.06	0.14	0.31	0.6
2016-11-13 17:33	2	250	249.70	248.53	0.12	0.18	-1.17	-0.5
2016-11-13 17:48	2	150	150.03	149.63	0.09	0.19	-0.40	-0.3
2016-11-13 18:03	3	0	0.11	0.78	0.08	0.07	0.67	NA
2016-11-13 18:18	3	40	40.04	40.21	0.07	0.19	0.17	0.4
2016-11-13 18:33	3	20	20.10	20.47	0.08	0.08	0.37	1.8
2016-11-13 18:48	3	80	79.93	79.86	0.10	0.07	-0.07	-0.1
2016-11-13 19:18	3	10	10.37	10.75	0.18	0.10	0.38	3.7
2016-11-13 19:33	3	30	29.91	30.09	0.08	0.10	0.18	0.6
2016-11-13 19:33	3	60	59.98	60.16	0.05	0.12	0.18	0.3
2016-11-13 19:48	3	90	89.88	89.92	0.08	0.09	0.04	0.0
2016-11-13 20:18	3	50	49.97	50.17	0.07	0.02	0.20	0.4
2016-11-13 20:33	3	70	69.90	70.01	0.03	0.07	0.11	0.2
2016-11-13 20:48	4	0	0.12	0.62	0.05	0.17	0.50	NA
2016-11-13 21:03	4	75	74.95	74.95	0.06	0.06	0.00	0.0
2016-11-13 21:18	4	225	224.75	223.90	0.13	0.15	-0.85	-0.4
2016-11-13 21:33	4	125	124.88	124.63	0.06	0.13	-0.25	-0.2
2016-11-13 21:48	4	175	174.88	174.43	0.06	0.19	-0.45	-0.3
2016-11-13 22:03	4	25	25.24	25.52	0.05	0.11	0.28	1.1
2016-11-13 22:18	5	0	0.10	0.66	0.05	0.10	0.56	NA
2016-11-13 22:33	5	90	89.85	89.75	0.05	0.13	-0.10	-0.1
2016-11-13 22:48	5	30	29.99	30.33	0.06	0.06	0.34	1.1
2016-11-13 23:03	5	60	59.88	59.96	0.06	0.05	0.08	0.1
2016-11-13 23:18	5	70	69.89	70.05	0.05	0.08	0.16	0.2
2016-11-13 23:33	5	40	39.97	40.16	0.05	0.10	0.19	0.5
2016-11-13 23:48	5	10	10.37	10.76	0.18	0.16	0.39	3.8
2016-11-14 00:03	5	20	19.93	20.35	0.08	0.17	0.42	2.1
2016-11-14 00:18	5	50	49.93	49.96	0.08	0.17	0.03	0.1
2016-11-14 00:33	5	80	79.87	79.83	0.12	0.15	-0.04	-0.1
2016-11-14 00:48	6	0	0.08	0.54	0.10	0.04	0.46	NA
2016-11-14 01:03	6	100	99.86	99.57	0.06	0.07	-0.29	-0.3
2016-11-14 01:18	6	200	199.76	198.91	0.11	0.19	-0.85	-0.4
2016-11-14 01:33	6	50	50.00	50.34	0.14	0.05	0.34	0.7
2016-11-14 01:48	6	250	249.71	248.88	0.07	0.11	-0.83	-0.3

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-14 02:03	6	150	149.92	149.57	0.08	0.18	-0.35	-0.2
2016-11-14 02:18	7	0	0.08	0.58	0.04	0.09	0.50	NA
2016-11-14 02:33	7	40	39.96	40.13	0.05	0.09	0.17	0.4
2016-11-14 02:48	7	20	20.06	20.27	0.14	0.08	0.21	1.0
2016-11-14 03:03	7	80	79.82	79.61	0.09	0.13	-0.21	-0.3
2016-11-14 03:33	7	10	10.43	10.79	0.15	0.17	0.36	3.5
2016-11-14 03:48	7	30	29.89	30.21	0.10	0.10	0.32	1.1
2016-11-14 03:48	7	60	60.01	60.03	0.06	0.08	0.02	0.0
2016-11-14 04:03	7	90	89.84	89.70	0.09	0.08	-0.14	-0.2
2016-11-14 04:33	7	50	49.99	50.12	0.10	0.09	0.13	0.3
2016-11-14 04:48	7	70	70.03	69.96	0.06	0.11	-0.07	-0.1
2016-11-14 05:03	8	0	0.17	0.52	0.07	0.09	0.35	NA
2016-11-14 05:18	8	75	74.92	74.77	0.10	0.10	-0.15	-0.2
2016-11-14 05:33	8	225	224.75	223.94	0.14	0.21	-0.81	-0.4
2016-11-14 05:48	8	125	125.08	124.69	0.09	0.15	-0.39	-0.3
2016-11-14 06:03	8	175	174.78	174.36	0.06	0.12	-0.42	-0.2
2016-11-14 06:18	8	25	25.25	25.40	0.15	0.13	0.15	0.6
2016-11-14 06:33	9	0	0.22	0.60	0.09	0.10	0.38	NA
2016-11-14 06:48	9	90	89.89	89.75	0.08	0.08	-0.14	-0.2
2016-11-14 07:03	9	30	30.03	30.20	0.07	0.07	0.17	0.6
2016-11-14 07:18	9	60	59.92	60.07	0.16	0.09	0.15	0.3
2016-11-14 07:33	9	70	69.91	69.96	0.05	0.13	0.05	0.1
2016-11-14 07:48	9	40	40.02	40.16	0.11	0.09	0.14	0.3
2016-11-14 08:03	9	10	10.31	10.69	0.11	0.12	0.38	3.7
2016-11-14 08:18	9	20	19.88	20.35	0.08	0.14	0.47	2.4
2016-11-14 08:33	9	50	49.86	49.93	0.07	0.08	0.07	0.1
2016-11-14 08:48	9	80	79.84	79.84	0.08	0.09	0.00	0.0
2016-11-14 09:03	10	0	0.20	0.60	0.06	0.06	0.40	NA
2016-11-14 09:18	10	100	99.83	99.71	0.11	0.17	-0.12	-0.1
2016-11-14 09:32	10	200	199.62	199.33	0.05	0.06	-0.29	-0.1

Table 7. Same as above for the Thermo Scientific 49i #0806127828.

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-15 12:56	1	0	0.02	0.08	0.01	0.09	0.06	NA
2016-11-15 13:13	1	90	89.92	90.78	0.05	0.16	0.86	1.0
2016-11-15 13:27	1	30	30.06	30.31	0.04	0.04	0.25	0.8
2016-11-15 13:41	1	60	59.95	60.79	0.08	0.07	0.84	1.4
2016-11-15 13:57	1	70	70.01	70.76	0.11	0.16	0.75	1.1
2016-11-15 14:12	1	40	40.05	40.57	0.03	0.27	0.52	1.3
2016-11-15 14:25	1	10	10.51	10.90	NA	NA	0.39	3.7
2016-11-15 14:42	1	20	19.93	19.97	0.08	0.22	0.04	0.2
2016-11-15 15:12	1	80	79.86	80.79	0.08	0.24	0.93	1.2
2016-11-15 15:27	2	0	0.14	0.10	0.05	0.12	-0.04	NA
2016-11-15 15:42	2	100	100.00	100.93	0.07	0.17	0.93	0.9
2016-11-15 15:57	2	200	199.81	202.21	0.15	0.20	2.40	1.2

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-15 16:12	2	50	50.09	50.81	0.10	0.12	0.72	1.4
2016-11-15 16:27	2	250	249.82	252.65	0.10	0.41	2.83	1.1
2016-11-15 16:42	2	150	149.92	151.82	0.09	0.16	1.90	1.3
2016-11-15 16:57	3	0	0.17	0.15	0.09	0.16	-0.02	NA
2016-11-15 17:12	3	40	40.02	40.51	0.09	0.26	0.49	1.2
2016-11-15 17:26	3	20	20.14	20.23	0.08	0.10	0.09	0.4
2016-11-15 17:41	3	80	80.05	81.05	0.19	0.13	1.00	1.2
2016-11-15 18:12	3	10	10.39	10.60	0.09	0.26	0.21	2.0
2016-11-15 18:27	3	30	29.91	30.40	0.06	0.16	0.49	1.6
2016-11-15 18:38	3	60	59.95	60.68	0.01	0.25	0.73	1.2
2016-11-15 18:41	3	90	89.92	90.98	0.05	0.12	1.06	1.2
2016-11-15 19:12	3	50	49.97	50.61	0.04	0.03	0.64	1.3
2016-11-15 19:27	3	70	69.91	70.63	0.09	0.05	0.72	1.0
2016-11-15 19:42	4	0	0.14	0.09	0.05	0.07	-0.05	NA
2016-11-15 19:57	4	75	74.96	75.95	0.11	0.16	0.99	1.3
2016-11-15 20:11	4	225	224.68	227.40	0.17	0.20	2.72	1.2
2016-11-15 20:27	4	125	124.94	126.41	0.10	0.17	1.47	1.2
2016-11-15 20:57	4	25	25.26	25.59	0.04	0.25	0.33	1.3
2016-11-15 21:12	5	0	0.18	0.21	0.11	0.10	0.03	NA
2016-11-15 21:27	5	90	89.92	91.16	0.15	0.18	1.24	1.4
2016-11-15 21:41	5	30	30.08	30.74	0.10	0.16	0.66	2.2
2016-11-15 21:55	5	60	59.89	60.59	0.13	0.15	0.70	1.2
2016-11-15 22:12	5	70	70.02	70.87	0.14	0.10	0.85	1.2
2016-11-15 22:27	5	40	40.00	40.58	0.07	0.13	0.58	1.4
2016-11-15 22:42	5	10	10.37	10.52	0.14	0.16	0.15	1.4
2016-11-15 22:57	5	20	19.95	20.06	0.10	0.09	0.11	0.6
2016-11-15 23:11	5	50	49.97	50.56	0.09	0.10	0.59	1.2
2016-11-15 23:27	5	80	80.06	81.09	0.10	0.02	1.03	1.3
2016-11-15 23:42	6	0	0.17	0.08	0.16	0.12	-0.09	NA
2016-11-15 23:57	6	100	99.90	101.13	0.13	0.02	1.23	1.2
2016-11-16 00:12	6	200	199.72	202.28	0.03	0.25	2.56	1.3
2016-11-16 00:27	6	50	50.11	50.56	0.11	0.19	0.45	0.9
2016-11-16 00:43	6	250	249.68	252.89	NA	NA	3.21	1.3
2016-11-16 00:57	6	150	150.01	152.17	0.12	0.22	2.16	1.4
2016-11-16 01:12	7	0	0.18	0.10	0.10	0.17	-0.08	NA
2016-11-16 01:27	7	40	40.06	40.49	0.04	0.08	0.43	1.1
2016-11-16 01:42	7	20	20.14	20.35	0.05	0.12	0.21	1.0
2016-11-16 01:56	7	80	79.90	80.79	0.02	0.26	0.89	1.1
2016-11-16 02:27	7	10	10.36	10.55	0.17	0.19	0.19	1.8
2016-11-16 02:42	7	30	29.93	30.38	0.13	0.23	0.45	1.5
2016-11-16 02:54	7	60	59.99	60.89	0.07	0.21	0.90	1.5
2016-11-16 02:57	7	90	89.90	91.16	0.10	0.13	1.26	1.4
2016-11-16 03:27	7	50	50.05	50.68	0.08	0.29	0.63	1.3
2016-11-16 03:41	7	70	69.91	70.77	0.02	0.04	0.86	1.2
2016-11-16 03:56	8	0	0.22	0.22	0.09	0.11	0.00	NA
2016-11-16 04:12	8	75	74.88	75.80	0.08	0.10	0.92	1.2
2016-11-16 04:27	8	225	224.67	227.70	0.13	0.18	3.03	1.3
2016-11-16 04:42	8	125	125.02	126.61	0.12	0.19	1.59	1.3

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-16 04:57	8	175	174.90	177.15	0.11	0.21	2.25	1.3
2016-11-16 05:12	8	25	25.38	25.65	0.04	0.17	0.27	1.1
2016-11-16 05:26	9	0	0.17	0.25	0.09	0.19	0.08	NA
2016-11-16 05:42	9	90	89.92	91.05	0.15	0.12	1.13	1.3
2016-11-16 05:57	9	30	30.14	30.39	0.07	0.14	0.25	0.8
2016-11-16 06:12	9	60	59.99	60.90	0.08	0.16	0.91	1.5
2016-11-16 06:27	9	70	70.00	70.85	0.03	0.22	0.85	1.2
2016-11-16 06:43	9	40	40.08	40.65	0.01	0.13	0.57	1.4
2016-11-16 06:56	9	10	10.44	10.68	0.19	0.26	0.24	2.3
2016-11-16 07:12	9	20	19.93	20.22	0.07	0.07	0.29	1.5
2016-11-16 07:27	9	50	49.77	50.66	0.12	0.15	0.89	1.8
2016-11-16 07:42	9	80	79.86	80.83	0.13	0.31	0.97	1.2
2016-11-16 07:57	10	0	0.19	0.21	0.09	0.16	0.02	NA
2016-11-16 08:11	10	100	100.17	101.31	NA	NA	1.14	1.1
2016-11-16 08:26	10	200	199.64	202.45	0.05	0.33	2.81	1.4
2016-11-16 08:42	10	50	50.07	50.71	0.11	0.24	0.64	1.3
2016-11-16 08:57	10	250	249.66	252.87	0.08	0.22	3.21	1.3
2016-11-16 09:12	10	150	149.99	151.94	0.06	0.22	1.95	1.3
2016-11-16 09:27	11	0	0.23	0.26	0.05	0.27	0.03	NA
2016-11-16 09:43	11	40	40.01	40.63	0.05	0.02	0.62	1.5
2016-11-16 10:10	11	80	79.88	80.95	0.10	0.03	1.07	1.3

Table 8. Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the CGO ozone analyser (OA) Thermo Scientific 49C #78058-387 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-14 12:39	1	0	0.16	0.03	0.15	0.12	-0.13	NA
2016-11-14 12:54	1	40	40.04	41.49	0.09	0.04	1.45	3.6
2016-11-14 13:09	1	20	20.12	20.77	0.06	0.13	0.65	3.2
2016-11-14 13:24	1	80	79.91	83.01	0.07	0.12	3.10	3.9
2016-11-14 13:54	1	10	10.37	10.77	0.20	0.11	0.40	3.9
2016-11-14 14:09	1	30	29.93	31.06	0.12	0.03	1.13	3.8
2016-11-14 14:09	1	60	59.97	62.26	0.12	0.12	2.29	3.8
2016-11-14 14:24	1	90	89.87	93.60	0.11	0.16	3.73	4.2
2016-11-14 14:54	1	50	50.09	51.96	0.04	0.14	1.87	3.7
2016-11-14 15:09	1	70	70.07	72.80	0.07	0.07	2.73	3.9
2016-11-14 15:24	2	0	0.15	0.04	0.08	0.05	-0.11	NA
2016-11-14 15:39	2	75	75.08	78.02	0.07	0.13	2.94	3.9
2016-11-14 15:54	2	225	224.74	234.12	0.06	0.11	9.38	4.2
2016-11-14 16:09	2	125	124.94	130.07	0.02	0.21	5.13	4.1
2016-11-14 16:24	2	175	174.80	181.97	0.12	0.17	7.17	4.1
2016-11-14 16:39	2	25	25.21	26.27	0.05	0.08	1.06	4.2
2016-11-14 16:54	3	0	0.09	-0.02	0.09	0.06	-0.11	NA
2016-11-14 17:09	3	90	89.97	93.52	0.09	0.06	3.55	3.9
2016-11-14 17:24	3	30	30.11	31.16	0.11	0.10	1.05	3.5

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-14 17:39	3	60	59.96	62.29	0.06	0.13	2.33	3.9
2016-11-14 17:54	3	70	69.99	72.65	0.09	0.08	2.66	3.8
2016-11-14 18:09	3	40	40.11	41.46	0.09	0.14	1.35	3.4
2016-11-14 18:24	3	10	10.21	10.52	0.11	0.14	0.31	3.0
2016-11-14 18:39	3	20	19.89	20.56	0.09	0.07	0.67	3.4
2016-11-14 18:54	3	50	49.91	51.93	0.12	0.11	2.02	4.0
2016-11-14 19:09	3	80	79.88	83.02	0.14	0.05	3.14	3.9
2016-11-14 19:24	4	0	0.19	0.00	0.09	0.03	-0.19	NA
2016-11-14 19:39	4	100	99.87	103.92	0.11	0.17	4.05	4.1
2016-11-14 19:54	4	200	199.71	208.03	0.12	0.05	8.32	4.2
2016-11-14 20:09	4	50	50.09	52.01	0.07	0.11	1.92	3.8
2016-11-14 20:24	4	250	249.79	259.95	0.09	0.17	10.16	4.1
2016-11-14 20:39	4	150	149.95	156.04	0.12	0.12	6.09	4.1
2016-11-14 20:54	5	0	0.10	-0.03	0.03	0.04	-0.13	NA
2016-11-14 21:09	5	40	40.03	41.45	0.11	0.06	1.42	3.5
2016-11-14 21:24	5	20	20.06	20.62	0.08	0.08	0.56	2.8
2016-11-14 21:39	5	80	79.90	83.05	0.04	0.16	3.15	3.9
2016-11-14 22:09	5	10	10.33	10.72	0.22	0.14	0.39	3.8
2016-11-14 22:24	5	30	29.95	31.04	0.12	0.18	1.09	3.6
2016-11-14 22:24	5	60	60.00	62.44	0.11	0.11	2.44	4.1
2016-11-14 22:39	5	90	89.91	93.52	0.09	0.11	3.61	4.0
2016-11-14 23:09	5	50	49.99	51.91	0.05	0.04	1.92	3.8
2016-11-14 23:24	5	70	70.03	72.85	0.08	0.05	2.82	4.0
2016-11-14 23:39	6	0	0.04	-0.06	0.09	0.12	-0.10	NA
2016-11-14 23:54	6	75	74.95	77.91	0.12	0.10	2.96	3.9
2016-11-15 00:09	6	225	224.74	233.85	0.06	0.13	9.11	4.1
2016-11-15 00:24	6	125	124.92	130.04	0.10	0.03	5.12	4.1
2016-11-15 00:39	6	175	174.84	182.03	0.06	0.16	7.19	4.1
2016-11-15 00:54	6	25	25.22	26.24	0.07	0.06	1.02	4.0
2016-11-15 01:09	7	0	0.14	-0.07	0.08	0.16	-0.21	NA
2016-11-15 01:24	7	90	89.96	93.56	0.04	0.08	3.60	4.0
2016-11-15 01:39	7	30	30.04	31.08	0.13	0.10	1.04	3.5
2016-11-15 01:54	7	60	59.96	62.29	0.11	0.10	2.33	3.9
2016-11-15 02:09	7	70	69.95	72.68	0.08	0.14	2.73	3.9
2016-11-15 02:24	7	40	40.04	41.64	0.07	0.08	1.60	4.0
2016-11-15 02:39	7	10	10.30	10.53	0.11	0.14	0.23	2.2
2016-11-15 02:54	7	20	19.97	20.61	0.13	0.11	0.64	3.2
2016-11-15 03:09	7	50	49.90	51.80	0.07	0.12	1.90	3.8
2016-11-15 03:24	7	80	79.81	83.06	0.11	0.13	3.25	4.1
2016-11-15 03:39	8	0	0.16	0.07	0.07	0.10	-0.09	NA
2016-11-15 03:54	8	100	99.94	103.98	0.02	0.09	4.04	4.0
2016-11-15 04:09	8	200	199.75	208.00	0.13	0.14	8.25	4.1
2016-11-15 04:24	8	50	50.04	51.92	0.05	0.09	1.88	3.8
2016-11-15 04:39	8	250	249.71	260.02	0.08	0.18	10.31	4.1
2016-11-15 04:54	8	150	150.04	156.14	0.14	0.15	6.10	4.1
2016-11-15 05:09	9	0	0.14	0.00	0.08	0.08	-0.14	NA
2016-11-15 05:24	9	40	40.11	41.50	0.09	0.14	1.39	3.5
2016-11-15 05:39	9	20	20.15	20.84	0.13	0.11	0.69	3.4

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2016-11-15 05:54	9	80	79.96	83.00	0.07	0.07	3.04	3.8
2016-11-15 06:24	9	10	10.38	10.70	0.14	0.13	0.32	3.1
2016-11-15 06:39	9	30	29.99	31.00	0.07	0.07	1.01	3.4
2016-11-15 06:39	9	60	60.05	62.33	0.11	0.08	2.28	3.8
2016-11-15 06:54	9	90	89.90	93.42	0.10	0.03	3.52	3.9
2016-11-15 07:24	9	50	50.03	51.95	0.07	0.10	1.92	3.8
2016-11-15 07:39	9	70	70.03	72.70	0.03	0.11	2.67	3.8
2016-11-15 07:54	10	0	0.15	-0.03	0.14	0.07	-0.18	NA
2016-11-15 08:09	10	75	74.96	77.84	0.09	0.09	2.88	3.8
2016-11-15 08:24	10	225	224.61	233.87	0.06	0.20	9.26	4.1
2016-11-15 08:39	10	125	124.98	129.97	0.09	0.12	4.99	4.0
2016-11-15 08:54	10	175	174.86	181.99	0.12	0.12	7.13	4.1
2016-11-15 09:09	10	25	25.26	26.26	0.07	0.04	1.00	4.0
2016-11-15 09:24	11	0	0.09	0.08	0.04	0.12	-0.01	NA
2016-11-15 09:39	11	90	89.90	93.52	0.12	0.16	3.62	4.0
2016-11-15 09:54	11	30	30.04	31.13	0.13	0.08	1.09	3.6
2016-11-15 10:09	11	60	59.97	62.29	0.12	0.13	2.32	3.9
2016-11-15 10:24	11	70	69.90	72.73	0.06	0.11	2.83	4.0
2016-11-15 10:39	11	40	39.96	41.46	0.06	0.07	1.50	3.8
2016-11-15 10:54	11	10	10.36	10.69	0.17	0.12	0.33	3.2
2016-11-15 11:09	11	20	19.92	20.52	0.05	0.16	0.60	3.0
2016-11-15 11:24	11	50	49.92	51.74	0.12	0.12	1.82	3.6
2016-11-15 11:39	11	80	79.80	82.95	0.30	0.48	3.15	3.9

Greenhouse Gas and Carbon Monoxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given further below.

Results

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

Table 9. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CSIRO GASLAB RGA-3 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-11-13 00:00:00)	160926_FB03367	85.8	0.1	85.7	0.1	2	-0.1	-0.1
(16-11-12 12:00:00)	160922_FA01469	52.4	0.2	53.0	0.3	2	0.6	1.2
(16-11-17 00:00:00)	160922_FB03376	67.4	0.4	68.3	0.6	3	1.0	1.5
(16-11-16 16:00:00)	160825_FB03382	170.9	0.2	168.6	0.3	3	-2.2	-1.3
(16-11-18 00:00:00)	160825_FB03887	190.1	0.2	188.1	0.3	3	-1.9	-1.0
(16-11-12 12:00:00)	160922_FF31496	44.8	0.1	45.8	0.0	2	1.0	2.2

Table 10. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CSIRO GASLAB GC/FID instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-11-13 00:00:00)	160926_FB03367	1855.06	0.09	1854.68	0.89	2	-0.38	-0.02
(16-11-12 12:00:00)	160922_FA01469	1736.60	0.18	1736.66	0.71	2	0.07	0.00
(16-11-17 00:00:00)	160922_FB03376	1776.15	0.07	1777.51	0.36	3	1.36	0.08
(16-11-16 16:00:00)	160825_FB03382	1918.64	0.13	1917.59	1.53	3	-1.05	-0.05
(16-11-18 00:00:00)	160825_FB03887	2027.18	0.17	2028.06	1.85	3	0.88	0.04
(16-11-12 12:00:00)	160922_FF31496	1726.74	0.09	1727.28	3.05	2	0.54	0.03

Table 11. CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CSIRO GASLAB GC/FID instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(16-11-13 00:00:00)	160926_FB03367	412.67	0.04	412.67	0.01	2	0.00	0.00
(16-11-12 12:00:00)	160922_FA01469	392.88	0.12	392.87	0.01	2	-0.01	0.00
(16-11-17 00:00:00)	160922_FB03376	400.02	0.04	400.07	0.04	3	0.05	0.01
(16-11-16 16:00:00)	160825_FB03382	412.36	0.04	412.29	0.05	3	-0.07	-0.02
(16-11-18 00:00:00)	160825_FB03887	457.61	0.05	457.52	0.06	3	-0.09	-0.02
(16-11-12 12:00:00)	160922_FF31496	397.37	0.12	397.40	0.02	2	0.03	0.01

Table 12. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CGO GC/MRD instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale). Note that CGO values are on the CSIRO-94 CO scale.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(17-03-02 02:38:00)	160825_FB03382	170.9	0.2	171.1	0.7	8	0.3	0.2
(17-03-06 03:19:00)	160825_FB03887	190.1	0.2	192.4	0.8	10	2.4	1.2
(17-03-03 03:06:00)	160922_FA01469	52.4	0.2	50.4	0.3	8	-2.0	-3.8
(17-03-07 02:49:00)	160922_FB03376	67.4	0.4	66.6	0.5	10	-0.8	-1.2
(17-02-28 03:09:00)	160922_FF31496	44.8	0.1	43.6	0.7	10	-1.1	-2.5
(17-03-01 02:54:00)	160926_FB03367	85.8	0.1	85.0	0.4	8	-0.8	-0.9

Table 13. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CGO GC/FID instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale). Note that CGO values refer to the Tohoku University scale.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(17-03-02 02:38:00)	160825_FB03382	1918.64	0.13	1919.40	1.44	10	0.76	0.04
(17-03-06 03:19:00)	160825_FB03887	2027.18	0.17	2028.26	1.07	10	1.08	0.05
(17-03-03 03:06:00)	160922_FA01469	1736.60	0.18	1736.57	0.71	10	-0.03	0.00
(17-03-07 03:04:33)	160922_FB03376	1776.15	0.07	1775.80	0.55	9	-0.35	-0.02
(17-02-28 03:19:00)	160922_FF31496	1726.74	0.09	1726.61	0.64	8	-0.13	-0.01
(17-03-01 02:49:00)	160926_FB03367	1855.06	0.09	1855.38	0.69	10	0.32	0.02

Table 14. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CSIRO GC/FID instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale). Note that CGO values refer to the SIO-16 scale.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(17-03-02 03:03:00)	160825_FB03382	318.14	0.02	318.61	0.09	8	0.47	0.15
(17-03-06 03:24:00)	160825_FB03887	331.67	0.03	332.11	0.09	8	0.44	0.13
(17-03-03 02:46:00)	160922_FA01469	320.14	0.05	320.75	0.12	9	0.61	0.19
(17-03-07 03:09:00)	160922_FB03376	327.39	0.06	327.94	0.14	9	0.55	0.17
(17-02-28 04:09:00)	160922_FF31496	323.54	0.10	324.13	0.03	7	0.59	0.18
(17-03-01 03:09:00)	160926_FB03367	339.80	0.09	340.15	0.17	9	0.35	0.10

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: Thermo Scientific 49C-PS #54509-300, BKG -0.3, COEF 1.009

Zero air source: Pressurized air - Dryer – Breitfuss zero air generator – Purafil – charcoal – outlet filter

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 15. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 31). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (ppb)} = ([TS] + 0.15 \text{ ppb}) / 1.0024 \quad (6a)$$

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

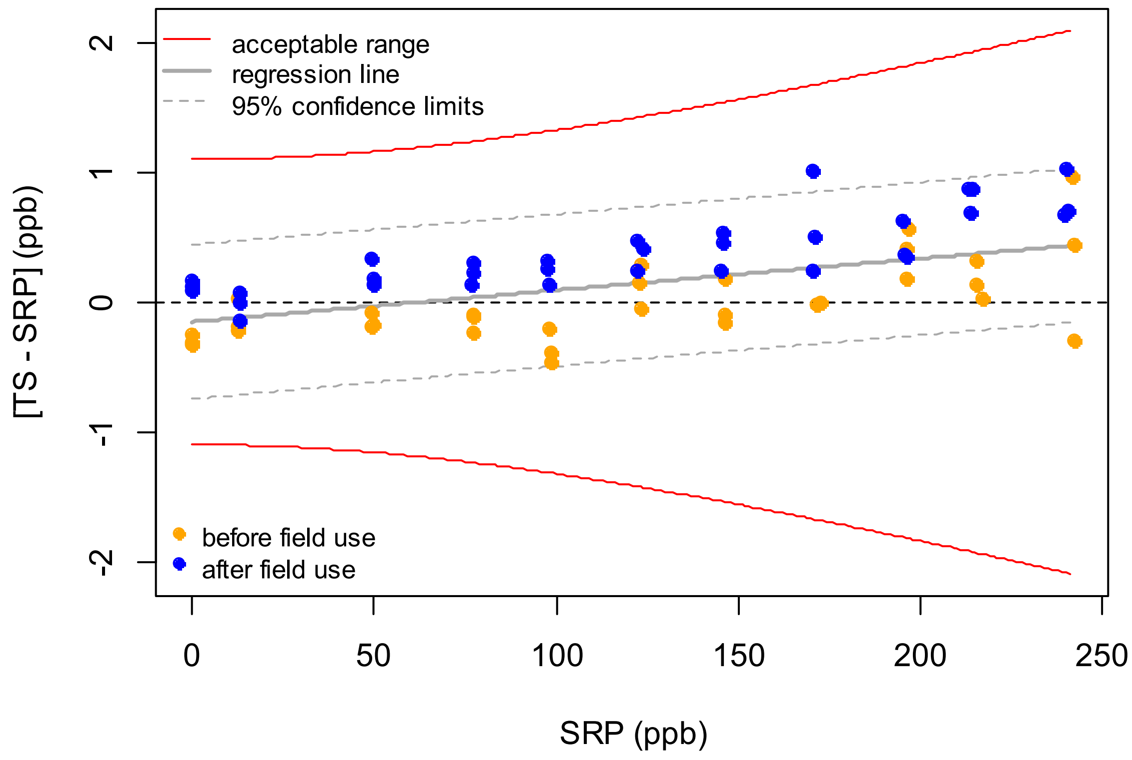

Figure 31. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 15. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2016-09-21	1	100	98.30	0.36	98.10	0.18
2016-09-21	1	75	77.10	0.13	76.87	0.07
2016-09-21	1	215	217.16	0.35	217.18	0.09
2016-09-21	1	0	-0.02	0.34	-0.35	0.06
2016-09-21	1	175	172.62	0.38	172.61	0.18
2016-09-21	1	125	122.81	0.32	122.96	0.08
2016-09-21	1	10	12.47	0.24	12.50	0.17
2016-09-21	1	50	49.71	0.25	49.53	0.09
2016-09-21	1	195	196.09	0.28	196.50	0.16
2016-09-21	1	145	146.23	0.30	146.41	0.08
2016-09-21	1	240	241.87	0.44	242.32	0.14
2016-09-21	2	75	77.28	0.47	77.18	0.07
2016-09-21	2	0	0.09	0.25	-0.22	0.07
2016-09-21	2	215	215.43	0.36	215.76	0.23
2016-09-21	2	125	123.24	0.26	123.19	0.11
2016-09-21	2	170	171.73	0.22	171.71	0.13
2016-09-21	2	195	195.90	0.30	196.08	0.06
2016-09-21	2	15	12.51	0.21	12.29	0.09
2016-09-21	2	50	49.51	0.20	49.42	0.08
2016-09-21	2	100	98.39	0.27	98.00	0.09
2016-09-21	2	145	146.26	0.13	146.17	0.06
2016-09-21	2	240	241.98	0.37	241.69	0.18
2016-09-21	3	75	76.97	0.25	76.86	0.10
2016-09-21	3	170	171.64	0.27	171.63	0.09
2016-09-21	3	15	12.53	0.20	12.35	0.10
2016-09-21	3	100	98.67	0.30	98.20	0.07
2016-09-21	3	215	215.42	0.28	215.56	0.15
2016-09-21	3	145	146.29	0.17	146.13	0.07
2016-09-21	3	50	49.38	0.38	49.20	0.13
2016-09-21	3	0	0.02	0.15	-0.23	0.14
2016-09-21	3	195	196.82	0.27	197.38	0.20
2016-09-21	3	125	123.20	0.22	123.49	0.09
2016-09-21	3	240	241.44	0.46	242.41	0.16
2017-05-04	4	75	77.05	0.29	77.28	0.10
2017-05-04	4	145	145.67	0.38	146.21	0.15
2017-05-04	4	15	13.13	0.23	12.98	0.12
2017-05-04	4	195	196.03	0.17	196.38	0.40
2017-05-04	4	170	170.96	0.18	171.47	0.13
2017-05-04	4	95	97.42	0.26	97.69	0.12
2017-05-04	4	50	49.82	0.25	49.95	0.12
2017-05-04	4	0	-0.06	0.35	0.06	0.15
2017-05-04	4	125	123.60	0.32	124.01	0.10
2017-05-04	4	215	214.31	0.25	215.18	0.19
2017-05-04	4	240	240.48	0.24	241.18	0.20
2017-05-04	5	75	76.97	0.38	77.28	0.13
2017-05-04	5	15	13.19	0.30	13.19	0.08
2017-05-04	5	50	49.86	0.20	50.04	0.13
2017-05-04	5	100	97.72	0.25	98.03	0.06
2017-05-04	5	195	195.03	0.26	195.66	0.12
2017-05-04	5	120	122.22	0.20	122.46	0.16

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2017-05-04	5	170	170.43	0.29	170.68	0.09
2017-05-04	5	145	145.19	0.53	145.43	0.14
2017-05-04	5	0	0.06	0.29	0.15	0.07
2017-05-04	5	215	213.84	0.23	214.53	0.36
2017-05-04	5	240	239.82	0.51	240.84	0.19
2017-05-04	6	120	122.06	0.28	122.53	0.15
2017-05-04	6	170	170.13	0.68	171.15	0.08
2017-05-04	6	215	213.20	0.22	214.07	0.13
2017-05-04	6	50	49.26	0.29	49.60	0.12
2017-05-04	6	0	0.02	0.18	0.19	0.09
2017-05-04	6	100	98.09	0.27	98.23	0.12
2017-05-04	6	195	195.35	0.34	195.72	0.18
2017-05-04	6	15	13.01	0.16	13.08	0.13
2017-05-04	6	145	145.66	0.56	146.13	0.15
2017-05-04	6	75	76.96	0.21	77.09	0.12
2017-05-04	6	240	239.51	0.48	240.19	0.16

#the level is only indicative.

Greenhouse gases and carbon monoxide

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

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

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

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

Table 16 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 17, and Figure 32 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS.

Table 16. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO (ppb)	CH_4 (ppb)	N_2O (ppb)	CO_2 (ppm)
CC339478	463.76	2485.25	357.19	484.39
CB11499	141.03	1933.77	329.15	407.33
CB11485	110.88	1844.78	328.46	394.30

Table 17. 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)
160922_FF31496	44.76	0.07	1726.74	0.09	397.37	0.12	323.54	0.10
160922_FA01469	52.39	0.19	1736.60	0.18	392.88	0.12	320.14	0.05
160922_FB03376	67.36	0.37	1776.15	0.07	400.02	0.04	327.39	0.06
160926_FB03367	85.81	0.14	1855.06	0.09	412.67	0.04	339.80	0.09
160825_FB03382	170.88	0.23	1918.64	0.13	412.36	0.04	318.14	0.02
160825_FB03887	190.08	0.19	2027.18	0.17	457.61	0.05	331.67	0.03

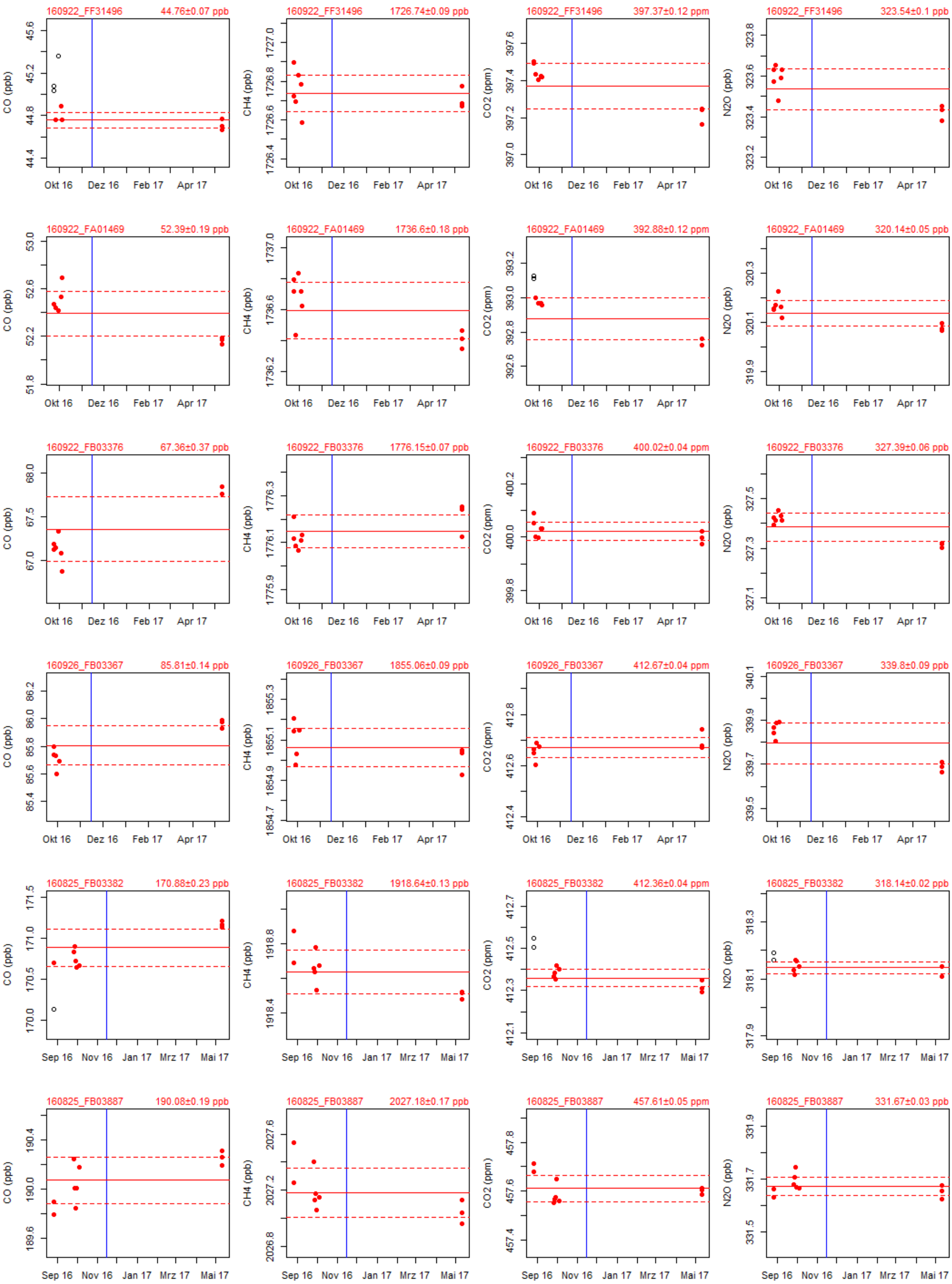

Figure 32. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

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LIST OF ABBREVIATIONS

AGAGE	Advanced Global Atmospheric Gases Experiment
ANSTO	Australian Nuclear Science and Technology Organisation
a.s.l	above sea level
BKG	Background
BoM	Bureau of Meteorology
CGO	Cape Grim GAW Station
COEF	Coefficient
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DQO	Data Quality Objective
ECD	Electron Capture Detector
eDQO	Extended Data Quality Objective
ESRL	Earth System and Research Laboratory
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatography
GHG	Greenhouse Gases
LS	Laboratory Standard
NA	Not Applicable
NIST	National Institute of Standards and Technology
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WCC-N_2O	World Calibration Centre for N_2O
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard