Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Materials Science & Technology
Laboratory Air Pollution / Environmental Technology

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Submitted to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, METHANE, CARBON DIOXIDE AND CARBON MONOXIDE AT THE GLOBAL GAW STATION CAPE POINT SOUTH AFRICA, MARCH 2011

Submitted by
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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The third system and performance audit at the Global GAW station Cape Point was conducted by WCC-Empa[1] from 16 through 23 March 2011 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Cape Point (CPT) atmospheric research station is 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. Beat Schwarzenbach	Empa Dübendorf, National Air Pollution Monitoring Network
Mr. Ernst-Günther Brunke	SAWS, Station Manager, Senior Scientist, SAG GHG member
Mr. Casper Labuschagne	SAWS, Senior Scientist
Mr. Bhawoodien Parker	SAWS, Senior Scientist
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 assessment criteria for the ozone comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer et al.*, 2000; *Klausen et al.*, 2003].

The report is distributed to the SAWS Cape Point, the CPT twinning partner from the Institute for Meteorology and Climate Research, Atmospheric Environmental Research (IMK-IFU) 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, serious and critical and are complemented with a priority (*** indicating highest priority) and a suggested completion date.

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, www.gaw.empa.ch/gawsis). No significant changes were made since the last audit by WCC-Empa.

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.

[1] WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. 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.

Recommendation 1 (, minor, 2012)**
WMO GAW recommends that data is disseminated as speedily as possible. Information provided in NRT can enhance the value of the data especially given the fact that newer instruments are able to provide high resolution data that goes beyond evaluating long term trends. To meet theses needs, the bandwidth of the internet connection needs to be increased.

Station Management and Operation

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). Retirement of the station manager is expected soon, and it is very important that the knowledge will be transferred to his successor.

Recommendation 2 (*, critical, ongoing)**
The current station management system with responsibilities of both technical and scientific staff is regarded as adequate and should be continued. However, with the ongoing expansion of the measuring programme at the SAWS Cape Point GAW station, especially over the recent few years, the current staff situation warrants a commensurate expansion. At least one new scientific post should be created for the programme in order to adhere to the QA/QC requirements of the international community. Furthermore, it should be ensured that scientific networking continues in future, given the large number of collaborative programmes, with regular meetings, workshops and conferences.

Air Inlet Systems

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). An additional ozone analyser was purchased following a recommendation made after the last audit by WCC-Empa. Data of the 4m inlet is considered for data submission.

Standards. A TEI49i-PS ozone calibrator was purchased following a recommendation made after the last audit by 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 are summarised below. All three ozone analysers and the station calibrator were compared against the WCC-Empa ozone reference. All instruments had severe problems, which were mainly caused by water damage and mistakes during instrument operation. The following problems were identified:

TEI 49iPS (station calibrator): The pressure correction was set to 'OFF'. Unfortunately this compensated some of the problems of the other analysers during the comparisons made by CPT staff, since the TEI 49i-PS readings were lower than the actual ozone delivery. The pressure and temperature correc-

	tion settings are not recorded by the instrument, and were also not part of the regular checks made at CPT.
TEI 49C (main analyser):	The instrument suffered from water damage; it was compared in its original state and after complete disassembling and cleaning. The analyser is working but needs to be serviced.
TEI 49i (backup analyser):	Also damaged by water. The instrument was disassembled, dried and cleaned by CPT staff before the audit. During re-assembling, a gasket was placed in a wrong position, which caused a leak. The instrument was compared in the original state and after correct re-assembling. The analyser was working after repair but the results were not satisfactory for this instrument type. The analyser should be serviced; one of the flow sensors is not working.
TEI 49 (backup analyser):	A large bias was found between WCC-Empa and this analyser. Since this instrument type has got stability issues compared to the newer C- and i-series analyser, repair is not recommended, and the analyser should be decommissioned.

Recommendation 3 (*, critical, immediately)**
The pressure and temperature correction must always be on for all ozone instruments. It is recommended to record this along with the calibration settings on the weekly check lists.

The results of the comparison made at Cape Point are summarised below. The data was acquired by both the WCC-Empa and the station data acquisition system. Data of the WCC-Empa DAQ was used for data evaluation, and the data was corrected using the correction function provided by CPT based on their calibrations and zero checks. 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] + 0.5 ppb) / 1.004 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.68e-05 * X_{O3}^2) (1b)

TEI 49C #5226513044 (BKG -0.5 ppb, SPAN 1.015) – main analyser, before cleaning:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 1.8 ppb) / 0.9830 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.5 ppb^2 + 2.73e-05 * X_{O3}^2) (1d)

After cleaning:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 0.3 ppb) / 0.9861 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.67e-05 * X_{O3}^2) (1f)

TEI 49i #802426999 (BKG 0.0 ppb, SPAN 1.038) – backup analyser, before repair:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] - 5.1 ppb) / 0.9496 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (8.0 ppb^2 + 2.92e-05 * X_{O3}^2) (1h)

After repair:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] – 1.9 ppb) / 0.9870 (1i)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.67e-05 * X_{O3}^2) (1j)

TEI 49 #51594-288 (ZERO 56 ppb, SPAN 507) – backup analyser:

Unbiased O_3 mole fraction (ppb): X_{O3} (ppb) = ([OA] + 11.3 ppb) / 0.9173 (1k)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (3.2 ppb^2 + 3.32e-05 * X_{O3}^2) (1l)

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

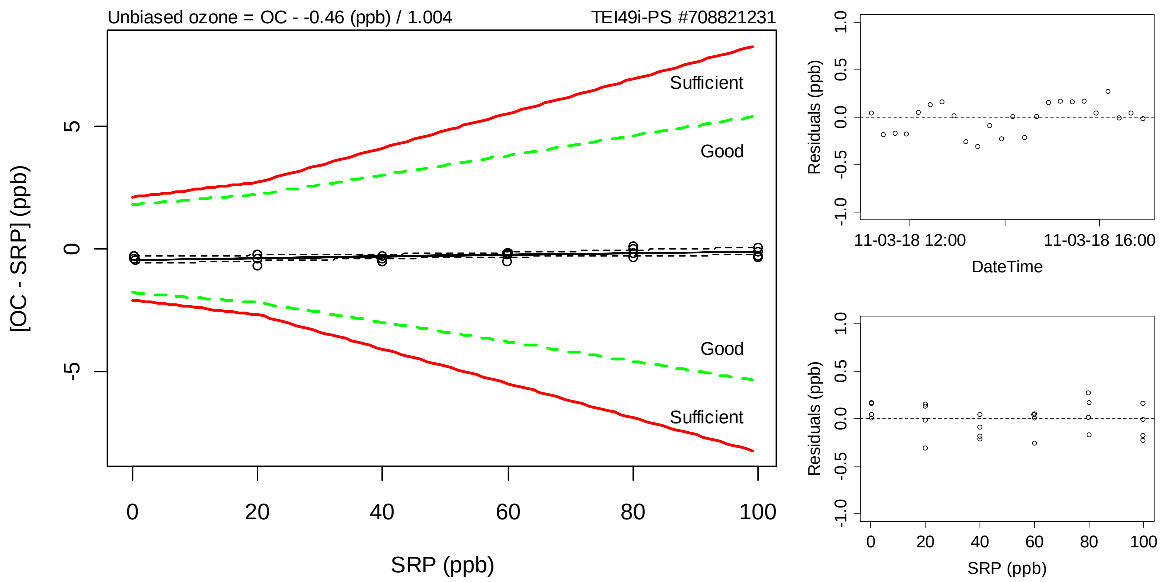

Figure 1. Left: Bias of the CPT ozone calibrator (TEI 49i-PS #7088211231) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining ‘good’ and ‘sufficient’ agreement according to GAW assessment criteria are delimited by green and red 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).

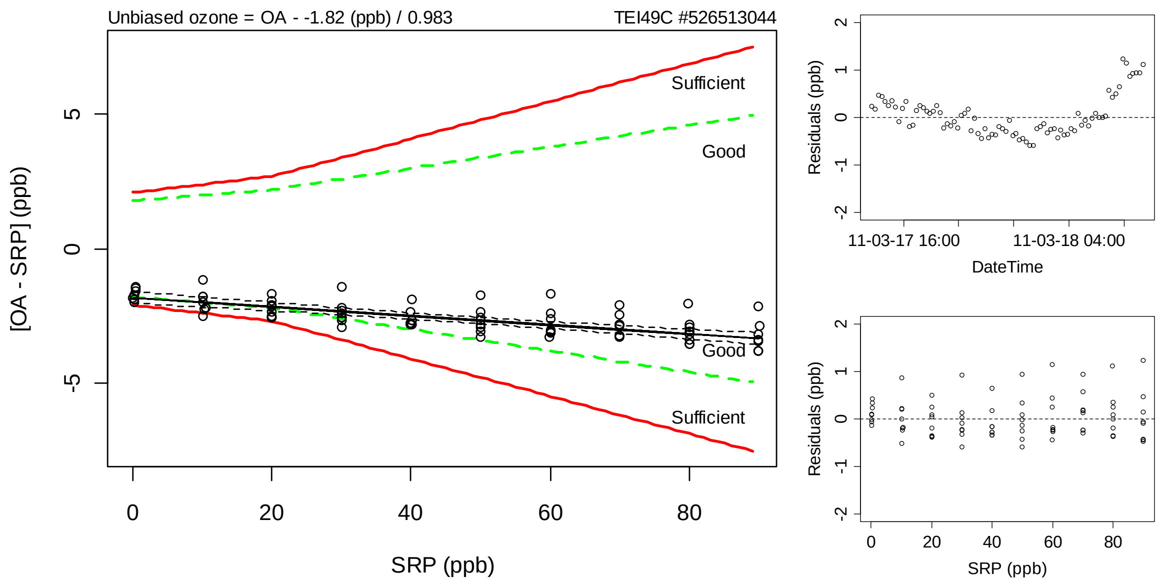

Figure 2. Same as Figure 1, for the TEI 49C #5226513044 main station analyser before cleaning.

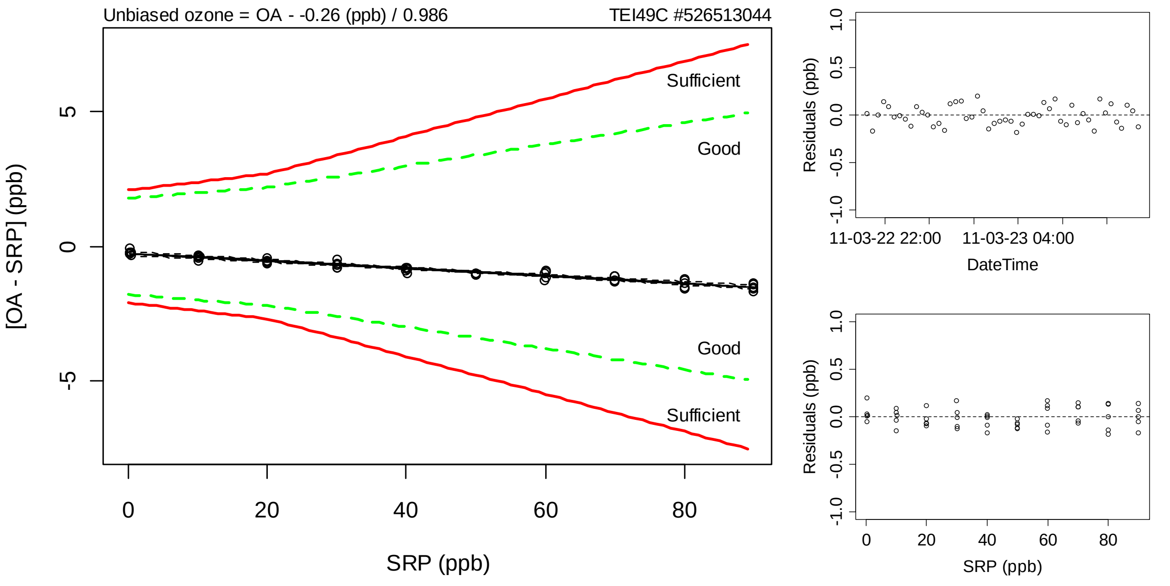

Figure 3. Same as above, for the TEI 49C #5226513044 main station analyser after cleaning.

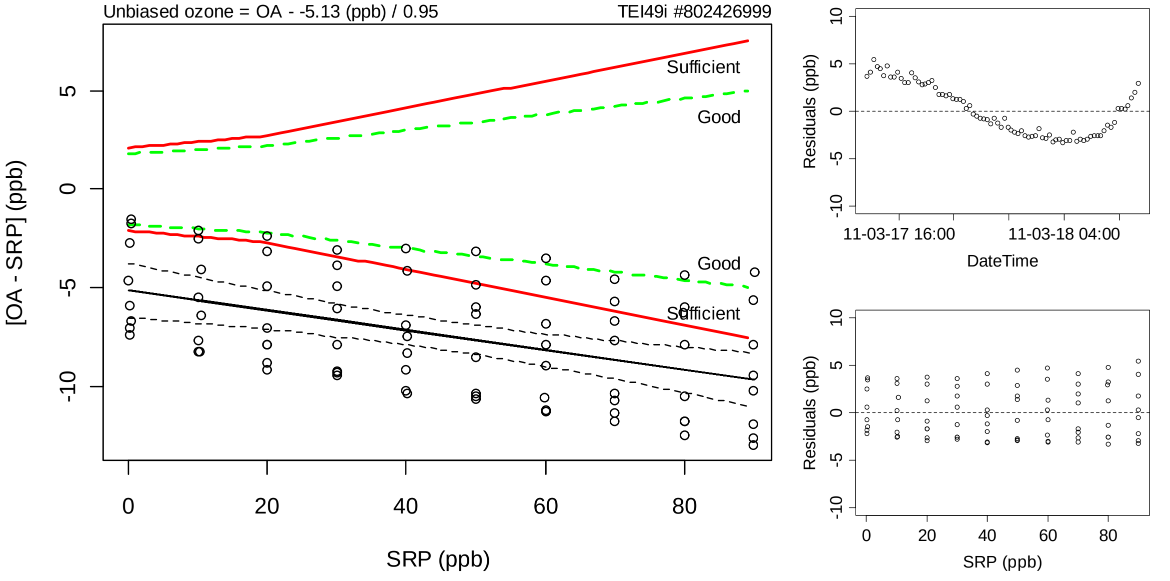

Figure 4. Same above, for the TEI 49i #802426999 backup analyser, before repair.

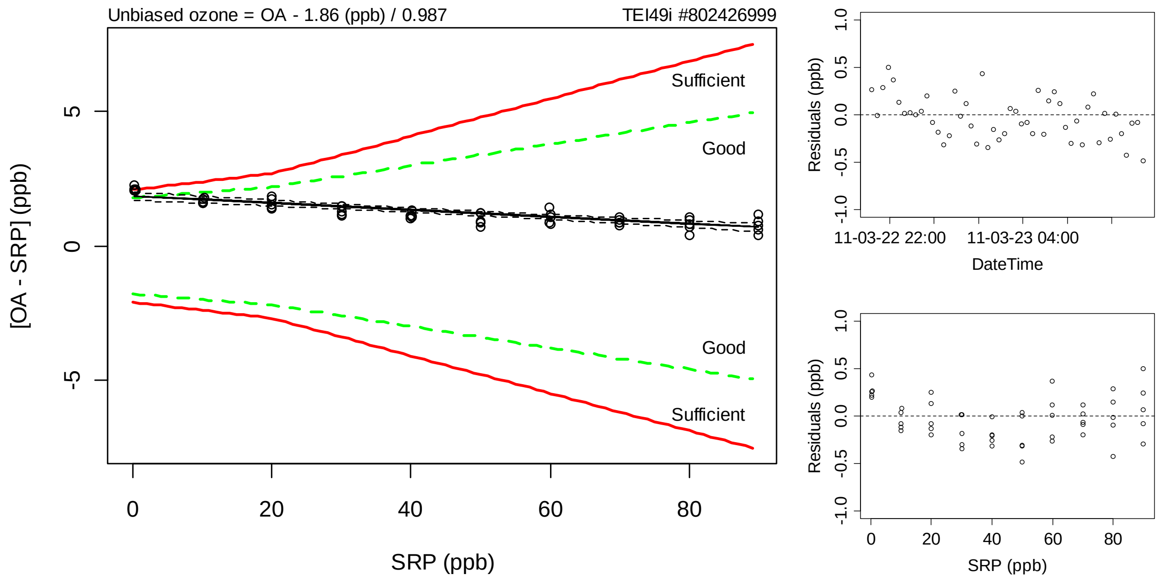

Figure 5. Same above, for the TEI 49i #802426999 backup analyser, after repair.

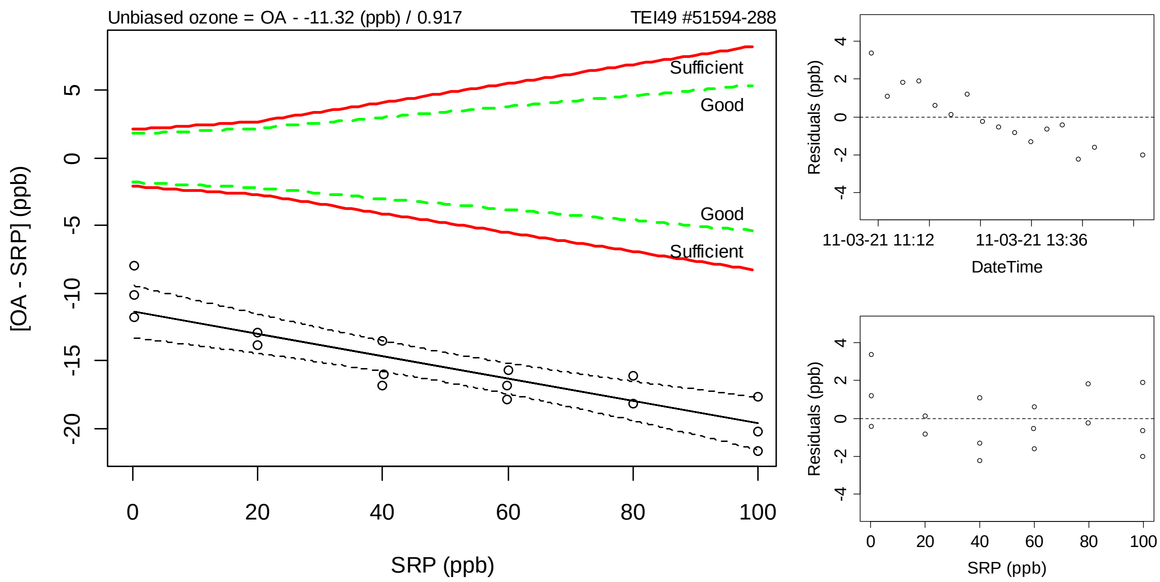

Figure 6. Same above, for the TEI 49 #51594-288 backup analyser.

Recommendation 4 (*, critical, immediately)**
The above comparisons show that the CPT station calibrator is working well. However, all ozone analysers showed a significant bias compared to the WCC-Empa ozone reference. The reason for this must be found, and instrument maintenance is necessary. The station calibrator can be used to verify the success of these corrective actions, and new calibration settings might be necessary.

Recommendation 5 (, serious, 2012)**
Existing ozone data needs to be reviewed and corrected if possible.

Recommendation 6 (*, minor, 2012)
The TEI 49 ozone analyser should be decommissioned, and replacement should be considered.

Carbon Monoxide Measurements

Cape Point has one of the longest CO time series in the Southern Hemisphere. Continuous measurements started in 1978, and currently data is available from WDCGG since 1995. No changes were made concerning the measurement setup since the last audit by WCC-Empa in 2006.

Instrumentation. At the time of the audit Cape Point was equipped with an RGA-3 CO analyser. In addition to the existing instrument, a Picarro G2302 CO and CO_2 analyser was installed after the audit. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with eight NOAA/ESRL carbon monoxide standards. Some of the standards have been calibrated or certified for both WMO-88 and WMO-2004 scales by NOAA. The standards span a mole fraction range from approx. 50 – 220 ppb CO. The NOAA/ESRL standards are used for the calibration of the working standards, which are filled at the site using a RIX compressor. With this equipment, adequate calibration of the carbon monoxide measurements is possible.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT instrument with randomised carbon monoxide levels from Travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 7 with respect to the WMO GAW DQOs [*WMO*, 2010; 2011]:

RGA-3 #113087-003:

Unbiased CO mole fraction: X_{CO} (ppb) = (CO – 2.2) / 0.9527 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (3.5 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

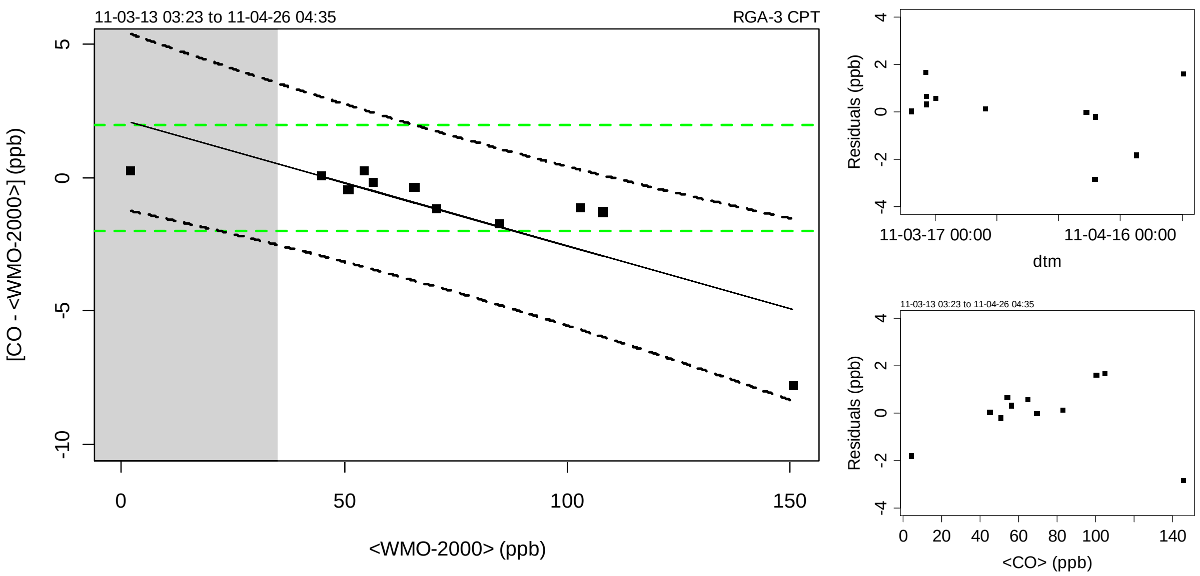

Figure 7. Left: Bias of Cape Point RGA-3 carbon monoxide instrument with respect to the WMO2000 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CPT, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

In addition to the current comparison, WCC-Empa provided in 2008 a set of six CO travelling standards to Cape Point with a mole fraction range of 35-110 ppb. The results in 2008 (shown in the Appendix) were not significantly different from the current comparison.

Methane Measurements

Cape Point comprises one of the longest methane time series in the Southern Hemisphere with continuous measurements starting in 1982 and data becoming available in 1983.

Instrumentation. A Varian CP-3800 GC/FID system is used for methane measurements at Cape Point. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with eight NOAA/ESRL methane standards. The NOAA/ESRL standards are used for the calibration of the working standards, which are filled at the site using a RIX compressor. With this equipment, adequate calibration of the methane measurements is possible.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT instrument with randomised methane levels from Travelling standards. The following equations (3a-b) characterise the instrument bias and remaining standard uncertainty after compensation of the bias. The results are further illustrated in Figure 8 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs. The green lines correspond to the recommendations made by the Experts Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques [*WMO*, 2011], whereas the red lines correspond to the recommended reproducibility of the WMO GAW Report No. 186 [*WMO*, 2009].

Varian CP-3800 #101605:

Unbiased CH_4 mole fraction: X_{CH4} (ppb) = $(CH_4 + 34.9) / 1.02019$ (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = $\text{sqrt}(3.9\ \text{ppb}^2 + 1.30\text{e-}07 * X_{CH4}^2)$ (3b)

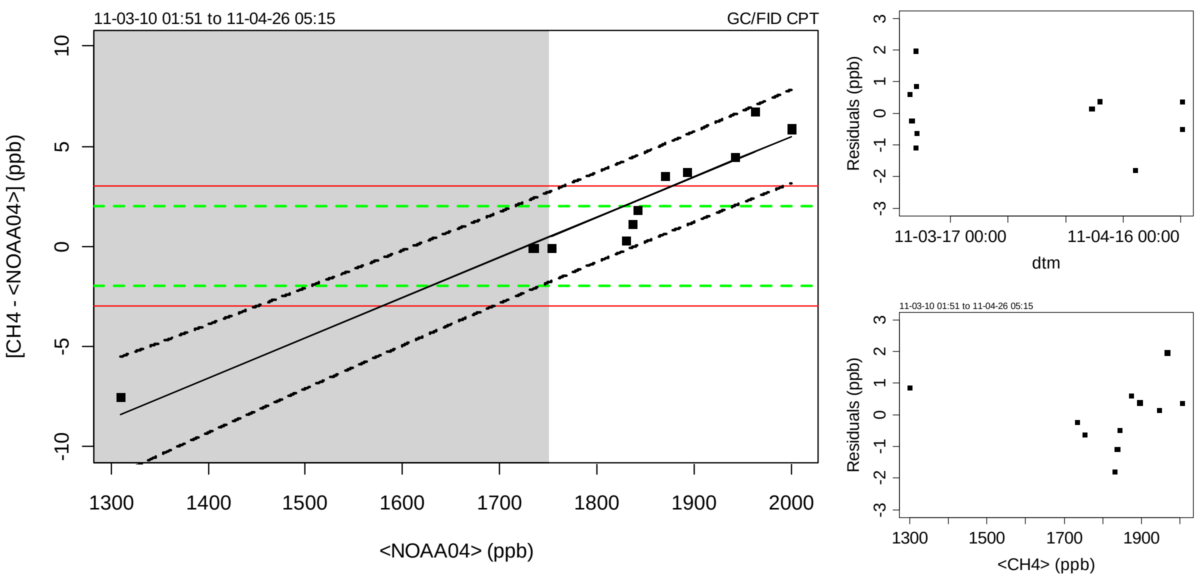

Figure 8. Left: Bias of Cape Point Varian CP-3800 methane GC with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CPT, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The comparison of the GC with WCC-Empa travelling standards showed good agreement for the mole fraction range of approx. 1700 to 1850 ppb; however, values below and above this range are exceeding the GAW DQOs of 2 ppb. The audit results clearly demonstrate that the CPT methane GC has either linearity issues even, or the NOAA standards used for the calibration of the instrument lead to the observed bias. Despite the fact that methane values above 1850 ppb are currently observed at CPT only a few times per year during pollution episodes, the reason for the non-linear behaviour of the FID detector needs to be identified, which might be related to the standards used for calibration of the instrument.

Recommendation 7 (, serious, 2012)**
The reason for the non-linear behaviour of the GC/FID instrument needs to be identified, and corrective actions are necessary to meet the GAW methane DQOs for values higher than 1850 ppb. In comparison to other techniques (CRDS), the GC/FID method has a significantly poorer repeatability, and replacement of the instrument should be considered.

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.

Instrumentation. An NDIR analyser (instrument-type URAS 4, Hartmann & Braun, Germany) is deployed at CPT. The measurement set-up was complemented with a Picarro G2302 CO and CO_2 analyser after the audit.

Standards. The station is equipped with ten NOAA/ESRL carbon dioxide standards. The NOAA/ESRL standards are used for the calibration of the working standards, which are filled at the site using a RIX compressor. With this equipment, adequate calibration of the methane measurements is possible.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CPT instrument with randomised carbon dioxide levels from Travelling standards. The following equations (4a-b) characterise the instrument bias and remaining standard uncertainty after compensation of the bias. The results are further illustrated in Figure 9 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red lines for northern hemisphere, green lines for southern hemisphere) [*WMO*, 2011].

URAS 4:

Unbiased CO_2 mole fraction: X_{CO2} (ppm) = (CO_2 – 4.65) / 0.988130 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.08 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4b)

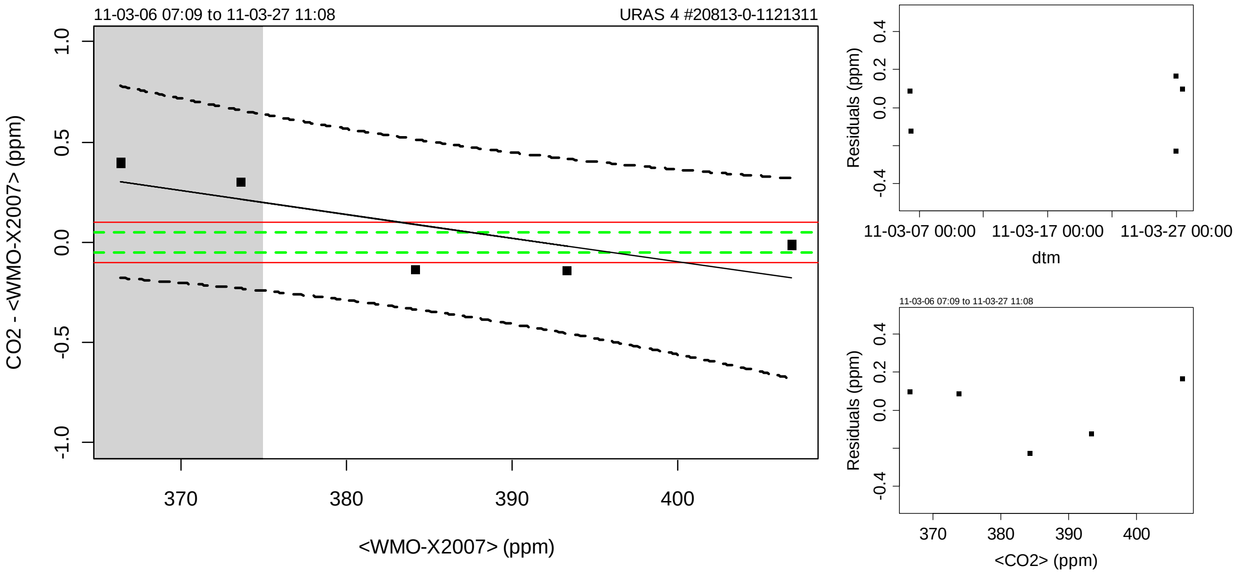

Figure 9. Left: Bias of Cape Point URAS 4 carbon dioxide instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CPT, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The overall agreement between WCC-Empa and CPT was relatively good but exceeded the GAW DQOs of 0.1 ppm, which might be explained by the uncertainty of the individual measurement points. The relative standard deviation of the multiple analyses of the TS was 0.037% based on single measurements of 5-15 min. This repeatability is not sufficient for meeting the GAW DQOs for averaging times of 15 min.

Recommendation 8 (, serious, 2012)**
The repeatability of the NDIR CO_2 instrument is a limiting factor for meeting the GAW DQOs. The recently purchased Picarro G2302 should have a better repeatability compared to the NDIR system, and it is recommended that the Picarro data are considered for future data submission after the method has been validated at the station. Parallel measurements of the two instruments should be made.

On-site Comparisons with a Picarro G2401 Analyser

Picarro Inc. provided a G2401 CO, CO_2, CH_4 and H_2O analyser for on-site comparisons as part of the WCC-Empa audit. The instrument was running in parallel to the CPT systems over a period of two months using a separate inlet line to the same air intake location. During the last five days, the Picarro G2401 was connected to the CPT drying system, and all instruments sampled the same dry air. In contrast to the comparisons of the travelling standards, much higher deviations between CPT and WCC-Empa were observed, especially for the CH_4 measurements.

Recommendation 9 (*, critical, 2012)**
The reason for the lower readings of the CPT methane GC/FID system during the comparison with the WCC-Empa travelling instrument needs to be identified. It is recommended that comparisons with the NOAA flask sampling are thoroughly analysed, and the whole measurement set-up is tested for potential leaks and CH_4 losses.

Recommendation 10 (*, serious, 2012)**
Comparisons between the recently purchased Picarro G2302 CO/CO_2 analyser and the existing instrumentation at CPT should be made to identify problems with the URAS-4 and RGA-3 instruments; however, the Picarro G2302 requires a correction for water vapour interference, which might be challenging for carbon monoxide. Alternatively, a measurement set-up using a drying system might be considered.

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 CD on a monthly basis. Data can be accessed through the internet from the main office in Stellenbosch. Data validation is carried out at Stellenbosch.

Ozone and carbon dioxide: 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 11 (, minor, 2012)**
It was recommended to acquire digital signals of the ozone instruments after the last WCC-Empa audit. This recommendation has not yet been implemented and remains valid. Additional instrument parameters such as flow rates, pressure and temperatures should be incorporated in a new DAQ system.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). For the parameters of the audit scope in-situ data for surface ozone (1997-2010), carbon monoxide (1995 – 2010), methane (1983-2010) and carbon dioxide (1993-2010) is available from WDCGG. Unfiltered and filtered data sets have been submitted for all of the above parameters.

Recommendation 12 (*, minor, future data submissions)**
It was noted that no scale versions have been submitted for CO and CO_2 time series. The version of the scale is an important parameter and needs to be specified for every data submission.

Conclusions

The Global GAW station Cape Point carries out a very comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the Cape Point station an important contribution to the GAW programme. The recent addition of a Picarro G2302 CO and CO2 analyser is a valuable addition to the existing instrumentation.

Several problems with the current instrumentation were identified during the audit, and corresponding recommendations were made by WCC-Empa to solve these issues.

Summary Ranking of the Cape Point GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access by road
Facilities		
Laboratory and office space	(5)	Large research facilities
Internet access	(3)	Available, bandwidth limited
Air Conditioning	(4)	Stable lab temperature
Power supply	(5)	Reliable, UPS
General Management and Operation		
Organisation	(4)	Well organised within CPT staff
Competence of staff	(4)	Experienced technical and scientific staff, retirement of station manager expected
Air Inlet System	(4)	Adequate inlets for all assessed parameters
Instrumentation		
Ozone	(3)	Adequate instruments, but service needed
Carbon monoxide	(4)	RGA-3, Picarro G2302
Methane	(4)	GC/FID
Carbon dioxide	(5)	URAS 4 and Picarro G2301
Standards		
Ozone	(5)	TEI 49i-PS
CO, CH_4 and CO_2	(5)	NOAA and working standards
Data Management		
Data acquisition	(3)	Only analogue signals are acquired (TEI instruments)
Data processing	(5)	Experienced staff, scientific use of the data
Data submission	(5)	Large suite of parameters submitted within acceptable submissions delay (1-2 yrs)

#0: inadequate through 5: adequate.

Dübendorf, January 2012

Dr. C. Zellweger	Dr. M. Steinbacher	Dr. B. Buchmann
WCC-Empa	QA/SAC Switzerland	Head of laboratory

APPENDIX

Global GAW Station Cape Point

Site description

Information about the Cape Point GAW station can be found in the previous audit report [*Zellweger et al.*, 2006], and the station is also registered in GAWSIS (http://gaw.empa.ch/gawsis). No significant changes were made at the station and the surroundings since the last WCC-Empa audit.

Measurement Programme

The Cape Point Observatory comprises one of the longest time series for reactive and greenhouse gases in the Southern Hemisphere. An overview of the measurement programme and its status as of July 2011 is shown in Table 1. Refer to GAWSIS for more details and a complete overview of the measurement programme.

Table 1. Measurement Programme at the CPT Station (gas and aerosol measurements only)

Parameter	*Current Instrument/method*
Reactive Gas	
CO	RGA-3 and Picarro G2302
NO_2, SO_2	Passive Samplers
Greenhouse Gas	
CO_2	URAS 4 and Picarro G2302
CH_4	GC/FID
N_2O	GC/ECD
Flask sampling	NOAA/GMD flask programme
Ozone	
Surface ozone	TEI Series (49C, 49i and 49)
Aerosol	
Carbonaceous/organic material (fine)	Optical particle counter (OPC)
Hemispheric backscattering coef	Nephelometry, integrating
Light absorption coef	Light absorption photometry
Light scattering coef	Nephelometry, integrating
Optical depth	Sunphotometry/Filter Radiometry
Number concentration	Condensation particle counter (CPC)
Radio Nuclide	
Beryllium [Be-7]	Filter / gamma spectrometry
Krypton [Kr-85]	Adsorption - scintillation counting
Lead [Pb-210]	Filter / gamma spectrometry
Radon [Rn-222]	Alpha counting

Trace Gas Distributions at Cape Point

The monthly and yearly distribution for surface ozone, carbon monoxide, methane and carbon dioxide (all for 2009 unfiltered hourly CPT data) at Cape Point is shown in Figure 10.

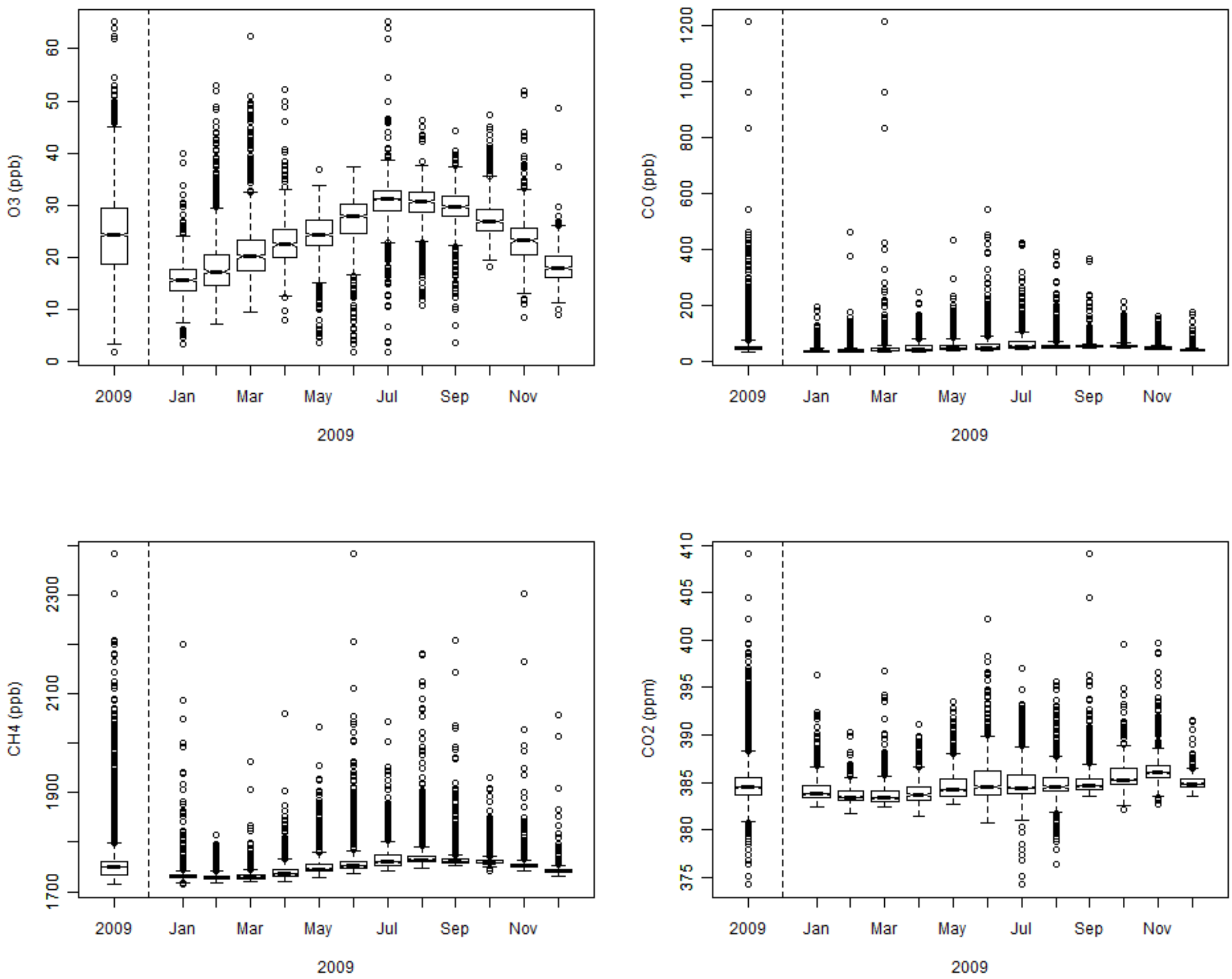

Figure 10. Yearly and monthly box plots for surface ozone surface ozone, carbon monoxide, methane and carbon dioxide (2009). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organisation and Contact Persons

The Cape Point Observatory is run and coordinated by the South African Weather Service (SAWS) with administrative offices located in Pretoria. The scientific and technical staff of the Cape Point Observatory is listed in Table 2. Refer also to GAWSIS for more contact and organisational information.

Table 2. CPT contact persons as of August 2011 (in-situ measurements only)

Name	*Responsibility*
Mr. Ernst-Günther Brunke	Station Manager, Senior Scientist
Mr. Casper Labuschagne	Senior Scientist
Mr. Bhawoodien Parker	Senior Scientist
Mr. Danie van der Spuy	Station Technician
Ms. Thumeka Mkololo	Junior Scientist

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The laboratories are air-conditioned, and the instruments are protected from direct sunlight. No modifications are necessary.

Air Inlet System

Location of air intake:	The air intake is mounted on the flat roof 2 m above the laboratory.
Inlet protection:	Protection against rain water / snow / insects by an upside-down stainless steel bucket.
Inlet design:	Straight stainless steel tubing, length = 4.3 m, inner diameter 10 cm, SCHOTT glass tube with 50 cm outer diameter inside. Flow rate 1.5 m^3 per minute.
Manifold:	SCHOTT glass, length 0.4 m, inner diameter 8 cm, flow rate 1.5 m^3 per minute.
Tubing / Material:	Instruments connected to manifold with 2 m 1/4" PFA tubing 2 m ¼, flow depending on instrument, approx. 1 l min^{-1}.
Inlet filter:	PFA filter holder with Pall Zylon PFTE filters, 5µm.
Residence time:	ca. 2 s

The backup analyser is normally sampling air directly from the tower using 35 m 1/4" PFA tubing. The residence time is approx. 20 s.

The main air inlet is fully adequate for ozone measurements.

Instrumentation

Currently, three instruments using UV absorption technique (TEI 49C, TEI 49i and TEI 49) are running in parallel at the station for continuous surface ozone measurements. Instrumental details are summarised in Table 3.

Standards

A TEI 49i-PS ozone standard is available, for details refer to Table 3.

Operation and Maintenance

Check for general operation:	Twice per week (usually Tuesday and Thursday).
Zero / Span check:	Automatic, daily.
Calibration/checks with standard:	Every 3 months, including check of pressure sensors.
Inlet filter exchange:	Monthly, more often in case of pollution episodes.
Other (cleaning, leak check etc.):	As required, usually yearly.

Data Acquisition and Data Transfer

Data acquisition is made with Testpoint (Keithley). Only analogue signals of the ozone instruments are acquired and 1-minute and 30-minute average signals are stored on the data acquisition computer. No additional instrument parameters are acquired. Data back-ups are made weekly.

Data Treatment

Data validation is carried out at the SAWS office in Stellenbosch by the station scientist. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. The values of the three different ozone analysers are regularly compared for QC/QA purposes, and the data of the main station analyser are considered for further scientific use and submission to data centres. In case of instrument problems, data of the backup instruments might be used.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone from 1997 to 2010 is available from WDCGG.

Documentation

All information is entered in paper log books and checklists. A SOP has been prepared by CPT, and weekly instrument check lists were available. The information was comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison of the Ozone Analyser

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 travelling standard was used for the 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 (including inlet filters) 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 and the station data acquisition systems.

Table 3. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
Settings	BKG = -0.2; COEFF = 1.009
Station Analyser (OA) – main instrument	
Model, S/N	TEI 49C #5226513044
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = -0.5; COEFF = 1.015
Pressure readings (torr)	Ambient 738.0, OA 737.7, no adjustments were made
Station Analyser (OA) – backup instrument	
Model, S/N	TEI 49i #802426999
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = 0.0; COEFF = 1.038
Pressure readings (torr)	Ambient 738.0, OA 738.0, no adjustments were made
Station Analyser (OA) – backup instrument	
Model, S/N	TEI 49 #51594-288
Principle	UV absorption
Range	0-1 ppm
Settings	ZERO = 506; SPAN = 507
Pressure readings (torr)	Ambient 738.9, OA 735, no adjustments were made
Station Calibrator (OC)	
Model, S/N	TEI 49i-PS #7088211231
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = -0.1; COEFF = 1.019
Pressure readings (torr)	Ambient 740.7, OC 741.0, no adjustments were made

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison as described elsewhere *[Klausen et al., 2003]*. 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 (Figures and Equations).

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main CPT ozone calibrator (OC) TEI 49i-PS #708821231 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2011-03-18 11:10	1	0	0.23	-0.12	0.22	0.02	-0.35	NA
2011-03-18 11:25	1	40	39.99	39.48	0.09	0.10	-0.51	-1.3
2011-03-18 11:40	1	80	80.02	79.61	0.12	0.08	-0.41	-0.5
2011-03-18 11:55	1	100	100.00	99.62	0.09	0.10	-0.38	-0.4
2011-03-18 12:10	1	60	60.03	59.80	0.10	0.05	-0.23	-0.4
2011-03-18 12:25	1	20	19.96	19.73	0.16	0.05	-0.23	-1.2
2011-03-18 12:40	2	0	0.14	-0.10	0.25	0.01	-0.24	NA
2011-03-18 12:55	2	80	80.02	79.78	0.06	0.11	-0.24	-0.3
2011-03-18 13:10	2	60	60.00	59.46	0.12	0.12	-0.54	-0.9
2011-03-18 13:25	2	20	19.98	19.31	0.17	0.07	-0.67	-3.4
2011-03-18 13:40	2	40	40.02	39.60	0.12	0.11	-0.42	-1
2011-03-18 13:55	2	100	99.99	99.56	0.11	0.14	-0.43	-0.4
2011-03-18 14:10	3	0	0.33	-0.06	0.21	0.03	-0.39	NA
2011-03-18 14:25	3	40	40.01	39.47	0.10	0.12	-0.54	-1.3
2011-03-18 14:40	3	60	59.99	59.71	0.12	0.10	-0.28	-0.5
2011-03-18 14:55	3	20	19.99	19.78	0.15	0.05	-0.21	-1.1
2011-03-18 15:10	3	80	80.03	79.95	0.07	0.14	-0.08	-0.1
2011-03-18 15:25	3	100	99.98	99.93	0.09	0.07	-0.05	-0.1
2011-03-18 15:40	4	0	0.21	-0.02	0.19	0.03	-0.23	NA
2011-03-18 15:55	4	40	40.02	39.74	0.14	0.09	-0.28	-0.7
2011-03-18 16:10	4	80	79.99	80.01	0.07	0.09	0.02	0
2011-03-18 16:25	4	100	99.96	99.75	0.07	0.10	-0.21	-0.2
2011-03-18 16:40	4	60	59.95	59.71	0.12	0.10	-0.24	-0.4
2011-03-18 16:55	4	20	20.00	19.62	0.20	0.08	-0.38	-1.9

Table 5. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main CPT ozone analyser (OA) TEI 49C #5226513044 with the WCC-Empa travelling standard (TS) before cleaning.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-17 13:40	1	0	0.30	-1.24	0.18	0.04	-1.54	NA
2011-03-17 13:55	1	40	39.99	37.65	0.09	0.09	-2.34	-5.9
2011-03-17 14:10	1	90	90.05	87.09	0.12	0.11	-2.96	-3.3
2011-03-17 14:25	1	60	59.99	57.55	0.13	0.05	-2.44	-4.1
2011-03-17 14:40	1	50	49.98	47.62	0.08	0.09	-2.36	-4.7
2011-03-17 14:55	1	20	20.03	18.14	0.12	0.05	-1.89	-9.4
2011-03-17 15:10	1	80	79.99	77.10	0.08	0.08	-2.89	-3.6
2011-03-17 15:25	1	10	10.03	8.29	0.19	0.05	-1.74	-17.3
2011-03-17 15:40	1	30	29.99	27.57	0.16	0.10	-2.42	-8.1
2011-03-17 15:55	1	70	70.03	67.15	0.09	0.05	-2.88	-4.1
2011-03-17 16:10	2	0	0.29	-1.15	0.21	0.07	-1.44	NA
2011-03-17 16:25	2	20	19.99	17.67	0.13	0.05	-2.32	-11.6
2011-03-17 16:40	2	40	40.03	37.35	0.11	0.09	-2.68	-6.7

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-17 16:55	2	90	90.02	86.73	0.09	0.09	-3.29	-3.7
2011-03-17 17:10	2	60	59.99	57.36	0.09	0.11	-2.63	-4.4
2011-03-17 17:25	2	10	10.08	8.34	0.23	0.04	-1.74	-17.3
2011-03-17 17:40	2	30	30.00	27.81	0.08	0.06	-2.19	-7.3
2011-03-17 17:55	2	50	49.99	47.38	0.08	0.09	-2.61	-5.2
2011-03-17 18:10	2	70	70.01	67.08	0.11	0.09	-2.93	-4.2
2011-03-17 18:25	2	80	79.97	76.96	0.14	0.08	-3.01	-3.8
2011-03-17 18:40	3	0	0.23	-1.45	0.18	0.07	-1.68	NA
2011-03-17 18:55	3	30	29.97	27.43	0.18	0.06	-2.54	-8.5
2011-03-17 19:10	3	50	50.02	47.20	0.18	0.08	-2.82	-5.6
2011-03-17 19:25	3	10	10.52	8.38	0.54	0.16	-2.14	-20.3
2011-03-17 19:40	3	90	90.00	86.47	0.11	0.08	-3.53	-3.9
2011-03-17 19:55	3	60	60.01	56.91	0.11	0.04	-3.10	-5.2
2011-03-17 20:10	3	20	19.98	17.88	0.18	0.12	-2.10	-10.5
2011-03-17 20:25	3	80	80.00	76.84	0.12	0.11	-3.16	-4
2011-03-17 20:40	3	70	70.00	67.10	0.13	0.14	-2.90	-4.1
2011-03-17 20:55	3	40	40.00	37.21	0.17	0.13	-2.79	-7
2011-03-17 21:10	4	0	0.06	-1.72	0.18	0.05	-1.78	NA
2011-03-17 21:25	4	40	40.03	37.18	0.12	0.09	-2.85	-7.1
2011-03-17 21:40	4	90	90.03	86.15	0.10	0.07	-3.88	-4.3
2011-03-17 21:55	4	60	60.00	56.89	0.13	0.07	-3.11	-5.2
2011-03-17 22:10	4	50	50.00	46.88	0.10	0.06	-3.12	-6.2
2011-03-17 22:25	4	20	19.98	17.49	0.14	0.07	-2.49	-12.5
2011-03-17 22:40	4	80	80.02	76.40	0.09	0.07	-3.62	-4.5
2011-03-17 22:55	4	10	10.37	8.22	0.48	0.18	-2.15	-20.7
2011-03-17 23:10	4	30	29.99	27.42	0.11	0.09	-2.57	-8.6
2011-03-17 23:25	4	70	69.97	66.61	0.10	0.06	-3.36	-4.8
2011-03-17 23:40	5	0	0.06	-1.76	0.19	0.05	-1.82	NA
2011-03-17 23:55	5	20	20.02	17.50	0.18	0.07	-2.52	-12.6
2011-03-18 00:10	5	40	40.00	37.16	0.07	0.05	-2.84	-7.1
2011-03-18 00:25	5	90	90.04	86.13	0.09	0.10	-3.91	-4.3
2011-03-18 00:40	5	60	59.98	56.66	0.11	0.06	-3.32	-5.5
2011-03-18 00:55	5	10	10.05	7.58	0.20	0.08	-2.47	-24.6
2011-03-18 01:10	5	30	30.02	27.10	0.17	0.12	-2.92	-9.7
2011-03-18 01:25	5	50	50.02	46.73	0.09	0.12	-3.29	-6.6
2011-03-18 01:40	5	70	70.01	66.70	0.07	0.07	-3.31	-4.7
2011-03-18 01:55	5	80	80.00	76.55	0.13	0.07	-3.45	-4.3
2011-03-18 02:10	6	0	0.11	-1.80	0.28	0.04	-1.91	NA
2011-03-18 02:25	6	30	30.00	27.36	0.13	0.10	-2.64	-8.8
2011-03-18 02:40	6	50	50.01	47.06	0.05	0.05	-2.95	-5.9
2011-03-18 02:55	6	10	10.33	8.13	0.52	0.16	-2.20	-21.3
2011-03-18 03:10	6	90	89.99	86.13	0.12	0.07	-3.86	-4.3
2011-03-18 03:25	6	60	60.00	56.85	0.11	0.08	-3.15	-5.2
2011-03-18 03:40	6	20	19.98	17.47	0.10	0.07	-2.51	-12.6
2011-03-18 03:55	6	80	79.98	76.38	0.10	0.07	-3.60	-4.5
2011-03-18 04:10	6	70	69.99	66.69	0.08	0.07	-3.30	-4.7
2011-03-18 04:25	6	40	40.00	37.21	0.12	0.10	-2.79	-7
2011-03-18 04:40	7	0	0.12	-1.56	0.29	0.03	-1.68	NA

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-18 04:55	7	40	40.03	37.36	0.14	0.12	-2.67	-6.7
2011-03-18 05:10	7	90	90.00	86.50	0.10	0.10	-3.50	-3.9
2011-03-18 05:25	7	60	60.00	56.94	0.07	0.07	-3.06	-5.1
2011-03-18 05:40	7	50	50.02	47.31	0.12	0.06	-2.71	-5.4
2011-03-18 05:55	7	20	19.98	17.93	0.22	0.06	-2.05	-10.3
2011-03-18 06:10	7	80	80.01	76.76	0.08	0.10	-3.25	-4.1
2011-03-18 06:25	7	10	10.02	8.07	0.19	0.08	-1.95	-19.5
2011-03-18 06:40	7	30	30.00	27.71	0.17	0.12	-2.29	-7.6
2011-03-18 06:55	7	70	70.03	67.54	0.10	0.15	-2.49	-3.6
2011-03-18 07:09	8	0	0.39	-0.95	0.28	0.03	-1.34	NA
2011-03-18 07:24	8	20	19.98	18.34	0.16	0.09	-1.64	-8.2
2011-03-18 07:39	8	40	40.04	38.17	0.15	0.09	-1.87	-4.7
2011-03-18 07:54	8	90	90.00	87.79	0.11	0.07	-2.21	-2.5
2011-03-18 08:09	8	60	60.00	58.26	0.13	0.08	-1.74	-2.9
2011-03-18 08:24	8	10	9.99	8.90	0.14	0.04	-1.09	-10.9
2011-03-18 08:39	8	30	30.00	28.60	0.12	0.06	-1.40	-4.7
2011-03-18 08:54	8	50	50.01	48.26	0.11	0.08	-1.75	-3.5
2011-03-18 09:09	8	70	70.00	67.86	0.10	0.07	-2.14	-3.1
2011-03-18 09:24	8	80	79.91	77.78	0.18	0.07	-2.13	-2.7

Table 6. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main CPT ozone analyser (OA) TEI 49C #5226513044 with the WCC-Empa travelling standard (TS) after cleaning.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-22 21:10	1	0	0.42	0.23	0.16	0.04	-0.19	NA
2011-03-22 21:25	1	40	40.04	39.05	0.12	0.04	-0.99	-2.5
2011-03-22 21:40	1	80	80.02	78.59	0.07	0.03	-1.43	-1.8
2011-03-22 21:55	1	90	90.01	88.56	0.10	0.08	-1.45	-1.6
2011-03-22 22:10	1	60	59.96	58.93	0.11	0.07	-1.03	-1.7
2011-03-22 22:25	1	20	19.98	19.45	0.11	0.07	-0.53	-2.7
2011-03-22 22:40	1	30	30.01	29.34	0.09	0.05	-0.67	-2.2
2011-03-22 22:55	1	70	70.00	68.68	0.07	0.03	-1.32	-1.9
2011-03-22 23:10	1	50	50.00	48.91	0.12	0.06	-1.09	-2.2
2011-03-22 23:25	1	10	10.01	9.74	0.11	0.04	-0.27	-2.7
2011-03-22 23:40	2	0	0.23	0.06	0.17	0.03	-0.17	NA
2011-03-22 23:55	2	90	89.98	88.39	0.10	0.06	-1.59	-1.8
2011-03-23 00:10	2	30	29.98	29.19	0.14	0.05	-0.79	-2.6
2011-03-23 00:25	2	40	40.00	39.10	0.16	0.06	-0.90	-2.2
2011-03-23 00:40	2	60	59.96	58.68	0.10	0.10	-1.28	-2.1
2011-03-23 00:55	2	20	19.99	19.60	0.23	0.05	-0.39	-2
2011-03-23 01:10	2	80	80.01	78.71	0.11	0.06	-1.30	-1.6
2011-03-23 01:25	2	70	69.99	68.86	0.08	0.08	-1.13	-1.6
2011-03-23 01:40	2	10	10.02	9.63	0.18	0.07	-0.39	-3.9
2011-03-23 01:55	2	50	49.99	49.00	0.12	0.06	-0.99	-2
2011-03-23 02:10	3	0	0.22	0.21	0.14	0.02	-0.01	NA

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-23 02:25	3	30	29.98	29.37	0.13	0.07	-0.61	-2
2011-03-23 02:40	3	10	10.00	9.49	0.16	0.05	-0.51	-5.1
2011-03-23 02:55	3	60	60.01	58.80	0.11	0.04	-1.21	-2
2011-03-23 03:10	3	70	70.01	68.66	0.09	0.07	-1.35	-1.9
2011-03-23 03:25	3	90	89.99	88.35	0.09	0.04	-1.64	-1.8
2011-03-23 03:40	3	50	50.00	48.96	0.12	0.11	-1.04	-2.1
2011-03-23 03:55	3	80	79.98	78.36	0.08	0.08	-1.62	-2
2011-03-23 04:10	3	20	20.01	19.41	0.16	0.09	-0.60	-3
2011-03-23 04:25	3	40	40.00	39.19	0.13	0.08	-0.81	-2
2011-03-23 04:40	4	0	0.25	0.05	0.06	0.05	-0.20	NA
2011-03-23 04:55	4	40	40.02	39.19	0.19	0.08	-0.83	-2.1
2011-03-23 05:10	4	80	79.98	78.67	0.11	0.07	-1.31	-1.6
2011-03-23 05:25	4	90	90.02	88.49	0.06	0.07	-1.53	-1.7
2011-03-23 05:40	4	60	60.00	59.04	0.08	0.07	-0.96	-1.6
2011-03-23 05:55	4	20	20.01	19.44	0.13	0.04	-0.57	-2.8
2011-03-23 06:10	4	30	30.03	29.26	0.10	0.07	-0.77	-2.6
2011-03-23 06:25	4	70	69.98	68.80	0.08	0.08	-1.18	-1.7
2011-03-23 06:40	4	50	50.02	48.97	0.11	0.08	-1.05	-2.1
2011-03-23 06:55	4	10	10.33	9.98	0.27	0.09	-0.35	-3.4
2011-03-23 07:10	5	0	0.33	0.07	0.18	0.03	-0.26	NA
2011-03-23 07:25	5	90	89.99	88.23	0.17	0.07	-1.76	-2
2011-03-23 07:40	5	30	29.98	29.49	0.08	0.05	-0.49	-1.6
2011-03-23 07:55	5	40	40.02	39.22	0.09	0.05	-0.80	-2
2011-03-23 08:10	5	60	59.99	58.98	0.10	0.04	-1.01	-1.7
2011-03-23 08:25	5	20	19.96	19.38	0.18	0.05	-0.58	-2.9
2011-03-23 08:40	5	80	79.99	78.41	0.13	0.06	-1.58	-2
2011-03-23 08:55	5	70	69.99	68.81	0.11	0.09	-1.18	-1.7
2011-03-23 09:10	5	10	9.98	9.67	0.17	0.07	-0.31	-3.1
2011-03-23 09:25	5	50	50.04	48.94	0.08	0.06	-1.10	-2.2

Table 7. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the backup CPT ozone analyser (OA) TEI 49i #802426999 with the WCC-Empa travelling standard (TS) before repair.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-17 13:40	1	0	0.30	-1.17	0.18	0.05	-1.47	NA
2011-03-17 13:55	1	40	39.99	36.96	0.09	0.09	-3.03	-7.6
2011-03-17 14:10	1	90	90.05	85.75	0.12	0.12	-4.30	-4.8
2011-03-17 14:25	1	60	59.99	56.46	0.13	0.06	-3.53	-5.9
2011-03-17 14:40	1	50	49.98	46.81	0.08	0.06	-3.17	-6.3
2011-03-17 14:55	1	20	20.03	17.65	0.12	0.08	-2.38	-11.9
2011-03-17 15:10	1	80	79.99	75.54	0.08	0.10	-4.45	-5.6
2011-03-17 15:25	1	10	10.03	7.99	0.19	0.08	-2.04	-20.3
2011-03-17 15:40	1	30	29.99	26.93	0.16	0.09	-3.06	-10.2
2011-03-17 15:55	1	70	70.03	65.40	0.09	0.07	-4.63	-6.6
2011-03-17 16:10	2	0	0.29	-1.37	0.21	0.05	-1.66	NA

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-17 16:25	2	20	19.99	16.90	0.13	0.05	-3.09	-15.5
2011-03-17 16:40	2	40	40.03	35.90	0.11	0.07	-4.13	-10.3
2011-03-17 16:55	2	90	90.02	84.31	0.09	0.11	-5.71	-6.3
2011-03-17 17:10	2	60	59.99	55.29	0.09	0.09	-4.70	-7.8
2011-03-17 17:25	2	10	10.08	7.58	0.23	0.07	-2.50	-24.8
2011-03-17 17:40	2	30	30.00	26.14	0.08	0.10	-3.86	-12.9
2011-03-17 17:55	2	50	49.99	45.15	0.08	0.08	-4.84	-9.7
2011-03-17 18:10	2	70	70.01	64.26	0.11	0.07	-5.75	-8.2
2011-03-17 18:25	2	80	79.97	73.95	0.14	0.08	-6.02	-7.5
2011-03-17 18:40	3	0	0.23	-2.42	0.18	0.05	-2.65	NA
2011-03-17 18:55	3	30	29.97	25.09	0.18	0.09	-4.88	-16.3
2011-03-17 19:10	3	50	50.02	44.06	0.18	0.07	-5.96	-11.9
2011-03-17 19:25	3	10	10.52	6.52	0.54	0.16	-4.00	-38
2011-03-17 19:40	3	90	90.00	82.02	0.11	0.08	-7.98	-8.9
2011-03-17 19:55	3	60	60.01	53.15	0.11	0.08	-6.86	-11.4
2011-03-17 20:10	3	20	19.98	15.10	0.18	0.11	-4.88	-24.4
2011-03-17 20:25	3	80	80.00	72.03	0.12	0.06	-7.97	-10
2011-03-17 20:40	3	70	70.00	62.30	0.13	0.14	-7.70	-11
2011-03-17 20:55	3	40	40.00	33.12	0.17	0.09	-6.88	-17.2
2011-03-17 21:10	4	0	0.06	-4.48	0.18	0.04	-4.54	NA
2011-03-17 21:25	4	40	40.03	32.57	0.12	0.10	-7.46	-18.6
2011-03-17 21:40	4	90	90.03	79.73	0.10	0.07	-10.30	-11.4
2011-03-17 21:55	4	60	60.00	51.02	0.13	0.09	-8.98	-15
2011-03-17 22:10	4	50	50.00	41.48	0.10	0.08	-8.52	-17
2011-03-17 22:25	4	20	19.98	12.94	0.14	0.08	-7.04	-35.2
2011-03-17 22:40	4	80	80.02	69.43	0.09	0.05	-10.59	-13.2
2011-03-17 22:55	4	10	10.37	4.01	0.48	0.16	-6.36	-61.3
2011-03-17 23:10	4	30	29.99	22.10	0.11	0.06	-7.89	-26.3
2011-03-17 23:25	4	70	69.97	59.56	0.10	0.09	-10.41	-14.9
2011-03-17 23:40	5	0	0.06	-5.77	0.19	0.08	-5.83	NA
2011-03-17 23:55	5	20	20.02	12.16	0.18	0.10	-7.86	-39.3
2011-03-18 00:10	5	40	40.00	30.81	0.07	0.06	-9.19	-23
2011-03-18 00:25	5	90	90.04	78.05	0.09	0.08	-11.99	-13.3
2011-03-18 00:40	5	60	59.98	49.41	0.11	0.10	-10.57	-17.6
2011-03-18 00:55	5	10	10.05	2.39	0.20	0.08	-7.66	-76.2
2011-03-18 01:10	5	30	30.02	20.80	0.17	0.11	-9.22	-30.7
2011-03-18 01:25	5	50	50.02	39.61	0.09	0.12	-10.41	-20.8
2011-03-18 01:40	5	70	70.01	58.62	0.07	0.08	-11.39	-16.3
2011-03-18 01:55	5	80	80.00	68.19	0.13	0.08	-11.81	-14.8
2011-03-18 02:10	6	0	0.11	-6.84	0.28	0.06	-6.95	NA
2011-03-18 02:25	6	30	30.00	20.54	0.13	0.11	-9.46	-31.5
2011-03-18 02:40	6	50	50.01	39.47	0.05	0.08	-10.54	-21.1
2011-03-18 02:55	6	10	10.33	2.17	0.52	0.14	-8.16	-79
2011-03-18 03:10	6	90	89.99	76.97	0.12	0.08	-13.02	-14.5
2011-03-18 03:25	6	60	60.00	48.80	0.11	0.07	-11.20	-18.7
2011-03-18 03:40	6	20	19.98	10.87	0.10	0.07	-9.11	-45.6
2011-03-18 03:55	6	80	79.98	67.45	0.10	0.08	-12.53	-15.7
2011-03-18 04:10	6	70	69.99	58.17	0.08	0.06	-11.82	-16.9

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-18 04:25	6	40	40.00	29.77	0.12	0.11	-10.23	-25.6
2011-03-18 04:40	7	0	0.12	-7.18	0.29	0.07	-7.30	NA
2011-03-18 04:55	7	40	40.03	29.69	0.14	0.07	-10.34	-25.8
2011-03-18 05:10	7	90	90.00	77.28	0.10	0.07	-12.72	-14.1
2011-03-18 05:25	7	60	60.00	48.72	0.07	0.09	-11.28	-18.8
2011-03-18 05:40	7	50	50.02	39.38	0.12	0.08	-10.64	-21.3
2011-03-18 05:55	7	20	19.98	11.21	0.22	0.08	-8.77	-43.9
2011-03-18 06:10	7	80	80.01	68.20	0.08	0.08	-11.81	-14.8
2011-03-18 06:25	7	10	10.02	1.86	0.19	0.11	-8.16	-81.4
2011-03-18 06:40	7	30	30.00	20.75	0.17	0.07	-9.25	-30.8
2011-03-18 06:55	7	70	70.03	59.26	0.10	0.17	-10.77	-15.4
2011-03-18 07:09	8	0	0.39	-6.22	0.28	0.05	-6.61	NA
2011-03-18 07:24	8	20	19.98	12.15	0.16	0.10	-7.83	-39.2
2011-03-18 07:39	8	40	40.04	31.69	0.15	0.10	-8.35	-20.9
2011-03-18 07:54	8	90	90.00	80.51	0.11	0.11	-9.49	-10.5
2011-03-18 08:09	8	60	60.00	52.05	0.13	0.10	-7.95	-13.2
2011-03-18 08:24	8	10	9.99	4.58	0.14	0.09	-5.41	-54.2
2011-03-18 08:39	8	30	30.00	23.97	0.12	0.09	-6.03	-20.1
2011-03-18 08:54	8	50	50.01	43.69	0.11	0.09	-6.32	-12.6
2011-03-18 09:09	8	70	70.00	63.24	0.10	0.12	-6.76	-9.7
2011-03-18 09:24	8	80	79.91	73.58	0.18	0.08	-6.33	-7.9

Table 8. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the backup CPT ozone analyser (OA) TEI 49i #802426999 with the WCC-Empa travelling standard (TS) after repair.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-22 21:10	1	0	0.42	2.60	0.16	0.04	2.18	NA
2011-03-22 21:25	1	40	40.04	41.37	0.12	0.06	1.33	3.3
2011-03-22 21:40	1	80	80.02	81.05	0.07	0.05	1.03	1.3
2011-03-22 21:55	1	90	90.01	91.11	0.10	0.08	1.10	1.2
2011-03-22 22:10	1	60	59.96	61.37	0.11	0.07	1.41	2.4
2011-03-22 22:25	1	20	19.98	21.74	0.11	0.05	1.76	8.8
2011-03-22 22:40	1	30	30.01	31.51	0.09	0.06	1.50	5
2011-03-22 22:55	1	70	70.00	70.91	0.07	0.06	0.91	1.3
2011-03-22 23:10	1	50	50.00	51.19	0.12	0.07	1.19	2.4
2011-03-22 23:25	1	10	10.01	11.82	0.11	0.09	1.81	18.1
2011-03-22 23:40	2	0	0.23	2.34	0.17	0.03	2.11	NA
2011-03-22 23:55	2	90	89.98	90.50	0.10	0.07	0.52	0.6
2011-03-23 00:10	2	30	29.98	31.27	0.14	0.06	1.29	4.3
2011-03-23 00:25	2	40	40.00	41.02	0.16	0.08	1.02	2.6
2011-03-23 00:40	2	60	59.96	60.78	0.10	0.12	0.82	1.4
2011-03-23 00:55	2	20	19.99	21.87	0.23	0.04	1.88	9.4
2011-03-23 01:10	2	80	80.01	80.74	0.11	0.07	0.73	0.9
2011-03-23 01:25	2	70	69.99	71.00	0.08	0.07	1.01	1.4
2011-03-23 01:40	2	10	10.02	11.68	0.18	0.09	1.66	16.6

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-23 01:55	2	50	49.99	50.87	0.12	0.07	0.88	1.8
2011-03-23 02:10	3	0	0.22	2.57	0.14	0.04	2.35	NA
2011-03-23 02:25	3	30	29.98	31.12	0.13	0.06	1.14	3.8
2011-03-23 02:40	3	10	10.00	11.61	0.16	0.07	1.61	16.1
2011-03-23 02:55	3	60	60.01	60.79	0.11	0.07	0.78	1.3
2011-03-23 03:10	3	70	70.01	70.70	0.09	0.11	0.69	1
2011-03-23 03:25	3	90	89.99	90.66	0.09	0.08	0.67	0.7
2011-03-23 03:40	3	50	50.00	51.22	0.12	0.12	1.22	2.4
2011-03-23 03:55	3	80	79.98	80.63	0.08	0.09	0.65	0.8
2011-03-23 04:10	3	20	20.01	21.56	0.16	0.09	1.55	7.7
2011-03-23 04:25	3	40	40.00	41.14	0.13	0.11	1.14	2.8
2011-03-23 04:40	4	0	0.25	2.42	0.06	0.04	2.17	NA
2011-03-23 04:55	4	40	40.02	41.14	0.19	0.08	1.12	2.8
2011-03-23 05:10	4	80	79.98	80.87	0.11	0.07	0.89	1.1
2011-03-23 05:25	4	90	90.02	90.86	0.06	0.05	0.84	0.9
2011-03-23 05:40	4	60	60.00	61.15	0.08	0.07	1.15	1.9
2011-03-23 05:55	4	20	20.01	21.50	0.13	0.05	1.49	7.4
2011-03-23 06:10	4	30	30.03	31.21	0.10	0.10	1.18	3.9
2011-03-23 06:25	4	70	69.98	70.81	0.08	0.09	0.83	1.2
2011-03-23 06:40	4	50	50.02	50.89	0.11	0.06	0.87	1.7
2011-03-23 06:55	4	10	10.33	12.17	0.27	0.08	1.84	17.8
2011-03-23 07:10	5	0	0.33	2.46	0.18	0.03	2.13	NA
2011-03-23 07:25	5	90	89.99	90.30	0.17	0.10	0.31	0.3
2011-03-23 07:40	5	30	29.98	31.48	0.08	0.06	1.50	5
2011-03-23 07:55	5	40	40.02	41.09	0.09	0.05	1.07	2.7
2011-03-23 08:10	5	60	59.99	61.04	0.10	0.07	1.05	1.8
2011-03-23 08:25	5	20	19.96	21.39	0.18	0.08	1.43	7.2
2011-03-23 08:40	5	80	79.99	80.31	0.13	0.08	0.32	0.4
2011-03-23 08:55	5	70	69.99	70.79	0.11	0.10	0.80	1.1
2011-03-23 09:10	5	10	9.98	11.68	0.17	0.05	1.70	17
2011-03-23 09:25	5	50	50.04	50.74	0.08	0.08	0.70	1.4

Table 9. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the backup CPT ozone analyser (OA) TEI 49 #8 51594-288 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-21 11:05	1	0	0.18	-7.74	0.13	0.08	-7.92	NA
2011-03-21 11:20	1	40	40.01	26.45	0.09	0.12	-13.56	-33.9
2011-03-21 11:35	1	80	80.01	63.83	0.09	0.12	-16.18	-20.2
2011-03-21 11:50	1	100	99.98	82.22	0.09	0.10	-17.76	-17.8
2011-03-21 12:05	1	60	60.01	44.32	0.10	0.14	-15.69	-26.1
2011-03-21 12:20	1	20	19.96	7.13	0.18	0.10	-12.83	-64.3
2011-03-21 12:35	2	0	0.19	-9.91	0.26	0.05	-10.10	NA
2011-03-21 12:50	2	80	80.00	61.77	0.10	0.14	-18.23	-22.8
2011-03-21 13:05	2	60	59.79	42.95	0.46	0.17	-16.84	-28.2

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-03-21 13:20	2	20	19.98	6.21	0.16	0.08	-13.77	-68.9
2011-03-21 13:35	2	40	40.05	24.10	0.11	0.06	-15.95	-39.8
2011-03-21 13:50	2	100	100.01	79.69	0.11	0.10	-20.32	-20.3
2011-03-21 14:05	3	0	0.11	-11.57	0.21	0.09	-11.68	NA
2011-03-21 14:20	3	40	39.97	23.11	0.06	0.10	-16.86	-42.2
2011-03-21 14:35	3	60	59.97	42.07	0.10	0.09	-17.90	-29.8
2011-03-21 15:21	3	100	100.00	78.30	0.09	0.27	-21.70	-21.7

Conclusions

The ozone measurements at Cape Point showed significant differences compared to WCC-Empa for the analysers. The main analyser was still within the GAW DQOs, but the reproducibility was poor before instrument cleaning. The TEI 49C and 49i ozone analysers need to be serviced (see recommendations in the Executive Summary); it is recommended to decommission the TEI 49 instrument.

Fortunately the station calibrator agreed perfectly compared to the WCC-Empa travelling standard. This instrument should be used to verify the performance of the TEI 49C and 49i analyser after service / repair.

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Location of air intake:	The air intake is mounted on top of the sampling tower 30 m above ground.
Inlet protection:	Protection against rain water / snow / insects.
Tubing / Material:	30 m ¼" stainless steel tubing to pump box at the base of the tower, MB158e pump, 12 m ¼" stainless steel tubing to two cryo traps (-5°C, -40°C, glass traps), flow rate 12 l min^{-1} in, 50 ml min^{-1} split to RGA-3 instrument.
Inlet filter:	NA
Residence time:	approx. 3s

Instrumentation

Cape Point is equipped with a RGA-3 CO GC; in the meantime a Picarro G2302 has been purchased, and the two instruments are running in parallel. The RGA-3 instrument is still considered as the main CO instrument, and the Picarro system is currently tested at CPT.

Standards

NOAA/ESRL laboratory and working standards (target and calibration gases) pressurised with CPT air using a RIX pump are available at CPT. Table 10 gives an overview of the CPT standards.

Table 10. CO, CO_2 and CH_4 Standards available at CPT.

Cylinder ID	Type	CO (ppb)	U_{CO} (ppb)	CH_4 (ppb)	U_{CH4} (ppb)	CO_2 (ppm)	U_{CO2} (ppb)	Start of use	End of use
CA02907	NOAA	53.4	NA	1730.7	NA	353.23	NA	1997	ongoing
CA02929	NOAA	77.1	NA	1788.1	NA	365.79	NA	1997	ongoing
CA05050	NOAA	105.9	NA	1806.7	NA	382.52	NA	2007	ongoing
CA05081	NOAA	59.4	NA	1741.8	NA	370.95	NA	2007	ongoing
CA05712	NOAA	219.2	NA	1902.4	NA	395.72	NA	2006	ongoing
CA05714	NOAA	60.8	NA	1749.9	NA	364.07	NA	2004	ongoing
CA05715	NOAA	131.1	NA	1857.9	NA	389.05	NA	2006	ongoing
CA05716	NOAA	90.8	NA	1801.6	NA	378.14	NA	2006	ongoing
CA08110	NOAA	NA	NA	NA	NA	410.36	NA	2009	ongoing
CA08138	NOAA	NA	NA	NA	NA	384.38	NA	2009	ongoing
CA03712	Target_CH4	NA	NA	1832.6	NA	NA	NA	Apr_09	ongoing
CA07975	Calgas_CH4	NA	NA	1744.0	NA	NA	NA	Apr_09	ongoing
CA04325	Calgas_CO	63.7	NA	NA	NA	NA	NA	Dec_05	ongoing
CA04035	Target_CO	50.1	NA	NA	NA	NA	NA	Dec_09	ongoing
ALM_78442	Target_CO2	NA	NA	NA	NA	381.96	NA	Nov_10	ongoing
CA04058	Calgas1_CO2	NA	NA	NA	NA	405.35	NA	Nov_10	ongoing
CA04037	Calgas2_CO2	NA	NA	NA	NA	381.88	NA	Oct_10	ongoing

Operation and Maintenance

Check for general operation:	Twice per week (usually Tuesday and Thursday).
Weekly checklist:	A weekly check list is used (RGA-3 test points, visual inspection of chromatogram, peak width, CO-retention time, cylinder pressures). Cold traps are exchanged when necessary.
Linearity check:	As required. A linearity check (range 40 to 80 ppb) with a dilution system is performed when significant changes of the instrument are made (e.g. replacement of the mercury bed).

Data Acquisition and Data Transfer

AZUR GC control software (see [C. Zellweger et al., 2006]).

Data Treatment

Data validation is carried out at the Stellenbosch office by the station scientist. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. Details of the data evaluation [C. Zellweger et al., 2006] and filtering [Brunke et al., 2004] have been described previously.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for carbon monoxide from 1995 to 2010 is available from WDCGG. Filtered (background conditions [*Brunke et al.*, 2004]) and unfiltered data sets have been submitted.

Documentation

All information is entered in paper log books and checklists. A SOP has been prepared by CPT staff, and weekly station check lists were available. The information was comprehensive and up-to-date. The instrument manual was available at the site.

Comparison of the Carbon Monoxide Analyser

All procedures were conducted according to the Standard Operating Procedure [WMO, 2007b] and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 20 below.

Setup and Connections

Table 11 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the CPT data acquisition system.

Table 11. Experimental details of CPT CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 20.	
Station Analyser (AL)	
Model, S/N	RGA-3 #113087-003
Principle	Gaschrommatographic separation, HgO/UV absorption detector
	Analytical column: Mole sieve 5Å 60/80
	Carrier: synthetic air - Mole sieve - Hopcalite – Sofnocat
	Column temp. 100°C, Detector temp. 200°C
	Sample loop 1 ml
	Sample air dried to dew point -40°C
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas port.

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 Table 12.

Table 12. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the RGA-3 instrument with the WCC-Empa TS (WMO-2000 CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(11-03-13 03:23:20)	080814_FA02488	44.96	0.33	45.03	0.38	3	0.07	0.16
(11-03-15 12:32:30)	080820_FA02686	108.03	0.20	106.75	1.43	4	-1.28	-1.18
(11-03-15 15:06:15)	100122_FA02789	56.53	0.92	56.35	0.34	4	-0.18	-0.32
(11-03-15 15:06:15)	100122_FA01469	54.50	0.39	54.75	0.70	4	0.25	0.46
(11-03-17 01:38:45)	080820_FA02785	65.70	0.34	65.33	0.62	4	-0.38	-0.58
(11-03-25 02:21:15)	080814_FA02466	84.87	0.32	83.15	1.14	4	-1.72	-2.03
(11-04-10 12:11:40)	100204_FA02464	70.58	0.05	69.40	0.26	3	-1.18	-1.67
(11-04-11 21:15:00)	070807_FA02770	150.62	0.31	142.83	0.95	3	-7.79	-5.17
(11-04-11 21:40:00)	100122_FA02479	50.98	0.28	50.53	0.50	3	-0.45	-0.88
(11-04-18 14:45:00)	100122_FA02469	2.05	0.63	2.30	0.28	2	0.25	NA
(11-04-26 04:35:00)	100204_FA02505	103.07	0.20	101.97	0.59	3	-1.10	-1.07

Additional comparisons in 2008

WCC-Empa provided in 2008 in collaboration with WCC-N_2O a set of six travelling standards to CPT. Details of the TS are summarised in Table 21 and Figure 18. Due to the longer time period between calibrations at WCC-Empa before and after the field measurements at CPT, these standards showed more significant drift, and the associated uncertainties are therefore larger compared to the current comparison.

The results of the comparison are illustrated in Figure 11 with respect to the WMO GAW DQOs [WMO, 2010; 2011], and the individual measurements of the TS are presented in Table 13. The following equations characterised the instrument bias during the comparison in 2008:

RGA-3 #113087-003:

Unbiased CO mole fraction: X_{CO} (ppb) = (CO + 0.1) / 0.9862 (5a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (4.0 ppb^2 + 1.01e-04 * X_{CO}^2) (5b)

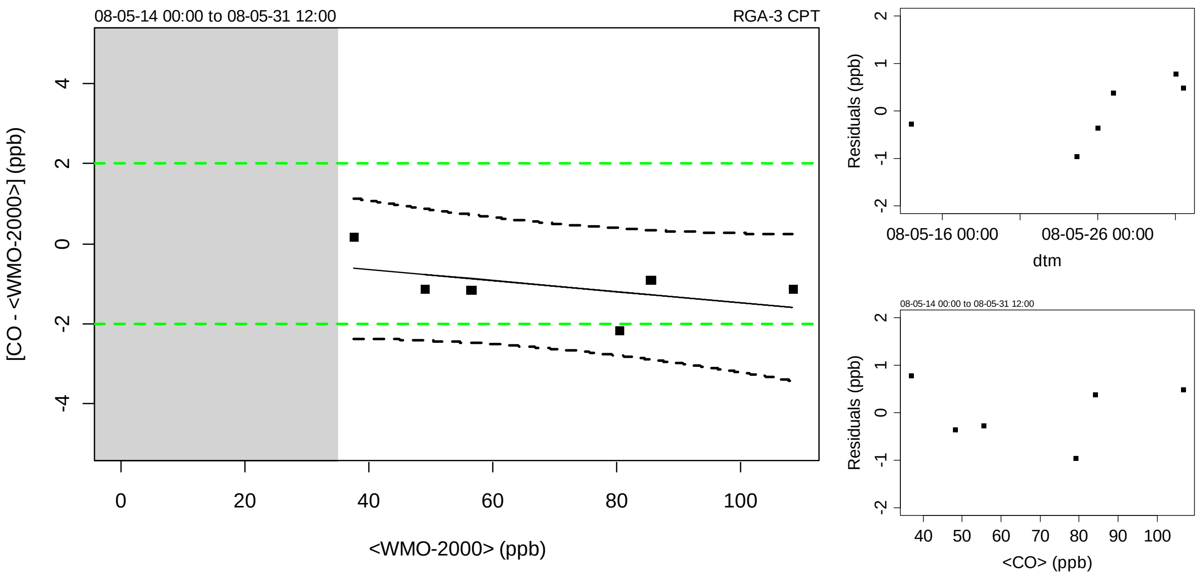

Figure 11. Comparison results with WCC-Empa travelling standard in 2008. Left: Bias of Cape Point RGA-3 carbon monoxide instrument with respect to the WMO2000 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CPT, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

Table 13. Comparison results between the CPT RGA-3 instrument and the WCC-Empa TS (WMO-2000 CO scale) in 2008.

Date / Time	TS Cylinder	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(08-05-14 00:00:00)	070808_FA02783	56.48	1.10	55.32	0.00	2	-1.16	-2.05
(08-05-24 16:00:00)	070807_FA02773	80.41	3.13	78.23	0.47	3	-2.18	-2.71
(08-05-26 00:00:00)	070808_FA02786	48.96	1.22	47.83	0.16	2	-1.13	-2.31
(08-05-27 00:00:00)	070808_FA02769	85.48	1.24	84.58	0.40	2	-0.9	-1.05
(08-05-31 00:00:00)	071122_FA30491	37.56	1.79	37.72	0.96	2	0.16	0.43
(08-05-31 12:00:00)	071122_FF31496	108.36	0.64	107.24	0.80	2	-1.12	-1.03

Conclusions

The carbon monoxide measurements at Cape Point agreed within the WMO GAW DQOs of 2 ppb up to mole fractions of 110 ppb. Significantly larger differences were found for higher CO levels, most likely due to the non-linearity of the RGA-3 GC. The calibrations function of the instrument is only determined for CO levels that correspond to undisturbed Southern Hemispheric conditions. Therefore data acquired during pollution episodes are associated with higher uncertainties with respect to the WMO GAW reference scale.

The recent addition of a Picarro G2302 CO analyser might improve this situation because this analytical technique is much more linear compared to the GC method.

The relative standard deviation of the multiple analyses of the TS was 0.9 % for the RGA-3 GC. This is comparable to other measurement techniques such as UV fluorescence, and significantly better compared to NDIR instruments. Therefore, the CPT instrumentation is fully adequate for CO measurements.

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

All instruments are installed in the same laboratory (see ozone).

Air Inlet System

The same air inlet system as for CO is used; the methane GC also uses a split of 50 ml min^{-1} to flush the sample loop.

Instrumentation

A Varian CP-3800 GC/FID system is used for methane measurements at Cape Point. The instrumentation was installed at the station in 2004.

Standards

See Table 10 above for a list of the currently available CH_4 and CO_2 standards at CPT.

Operation and Maintenance

Check for general operation:	Twice per week (usually Tuesday and Thursday).
Weekly checklist:	A weekly check list is used (retention times, peak shape and integration, flow rates, cylinder pressures). Cold traps are exchanged when necessary.

Data Acquisition and Data Transfer

Unchanged since the last audit, the AZUR GC control software (Version 2.0.4.0) is used for data acquisition and processing. Raw data including chromatograms are archived on a monthly basis. The Testpoint analogue data acquisition is running as a backup system.

Data Treatment

Data validation is carried out at the Stellenbosch office by the station scientist. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. Details of the data evaluation [C. Zellweger et al., 2006] and filtering [*Brunke et al.*, 2004] have been described previously.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for methane since the start of the measurements in 1983 until 2010 is available from WDCGG. Filtered (background conditions [*Brunke et al.*, 2004]) and unfiltered data sets have been submitted.

Documentation

All information is entered in paper log books and checklists. A SOP has been prepared by CPT staff, and weekly station check lists were available. The information was comprehensive and up-to-date. The instrument manual was available at the site.

Comparison of the GC/FID instrument with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure [WMO, 2007b] and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 20 below.

Setup and Connections

Table 14 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the Picarro data acquisition system.

Table 14. Experimental details of the Varian CP-3800 GC/FID comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 20.	
Station Analyser (OA)	
Model, S/N	Varian CP-3800 GC/FID
Principle	GC with FID detector
	Analytical column: Hayesep 80/100, 12 ft x 3/16″
	Carrier: N2 (5.0) – activated charcoal, 180 ml/min
	FID: Air 285 ml/min, H_2 33 ml/min
	Loop 60°C, Column 60°C, FID 170°C
	Sample loop size 7 ml
	Sample air dried to dew point -40°C
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas port.

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 Table 15.

Table 15. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Varian CP-3800 instrument with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(11-03-10 01:51:15)	080820_FA02686	1871.16	0.05	1874.66	1.00	4	3.50	0.19
(11-03-10 08:13:45)	080814_FA02466	1734.91	0.05	1734.81	0.58	4	-0.10	-0.01
(11-03-10 23:15:00)	080820_FA02785	1962.86	0.04	1969.56	0.16	3	6.70	0.34
(11-03-10 23:53:20)	100122_FA01469	1836.47	0.11	1837.57	0.12	3	1.10	0.06
(11-03-11 04:08:20)	080814_FA02488	1309.97	0.05	1302.38	0.47	3	-7.59	-0.58
(11-03-11 05:10:00)	100122_FA02789	1753.40	0.11	1753.29	0.51	3	-0.11	-0.01
(11-04-10 12:48:20)	100204_FA02464	1942.22	0.08	1946.68	1.57	3	4.46	0.23
(11-04-11 21:38:20)	100122_FA02479	1893.25	0.13	1896.95	1.28	3	3.70	0.20
(11-04-18 03:53:45)	100204_FA02470	1830.79	0.07	1831.06	2.14	4	0.27	0.01
(11-04-26 04:51:40)	100204_FA02505	2000.45	0.16	2006.31	1.25	3	5.86	0.29
(11-04-26 05:15:00)	100122_FA02469	1842.38	0.10	1844.18	1.37	3	1.80	0.10

Conclusions

The GC/FID system used at CPT was within the GAW DQOs for levels corresponding to the typical Southern Hemispheric methane background (1700-1850 ppb); however, a larger bias was found for values below and above this limit. The results showed that the instrument is having linearity issues which need further attention.

The relative standard deviation of the multiple analyses of the TS was 0.05% based on single injections. Optimised GC/FID reach values between 0.03 and 0.10% for the relative standard deviation, which shows that the CPT GC/FID system is in a good condition concerning repeatability of the measurements. Besides the linearity issues the Varian CP-3800 instrument is fully adequate for CH_4 measurements.

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

All instruments are installed in the same laboratory (see ozone).

Air Inlet System

The same air inlet system as for CO is used, with the following differences: Additional cold trap at -70°C, split off flow to instrument controlled by a mass flow controller (300 ml min^{-1}), magnesium perchlorate cartridge before instrument for further drying of the sampled air. Residence time approx. 5 s.

Instrumentation

An NDIR analyser (instrument-type URAS 4, Hartmann & Braun, Germany) is deployed at CPT. The measurement set-up was complemented with a Picarro G2302 CO and CO_2 analyser after the audit. The instrumentation was installed at the station in 1993 in collaboration with the twinning partner at IMK-IFU.

Standards

See Table 10 above for a list of the currently available CO_2 standards at CPT.

Operation and Maintenance

Check for general operation:	Twice per week (usually Tuesday and Thursday).
Weekly checklist:	A weekly check list is used. Cold traps are exchanged when necessary.
Linearity check:	A linearity check in the range from 340-450 ppm CO_2 is made once per year.

Automatic measurements of the working standards (every 6 hour) and a target gas (working standard with mole fraction close to ambient background level, daily) are made.

Data Acquisition and Data Transfer

Data acquisition is made using ADAM 4017 D/A converter units with Testpoint (Keithley) software. The analogue signal of the CO_2 instrument is acquired, and 1-minute and 30-minute average signals are stored on the data acquisition computer. 10-second data can also be acquired but is not routinely stored. No additional instrument parameters are acquired. Data back-ups are made weekly.

Data Treatment

Data validation is carried out at the Stellenbosch office by the station scientist. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. Details of the data treatment and filtering [*Brunke et al.*, 2004] have been described previously.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for methane since the start of the measurements in 1993 until 2010 is available from WDCGG. Filtered (background conditions [*Brunke et al.*, 2004]) and unfiltered data sets have been submitted. It was noted that the scale version was not correctly submitted (see recommendation 10).

Documentation

All information is entered in paper log books and checklists. A SOP has been prepared by CPT staff, and weekly station check lists were available. The information was comprehensive and up-to-date. The instrument manual was available at the site.

Comparison of the NDIR CO_2 instrument with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure [WMO, 2007b] and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 20 below.

Setup and Connections

Table 16 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the URAS 4 data acquisition system.

Table 16. Experimental details of the Hartmann & Braun URAS 4 comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 20.	
Station Analyser (OA)	
Model, S/N	Hartmann & Braun URAS 4
Principle	NDIR
	Sample air dried to dew point -70°C
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas port.

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 Table 17.

Table 17. CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Hartmann & Braun URAS 4 instrument with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	uTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(11-03-06 07:09:00)	100122_FA02789	373.64	0.03	373.94	0.13	5	0.30	0.08
(11-03-06 07:44:36)	100122_FA01469	393.35	0.04	393.20	0.10	5	-0.15	-0.04
(11-03-26 23:19:15)	100122_FA02479	406.88	0.03	406.87	0.13	4	-0.01	0.00
(11-03-26 23:22:30)	100122_FA02469	384.16	0.01	384.02	0.20	4	-0.14	-0.04
(11-03-27 11:08:36)	100204_FA02505	366.40	0.03	366.80	0.15	5	0.40	0.11

Conclusions

Individual carbon dioxide measurements at Cape Point exceeded the WMO GAW DQOs for the Southern Hemisphere of 0.05 ppm in the mole fraction range of 360 to 410 ppm; however, the agreement was within 0.01 ppm when all comparison data was aggregated. The larger bias of the individual measurements is likely caused by the relatively high standard deviation of the multiple analyses of the TS, which was ranging from 0.025 to 0.052% for the TS comparisons. In absolute terms, this corresponds to 0.1 to 0.2 ppm, which is clearly insufficient for meeting the WMO GAW DQO of 0.05 ppm.

The recent addition of a Picarro G2302 CO_2 analyser might improve this situation because this analytical technique usually shows much better reproducibility.

On-site Comparisons with a Picarro G2401 Analyser

Picarro Inc. provided a G2401 CO, CO_2, CH_4 and H_2O analyser for on-site comparisons as part of the WCC-Empa audit. The instrument was running in parallel to the CPT systems over a period of two months using a separate inlet line to the same air intake location. For this purpose, the existing ¼ inch Dekabon line which is normally deployed for flask sampling was used. This line leads to the exact same intake location as for the other measurements on the 30 m tower. The line was flushed with a bypass pump at 2 l/min, and then a custom made sampling unit was used for air delivery to the Picarro G2401. Three WCC-Empa standards were injected every 1-3 days, and no significant drift was observed for these standard injections during the 2-month period. The results of the standard injections were used to calibrate the Picarro G2401 instrument.

During the last five days of the comparison period, the Picarro G2401 was connected to the CPT drying system, and all instrument sampled the same dry air. In contrast to the comparisons of the travelling standards, much higher deviations between CPT and WCC-Empa were observed, which cannot easily be explained and need further attention. The main results of the 2-month measurement campaign are described below.

Parallel CO_2 measurements

One-hourly CO_2 data measured by both the CPT URAS-4 and the WCC-Empa Picarro G2401 instruments is shown in in Figure 12. It can be seen that the deviation between the instruments was relatively good until 11-04-14; afterwards, some periods showed significant deviations between the instruments, and the bias between the two analysers was less stable. One possible cause of these differences could be the exchange of the freezing traps; however, further investigation by CPT staff is needed to identify the reasons for this behaviour. (Note 2011-12-20: the longer period with larger deviation could clearly be attributed to a freeze trap issue.)

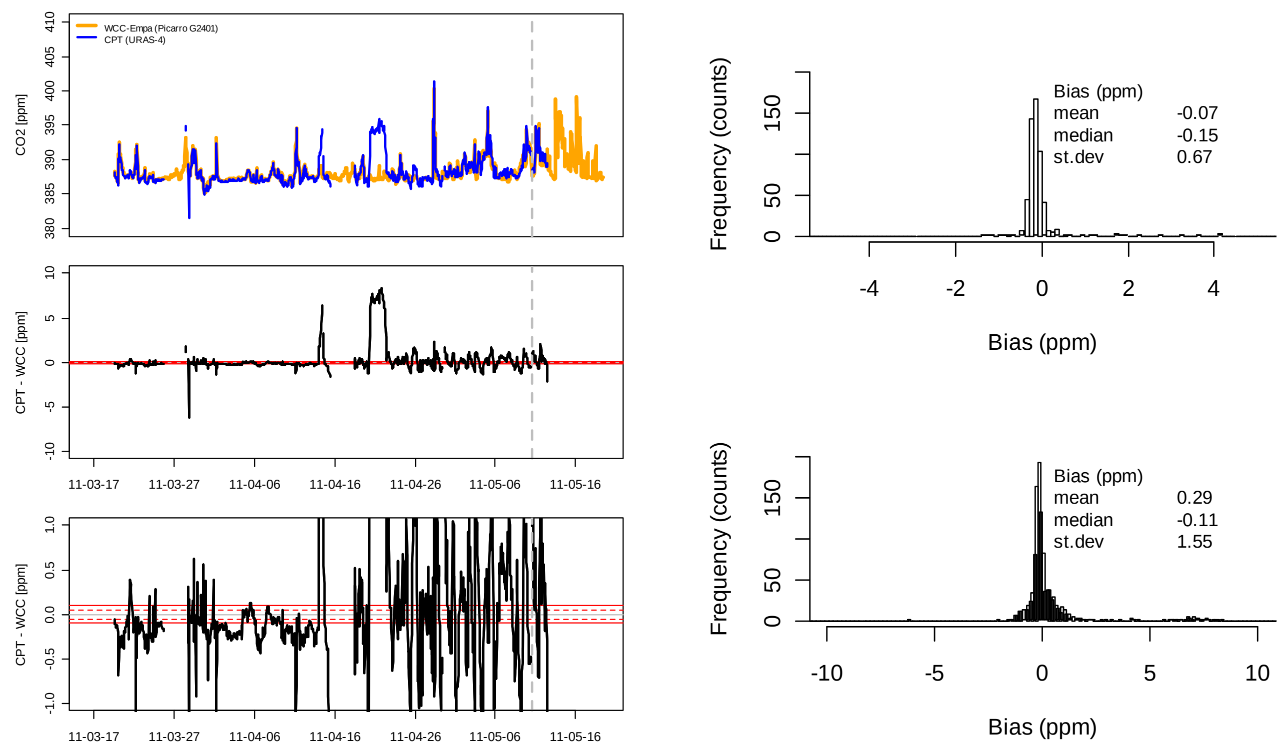

Figure 12. Left: Parallel measurements of CO_2 at CPT (upper panel), and difference between CPT and WCC-Empa (lower panels). The red lines indicate the WMO/GAW DQOs. Right: Frequency distributions of the bias between CPT and WCC-Empa until 11-04-14 (top panel) and for all data (bottom panel).

Parallel CH_4 measurements

One-minute CH_4 data measured by the WCC-Empa Picarro analyser and single injections by the CPT GC/FID system are shown in in Figure 13. The deviation between the instruments clearly exceeded the WMO/GAW DQOs of 2 ppb for most of the comparison period. This was not expected based on the audit results, and the reason for the bias needs further investigation. The observed bias is comparable with comparisons between CPT in-situ measurements and the NOAA flask sampling programme.

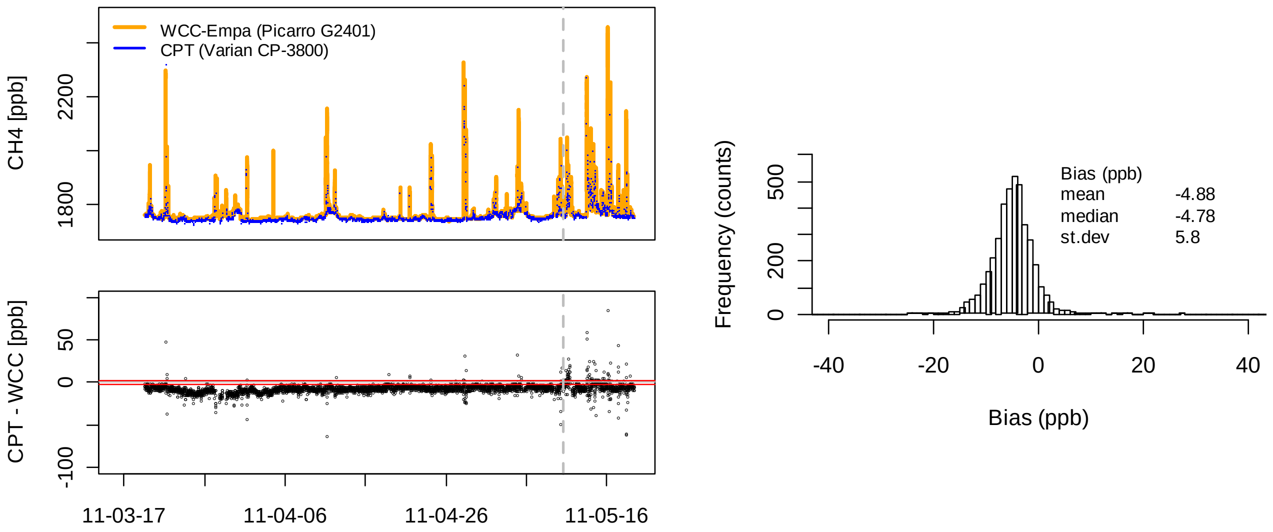

Figure 13. Left: Parallel measurements of CH_4 at CPT (upper panel), and difference between CPT and WCC-Empa (lower panel). The red lines indicate the WMO/GAW DQOs. Right: Frequency distributions of the bias between CPT and WCC-Empa for all data.

Parallel CO measurements

One-minute CO data measured by the WCC-Empa Picarro analyser and single injections by the CPT RGA-3 system are shown in in Figure 14. The deviation between the instruments clearly exceeded the WMO/GAW DQOs of 2 ppb for the comparison period without sample drying for the Picarro measurements. The bias can to a large part be explained by the mole fraction dependent water vapour interference of the Picarro G2401 analyser. The agreement became significantly better when the sample air was dried; however, most of this period was characterised by large CO variability, and mole fractions exceeded the calibrated range of the CPT instrument. In conclusion, the observed bias between the two systems are mainly attributable to imperfect compensation of the H2O interference of the Picarro system, whereas the CPT RGA-3 analyser seems to work fine within its limitations (non-linear response, insufficient characterisation of the instrument response function for a complete coverage of CPT CO variability).

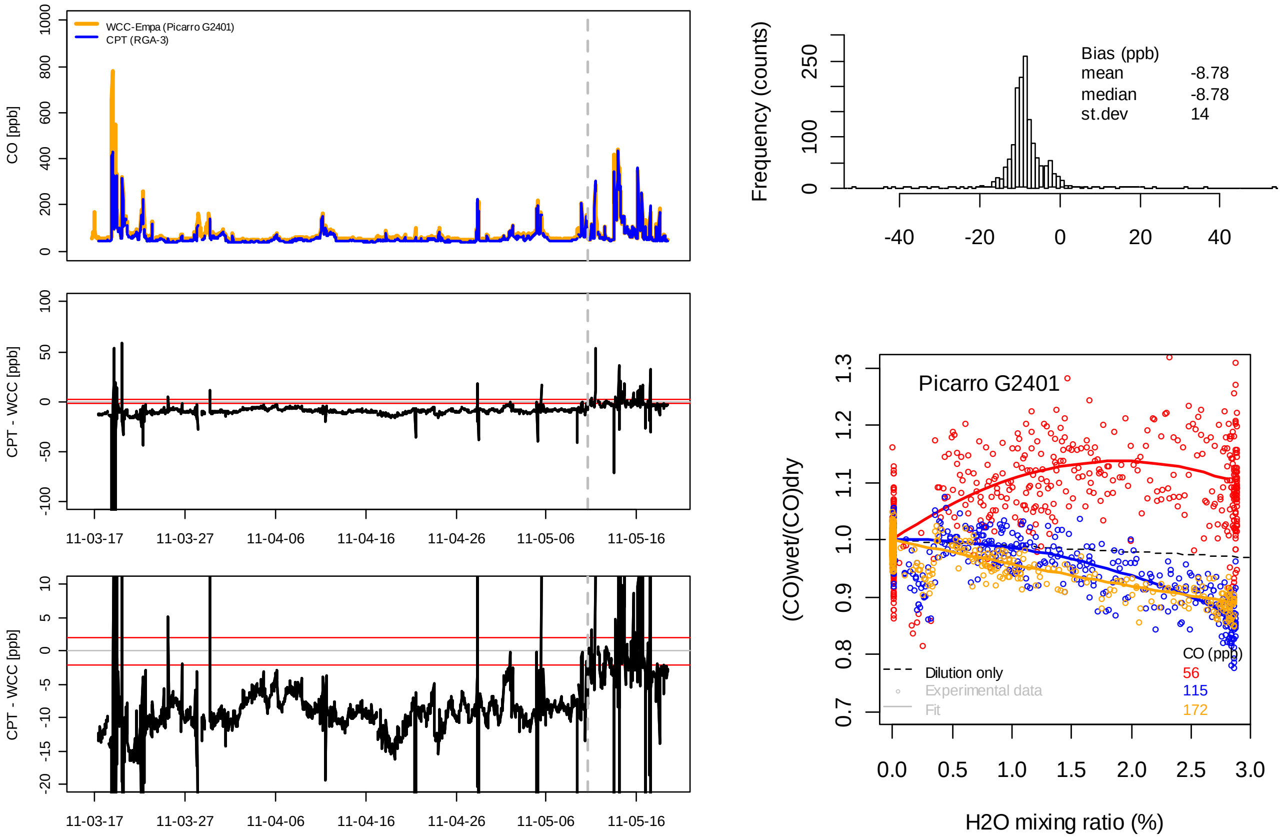

Figure 14. Left: Parallel measurements of CO at CPT (upper panel), and difference between CPT and WCC-Empa (lower panels). The red lines indicate the WMO/GAW DQOs, and the grey dotted line the time when the Picarro instrument was connected to the drying system. Right top: Frequency distributions of the bias between CPT and WCC-Empa for all data. Right bottom: Influence of water vapour mixing ratios on Picarro G2401 CO as a function of CO mole fraction.

WCC-Empa Travelling Standards

Ozone

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

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

WCC-Empa TS: TEI 49i-PS #0810-153, BKG -0.2, COEF 1.009

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 18. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 15). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mole fraction 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] - 0.06 ppb) / 1.002 (6a)

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

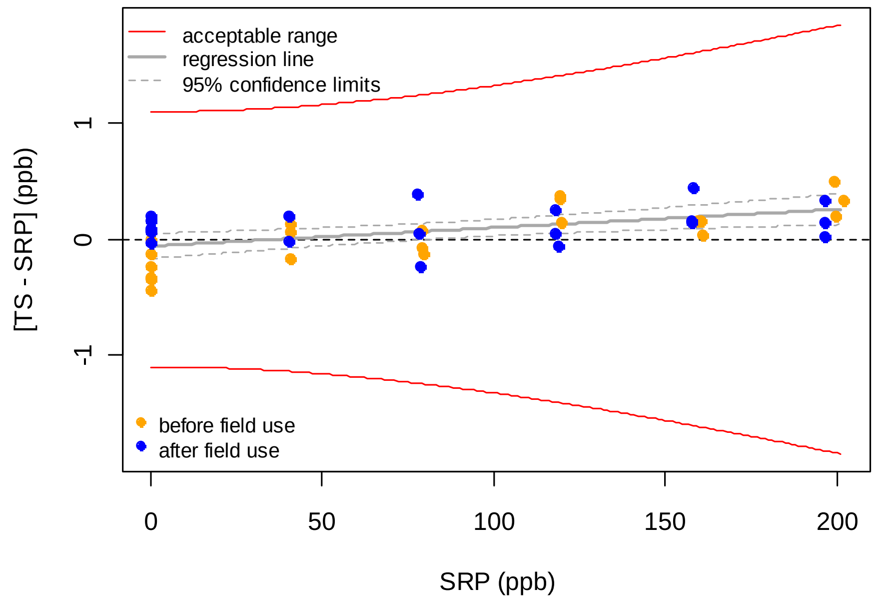

Figure 15. Deviations between Travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 18. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa Travelling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2011-01-28	1	0	0.07	0.16	-0.16	0.23
2011-01-28	1	80	79.39	0.14	79.27	0.25
2011-01-28	1	160	160.26	0.42	160.42	0.43
2011-01-28	1	40	40.70	0.17	40.77	0.17
2011-01-28	1	120	119.11	0.22	119.46	0.38
2011-01-28	1	200	199.80	0.12	200.00	0.40
2011-01-28	1	0	0.13	0.13	-0.21	0.11
2011-01-28	2	0	0.11	0.19	-0.32	0.26
2011-01-28	2	160	160.91	0.33	160.94	0.22
2011-01-28	2	120	119.57	0.24	119.72	0.22
2011-01-28	2	40	40.59	0.26	40.73	0.20
2011-01-28	2	200	199.52	0.26	200.01	0.38
2011-01-28	2	80	79.02	0.21	79.10	0.25
2011-01-28	2	0	0.18	0.19	-0.15	0.26
2011-01-28	3	0	0.02	0.30	0.01	0.33
2011-01-28	3	200	201.91	0.39	202.25	0.23
2011-01-28	3	160	159.69	0.17	159.84	0.30
2011-01-28	3	120	119.27	0.44	119.64	0.27
2011-01-28	3	80	79.03	0.20	78.96	0.23
2011-01-28	3	40	40.64	0.27	40.48	0.20
2011-01-28	3	0	0.03	0.29	-0.09	0.21
2011-06-01	4	0	0.11	0.44	0.20	0.18
2011-06-01	4	80	78.48	0.11	78.25	0.15
2011-06-01	4	160	157.69	0.27	157.83	0.19
2011-06-01	4	40	40.16	0.24	40.36	0.24
2011-06-01	4	200	196.55	0.22	196.57	0.25
2011-06-01	4	120	117.91	0.38	117.96	0.20
2011-06-01	4	0	-0.09	0.35	0.00	0.15
2011-06-01	5	0	0.03	0.20	0.09	0.19
2011-06-01	5	120	118.89	0.31	118.83	0.15
2011-06-01	5	80	78.22	0.36	78.28	0.12
2011-06-01	5	160	157.65	0.19	157.81	0.20
2011-06-01	5	200	196.75	0.23	197.09	0.31
2011-06-01	5	40	40.15	0.24	40.14	0.34
2011-06-01	5	0	0.00	0.16	-0.04	0.19
2011-06-01	6	0	-0.08	0.30	0.11	0.26
2011-06-01	6	160	158.33	0.27	158.77	0.33
2011-06-01	6	40	40.18	0.21	40.38	0.28
2011-06-01	6	120	118.11	0.34	118.36	0.10
2011-06-01	6	200	196.75	0.55	196.90	0.31
2011-06-01	6	80	77.73	0.27	78.12	0.20
2011-06-01	6	0	0.03	0.29	0.20	0.14

#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 Travelling 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-2000/2004 scale [*Novelli et al.*, 2003]

CO_2: WMOX2007 scale [*Zhao and Tans*, 2006]

CH_4: NOAA04 scale [*Dlugokencky et al.*, 2005]

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 at WCC-Empa:

CO: Aerolaser AL5001 (Vacuum UV Fluorescence) and Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).

CO_2 and CH_4: Picarro G1301 (Cavity Ring Down Spectroscopy).

Table 19 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. For internal consistency among the available LS at WCC-Empa, new values have been assigned to the NOAA standards for some tanks. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 20, and Figure 16 and Figure 17 show 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.

TS #100204_FA02470 was not used for the CO assessment because of drift during the audit period.

Table 21 and Figure 18 summarise the results of the TS used in the comparison in 2008. The uncertainty of these standards is slightly higher due to the fact that the time span before and after comparison against the WCC-Empa laboratory standards was longer, which resulted in more significant drift.

Table 19. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO	sd	CH_4	sd	N_2O	sd	CO_2	sd	CO	sd	CH_4	sd	N_2O	sd	CO_2	sd
	NOAA assigned values								WCC-Empa assigned values							
	(ppb)		(ppb)		(ppb)		(ppm)		(ppb)		(ppb)		(ppb)		(ppm)	
CA05373	130.0*	0.4	1608.57	0.08	NA	NA	326.96	0.00	131.7	0.2	1607.82	0.04	294.43	0.03	326.77	0.01
CC339523	347.9*	0.3	1854.60	0.13	322.52	0.12	396.88	0.06	352.2	0.3	1855.31	0.03	322.66	0.02	396.97	0.02
CC339524	390.7*	0.2	1980.28	0.30	355.24	0.16	795.42	0.06	395.4	0.4	1981.77	0.04	355.32	0.02	796.60	0.04
CC311846	166.4*	0.1	1805.24	0.12	317.24	0.11	377.86	0.04	168.9	0.3	1805.61	0.11	317.40	0.01	377.86	0.02
CA02854	295.5#	3.0	NA	NA	NA	NA	NA	NA	295.3	0.6	1677.14	0.08	NA	NA	347.36	0.03

*WMO-2004, #WMO-2000

Table 20. Calibration summary of the WCC-Empa travelling standards.

TS	CO	sdCO	CH_4	$sdCH_4$	CO_2	$sdCO_2$
	(ppb)	(ppb)	(ppb)	(ppb)	(ppm)	(ppm)
070807_FA02770	150.62	0.31	1861.44	0.04	391.62	0.03
080814_FA02466	84.87	0.32	1734.91	0.05	179.25	0.02
080814_FA02488	44.96	0.33	1309.97	0.05	149.79	0.03
080820_FA02686	108.03	0.20	1871.16	0.05	172.93	0.01
080820_FA02785	65.70	0.34	1962.86	0.04	245.03	0.01
100122_FA01469	54.50	0.39	1836.47	0.11	393.35	0.04
100122_FA02469	2.05	0.63	1842.38	0.10	384.16	0.01
100122_FA02479	50.98	0.28	1893.25	0.13	406.88	0.03
100122_FA02789	56.53	0.92	1753.40	0.11	373.64	0.03
100204_FA02464	70.58	0.05	1942.22	0.08	347.12	0.02
100204_FA02470	55.80	2.60	1830.79	0.07	342.71	0.01
100204_FA02505	103.07	0.20	2000.45	0.16	366.40	0.03

Table 21. Calibration summary of the WCC-Empa CO travelling standards sent to CPT in 2008.

TS	CO	sdCO
	(ppb)	(ppb)
070807_FA02773	80.41	3.13
070808_FA02769	85.48	1.24
070808_FA02783	56.48	1.10
070808_FA02786	48.96	1.22
071122_FA30491	108.36	0.64
071122_FF31496	37.56	1.79

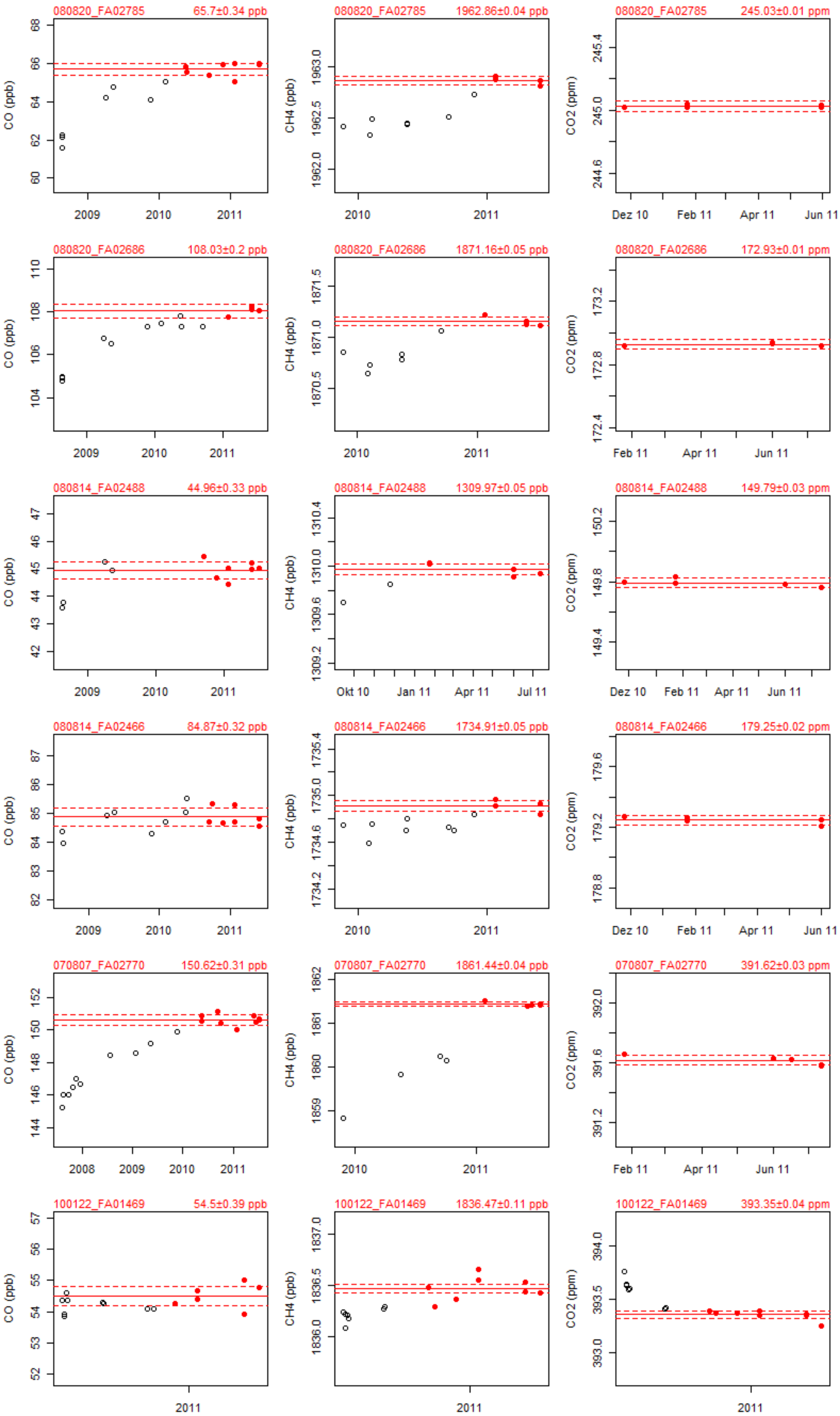

Figure 16. Results of the WCC-Empa TS calibrations. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard uncertainty and includes the uncertainty of the reference scale.

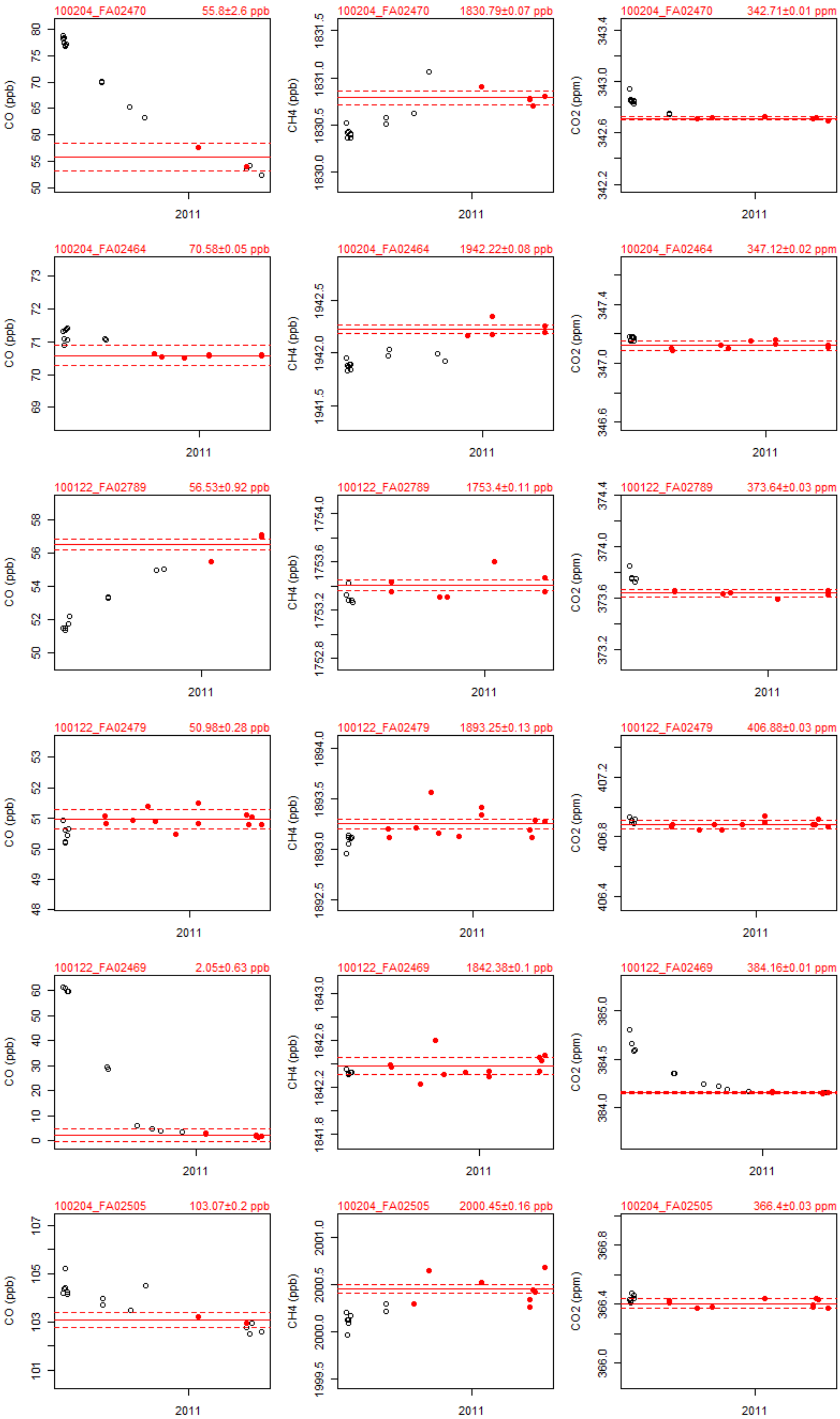

Figure 17. Results of the WCC-Empa TS calibrations. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard uncertainty and includes the uncertainty of the reference scale.

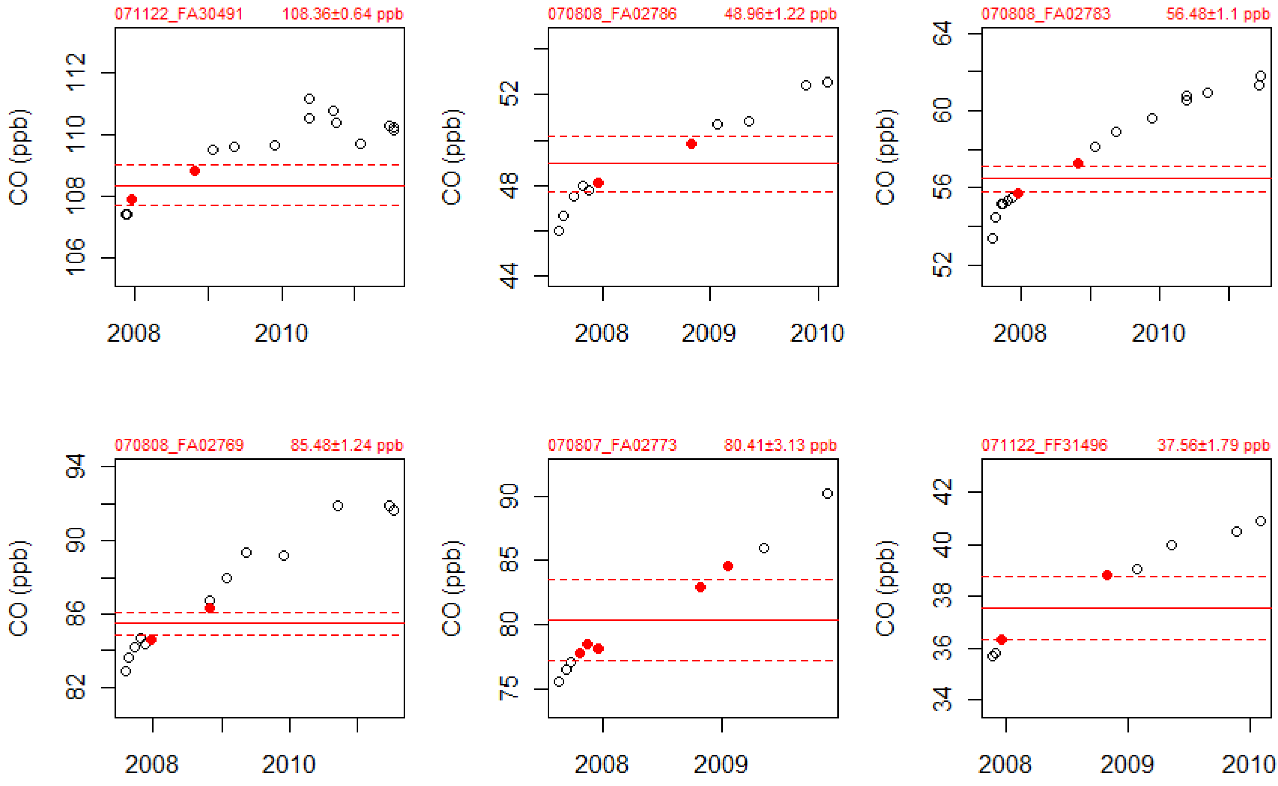

Figure 18. Results of the WCC-Empa TS calibrations for the standards used in 2008. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard uncertainty and includes the uncertainty of the reference scale. The measurements at CPT were made in May/June 2008, and linear drift of the WCC-Empa TS was assumed.

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Ozone Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.35348°S 18.48968°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2011-03-18
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
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 -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.002±0.001) • [SRP] - (0.1±0.2)
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; COEFF = 1.019
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.004±0.001) • [SRP] - (0.5±0.1)
1.6.5	Unbiased ozone mole fraction (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.5 ppb) / 1.004
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.68e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mole fraction (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments: NA	
1.8	Reference:	WCC-Empa Report 11/1

[OC]: Instrument readings; [SRP]: SRP readings; X_{O3}: mole fractions on SRP scale

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Parameter:		Surface Ozone

1.1	Date of Audit:	2011-03-18
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
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 -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.002±0.001) • [SRP] - (0.1±0.2)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #5226513044
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = -0.5; COEFF = 1.015
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9830±0.001) • [SRP] - (1.8±0.1)
1.6.5	Unbiased ozone mole fraction (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 1.8 ppb) / 0.9830
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.5 ppb^2 + 2.73e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	[OA] = (0.9861±0.000) • [SRP] - (0.3±0.1)
1.6.9	Unbiased ozone mole fraction (ppb) after audit:	X_{O3} (ppb) = ([OA] + 0.3 ppb) / 0.9861
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.5 ppb^2 + 2.67e-05 * X_{O3}^2)
1.7	Comments: First results in initial state, 2nd comparison after disassembling and cleaning	
1.8	Reference:	WCC-Empa Report 11/1

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mole fractions on SRP scale

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0.3	Coordinates/Elevation:	34.35348°S 18.48968°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2011-03-18
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
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 -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.002±0.001) · [SRP] - (0.1±0.2)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #802426999
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.0; COEFF = 1.038
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9496±0.001) · [SRP] - (5.1±0.1)
1.6.5	Unbiased ozone mole fraction (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 5.1 ppb) / 0.9496
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (8.0 ppb^2 + 2.92e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	[OA] = (0.9870±0.000) · [SRP] + (1.9±0.1)
1.6.9	Unbiased ozone mole fraction (ppb) after audit:	X_{O3} (ppb) = ([OA] – 1.9 ppb) / 0.9870
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.67e-05 * X_{O3}^2)
1.7	Comments: First results in initial state, 2nd comparison after disassembling and repair	
1.8	Reference:	WCC-Empa Report 11/1

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mole fractions on SRP scale

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Ozone Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.35348°S 18.48968°E (230 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2011-03-18
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
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 -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.002±0.001) • [SRP] - (0.1±0.2)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49 # 51594-288
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	ZERO = 56; SPAN = 507
1.6.4	Calibration at start of audit (ppb):	[OA] = (0. 9173±0.001) • [SRP] - (11.3±0.9)
1.6.5	Unbiased ozone mole fraction (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 11.3 ppb) / 0.9173
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (3.2 ppb^2 + 3.32e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mole fraction (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments: Analyser was not working properly and should be decommissioned	
1.8	Reference:	WCC-Empa Report 11/1

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mole fractions on SRP scale

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Carbon Monoxide Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.35348°S 18.48968°E (230 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2011-03-13 to 2011-04-26
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2000 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2000 scale
1.6	Station CO Reference:	NOAA/GMD WMO-2004 laboratory standards
1.6.1	Analyser Model:	RGA-3 #113087-003
1.6.2	Range of calibration:	0 – 150 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9527±0.0113) · X_{CO} + (2.2±0.9)
1.6.5	Unbiased CO mole fraction (ppb) at start of audit:	X_{CO} (ppb) = (CO – 2.2) / 0.9527
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (3.5 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 mole fraction (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	Calculations based on WMO-2000 CO scale
1.8	Reference:	WCC-Empa Report 11/1

[CO]: Instrument readings; X: mole fractions on the WMO-2000 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:	34.35348°S 18.48968°E (230 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2011-03-10 to 2011-04-26
1.2	Auditor:	Dr. C. Zellweger, Mr. B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station CH_4 Reference:	WS and NOAA laboratory standards (NOAA04 scale)
1.6.1	Analyser Model:	Varian CP-3800 GC/FID
1.6.2	Range of calibration:	1310 – 2000 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (1.02019 \pm 0.00182) \cdot X_{CH4} - (34.9 \pm 3.3)$
1.6.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 + 34.9) / 1.02019$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = $\mathrm{sqrt}(3.9\ \mathrm{ppb}^2 + 1.30\mathrm{e}{-07} * X_{CH4}^2)$
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 mole fraction (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 11/1

[CH_4]: Instrument readings; X: mole fractions on the NOAA04 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:	34.35348°S 18.48968°E (230 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2011-03-10 to 2011-04-26
1.2	Auditor:	Dr. C. Zellweger, Mr. B. Schwarzenbach
1.3	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, T. Mkololo
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 CO_2 Reference:	WS and NOAA laboratory standards (WMO-X2007 scale)
1.6.1	Analyser Model:	Hartmann & Braun URAS 4
1.6.2	Range of calibration:	366 – 407 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.988130 \pm 0.006142) \cdot X_{CO2} + (4.65 \pm 2.37)$
1.6.5	Unbiased CO_2 mole fraction (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 – 4.65) / 0.988130$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.08 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 mole fraction (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 11/1

[CO_2]: Instrument readings; X: mole fractions on the WMO-X2007 CO_2 scale.

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LIST OF ABBREVIATIONS

BKG	Background
CCL	Central Calibration Laboratory
COEF	Coefficient
CPT	Cape Point GAW Station
CRDS	Cavity Ring-Down Spectroscopy
DAQ	Data Acquisition System
DQO	Data Quality Objective
dtm	Date/Time
ESRL	Earth System Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
IMK-IFU	Institute for Meteorology and Climate Research, Atmospheric Environmental Research
LS	Laboratory Standard
MFC	Mass Flow Controller
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
SAWS	South African Weather Service
QCL	Quantum Cascade Laser
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
TS	Travelling Standard
UV	Ultra Violet
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard