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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 06/5

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE, CARBON MONOXIDE AND METHANE

AT THE

GLOBAL GAW STATION CAPE POINT

SOUTH AFRICA, SEPTEMBER 2006

Submitted by

C. Zellweger, J. Klausen, B. Buchmann

WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane

Empa Dübendorf, Switzerland

Empa is accredited as a calibration laboratory for ozone measuring instruments in accordance with ISO/IEC 17025

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ASSESSMENT AND RECOMMENDATIONS

The fourth system and performance audit at the Global GAW station Cape Point (CPT) was conducted by WCC-Empa[1] from 13 through 16 September 2006 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007]. The CPT observatory is operated 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] and in April 2002 [*Zellweger, et al.*, 2002].

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Ernst-Günther Brunke	SAWS, Station Manager
Casper Labuschagne	SAWS, Station Scientist
Danie van der Spuy	SAWS, Station Operator
Bhawoodien Parker	SAWS, Station Operator

Our assessment of the Cape Point observatory in general, as well as the surface ozone, carbon monoxide and methane measurements in particular, is summarised below. The assessment criteria for the ozone inter-comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003].

This report is distributed to the GAW Country Contact (SAWS, Gerrie J. R. Coetzee), the station manager (SAWS, Ernst-Günther Brunke) and the World Meteorological Organization in Geneva. The executive summaries will be posted on the internet.

The recommendations found in this report 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 GAWSIS (www.empa.ch/gaw/gawsis).

Station Facilities

The Cape Point observatory comprises extensive laboratory and office facilities. It is an ideal platform for continuous atmospheric monitoring as well as measurement campaigns.

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).

[1] WMO/GAW 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.

Air Inlet System

The design of the air inlet system is state of the art (for all parameters) and no further recommendations are made by WCC-Empa. However, it was recognized during the audit that the filter holders used for the surface ozone measurements were leaking. Replacement is required immediately.

> **Recommendation 1 (***, immediately)**
> *Filter holders of the ozone instruments need to be replaced due to leakages. All other filter holders should be checked for tightness. It is further recommended to include the check of the inlet filters in the regular maintenance schedule of the station.*

Surface Ozone Measurements

Instrumentation. Two ozone analysers are currently used at the station for continuous parallel surface ozone measurements (TEI 49 and TEI 49C instruments) at two levels (inlet height 4 m and 30 m above the station). Automatic zero and span checks (approx. 50 ppb) are made once per day. The instrumentation is adequate for its intended purpose, though only data of the new TEI 49C should be considered for the final ozone data as after the audit.

> **Recommendation 2 (***, immediately)**
> *Only data of the TEI 49C instrument should be considered for submission to WDCGG. This was already initiated during the audit with the connection of this instrument to the 4 m inlet.*
>
> **Recommendation 3 (*, 2007-2009)**
> *The TEI 49 instrument should be replaced by a new model.*
>
> **Recommendation 4 (***, 2007)**
> *WCC-Empa recommends to perform the automatic span checks at a higher level, e.g. 100 ppb ozone to recognise changes in the instrument performance earlier.*

Standards. No ozone standard is available at the site, nor in South Africa. Calibrations were only performed during WCC-Empa audits, and with comparisons to a transfer standard from IMK-IFU.

> **Recommendation 4 (**, 2007)**
> *It should be considered to purchase an ozone calibrator for additional instrument calibrations and performance tests.*

Intercomparison (Performance Audit). The inter-comparisons extended over a period of several days. Both instruments were inter-compared during the audit. The following issues were encountered during the audit:

TEI 49:

This instrument was the main station analyser until the audit by WCC-Empa. The instrument was found to measure significantly lower when compared to WCC-Empa. The result of this first assessment is summarised below (1a). [OA] (ozone analyser) represents surface ozone readings obtained from the station data acquisition (TEI49).

Initial calibration:

TEI49 #51594-288: 0 – 90 ppb good agreement

Unbiased O3 mole fraction (ppb) X_{O3} (ppb) = ([OA] + 0.23 ppb) / 0.953 (1a)

The reason for these low readings were identified to be caused by a leaking valve (internal ozone/reference valve). The valve could be replaced, and the assessment after repair is summarised below (1b).

Calibration after repair, including the inlet filter:

TEI49 #51594-288:	0 – 90 ppb good agreement	
Unbiased O_3 mole fraction (ppb)	X_{O3} (ppb) = ([OA] + 0.17 ppb) / 0.983	(1b)

It was found that a further ozone loss occurred over the inlet filter. A final assessment after repair excluding the filter is summarised below (1c).

Calibration after repair, excluding the inlet filter:

TEI49 #51594-288:	0 – 90 ppb good agreement	
Unbiased O3 mole fraction (ppb)	X_{O3} (ppb) = ([OA] + 0.39 ppb) / 0.999	(1c)

The results of these inter-comparisons are presented in Figure 1.

The final calibration confirmed the good agreement between the station analyser and WCC-Empa that was found in the previous audit in 2002. Data should carefully be revised to identify the period where lower measurements were observed due to the defective valve and losses over the inlet filter. This can be done analysing the automatic span data; however, small percentage changes are difficult to identify due to the relatively low span level of approx. 50 ppb.

Recommendation 5 (*, 2007)**
Data acquired with the TEI 49 analyser need to be carefully revised before submission to the data centre or further scientific analysis. The time period with invalid data needs to be identified using existing ancillary information such as span checks.

Recommendation 6 (*, 2007)**
WCC-Empa recommends to submit data of the TEI 49C analyzer to WDCGG; Data acquired with this instrument for the period before the audit should be corrected using equation (1d) below.

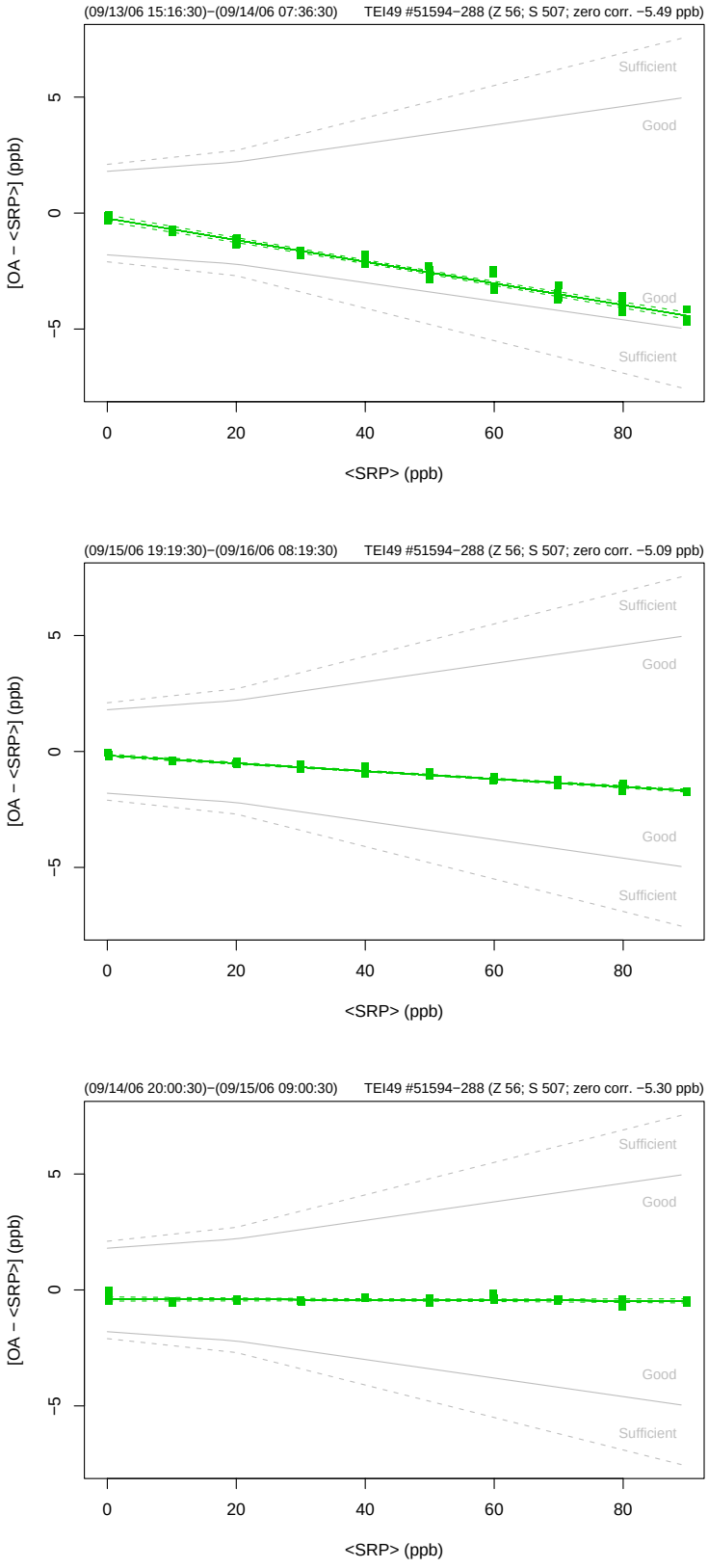

Figure 1. Bias of the Cape Point ozone analyser (TEI 49) with respect to the SRP (Standard Reference Photometer) as a function of mole fraction (upper panel: initial calibration; middle panel: after repair with inlet filter; lower panel: after repair without inlet filter). Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen, et al., 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

TEI 49C:

This instrument was purchased in January 2006 and has been running as a backup instrument since then. The opportunity for a detailed calibration had not arisen yet and as such the coefficients (BKG 0.0 ppb, COEF 1.013) determined by the factory were still those in use at the beginning of the audit. The analyser was initially compared with these settings, and the result of this first assessment is summarised below (1d). The calibration settings were then adjusted by WCC-Empa (BKG -0.5 ppb, COEF 1.015), which resulted in a relationship given in (1e). Both assessment results are presented in Figure 1.

Initial calibration (BKG 0.0 ppb, COEF 1.013):

TEI 49C #526513044: 0 – 90 ppb good agreement

Unbiased O_3 mole fraction (ppb) X_{O3} (ppb) = ([OA] + 0.75 ppb) / 0.993 (1d)

Calibration after adjustment (BKG -0.5 ppb, COEF 1.015):

TEI 49C #526513044: 0 – 90 ppb good agreement

Unbiased O_3 mole fraction (ppb) X_{O3} (ppb) = ([OA] + 0.25 ppb) / 1.000 (1e)

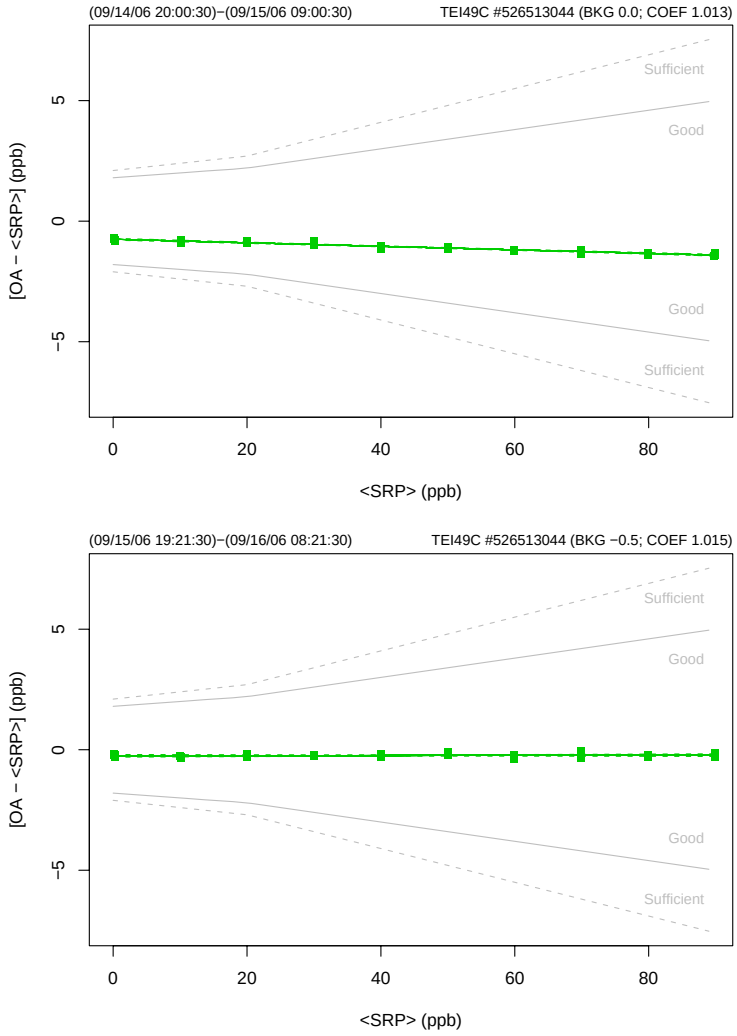

Figure 2. Bias of the new Cape Point ozone analyser (TEI 49C) with respect to the SRP as a function of mole fraction (upper panel: initial calibration; lower panel: after calibration factor adjustment). Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen, et al., 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Carbon Monoxide Measurements

Instrumentation. Cape Point is currently equipped with an RGA-3 carbon monoxide GC. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with eight carbon monoxide standards from NOAA/ESRL (National Oceanic & Atmospheric Administration / Earth System Research Laboratory). The standards have been calibrated or certified for both WMO-88 and WMO-2000 scales by NOAA/ESRL. The standards span a mole fraction range from approx. 50 – 220 ppb CO. In addition, two standards from IMK-IFU are available at the site. 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 inter-comparison involved repeated challenges of the instruments with randomised carbon monoxide mole fractions from travelling standards. The following equation (2) characterises the instrument bias (cf. Figure 3):

RGA-3, S/N 113087-003:

Unbiased CO mole fraction (ppb): X_{CO} (ppb) = ([CO] + 1.9 ppb) / 1.008 (2)

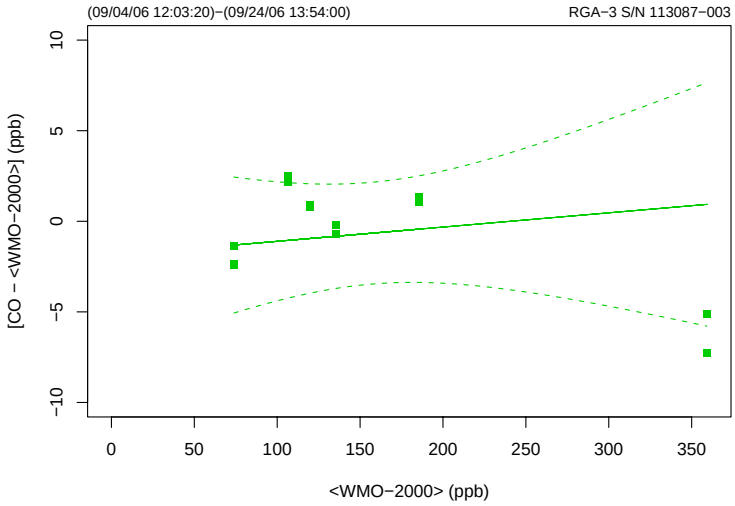

Figure 3. Bias of the Cape Point carbon monoxide GC (RGA-3) with respect to the WMO-2000 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

The results show that the instrument is in good calibration at lower mole fractions, but reproducibility might be improved. The instrument is only calibrated for low mole fractions as they are usually measured in Cape Point during clean conditions. A full characterisation of the instrument should therefore include more standards at low mole fractions. It was agreed with the station operator that additional standards will be sent to the station in the mole fraction range from 40 – 100 pbb CO. However the following recommendations are made by WCC-Empa based on the present results:

Recommendation 7 (, 2007)**
It should be considered apply a calibration function which fully covers the range of mole fractions encountered at the site.

Recommendation 8 (*, 2007-2009)
The current analytical equipment was installed in 1989. Replacement of this system should be planned as spare parts will become unavailable in future. Alterative techniques such as VUV resonance fluorescence (very fast and precise measurements) or GC/FID with methaniser should be considered.

Recommendation 9 (*, 2007)
The system integrates also the hydrogen peak but the data is not further used. It should be considered to calibrate the system for H_2 and to make use of these measurements.

Methane Measurements

Instrumentation. The methane instrumentation of Cape Point was replaced by a new system in 2004. The new Varian CP-3800 GC-FID shows an improved repeatability compared to the old instrument. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with eight methane standards from NOAA/ESRL. The standards have been calibrated and certified based on the CMDL83 methane scale by NOAA/ESRL. These numbers were converted to the NOAA04 methane scale after the revised scale was published [*Dlugokencky, et al.*, 2005]. The standards span a mole fraction range from approx. 1730 – 1900 ppb CH_4. Furthermore, working standards filled using a RIX compressor are available at the site. The working standards are calibrated using the NOAA/ESRL cylinders. With this equipment, adequate calibration of the methane measurements is possible.

Intercomparison (Performance Audit). The inter-comparison involved repeated measurements of WCC-Empa travelling standards with the CPT instrument. No formal data quality objectives have been established for methane. The following equations characterise the instrument bias (cf. Figure 4):

Varian CP-3800 S/N 101605

Unbiased CH_4 mole fraction (ppb): X_{CH4} (ppb) = (CH_4) / 1.0004 (3)

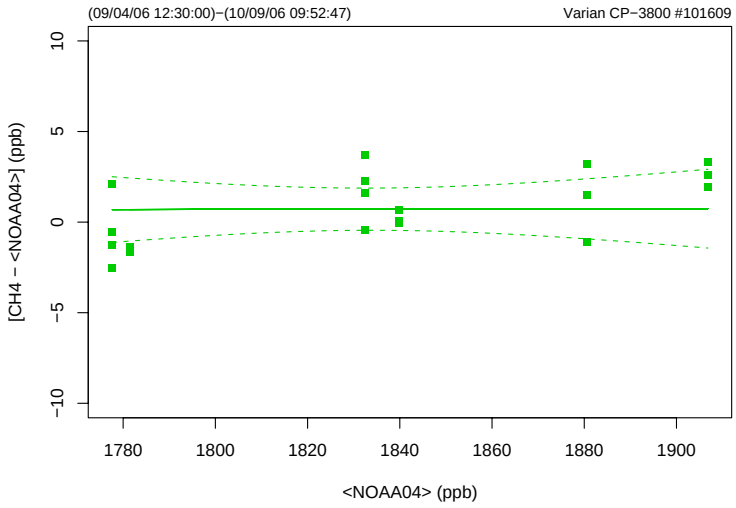

Figure 4. Bias of the Cape Point methane GC (Varian CP-3800) with respect to the NOAA04 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

The agreement between Cape Point and WCC-Empa was very good, and no significant differences were observed. No further recommendations are made by WCC-Empa concerning methane measurements.

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: Testpoint data acquisition (Keithley) is used to acquire the analog signals of the ozone analysers. 1-minute and 30-minute averages are stored on the data acquisition computer. Data back-ups are made weekly, and the data evaluation is made at the office in Stellenbosch.

Recommendation10 (, 2007)**
It should be considered to acquire the digital signal of the TEI 49C ozone monitor .

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). At the time of the audit data for all parameters of the scope of WCC-Empa were available at the data centre, however, the greenhouse gases have been only submitted in daily and monthly averages. In contrast, surface ozone data was also available as hourly values.

Recommendation 11 (, 2007)**
Greenhouse gas data should be submitted as hourly values to WDCGG.

Conclusions

The Global GAW station Cape Point comprises an extensive suite of ongoing measurements. The combination of long time series with the large number of measured parameters at this unique location in the Southern Hemisphere makes the CPT station an important contribution to the GAW programme. All assessed measurements were of high quality, though one ozone analyser was reading significantly lower values compared to WCC-Empa due to an instrument defect.

Summary Ranking of Cape Point Station

System Audit	Adequacy[#]	Comment
Access	(5)	
Facilities		
Laboratory and office space	(5)	
Air Conditioning	(4)	
Power supply	(5)	
General Management and Operation		
Organisation	(5)	
Competence of staff	(5)	
Air Inlet System	(3)	Inlet filters need to be replaced
Instrumentation*		
Ozone	(5)	TEI 49C
Carbon Monoxide	(3)	Old instrument, replacement should be considered
Methane	(5)	
CFCs	(4)	Old instrument, replacement should be considered
Nitrous Oxide	(2)	instrument replacement urgent
Carbon Dioxide	(4)	
Meteo* (PTU, wind speed / dir.)	(5)	
Standards		
Ozone	(1)	No standard available at the site
Carbon monoxide	(5)	
Methane	(5)	
Data Management		
Data acquisition	(4)	Only analogue signal of TEI 49C is acquired
Data processing	(5)	
Data submission	(4)	Hourly values should be submitted for all parameters

[#]0: inadequate through 5: adequate; *refer to GAWSIS (www.empa.ch/gaw/gawsis) for a complete overview of measured parameters.

Dübendorf, May 2007

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

APPENDIX

Global GAW Station Cape Point

Site description

The Cape Point GAW station has been described in detail elsewhere, e.g. [*Brunke, et al.*, 2004], and the station is also registered in GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Programme

The observatory Cape Point has a long research history dating back to the late 1970's and comprises today an extensive suite of observations of the atmosphere. The status of the programme as of September 2006 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the CPT Station

Parameter	Current Instrument	Data Coverage (%) *		
		<12 m	<3 y	Overall
Aerosols				
absorption/scattering: fine/course fractions for 3 wave-lengths	Nephelometer and PSAP			~95 #
Ozone				
Surface ozone	UV absorption (TEI 49 and 49C)			88
Greenhouse Gas				
CFCs	GC-ECD (HP 5890)			36
CH_4	GC-FID (Varian CP-3800)			84
CO_2	NDIR (Hartmann & Braun URAS 4)			91
N_2O	GC-ECD (Carlo Erba)			72
Reactive Gas				
CO	GC-HgO (RGA-3)			89
NO_2	Passive Sampler			~90
SO_2	Passive Sampler			~90
Solar radiation				
Global irradiance	Pyranometer (Kipp & Zonen)			~95
Diffuse irradiance	Kipp & Zonen			~95
UVB Broadband	Solar Light UV Biometer			~95
UVA Broadband	Eppley Pyranometer			~95
Radio Nuclide				
Radon	ZnS(Ag) scintillation cell + alpha counting			92 ##
Ancillary Measurements				
Meteo (complete set of parameters)				~90

* Only overall data coverage for the period 1998 – 2006 is given; Missing data availability: no data coverage information was available at the time of the audit. # Since October 2005; ## Since March 1999

Ozone, Carbon Monoxide and Methane Distribution at Cape Point

The monthly and yearly distributions of one hourly mean values for surface ozone, carbon monoxide and methane for the years 2005 (O_3) and 2006 (CO and CH_4) are shown in Figure 5.

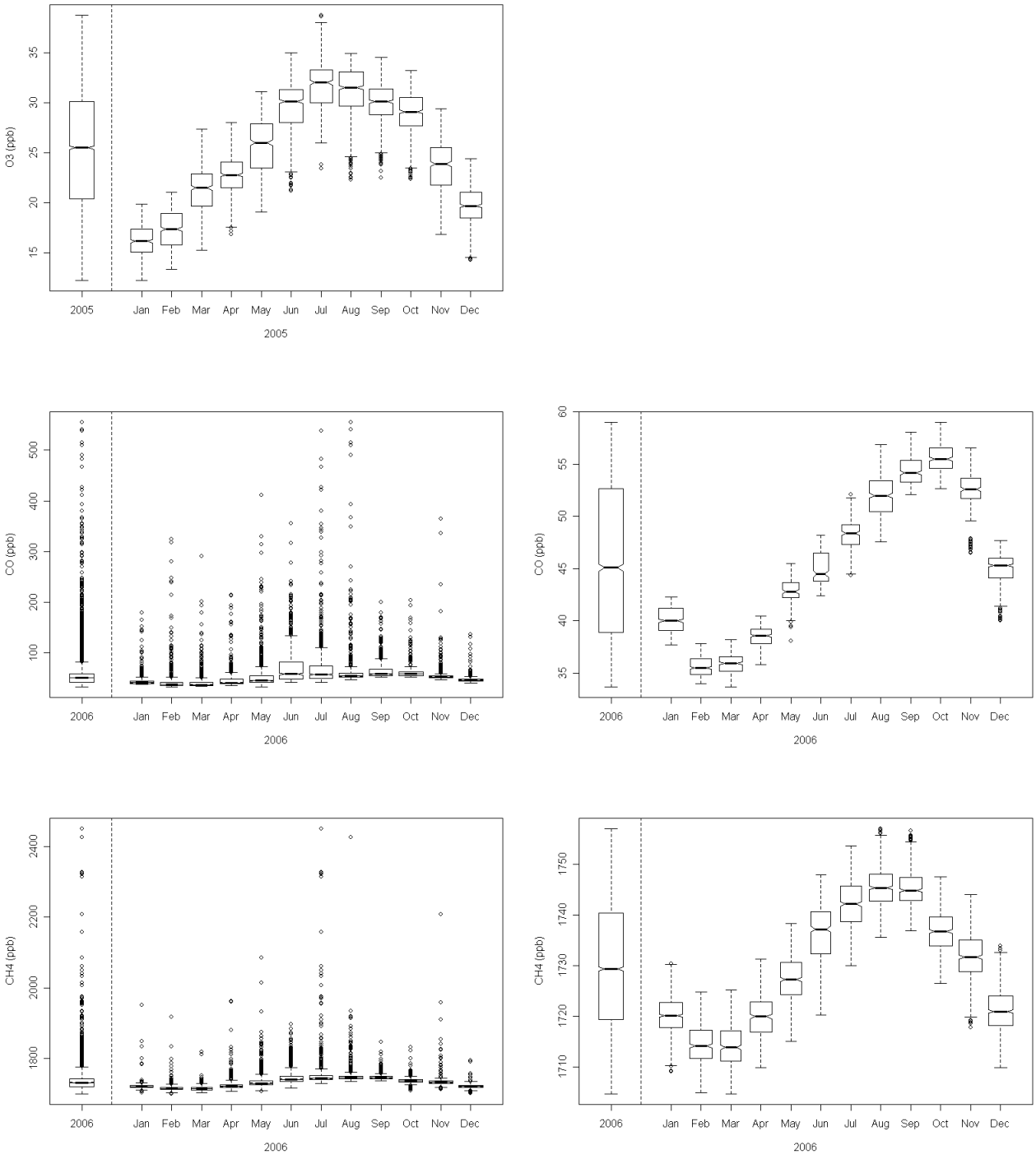

Figure 5. Yearly and Monthly Box Plots of 1-hourly aggregates for the years 2005 (Surface Ozone, upper panel), 2006 (Carbon Monoxide, middle panel and Methane, lower panel). Box plots on the left side show all data, and box plots on the right side show filtered data (CO and CH_4 only). The boxes indicate 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 GAW activities of South Africa are coordinated by the South African Weather Service, and an organisational chart is shown in Figure 6

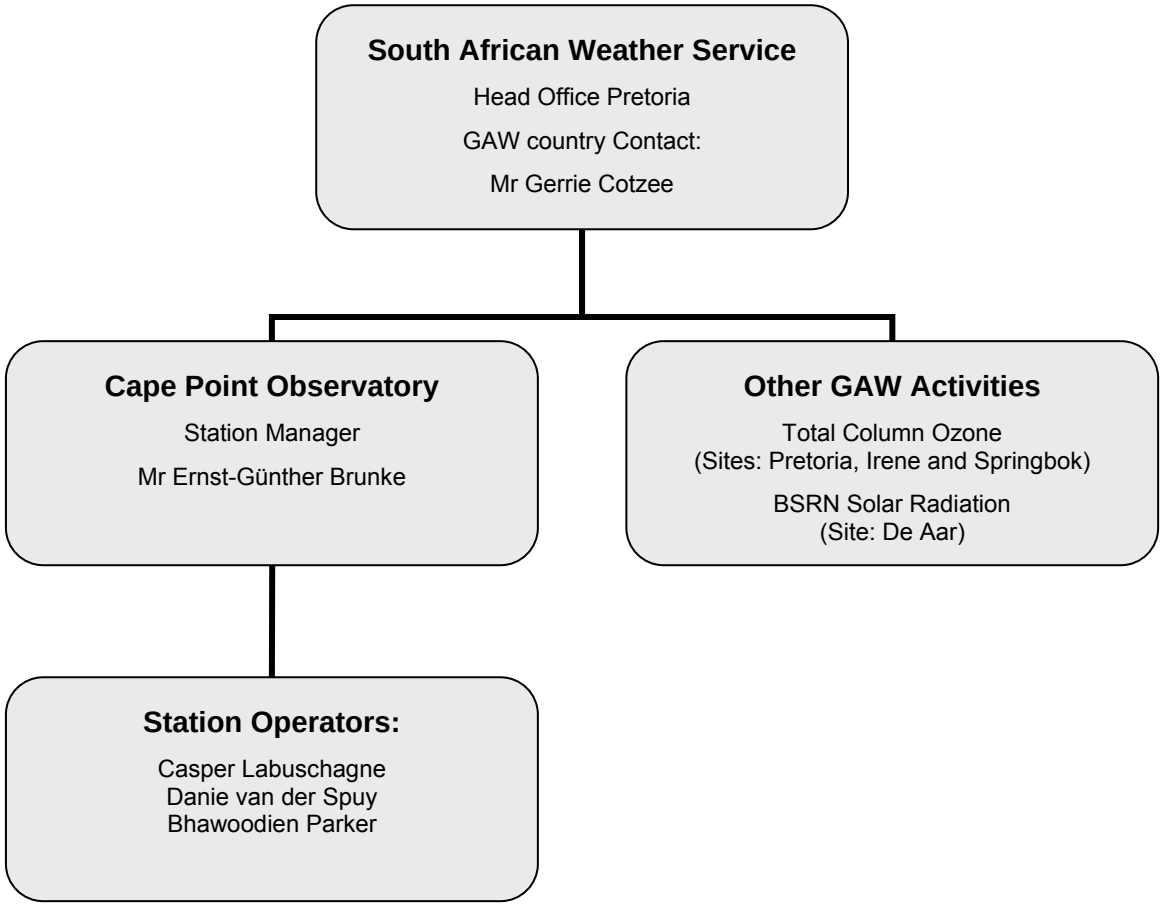

Figure 6. Organisation of GAW Activities in South Africa as of September 2006.

Surface Ozone Measurements

Surface ozone measurements started in 1982 at the Cape Point site, and continuous time series are available since then. Major changes since the last audit by WCC-Empa in 2002 include the replacement of the Dasibi monitor by a new instrument (TEI 49C). All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-a].

Monitoring Set-up and Procedures

Air Conditioning

The laboratory is not air conditioned but the temperature remains stable at approx. 22°C.

Air Inlet System

The main air intake is mounted on the flat roof above the laboratory and has been described in the previous audit report [*Zellweger, et al.*, 2002]. The residence time is estimated to be approx. 2 s. The backup instrument is taking air from the 30 m tower with approx. 35 m of ¼" Teflon tubing. Residence time is estimated to be approx. 25 s. Each instrument is protected by a Teflon inlet filter. The filter holders were leaking during the audit and need to be replaced (cf. Recommendation 1).

Instrumentation
The station is equipped with two ozone analysers (TEI 49 and 49C). Instrumental details for the ozone analysers (OA) are summarised in Table 2 below.

Standards
No ozone standard is available at the site. Occasionally, an ozone standard is shipped from IMK-IFU to the site for instrument calibration. WCC-Empa recommends purchasing an ozone standard, which should be calibrated at an ozone calibration laboratory (e.g. NIST, WCC-Empa) (cf. Recommendation 4).

Operation and Maintenance
Preventive instruments maintenance includes several instrument checks, and adjustment of the pressure transducer is made when necessary. The instrument cells are cleaned yearly. Inlet filters are exchanged monthly or when dirty.

Data Acquisition and Data Transfer
Data acquisition is made with Testpoint (Keithley). The analogue signals of the ozone instruments are acquired, and 1-minute and 30-minute average signals are stored on the data acquisition computer. Data back-ups are made weekly, and the data evaluation is made at the office in Stellenbosch.

Data Treatment
The raw data as it was collected from the data acquisition is inspected by the station operators (time series plot, check with instrument log book). A correction is made for the zero offset based on the monthly average value of the daily zero checks (TEI 49 only).

Data Submission
Ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG). Hourly data were available for the years 1997 – 2005 at the time of the audit.

Documentation
All information is entered in a hand-written log book. Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. The instrument manuals are available at the site.

Inter-Comparison of Ozone Analyzer
All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation-a] and included inter-comparisons of the transfer standard with the Standard Reference Photometer at Empa before and after the inter-comparison of the analyser.

Setup and Connections
Table 2 details the experimental setup during the inter-comparison of transfer standard with the station analysers. The data used for the evaluation was recorded by both WCC-Empa and Cape Point data acquisition systems as indicated. Data of the CPT data acquisition system (CPT analysers) was used for the evaluation of the results. Data of the TEI 49 instrument were corrected for the zero offset; otherwise no further corrections were applied.

Table 2. Experimental details of the ozone inter-comparison.

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.011
Main analyzer (OA) This instrument is the main ozone analyser since the current audit.	Model, S/N	TEI 49C #0526513044
	Principle	UV absorption
	Range	1 ppm
	Settings	Before audit: BKG = 0.0; COEFF = 1.013 After audit: BKG = -0.5; COEFF = 1.015
Backup analyzer (OA) This instrument was the main ozone analyser before the current audit.	Model, S/N	TEI 49 #51594-288
	Principle	UV absorption
	Range	1 ppm
	Settings	Offset 56, Slope 507
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm (WCC-Empa)
Connection between instruments		Ca. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS	WCC-Empa DAQ (one minute aggregates from digital output, custom designed LabView programme)
	Analyser OA	Station Data Acquisition and WCC-Empa DAQ (TEI 49C only)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	996.9 (Station reference)
	TS	1000.5, adjusted to 996.9
	TEI 49C	1002.9, adjusted to 996.9
	TEI 49	994, adjusted to 996
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90 (OA)
Duration per level (min)		20
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		TEI 49: 5 runs with original set-up (13 - 14 Sep 06) 4 runs after repair without filter (14 - 15 Sep 06) 4 runs after repair with filter (15 - 16 Sep 06) TEI 49C: 4 runs with initial cal. settings (14 - 15 Sep 06) 4 runs with new cal. settings (15 - 16 Sep 06)

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 inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results refer to the calibration factors as given in Table 2 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

TEI 49 #51594-288

The instrument was found to measure significantly lower (circa 1.5 ppb on an ambient level of 30 ppb) when compared to WCC-Empa during the first inter-comparison. The reason for the lower readings was found to be a leaking valve. The result of this first assessment is shown in Table 3. After this, the valve was replaced and the instrument was again inter-compared (without the inlet filter) against the WCC-Empa travelling standard. Results are presented in Table 4. A final inter-comparison was done afterwards and included also the inlet filter (Table 5).

Figure 7 shows the regression residuals of the TEI 49 ozone analyser for the inter-comparisons described above with respect to the SRP as a function of ozone mole fraction for the range 0 – 90 ppb and as a function of time.

Table 3. Ten-minute aggregates (initial inter-comparison, broken instrument) computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the CPT ozone analyser (OA) TEI 49 #51594-288 with the WCC-Empa transfer standard (TS).

DateTime (UTC+2)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-09-13 15:21	1	0	0.05	-0.23	0	0.08	0.09
2006-09-13 15:41	1	40	39.89	37.99	0	0.07	0.06
2006-09-13 16:01	1	70	69.88	66.44	0	0.07	0.11
2006-09-13 16:21	1	30	29.97	28.40	0	0.07	0.06
2006-09-13 16:41	1	90	89.85	85.68	0	0.04	0.08
2006-09-13 17:01	1	20	20.00	18.96	0	0.07	0.12
2006-09-13 17:21	1	10	10.00	9.37	0	0.10	0.04
2006-09-13 17:41	1	60	59.90	57.29	0	0.07	0.07
2006-09-13 18:01	1	50	49.93	47.50	0	0.08	0.06
2006-09-13 18:21	1	80	79.87	76.29	0	0.10	0.08
2006-09-13 18:41	2	0	0.13	0.04	0	0.11	0.07
2006-09-13 19:01	2	90	89.86	85.66	0	0.07	0.09
2006-09-13 19:21	2	70	69.94	66.81	0	0.07	0.07
2006-09-13 19:41	2	40	39.98	38.21	0	0.08	0.07
2006-09-13 20:01	2	50	49.90	47.62	0	0.07	0.07
2006-09-13 20:21	2	20	19.97	18.89	0	0.05	0.08
2006-09-13 20:41	2	80	79.91	76.28	0	0.08	0.07
2006-09-13 21:01	2	30	29.92	28.31	0	0.10	0.03
2006-09-13 21:21	2	60	59.87	57.42	0	0.09	0.05
2006-09-13 21:41	2	10	10.01	9.36	0	0.11	0.03
2006-09-13 22:01	3	0	0.13	0.00	0	0.12	0.07
2006-09-13 22:21	3	30	29.93	28.33	0	0.05	0.02
2006-09-13 22:41	3	60	59.90	57.37	0	0.07	0.05
2006-09-13 23:01	3	40	39.95	37.95	0	0.08	0.10
2006-09-13 23:21	3	90	89.87	85.21	0	0.07	0.04
2006-09-13 23:41	3	50	49.93	47.36	0	0.06	0.07
2006-09-14 00:01	3	80	79.89	76.00	0	0.06	0.09
2006-09-14 00:21	3	10	10.04	9.30	0	0.09	0.04
2006-09-14 00:41	3	20	19.96	18.65	0	0.09	0.10
2006-09-14 01:01	3	70	69.94	66.29	0	0.12	0.07
2006-09-14 01:21	4	0	0.08	0.01	0	0.10	0.07
2006-09-14 01:41	4	40	39.92	37.78	0	0.05	0.10
2006-09-14 02:01	4	70	69.91	66.23	0	0.06	0.04
2006-09-14 02:21	4	30	29.98	28.19	0	0.08	0.07
2006-09-14 02:41	4	90	89.88	85.28	0	0.09	0.04
2006-09-14 03:01	4	20	20.03	18.77	0	0.07	0.09
2006-09-14 03:21	4	10	10.01	9.28	0	0.12	0.04
2006-09-14 03:41	4	60	59.94	56.61	0	0.07	0.05
2006-09-14 04:01	4	50	50.01	47.14	0	0.06	0.06
2006-09-14 04:21	4	80	79.93	75.65	0	0.09	0.11
2006-09-14 04:41	5	0	0.11	0.08	0	0.09	0.09
2006-09-14 05:01	5	90	89.89	85.18	0	0.03	0.05
2006-09-14 05:21	5	70	69.91	66.16	0	0.06	0.07
2006-09-14 05:41	5	40	39.95	37.78	0	0.08	0.06
2006-09-14 06:01	5	50	49.96	47.32	0	0.07	0.07
2006-09-14 06:21	5	20	19.97	18.65	0	0.08	0.09
2006-09-14 06:41	5	30	29.98	28.20	0	0.10	0.03
2006-09-14 07:01	5	60	59.94	56.78	0	0.10	0.09
2006-09-14 07:21	5	10	10.02	9.25	0	0.11	0.03
2006-09-14 07:41	5	80	79.91	75.70	0	0.08	0.07

[#]0: valid data; 1: invalid data.

Table 4. Ten-minute aggregates (after repair, without inlet filter) computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the CPT ozone analyser (OA) TEI 49 #51594-288 with the WCC-Empa transfer standard (TS).

DateTime (UTC+2)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-09-14 20:05	1	0	0.13	0.15	0	0.09	0.09
2006-09-14 20:25	1	40	39.95	39.64	0	0.09	0.05
2006-09-14 20:45	1	70	69.92	69.53	0	0.10	0.03
2006-09-14 21:05	1	30	29.98	29.55	0	0.08	0.03
2006-09-14 21:25	1	90	89.88	89.28	0	0.07	0.06
2006-09-14 21:45	1	20	20.02	19.68	0	0.09	0.04
2006-09-14 22:05	1	10	10.02	9.52	0	0.09	0.04
2006-09-14 22:25	1	60	59.93	59.56	0	0.09	0.03
2006-09-14 22:45	1	50	49.99	49.60	0	0.08	0.03
2006-09-14 23:05	1	80	79.91	79.38	0	0.09	0.06
2006-09-14 23:25	2	0	0.12	-0.04	0	0.08	0.06
2006-09-14 23:45	2	90	89.84	89.38	0	0.08	0.04
2006-09-15 00:05	2	70	69.92	69.45	0	0.10	0.02
2006-09-15 00:25	2	40	40.01	39.71	0	0.10	0.03
2006-09-15 00:45	2	50	49.96	49.63	0	0.10	0.02
2006-09-15 01:05	2	20	20.01	19.56	0	0.11	0.03
2006-09-15 01:25	2	80	79.88	79.45	0	0.06	0.04
2006-09-15 01:45	2	30	29.94	29.53	0	0.07	0.03
2006-09-15 02:05	2	60	59.89	59.56	0	0.07	0.03
2006-09-15 02:25	2	10	10.06	9.64	0	0.12	0.07
2006-09-15 02:45	3	0	0.20	-0.21	0	0.10	0.08
2006-09-15 03:05	3	30	29.95	29.52	0	0.11	0.02
2006-09-15 03:25	3	60	59.90	59.75	0	0.09	0.08
2006-09-15 03:45	3	40	39.98	39.69	0	0.07	0.03
2006-09-15 04:05	3	90	89.90	89.40	0	0.11	0.05
2006-09-15 04:25	3	50	49.96	49.61	0	0.09	0.01
2006-09-15 04:45	3	80	79.85	79.28	0	0.06	0.05
2006-09-15 05:05	3	10	10.08	9.60	0	0.13	0.09
2006-09-15 05:25	3	20	20.00	19.63	0	0.08	0.05
2006-09-15 05:45	3	70	69.94	69.53	0	0.07	0.03
2006-09-15 06:05	4	0	0.15	-0.19	0	0.08	0.06
2006-09-15 06:25	4	40	39.95	39.63	0	0.07	0.03
2006-09-15 06:45	4	70	69.92	69.43	0	0.07	0.03
2006-09-15 07:05	4	30	30.01	29.53	0	0.07	0.02
2006-09-15 07:25	4	90	89.88	89.38	0	0.05	0.05
2006-09-15 07:45	4	20	20.01	19.59	0	0.07	0.04
2006-09-15 08:05	4	10	10.05	9.56	0	0.07	0.03
2006-09-15 08:25	4	60	59.95	59.53	0	0.07	0.05
2006-09-15 08:45	4	50	49.98	49.43	0	0.05	0.04
2006-09-15 09:05	4	80	79.93	79.17	0	0.05	0.08

[#]0: valid data; 1: invalid data.

Table 5. Ten-minute aggregates (after repair, with inlet filter) computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the CPT ozone analyser (OA) TEI 49 #51594-288 with the WCC-Empa transfer standard (TS).

DateTime (UTC+2)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-09-15 19:25	1	0	0.09	0.09	0	0.08	0.06
2006-09-15 19:45	1	40	39.94	39.00	0	0.08	0.07
2006-09-15 20:05	1	70	69.90	68.41	0	0.10	0.07
2006-09-15 20:25	1	30	30.00	29.33	0	0.08	0.06
2006-09-15 20:45	1	90	89.90	88.15	0	0.07	0.08
2006-09-15 21:05	1	20	20.03	19.58	0	0.09	0.05
2006-09-15 21:25	1	10	10.00	9.69	0	0.08	0.02
2006-09-15 21:45	1	60	59.92	58.71	0	0.04	0.03
2006-09-15 22:05	1	50	49.95	49.07	0	0.08	0.05
2006-09-15 22:25	1	80	79.90	78.18	0	0.08	0.04
2006-09-15 22:45	2	0	0.11	0.03	0	0.10	0.04
2006-09-15 23:05	2	90	89.87	88.08	0	0.07	0.09
2006-09-15 23:25	2	70	69.93	68.71	0	0.07	0.03
2006-09-15 23:45	2	40	39.99	39.38	0	0.09	0.12
2006-09-16 00:05	2	50	49.95	48.90	0	0.08	0.06
2006-09-16 00:25	2	20	20.00	19.50	0	0.05	0.07
2006-09-16 00:45	2	30	30.00	29.48	0	0.06	0.04
2006-09-16 01:05	2	80	79.91	78.42	0	0.11	0.06
2006-09-16 01:25	2	60	59.92	58.70	0	0.08	0.03
2006-09-16 01:45	2	10	10.07	9.71	0	0.06	0.00
2006-09-16 02:05	3	0	0.14	0.03	0	0.07	0.06
2006-09-16 02:25	3	30	29.96	29.38	0	0.09	0.08
2006-09-16 02:45	3	60	59.91	58.67	0	0.07	0.04
2006-09-16 03:05	3	40	39.94	39.14	0	0.08	0.07
2006-09-16 03:25	3	90	89.89	88.12	0	0.07	0.05
2006-09-16 03:45	3	50	49.98	48.93	0	0.02	0.05
2006-09-16 04:05	3	80	79.87	78.34	0	0.07	0.05
2006-09-16 04:25	3	10	10.06	9.74	0	0.07	0.02
2006-09-16 04:45	3	20	19.98	19.51	0	0.07	0.07
2006-09-16 05:05	3	70	69.93	68.59	0	0.05	0.06
2006-09-16 05:25	4	0	0.16	0.03	0	0.09	0.08
2006-09-16 05:45	4	40	39.93	39.20	0	0.08	0.07
2006-09-16 06:05	4	70	69.90	68.54	0	0.09	0.07
2006-09-16 06:25	4	30	30.00	29.29	0	0.08	0.05
2006-09-16 06:45	4	90	89.86	88.11	0	0.07	0.10
2006-09-16 07:05	4	20	20.01	19.63	0	0.10	0.04
2006-09-16 07:25	4	10	10.05	9.70	0	0.11	0.03
2006-09-16 07:45	4	60	59.92	58.84	0	0.08	0.02
2006-09-16 08:05	4	50	49.99	48.99	0	0.08	0.05
2006-09-16 08:25	4	80	79.97	78.58	0	0.07	0.05

[#]0: valid data; 1: invalid data.

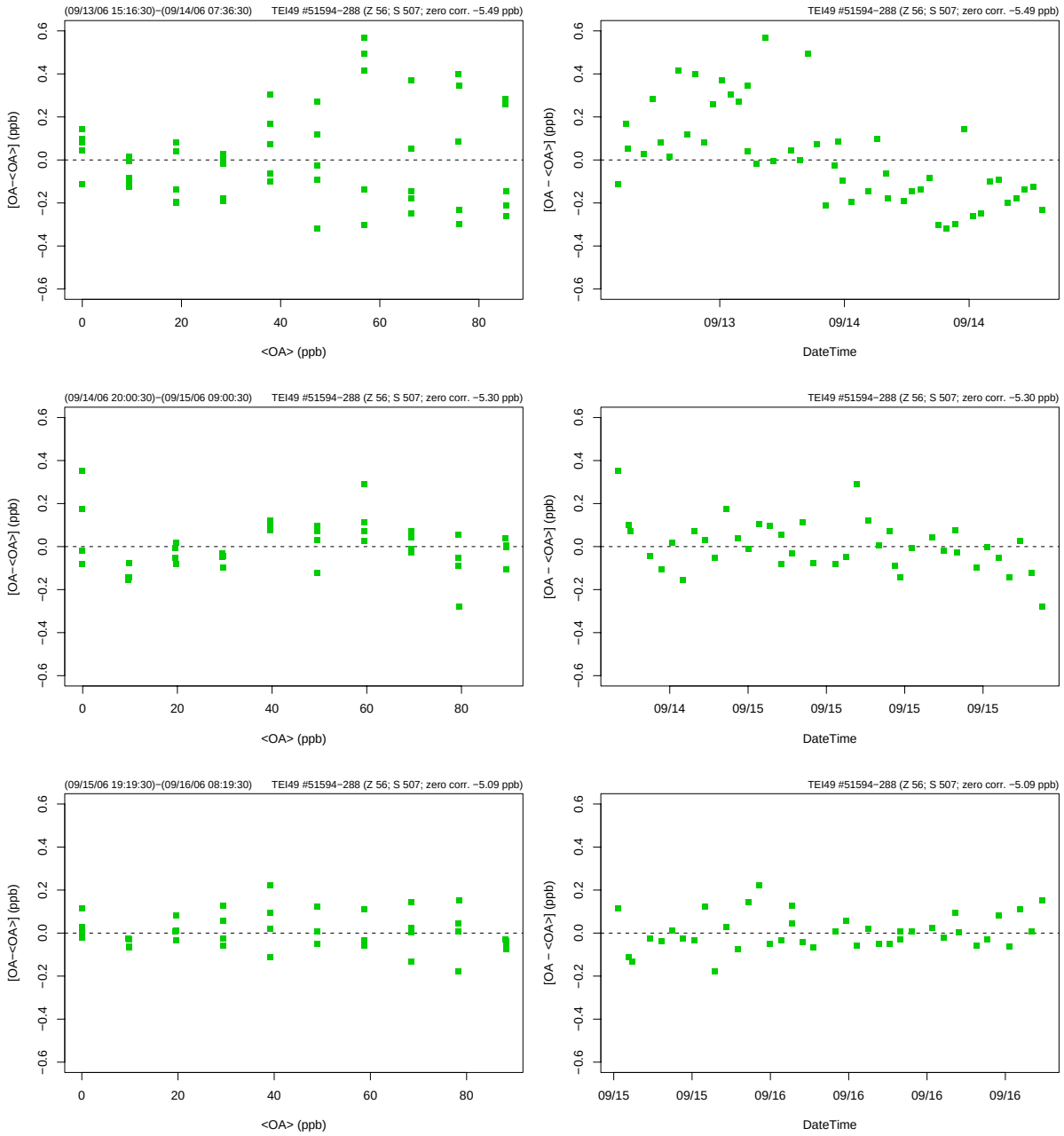

Figure 7. Regression residuals of the CPT ozone analyser (TEI 49) as a function of mole fraction (left) and time (right). The upper panel shows the initial inter-comparison (broken instrument), the middle panel after instrument repair without inlet filter, and the lower panel after repair with inlet filter.

Based on these inter-comparison results, unbiased ozone volume mole fractions X_{O3} and an estimate for the remaining combined standard uncertainty u_{O3} can be computed from the one-minute data [OA] using equation (1) [*Klausen, et al.*, 2003].

TEI 49 #51594-288:

Initial calibration:

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.23\ ppb) / 0.953}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.34\ ppb^2 + 2.85e\text{-}05 * X_{O3}^2)} \quad (1a)$$

Calibration after repair with inlet filter:

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.17\ ppb) / 0.983}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.28\ ppb^2 + 2.69e\text{-}05 * X_{O3}^2)} \quad (1b)$$

Calibration after repair without inlet filter:

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.39\ ppb) / 0.999}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.27\ ppb^2 + 2.60e\text{-}05 * X_{O3}^2)} \quad (1c)$$

TEI 49C #0526513044:

The instrument was installed at the station in January 2006. It was never inter-compared with an ozone standard, and was running as a back-up system until the audit. The results of the initial inter-comparison with unchanged calibrations settings are presented in Table 6. Based on these results, the calibration settings were adjusted, and a final inter-comparison was done afterwards (Table 7). Both inter-comparisons were made without inlet filter because the filter holders were leaking.

Figure 8 shows the regression residuals of the TEI 49C ozone analyser for the inter-comparisons described above with respect to the SRP as a function of ozone mole fraction for the range 0 – 90 ppb and as a function of time.

Table 6. Ten-minute aggregates (original calibration settings, BKG 0.0 ppb, COEF 1.013) computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the CPT ozone analyser (OA) TEI 49 #0526513044 with the WCC-Empa transfer standard (TS).

DateTime (UTC+2)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-09-14 20:05	1	0	0.13	-0.56	0	0.09	0.03
2006-09-14 20:25	1	40	39.95	38.89	0	0.09	0.04
2006-09-14 20:45	1	70	69.91	68.57	0	0.10	0.05
2006-09-14 21:05	1	30	29.98	29.03	0	0.08	0.05
2006-09-14 21:25	1	90	89.88	88.52	0	0.07	0.05
2006-09-14 21:45	1	20	20.02	19.16	0	0.09	0.04
2006-09-14 22:05	1	10	10.02	9.22	0	0.09	0.02
2006-09-14 22:25	1	60	59.93	58.69	0	0.09	0.03
2006-09-14 22:45	1	50	49.99	48.93	0	0.08	0.03
2006-09-14 23:05	1	80	79.89	78.53	0	0.08	0.02
2006-09-14 23:25	2	0	0.12	-0.54	0	0.08	0.03
2006-09-14 23:45	2	90	89.84	88.38	0	0.08	0.05
2006-09-15 00:05	2	70	69.92	68.69	0	0.10	0.06
2006-09-15 00:25	2	40	40.01	38.89	0	0.10	0.06
2006-09-15 00:45	2	50	49.96	48.89	0	0.10	0.06
2006-09-15 01:05	2	20	20.01	19.21	0	0.11	0.04
2006-09-15 01:25	2	30	29.94	29.16	0	0.07	0.04
2006-09-15 01:45	2	60	59.89	58.71	0	0.07	0.03
2006-09-15 02:05	2	10	10.06	9.32	0	0.12	0.04
2006-09-15 02:25	2	80	79.87	78.51	0	0.06	0.04
2006-09-15 02:45	3	0	0.20	-0.51	0	0.10	0.03
2006-09-15 03:05	3	30	29.95	29.07	0	0.11	0.04
2006-09-15 03:25	3	60	59.90	58.72	0	0.09	0.03
2006-09-15 03:45	3	40	39.98	38.96	0	0.07	0.03
2006-09-15 04:05	3	90	89.90	88.45	0	0.11	0.06
2006-09-15 04:25	3	50	49.96	48.82	0	0.09	0.03
2006-09-15 04:45	3	10	10.08	9.30	0	0.13	0.04
2006-09-15 05:05	3	20	20.00	19.20	0	0.08	0.03
2006-09-15 05:25	3	80	79.86	78.53	0	0.07	0.03
2006-09-15 05:45	3	70	69.95	68.73	0	0.06	0.03
2006-09-15 06:05	4	0	0.15	-0.60	0	0.08	0.04
2006-09-15 06:25	4	40	39.95	38.88	0	0.07	0.05
2006-09-15 06:45	4	70	69.90	68.53	0	0.07	0.04
2006-09-15 07:05	4	30	30.01	29.13	0	0.07	0.03
2006-09-15 07:25	4	90	89.88	88.47	0	0.05	0.05
2006-09-15 07:45	4	20	20.01	19.18	0	0.07	0.05
2006-09-15 08:05	4	10	10.05	9.22	0	0.07	0.04
2006-09-15 08:25	4	60	59.95	58.77	0	0.07	0.05
2006-09-15 08:45	4	50	49.98	48.83	0	0.05	0.05
2006-09-15 09:05	4	80	79.93	78.53	0	0.05	0.04

[#]0: valid data; 1: invalid data.

Table 7. Ten-minute aggregates (new calibration settings, BKG -0.5 ppb, COEF 1.015) computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the CPT ozone analyser (OA) TEI 49 #0526513044 with the WCC-Empa transfer standard (TS)..

DateTime (UTC+2)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-09-15 19:26	1	0	0.08	-0.07	0	0.09	0.04
2006-09-15 19:46	1	40	39.95	39.77	0	0.08	0.05
2006-09-15 20:06	1	70	69.92	69.55	0	0.08	0.04
2006-09-15 20:26	1	30	30.00	29.80	0	0.09	0.02
2006-09-15 20:46	1	90	89.89	89.60	0	0.07	0.03
2006-09-15 21:06	1	20	20.03	19.77	0	0.11	0.03
2006-09-15 21:26	1	10	10.00	9.79	0	0.09	0.04
2006-09-15 21:46	1	60	59.91	59.69	0	0.04	0.03
2006-09-15 22:06	1	50	49.96	49.85	0	0.07	0.04
2006-09-15 22:26	1	80	79.91	79.66	0	0.09	0.05
2006-09-15 22:46	2	0	0.13	0.01	0	0.10	0.04
2006-09-15 23:06	2	90	89.88	89.56	0	0.06	0.03
2006-09-15 23:26	2	70	69.94	69.89	0	0.04	0.04
2006-09-15 23:46	2	40	40.00	39.84	0	0.10	0.05
2006-09-16 00:06	2	50	49.94	49.73	0	0.08	0.05
2006-09-16 00:26	2	20	20.01	19.80	0	0.07	0.04
2006-09-16 00:46	2	30	30.02	29.81	0	0.06	0.04
2006-09-16 01:06	2	60	59.91	59.54	0	0.08	0.05
2006-09-16 01:26	2	10	10.07	9.80	0	0.06	0.04
2006-09-16 01:46	2	80	79.90	79.67	0	0.09	0.05
2006-09-16 02:06	3	0	0.15	-0.09	0	0.06	0.05
2006-09-16 02:26	3	30	29.95	29.78	0	0.08	0.03
2006-09-16 02:46	3	60	59.91	59.60	0	0.07	0.05
2006-09-16 03:06	3	40	39.95	39.68	0	0.08	0.05
2006-09-16 03:26	3	90	89.89	89.61	0	0.07	0.05
2006-09-16 03:46	3	50	49.99	49.79	0	0.03	0.03
2006-09-16 04:06	3	10	10.03	9.79	0	0.08	0.03
2006-09-16 04:26	3	20	19.96	19.73	0	0.08	0.03
2006-09-16 04:46	3	80	79.88	79.66	0	0.07	0.06
2006-09-16 05:06	3	70	69.93	69.59	0	0.07	0.03
2006-09-16 05:26	4	0	0.14	-0.01	0	0.08	0.04
2006-09-16 05:46	4	40	39.94	39.64	0	0.11	0.03
2006-09-16 06:06	4	70	69.89	69.63	0	0.09	0.07
2006-09-16 06:26	4	30	29.99	29.80	0	0.06	0.04
2006-09-16 06:46	4	90	89.87	89.69	0	0.07	0.06
2006-09-16 07:06	4	20	20.02	19.88	0	0.07	0.04
2006-09-16 07:26	4	10	10.02	9.75	0	0.09	0.04
2006-09-16 07:46	4	60	59.96	59.59	0	0.07	0.04
2006-09-16 08:06	4	50	49.99	49.90	0	0.08	0.05
2006-09-16 08:26	4	80	79.98	79.64	0	0.07	0.05

[#]0: valid data; 1: invalid data.

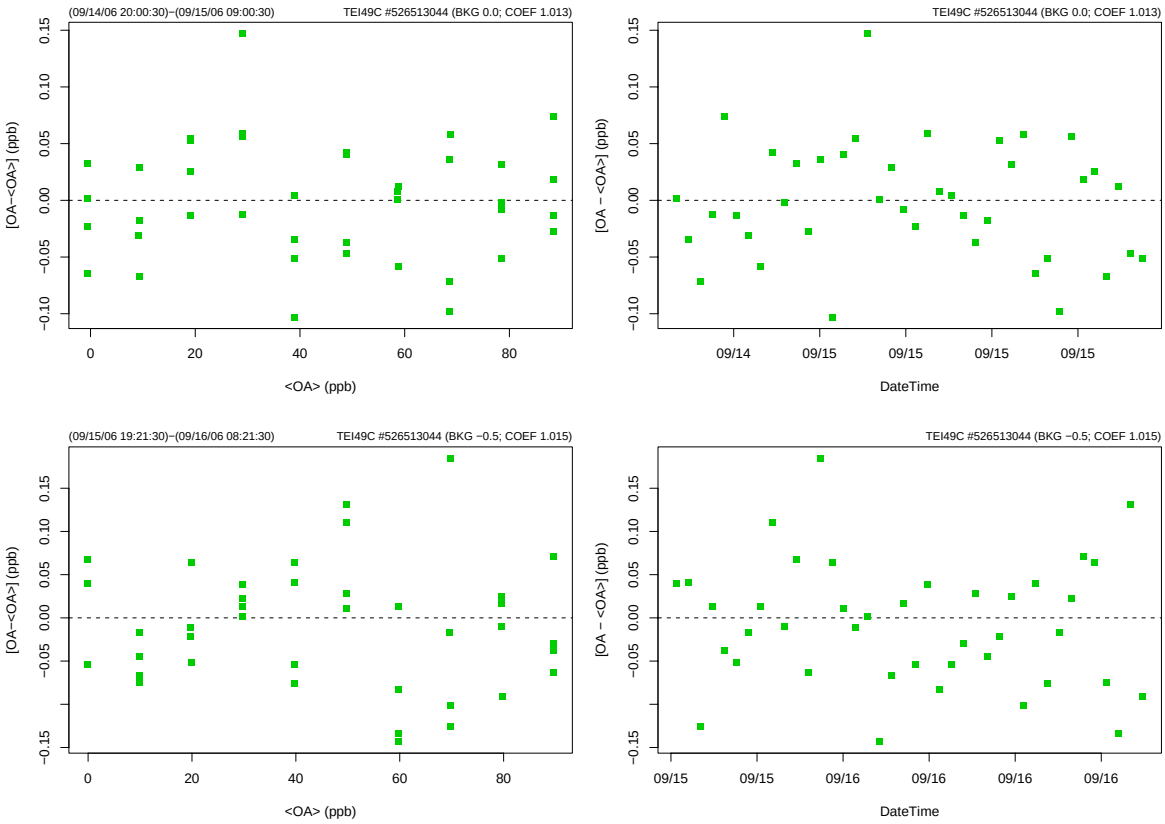

Figure 8. Regression residuals of the CPT ozone analyser (TEI 49C) s a function of mole fraction (left) and time (right). Upper panel: Initial inter-comparison with unchanged calibration settings. Lower panel: New calibration settings.

Based on these inter-comparison results, unbiased ozone volume mole fractions X_{O3} and an estimate for the remaining combined standard uncertainty u_{O3} can be computed from the one-minute data [OA] using equation (1) [*Klausen, et al.*, 2003].

TEI 49C #0526513044:

Initial calibration (BKG 0.0 ppb, COEF 1.013):

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.75\ ppb) / 0.993}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.27\ ppb^2 + 2.64e\text{-}05 * X_{O3}^2)} \quad (1d)$$

Calibration after adjustment (BKG -0.5 ppb, COEF 1.015):

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.25\ ppb) / 1.000}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.26\ ppb^2 + 2.60e\text{-}05 * X_{O3}^2)} \quad (1e)$$

Changes Made to Instrument

TEI 49: Replacement of an internal valve, details see above.
TEI 49C: New calibration settings, details see above.

Conclusions

The findings of this audit demonstrate good agreement between CPT ozone measurements and WCC-Empa after repair of the TEI 49 and calibration of the TEI 49C instrument. Significant deviations were found during the initial inter-comparison. Existing data need to be revised (cf. Recommendation 5).

Carbon Monoxide Measurements

The current set-up of carbon monoxide measurements remained unchanged since the last audit by WCC-Empa [*Zellweger, et al.*, 2002]. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-b].

Monitoring Set-up and Procedures

Air Conditioning

The air-conditioning is identical to the one for surface ozone as described above.

Air Inlet System

See previous audit report [*Zellweger, et al.*, 2002].

Instrumentation

See previous audit report [*Zellweger, et al.*, 2002]. Instrumental details are also listed in Table 9.

Standards and Calibration

The carbon monoxide instrument is equipped with a working standard and a target gas. These working standards are calibrated at the site using the laboratory standards. Table 8 gives details of the cylinders currently available at the station.

Injections are made every 12 minutes, and the working standard is injected after nine ambient samples (every two hours). A moving average over three working standard injections is then used to calculate the ambient data. In addition, daily automatic injections of the target gas are made. A zero check using synthetic air and Sofnocat is made every six month. A full characterisation of the instrument's non-linearity is made in irregular intervals (e.g. after significant instrument changes).

Table 8. Carbon monoxide standards available at the CPT station

Manufacturer, S/N, Use	CO Content (ppb) and matrix*	Calibration		In service	
		Date	By	From	To
NOAA/ESRL CA02907 laboratory standard	49.7 ppb CO[1] 53.4 ppb CO[2]	1997 2004	NOAA/ESRL	1997	cont.
NOAA/ESRL CA02929 laboratory standard	74.1 ppb CO[1] 77.1 ppb CO[2]	1997 2004	NOAA/ESRL	1997	cont.
NOAA/ESRL CA05050 laboratory standard	101.9 ppb CO[1] 102.2 ppb CO[2]	2002 2002	NOAA/ESRL	2002	cont.
NOAA/ESRL CA05081 laboratory standard	49.7 ppb CO[1] 53.0 ppb CO[2]	2002 2002	NOAA/ESRL	2002	cont.
NOAA/ESRL CA05712 laboratory standard	217.7 ppb CO[1] 217.7 ppb CO[2] 219.9 ppb CO[3]	2004 2004 2006	NOAA/ESRL	2004	cont.
NOAA/ESRL CA05714 laboratory standard	55.8 ppb CO[1] 60.8 ppb CO[2]	2004 2004	NOAA/ESRL	2004	cont.
NOAA/ESRL CA05715 laboratory standard	126.0 ppb CO[1] 130.0 ppb CO[2] 131.1 ppb CO[3]	2004 2004 2006	NOAA/ESRL	2004	cont.
NOAA/ESRL CA05716 laboratory standard	84.9 ppb CO[1] 90.2 ppb CO[2] 90.8 ppb CO[3]	2004 2004 2006	NOAA/ESRL	2004	cont.
Messer 4574D laboratory standard	84.9 ppb CO	2003	IMK-IFU	2003	cont.
Messer 4539D laboratory standard	163.4 ppb CO	2003	IMK-IFU	2003	2006
Messer 4574D laboratory standard	244.0 ppb CO	2003	IMK-IFU	2003	cont.
Scott-Marin /CPT CA04325 working standard	63.7 ppb CO	2005	CPT	2005	cont.
Scott-Marin /CPT CA04325 target gas	56.8 ppb CO	2005	CPT	2005	cont.

* All standards are in natural air except the Messer standards (synthetic air)
[1] WMO-88 carbon monoxide scale, RGA-3 instrument at NOAA/ESRL
[2] WMO-2000 carbon monoxide scale, VURF instrument at NOAA/ESRL
[3] WMO-2000 carbon monoxide scale, VURF instrument at NOAA/ESRL, re-analysis.

Operation and Maintenance
See previous audit report [*Zellweger, et al.*, 2002].

Data Acquisition and Data Transfer
AZUR GC control software (Version 2.0.4.0) is used for data acquisition and processing. Raw data including chromatograms are archived on CD on a monthly basis. The system remained unchanged since the last audit [*Zellweger, et al.*, 2002].

Data Treatment
See previous audit report [*Zellweger, et al.*, 2002].

Data Submission
Data is submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG). However, only daily and monthly averages have been submitted. WCC-Empa encourages the submission of hourly averages (cf. Recommendation 11).

Documentation
All information is entered in a hand-written log book. Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. The instrument manuals are available at the site.

Inter-Comparison of Carbon Monoxide Analysers
All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation-b] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 9 below.

Setup and Connections
The RGA-3 instrument was inter-compared by direct measurements of travelling standards. Details of this experiment are shown in Table 9. The data used for the evaluation was recorded by the CPT data acquisition system.

Table 9. Experimental details of the carbon monoxide inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (2 and 6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / FF31496 / 73.89 / 0.38 2 / 050419_FA02482 / 106.59 / 0.79 3 / 050419_FA02479 / 119.95 / 0.98 4 / 041109_FA01467 / 135.21 / 0.73 5 / 030703_FA01469 / 185.54 / 0.94 6 / 050701_FA02505 / 359.36 / 1.86
Field instrument	Model, S/N	RGA3, S/N 113087-003
	Principle	GC with HgO Reduction 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
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Duration per level (min)		Injections every 12 min; total 9-25 injections per level
Sequence of levels		Randomised sequence
Runs		Each level was repeated 2 times (2 runs) with the exception of the lowest level (3 repetitions) 04-24 September, 2006

Results

The RGA-3 system was audited using WCC-Empa travelling standards. Each level was injected between 9 and 25 times, and repeated two times with the exception of the lowest level with three repetitions. This resulted in a maximum of 25 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 10).

Table 10. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the CPT RGA-3 with WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	RGA-3 CO (ppb)	sdCO (ppb)	No. of inj.
2006-09-04	FF31496	73.89	0.38	71.52	0.17	18
2006-09-04	050419_FA02482	106.59	0.79	108.74	0.51	10
2006-09-04	030703_FA01469	185.54	0.94	186.87	0.46	11
2006-09-05	050419_FA02479	119.95	0.98	120.76	0.43	11
2006-09-05	050701_FA02505	359.36	1.86	354.25	0.48	12
2006-09-05	FF31496	73.89	0.38	72.52	0.20	16
2006-09-06)	041109_FA01467	135.21	0.73	134.53	0.17	12
2006-09-08	030703_FA01469	185.54	0.94	186.62	0.45	25
2006-09-11	050419_FA02482	106.59	0.79	109.08	0.21	9
2006-09-11	050419_FA02479	119.95	0.98	120.83	0.22	10
2006-09-11	041109_FA01467	135.21	0.73	135.03	0.43	15
2006-09-24	FF31496	73.89	0.38	71.46	0.21	18
2006-09-24	050701_FA02505	359.36	1.86	352.07	0.48	16

Figure 9 shows the regression residuals of the GC-FID instrument plotted against time and mole fraction. The absence of a temporal trend (lower panel) indicates stable instrument conditions; however, a slight mole fraction dependence (upper panel) in the residuals indicates that the non-linearity correction of the instrument is not able to cover the tested mole fraction range. This was expected since the instrument is only calibrated with focus on low carbon monoxide mole fractions (below 150 ppb). However, it should be considered to expand the calibration range to higher values (cf. Recommendation 7).

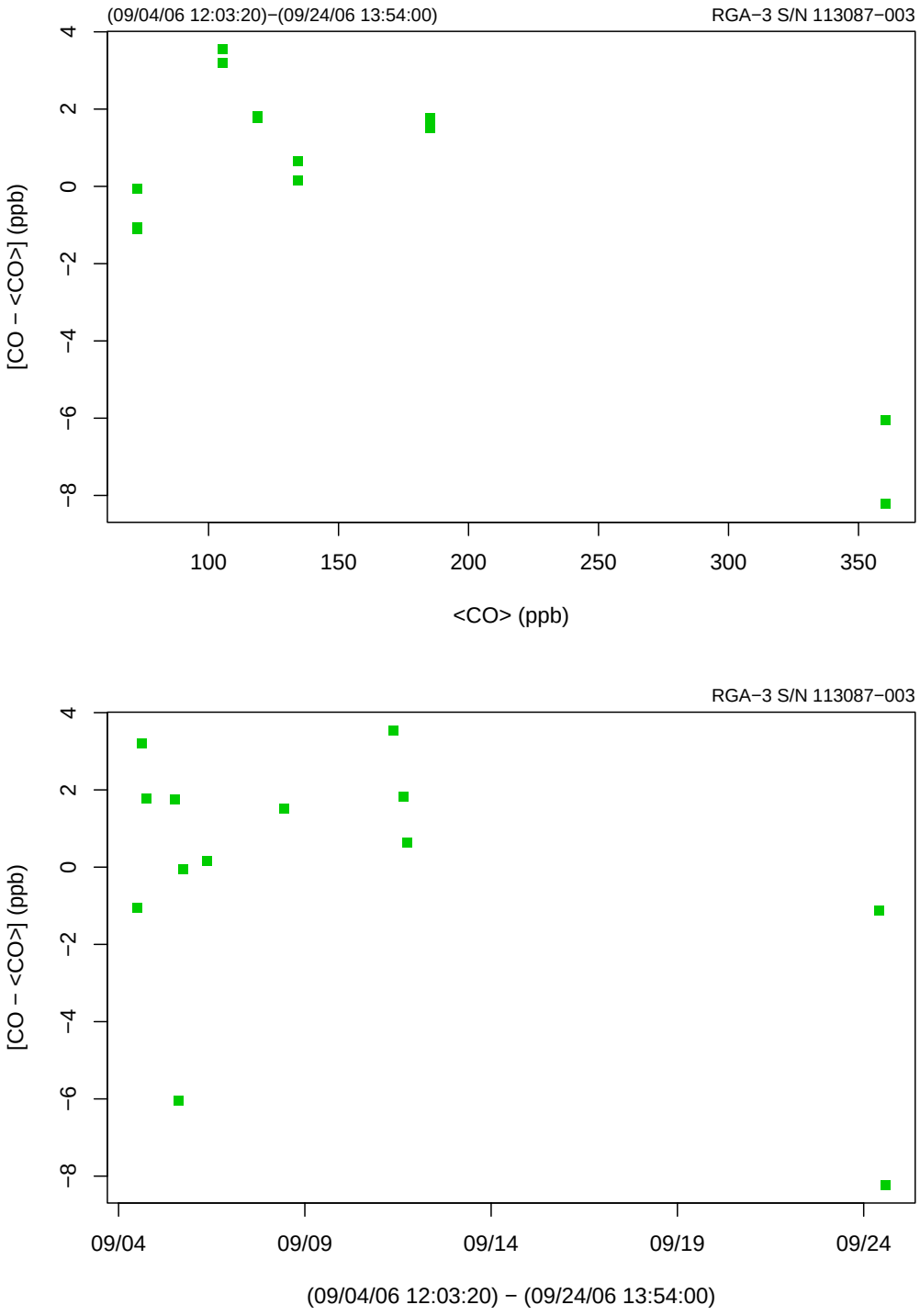

Figure 9. Regression residuals of the CPT RGA-3 based on the inter-comparison with travelling standards. Points represent averages of valid single injections. Upper panel: mole fraction dependence; Lower panel: time dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mole fractions of the RGA-3 system X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed using equation (2).

$$\mathbf{X_{CO}\ (ppb) = ([CO] + 1.9\ ppb) / 1.008}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(11.8\ ppb^2 + 3.71e\text{-}05 * X_{CO}^2)} \quad (2)$$

The estimate of the remaining standard uncertainty u_{CO} based on instrument noise and a linear mole fraction dependent contribution of 0.5%.

Changes made to the instrument

No changes were made to the instruments, all settings remained.

Conclusions

The WCC-Empa travelling standards were at relatively high mole fractions compared to the levels that are usually encountered at the site. Nevertheless, the agreement between WCC-Empa and Cape Point was good for carbon monoxide mole fractions below 150 ppb. The carbon monoxide GC was found to operate well within the limits of the instrument specifications.

Despite this good it was agreed during the audit that the low mole fractions below 70 ppb should be further investigated, and WCC-Empa will provide three carbon monoxide travelling standards which cover a mole fraction range of approx. 40 – 70 ppb. These results will also be considered for the final assessment, and will be published in a separate WCC-Empa report.

Methane Measurements

Methane measurements commenced in 1983 at the Cape Point Observatory. The instrument that was originally installed in 1983 was replaced in 2004 by a new GC-FID.

All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-b].

Monitoring Set-up and Procedures

Air Conditioning

The air-conditioning is identical to the one for surface ozone as described above.

Air Inlet System

See previous audit report [*Zellweger, et al.*, 2002].

Instrumentation

The station was equipped in 2004 with a new Varian CP-3800 with FID detector. The old instrument (see [*Zellweger, et al.*, 2002]) was decommissioned after the replacement. Instrumental details are listed in Table 12.

Standards and Calibration

The methane instrument is equipped with a working and a target gas. These working standards are calibrated at the site using the laboratory standards. Table 11 gives details of the cylinders currently available at the station.

Injections are made every 15 minutes, and the working standard is injected after three ambient samples. A moving average over three working standard injections is then used to calculate the ambient data. In addition, daily automatic injections of the target gas are made.

Table 11. Methane standards available at the CPT station

Manufacturer, S/N, Use	CH_4 Content* (ppb) and matrix**	Calibration		In service	
		Date	By	From	To
NOAA/ESRL CA02907 laboratory standard	1730.8 ppb CH_4	1997	NOAA/ESRL	1997	cont.
NOAA/ESRL CA02929 laboratory standard	1787.5 ppb CH_4	1997	NOAA/ESRL	1997	cont.
NOAA/ESRL CA05050 laboratory standard	1806.7 ppb CH_4	2002	NOAA/ESRL	2002	cont.
NOAA/ESRL CA05081 laboratory standard	1741.8 ppb CH_4	2002	NOAA/ESRL	2002	cont.
NOAA/ESRL CA05712 laboratory standard	1902.4 ppb CH_4 1902.4 ppb CH_4	2004 2006	NOAA/ESRL	2004	cont.
NOAA/ESRL CA05714 laboratory standard	1749.9 ppb CH_4	2004	NOAA/ESRL	2004	cont.
NOAA/ESRL CA05715 laboratory standard	1857.6 ppb CH_4 1857.6 ppb CH_4	2004 2006	NOAA/ESRL	2004	cont.
NOAA/ESRL CA05716 laboratory standard	1801.6 ppb CH_4 1801.6 ppb CH_4	2004 2006	NOAA/ESRL	2004	cont.
Scott-Marin /CPT CA03712 working standard	1744.3 ppb CH_4	2005	CPT	2005	cont.
Messer /CPT 5662D target gas	1740.8 ppb CH_4	2005	CPT	2005	cont.

* All standards are referenced to the NOAA04 methane scale
** All standards are in natural air

Operation and Maintenance
Weekly checks of general instrument operation are made (retention times, peak shape and integration, flow rates, cylinder pressures etc). The cold trap is exchanged when necessary.

Data Acquisition and Data Transfer
AZUR GC control software (Version 2.0.4.0) is used for data acquisition and processing. Raw data including chromatograms are archived on CD on a monthly basis. The system remained unchanged since the last audit [*Zellweger, et al.*, 2002]. The Testpoint analogue data acquisition is running as a backup system.

Data Treatment
Final ambient values are calculated using the injections of the working standard (moving average of three injections of the working standard is considered). The validated data set is further

aggregated to half hourly average values. Finally, data are filtered to exclude pollution events before submission to WDCGG. Filter procedures are described in [*Brunke, et al.*, 2004].

Data Submission
Data are submitted to the GAW World Data Centre for Methane at JMA (World Data Centre for Greenhouse Gases, WDCGG). However, only daily and monthly averages have been submitted. WCC-Empa encourages the submission of hourly averages (cf. Recommendation 11).

Documentation
All information is entered in a hand-written log book. Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. The instrument manuals are available at the site.

Inter-Comparison of the Methane Analyser
All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation-b] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standard to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 12 below.

Setup and Connections
Table 12 shows details of the experimental setup during the inter-comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the CPT data acquisition system, and no further corrections were applied.

Table 12. Experimental details of the methane inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (2 and 6 l aluminium cylinder containing natural air); NOAA04 methane scale
Field instrument	Model, S/N	Varian CP-3800 #101609 GC with FID detector Analytical column: Hayesep 80/100, 12 ft x 3/16” Carrier: N_2 (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
Connection of TS to field instrument		TS were connected to a spare port of the sample selection valve of the CPT system
Data Acquisition		Station data acquisition
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 050419_FA02482 / 1777.62 / 0.74 2 / 030703_FA01469 / 1781.38 / 1.50 3 / 050701_FA02505 / 1832.53 / 1.29 4 / FF31496 / 1839.82 / 0.54 5 / 050419_FA02479 / 1880.50 / 0.51 6 / 041109_FA01467 / 1906.82 / 0.67
Number of injections		One injection per hour; total 10-42 injections per level/run
Sequence of levels		Randomised sequence
Runs		Each level was repeated 3 times (3 runs) with the exception of levels 1 and 3 (4 repetitions) 04 September – 9 October, 2006

Results

Each level was injected between 10 and 42 times, and repeated three to four times. This resulted in a maximum of 42 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 13).

Table 13. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the inter-comparison of the CPT methane analyser with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	CH_4 (ppb)	uCH_4 (ppb)	No. of inj.
2006-09-04	041109_FA01467	1906.82	0.67	1908.78	0.28	21
2006-09-04	FF31496	1839.82	0.54	1839.76	0.23	17
2006-09-06	FF31496	1839.82	0.54	1840.49	0.47	17
2006-09-06	050419_FA02479	1880.50	0.51	1879.38	0.24	12
2006-09-06	050701_FA02505	1832.53	1.29	1832.08	0.45	14
2006-09-06	030703_FA01469	1781.38	1.50	1779.87	0.86	11
2006-09-06	041109_FA01467	1906.82	0.67	1910.16	0.46	14
2006-09-08	030703_FA01469	1781.38	1.50	1780.03	0.50	19
2006-09-11	050419_FA02482	1777.62	0.74	1779.75	0.23	15
2006-09-11	050701_FA02505	1832.53	1.29	1836.26	0.47	10
2006-09-13	041109_FA01467	1906.82	0.67	1909.41	0.35	21
2006-09-13	050419_FA02479	1880.50	0.51	1882.01	0.24	20
2006-09-13	050419_FA02482	1777.62	0.74	1775.07	0.23	19
2006-09-28	FF31496	1839.82	0.54	1839.89	0.30	25
2006-09-28	050701_FA02505	1832.53	1.29	1834.79	0.16	42
2006-09-28	050419_FA02482	1777.62	0.74	1776.37	0.33	20
2006-09-29	030703_FA01469	1781.38	1.50	1779.75	0.03	12
2006-10-02	050419_FA02479	1880.50	0.51	1883.69	0.52	14
2006-10-02	050419_FA02482	1777.62	0.74	1777.06	0.21	35
2006-10-09	050701_FA02505	1832.53	1.29	1834.11	0.18	32

Figure 10 shows the regression residuals of the Varian CP-3800 GC plotted against time and mole fraction. The absence of a temporal trend (upper panel) indicates stable instrument conditions. The absence of mole fraction dependence (lower pane) indicates linearity of the instrument.

Based on these inter-comparison results, unbiased methane volume mole fractions of the Varian CP-3800 GC X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed from the single injection inter-comparison data using equation (3).

$$X_{CH4}\ (\text{ppb}) = (CH_4) / 1.0004$$

$$u_{CH4}\ (\text{ppb}) = \text{sqrt}(3.6\ \text{ppb}^2 + 7.11\text{e-}08 * X_{CH4}^2) \quad (3)$$

Conclusions

No significant deviations between CPT and WCC-Empa were found. The good result of the inter-comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. The repeatability of the CPT GC was good, with an average standard deviation of 0.02% (10-42 injections). This value is among the best compared to other GC-FID systems at GAW stations. Therefore no further technical recommendations are made by WCC-Empa.

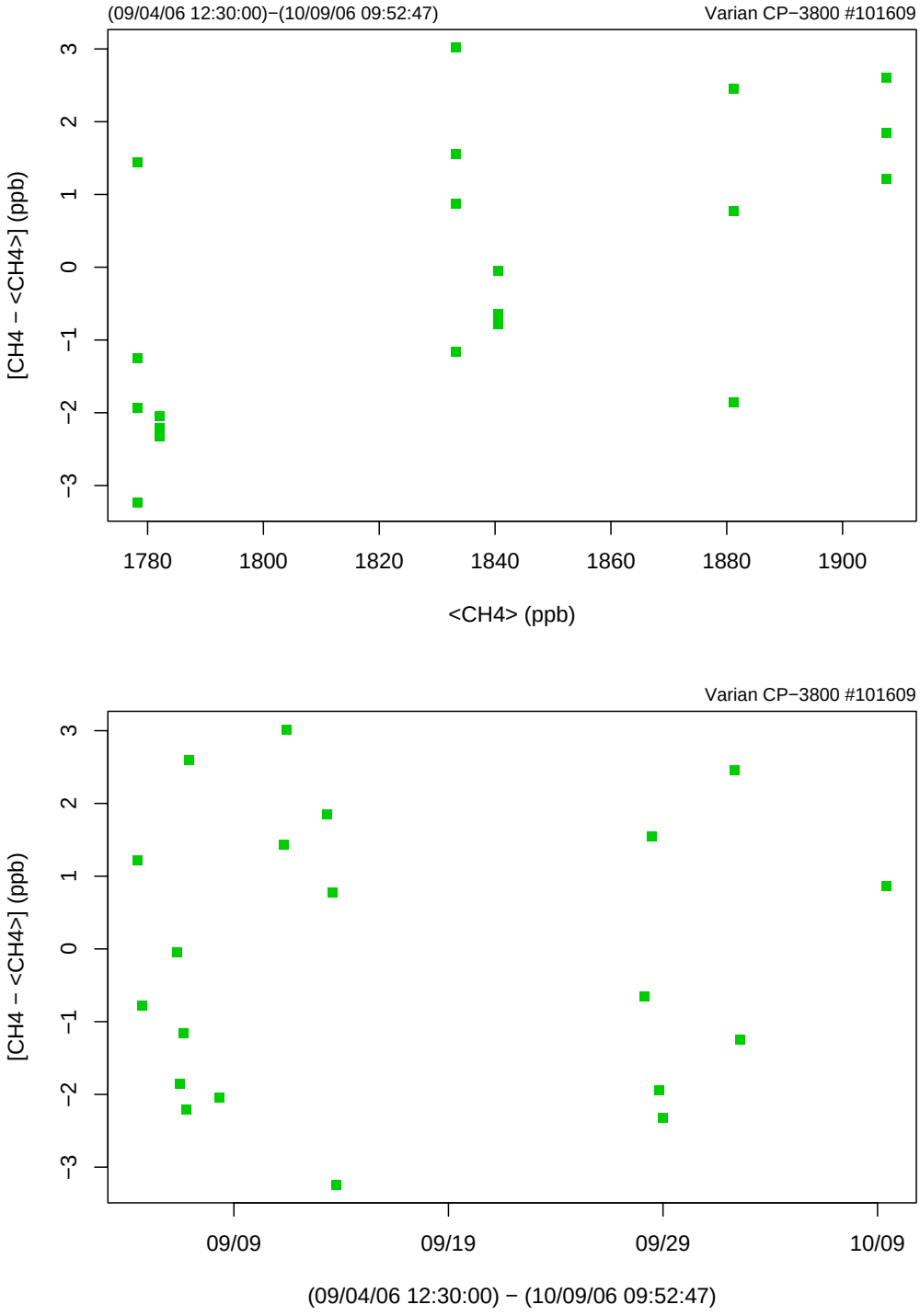

Figure 10. Regression residuals of the CPT methane GC. Points represent averages of valid single injections. Upper panel: mole fraction dependence; Lower panel: time dependence.

WCC-Empa Transfer Standards

Ozone

The WCC-Empa transfer standard (TS) was compared with the Standard Reference Photometer before and after use during the field audit. Details of these inter-comparisons at the Empa calibration laboratory are summarised in Table 14, the inter-comparison data is given in Table 15.

Table 14. Experimental details of the inter-comparison of transfer standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.011
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (8 August, 2006) 3 runs after return of TS (27 November, 2006)

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

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2006-08-08	1	0	-0.09	0.46	0.11	0.11
2006-08-08	1	90	89.91	0.30	89.69	0.08
2006-08-08	1	190	187.60	0.21	187.87	0.09
2006-08-08	1	60	59.95	0.41	59.85	0.09
2006-08-08	1	140	139.26	0.20	139.45	0.13
2006-08-08	1	30	31.75	0.39	31.79	0.06
2006-08-08	1	0	-0.04	0.36	0.11	0.07
2006-08-08	2	0	-0.01	0.36	0.15	0.19
2006-08-08	2	30	31.77	0.20	31.78	0.07
2006-08-08	2	190	188.78	0.41	188.91	0.09
2006-08-08	2	90	90.39	0.31	90.62	0.09
2006-08-08	2	140	139.85	0.43	140.06	0.10
2006-08-08	2	60	60.06	0.51	60.33	0.13
2006-08-08	2	0	-0.11	0.35	0.11	0.07
2006-08-08	3	0	0.22	0.40	0.09	0.07
2006-08-08	3	90	90.46	0.34	90.61	0.11
2006-08-08	3	190	188.32	0.15	188.93	0.08
2006-08-08	3	30	32.25	0.27	32.00	0.06
2006-08-08	3	140	139.68	0.35	139.76	0.10
2006-08-08	3	60	60.15	0.40	60.23	0.06
2006-08-08	3	0	-0.08	0.43	-0.01	0.05
2006-11-27	4	0	0.18	0.51	-0.21	0.11
2006-11-27	4	140	135.39	0.31	135.06	0.18
2006-11-27	4	90	87.40	0.38	87.23	0.08
2006-11-27	4	30	30.59	0.21	30.19	0.12
2006-11-27	4	190	182.32	0.29	182.26	0.22
2006-11-27	4	60	58.54	0.31	58.32	0.08
2006-11-27	4	0	-0.15	0.38	-0.13	0.11
2006-11-27	5	0	0.13	0.35	-0.20	0.06
2006-11-27	5	90	87.88	0.22	87.48	0.08
2006-11-27	5	190	183.00	0.43	183.15	0.11
2006-11-27	5	60	58.61	0.16	58.57	0.08
2006-11-27	5	140	135.90	0.43	135.95	0.11
2006-11-27	5	30	30.86	0.29	30.83	0.09
2006-11-27	5	0	-0.02	0.28	-0.20	0.12
2006-11-27	6	0	-0.27	0.60	-0.14	0.12
2006-11-27	6	30	30.81	0.48	30.76	0.06
2006-11-27	6	190	183.02	0.25	183.25	0.14
2006-11-27	6	90	87.96	0.22	88.07	0.13
2006-11-27	6	140	136.07	0.21	136.15	0.11
2006-11-27	6	60	58.78	0.29	58.79	0.11
2006-11-27	6	0	-0.14	0.19	-0.13	0.08

[#]The level is only indicative.

The transfer standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 11). 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 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [*Klausen, et al.*, 2003]).

$$X_{TS}\ (\text{ppb}) = ([TS] + 0.06\ \text{ppb}) / 1.0011$$

$$u_{TS}\ (\text{ppb}) = \text{sqrt}((0.43\ \text{ppb})^2 + (0.0034 * X)^2) \quad (3)$$

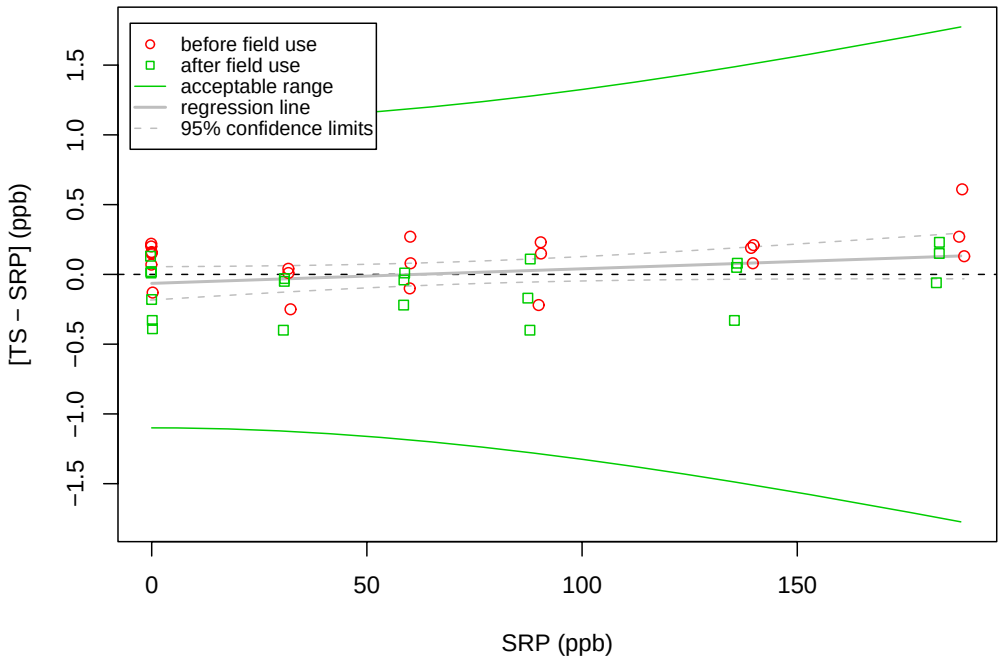

Figure 11. Deviations between transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly inter-compared with the CCL by way of travelling standards. The scale was transferred to the travelling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. Details are given in Table 16 - Table 17.

Table 16. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the travelling standard (TS) used during the field inter-comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale is based on two specific cylinders, CA02859 (194.7±1.9 ppb) CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Travelling standard (TS)		Carbon monoxide cylinders for direct inter-comparisons. (cf. Table 17)
Connection between instruments		Ca. 2 meter 1/8” stainless steel tubing (cylinders).
Levels (ppb)		70 – 360 ppb cf. Table 17
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 17. Calibration of the carbon monoxide travelling standards with the WCC-Empa reference before and after the audit.

Date	2006-06-27			2006-11-24		
Cylinder identification	CO (ppb)#			CO (ppb)#		
FF31496	73.82	±	0.15	73.96	±	0.36
050419_FA02482	106.17	±	0.19	107.00	±	0.46
050419_FA02479	119.41	±	0.27	120.49	±	0.34
041109_FA01467	135.02	±	0.25	135.40	±	0.30
030703_FA01469	185.50	±	0.31	185.63	±	0.48
050701_FA02505	359.02	±	0.44	359.71	±	0.87

Average±sd (n = approx. 100)

Methane

WCC-Empa refers to the latest WMO/GAW methane scale (hereafter: NOAA04 scale) [*Dlugokencky, et al.*, 2005] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 18). The scale was transferred to the travelling standards using a Varian 3400 gas chromatograph with an FID detector. Details of the travelling standards are given in Table 19.

Table 18. NOAA/ESRL CH_4 laboratory standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Cylinder#	Methane [ppb]* (NOAA04)
CA05316	1712.5 ± 0.30 ppb
CA04462	1817.4 ± 0.19 ppb
CA04580	1905.1 ± 0.24 ppb

* Certificates (CMDL83) from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316). Values were converted to NOAA04 scale by applying a factor of 1.0124.

Table 19. Calibration of the methane travelling standards with the WCC-Empa reference before and after the audit.

Date	2006-05-16			2006-06-26			2006-08-07			2006-11-22		
Cylinder identification	CH_4 (ppb)#			CH_4 (ppb)#			CH_4 (ppb)#			CH_4 (ppb)#		
050419_FA02482				1778.10	±	0.98				1777.14	±	1.55
030703_FA01469	1782.43	±	1.45							1780.34	±	1.76
050701_FA02505				1833.32	±	1.19	1831.08	±	1.42	1833.19	±	1.71
FF31496				1840.14	±	1.58				1839.51	±	0.93
050419_FA02479				1880.22	±	1.30				1880.79	±	1.93
041109_FA01467				1906.51	±	1.39	1907.51	±	1.66	1906.43	±	1.91

#Average±sd (n = 10)

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.353°S, 18.490°E (230 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	13 – 16 September, 2006
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, D. van der Spuy
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #54509-300
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(1.0011\pm0.0010) \times [SRP] - (0.06\pm0.09)$
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49 #51594-288
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	OFFSET: 56 SPAN: 507
1.5.4	Calibration at start of audit (ppb):	$[OA] = (0.953\pm0.000) \times [SRP] - (0.23\pm0.05)$
1.5.5	Unbiased ozone mole fraction (ppb) at start of audit:	$X = ([OA] + 0.23) / 0.953$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.33\ ppb^2 + 2.85e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	$[OA] = (0.999\pm0.000) \times [SRP] - (0.39\pm0.05)$
1.5.9	Unbiased ozone mole fraction (ppb) after audit:	$X = ([OA] + 0.39) / 0.999$
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.61e\text{-}5 \times X^2)^{1/2}$
1.6	Comments:	-Instrument was repaired during the audit -Results after audit without inlet filter -Run as the main instrument until the audit -Run as the back-up instrument after the audit
1.7	Reference:	WCC-Empa Report 06/5

[OA]: Instrument readings; [SRP]: SRP readings; X: mole fractions on SRP scale

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.353°S, 18.490°E (230 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	14 – 16 September, 2006
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, D. van der Spuy
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #54509-300
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0011±0.0010) × [SRP] - (0.06±0.09)
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49C #0526513044
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG: 0.0 COEF: 1.013
1.5.4	Calibration at start of audit (ppb):	[OA] = (0.993±0.000) × [SRP] - (0.75±0.05)
1.5.5	Unbiased ozone mole fraction (ppb) at start of audit:	X = ([OA] + 0.75) / 0.993
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.64e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	BKG: -0.5 COEF: 1.015
1.5.8	Calibration after audit (ppb):	[OA] = (1.000±0.000) × [SRP] - (0.25±0.05)
1.5.9	Unbiased ozone mole fraction (ppb) after audit:	X = ([OA] + 0.25) / 1.000
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.60e\text{-}5 \times X^2)^{1/2}$
1.6	Comments:	-Run as the back-up instrument until the audit -Run as the main instrument after the audit
1.7	Reference:	WCC-Empa Report 06/5

[OA]: Instrument readings; [SRP]: SRP readings; X: mole fractions on SRP scale

GAW World Calibration Centre for Carbon Monoxide
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Carbon Monoxide Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.353°S, 18.490°E (230 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	04 – 24 September, 2006	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, D. van der Spuy	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinder:	FF31496	73.89±0.38 ppb
		050419_FA02482	106.59±0.79 ppb
		050419_FA02479	119.95±0.98 ppb
		041109_FA01467	135.21±0.73 ppb
		030703_FA01469	185.54±0.94 ppb
		050701_FA02505	359.36±1.86 ppb
1.5	CO analyzer [CA]		
1.5.1	Model:	RGA3, S/N 113087-003	
1.5.2	Range of calibration:	0 – 360 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	CO = (1.008±0.004) × X - (1.9±0.4)	
1.5.5	Unbiased CO mole fraction (ppb) at start of audit:	X = (CO + 1.9) / 1.008	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (11.8\ ppb^2 + 3.71e\text{-}05 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	unchanged	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CO mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged	
1.6	Comments:	Standards used for the audit were partially out of the calibrated range of the instrument	
1.7	Reference:	WCC-Empa Report 06/5	

[CO]: Instrument readings; X: mole fractions on the WMO-2000 CO scale.

GAW World Calibration Centre for Methane
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Methane Audit Executive Summary (CPT)

0.1	Station Name:	Cape Point
0.2	GAW ID:	CPT
0.3	Coordinates/Elevation:	34.353°S, 18.490°E (230 m a.s.l)
Parameter:		Methane

1.1	Date of Audit:	04 September – 09 October, 2006
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	E.-G. Brunke, C. Labuschagne, B. Parker, D. van der Spuy
1.3	CH_4 Reference:	NOAA04
1.4	CH_4 Transfer Standard [TS]	
1.4.1	CH_4 Cylinders:	050419_FA02482 1777.62±0.74 ppb 030703_FA01469 1781.38±1.50 ppb 050701_FA02505 1832.53±1.29 ppb FF31496 1839.82±0.54 ppb 050419_FA02479 1880.50±0.51 ppb 041109_FA01467 1906.82±0.67 ppb
1.5	CH_4 analyzer [CA]	
1.5.1	Model:	Varian CP-3800 #101609
1.5.2	Range of calibration:	1775 –1910 ppb
1.5.3	Coefficients at start of audit	not applicable
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00039 \pm 0.00024) \times X$
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00039$
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (3.6\ ppb^2 + 7.11e\text{-}08 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 06/5

[CH_4]: Instrument readings; X: mole fractions on the NOAA04 CH_4 scale.

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LIST OF ABBREVIATIONS

CCL	Central Calibration Laboratory
GMD	Global Monitoring Division
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyser
SRP	Standard Reference Photometer
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases