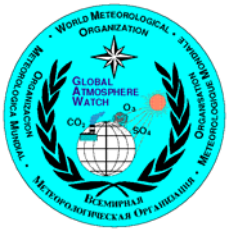

Materials Science & Technology

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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 07/3

Submitted to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE AND METHANE AT THE GLOBAL GAW STATION PALLAS FINLAND, SEPTEMBER 2007

Submitted by
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Empa Dübendorf, Switzerland

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ASSESSMENT AND RECOMMENDATIONS

The third system and performance audit at the Global GAW station Pallas (PAL) was conducted by WCC-Empa[1] from 5 thru 7 September 2007 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The PAL observatory is operated by the Finnish Meteorological Institute (FMI).

Previous audits at Pallas were conducted in June 1997 [*Herzog, et al.*, 1997] and in April 2003 [*Zellweger, et al.*, 2003].

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Mr Juha Hatakka	FMI, Primary station contact, Measurement leader
Mr Heikki Lättilä	FMI, Station operator
Mr Eero Yliniemi	FMI, Station operator

Our assessment of the Pallas 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 (FMI, Prof. Dr. Yrjö Viisanen), the primary station contact (FMI, Mr Juha Hatakka) and the World Meteorological Organization in Geneva. The report including 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 Pallas GAW station is part of the global station Pallas-Sodankylä and is located in the Pallas-Yllästunturi National Park within the northern boreal forest zone. The Pallas area is free of large local and regional pollution sources with the nearest town, Muonio with some 2500 inhabitants, being 19 km to the west. The second-nearest town, Kittilä, with 6000 inhabitants, is 46 km to the south-east. The main station, Sammaltunturi (67°58'N 24°07'E, 560 m a.s.l.) is on top of a fjeld (an arctic hill), ca. 300 m above the surrounding area and some 100 m above the tree line. The station is reached over a small access road which is closed to the public. Access is possible by snow mobile during winter and quad ATV (four wheel motorcycle) during the snow free period.

Station Facilities

The station building consists of a 120 m^2 room for the analytical equipment and a separate room for instrument pumps. Two 8 m towers are attached to either end (east and west) of the building for air sampling. These towers are electrically heated to prevent clogging of the inlets by ice and snow. It is an ideal platform for continuous atmospheric monitoring as well as measurement campaigns.

Station Management and Operation

The station is managed by the Finnish Forest Research Institute (METLA), while measurements are made by the Finnish Meteorological Institute (FMI). The station is visited twice per week (Monday and Friday) by a station operator from METLA. In case of instrument calibrations or maintenance, staff from FMI visits the site.

[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.

Recommendation 1 (*, ongoing)
The good working relationship and collaboration between the Forest Research Institute and the Meteorological Institute is important for the station and should be continued.

Air Inlet System

The station has a state-of-the art inlet system, where the east tower serves as the main inlet tower. The main inlet manifold is made of acid-proof stainless steel with an outer diameter of 60 mm, and is continuously flushed with a nominal flow rate of 150 m^3h^{-1}. All instruments are connected to this manifold, except for aerosol instruments and radon measurements, which have dedicated inlet systems.

Surface Ozone Measurements

Instrumentation. One ozone analyser (TEI 49i) is currently used at the station for continuous surface ozone measurements. The instrumentation is adequate for its intended purpose.

Standards. No ozone standard is available at the site. However, FMI uses a travelling standard (TEI 49C-PS) to check the calibration of the instrument four times per year. A Standard Reference Photometer (SRP#37) is available at FMI.

Intercomparison (Performance Audit). The inter-comparisons of the station ozone analyzer extended over a period of approx. 22 hours. The result is summarised below and the following equation characterises the instrument bias:

TEI 49i #619917500: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.25 ppb) / 1.001 (1)

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

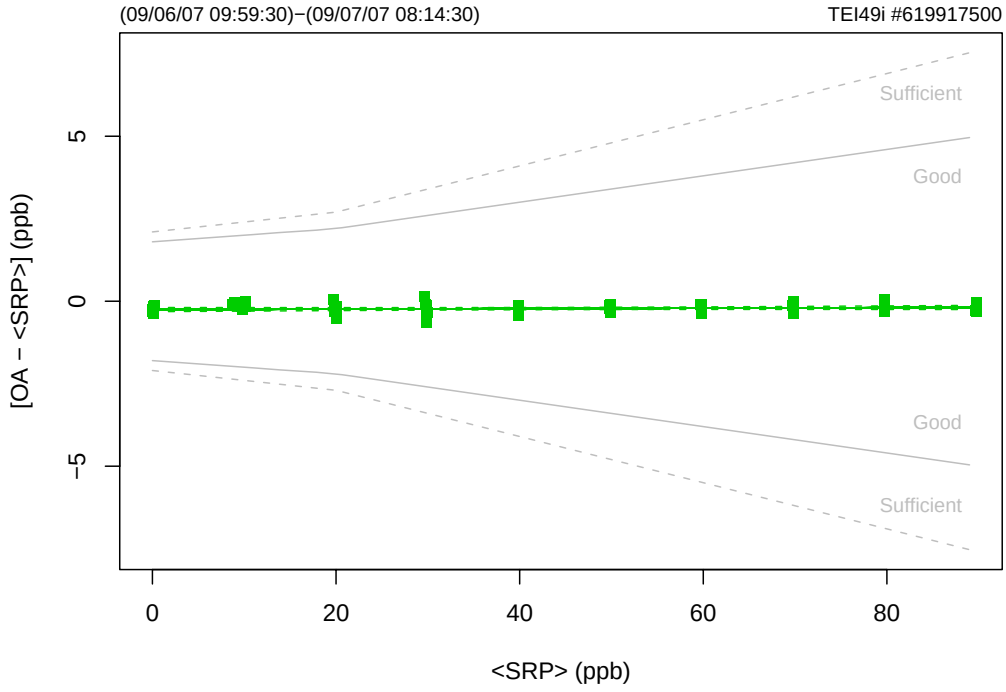

Figure 1. Bias of the Pallas ozone analyser (TEI 49i) with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Carbon Monoxide Measurements

Instrumentation. Pallas is equipped with an Agilent 6890N GC-FID/ECD system for simultaneous measurements of CH_4, CO, SF_6 and N_2O. The GC system was built in analogy to the systems used by Environment Canada (Group of Doug Worthy). The instrumentation is adequate for the intended purpose and shows a good reproducibility for multiple injections of a gas sample.

Standards. The station is equipped with three laboratory standards from NOAA/ESRL, which span the concentration range between 70 and 230 ppb. All standards have been certified by NOAA/ESRL based on the WMO-2000 carbon monoxide calibration scale in 2005.

Recommendation 2 (*, 2008)**
The laboratory standards need to be re-calibrated at NOAA/ESRL because significant deviations were found between Pallas and WCC-Empa measurements.

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instrument with randomised carbon monoxide concentrations from travelling standards. The following equation (2) characterises the instrument bias (cf. Figure 2):

AGILENT 6890N:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 0.4 ppb) / 0.977 (2)

The results show that the measurements of the Pallas instrument are lower compared to WCC-Empa. The most likely reason is a bias of the laboratory standards, which should be re-calibrated (cf. recommendation 2).

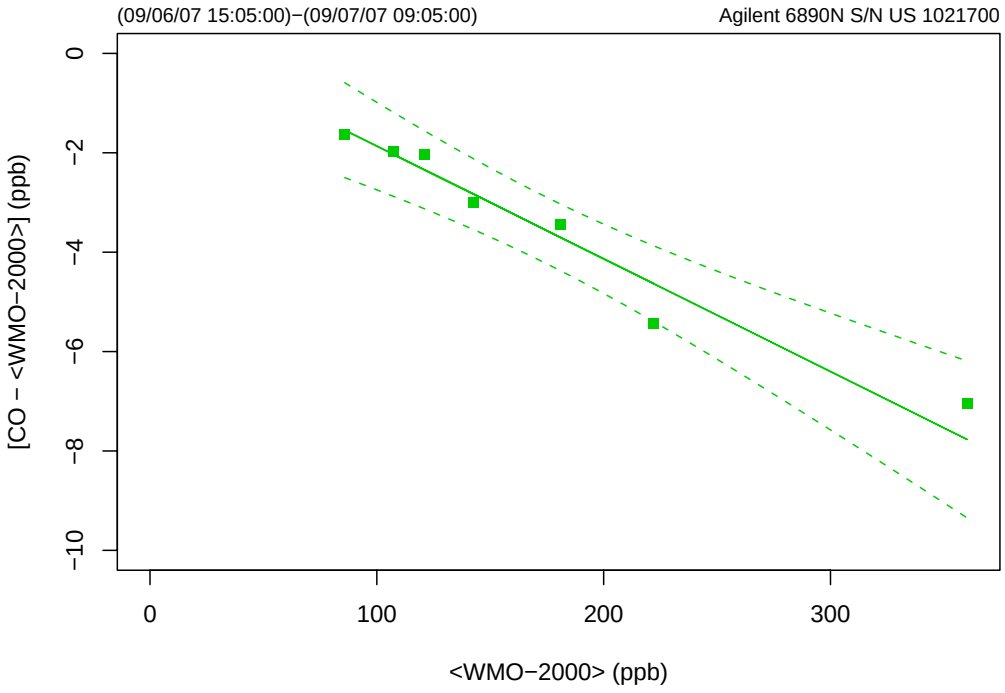

Figure 2. Bias of the Pallas carbon monoxide instrument (AGILENT 6890N) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Methane Measurements

Instrumentation. The same GC system as for the analysis of carbon monoxide is used.

Standards. The station is equipped with three laboratory standards from NOAA/ESRL, which span the concentration range between 1790 and 2000 ppb. All standards have been certified by NOAA/ESRL based on the CMDL-83 methane calibration scale in 2005, and were converted to NOAA-04 scale in 2006 (Factor 1.0124).

Intercomparison (Performance Audit). The inter-comparison involved repeated measurements of WCC-Empa travelling standards with the PAL instrument. No significant deviations between the Pallas instrument and WCC-Empa were found. The following equation characterises the instrument bias (cf. Figure 3):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 1.0002 (3)

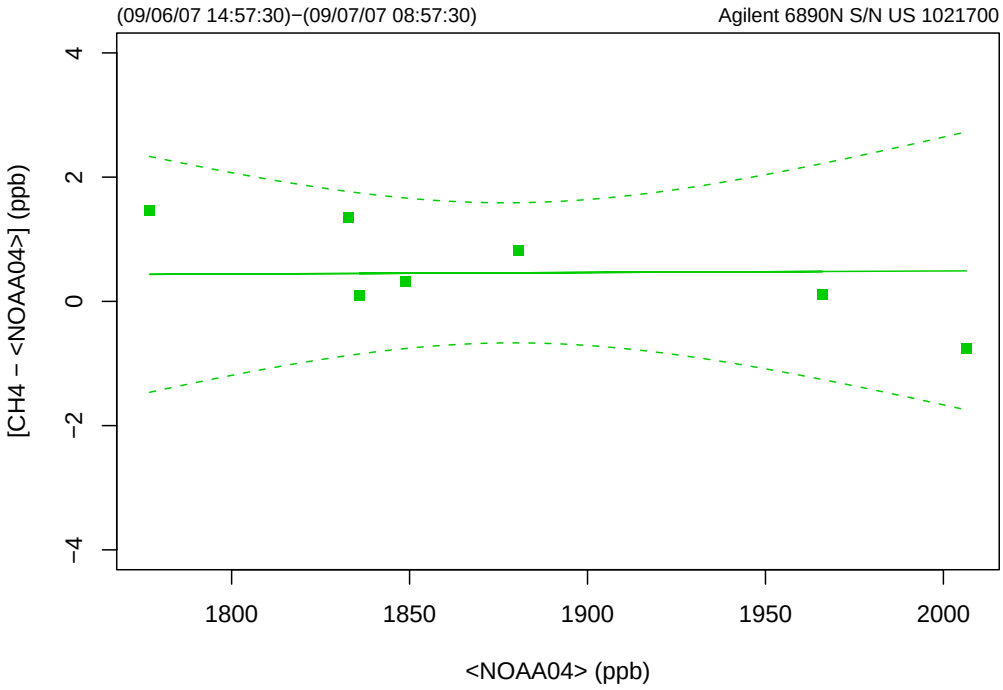

Figure 3. Bias of the Pallas methane GC (AGILENT 6890N Series) with respect to the NOAA04 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Data Acquisition and Management

Ozone: A commercial system (Envidas, Envitech Ltd.) is used for data acquisition. Data is automatically transferred to FMI. Data validation is carried out at FMI using also a programme of Envitech (Enview-2000). Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. Data is re-calculated using the three-monthly calibrations of the station instrument with the travelling standard.

GC instrument: The entire instrument is under the control of a Linux based PC using multiple RS-232 serial data ports and a GC control software written in Python. The software controls the Agilent 6890 GC including all the pneumatically actuated Valco valves.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). At the time of the audit data for surface ozone (1955 – 2005) and carbon dioxide (1999 – 2005) have been submitted by FMI. However, ozone data were submitted in μgm^{-3} units, without information about the reference pressure/temperature or conversion factor to ppb units. Other data (CO, CH_4, N_2O, SF_6) has not yet been submitted due to the relatively recent start of these measurements.

Recommendation 3 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year.

Recommendation 4 (*, ongoing)**
All data must be submitted as mole fractions.

Conclusions

The Global GAW station Pallas carries out a comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the PAL station an important contribution to the GAW programme. All assessed measurements were of high quality.

Summary Ranking of Pallas Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access possible
Facilities		
Laboratory and office space	(5)	State-of-the-art
Air Conditioning	(4)	Small temperature changes
Power supply	(5)	
Internet access	(4)	Low connection speed
General Management and Operation		
Organisation	(5)	
Competence of staff	(5)	
Air Inlet System	(5)	State-of-the-art
Instrumentation		
Ozone	(5)	TEI49i
Carbon monoxide	(5)	Agilent 6890N
Methane	(5)	Agilent 6890N
Other gases*	(5)	CO_2, SF_6, N_2O, SO_2, NO, NO_y, Rn-222, H_2
Aerosol parameters*	(5)	Comprehensive programme
Flask sampling	(5)	NOAA/ESRL
Meteo	(5)	
Standards		
Ozone	(5)	SRP, TEI49C-PS (off site)
Carbon monoxide	(3)	Re-calibration needed
Methane	(5)	NOAA standards
Data Management		
Data acquisition	(5)	
Data processing	(5)	
Data submission	(3)	Not all data submitted yet

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

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Dübendorf, February 2008

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

APPENDIX

Global GAW Station Pallas

Site description

The Pallas GAW station has been described e.g. in [*Hatakka, et al.*, 2003]. Further information can also be found in previous audit reports [*Herzog, et al.*, 1997; *Zellweger, et al.*, 2003] and from the station web site (http://fmigaw.fmi.fi). The station is also registered in GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Programme

The Pallas station started its operation in 1994, and was completely re-built in 2001. An overview of the measurement programme and its status as of September 2007 is shown in Table 1. Refer to GAWSIS or the station web page for more details.

Table 1. Measurement Programme at the PAL Station (Sammaltunturi station only)

Parameter	**Current Instrument**	**Data Coverage (%)**[#]		
		<12 m	<3 y	Overall
Aerosol				
Light absorption coefficient[#]	Aethalometer AE31 and MAAP			
Light scattering coefficient	TSI Nephelometer 3560			
Mass concentration (PM10)	Environnement MP101M			
Size distribution (7-500 nm)	DMPS			
Size distribution (>500 nm)	APS			
Total number concentration	TSI CPC model 3010			
Ozone				
Surface ozone	UV absorption (TEI 49i)	99	>90	>90
Greenhouse Gas				
CO_2	NDIR (LICOR)			
CH_4, SF_6, N_2O	Agilent 6890N with FID/ECD	>90	>90	>90
Reactive Gas				
CO	Agilent 6890N with FID	>90	>90	>90
H_2	RGD (GC - HgO reduction/UV absorption)			
NO, NO_2, NO_X	TEI 42i			
SO_2	TEI 43i			
Flask Sampling				
VOC	850-mL stainless steel flasks			
CO_2, N_2O, CH_4, CO, H_2, SF_6	NOAA Glass flask samples			
Radio Nuclide				
Rn-222	Aerosol beta activity measurement			
Solar radiation				
Global irradiance	Pyranometer (Kipp & Zonen CM11)			
$J(NO_2)$	Radiometer (Meteoroloogie Consult)			
Meteo				
PTU, wind speed + direction	Vaisala MILOS500+sensors			
Visibility, Precipitation	Vaisala FD12P			

[#] Missing information about data coverage: information was not available, but general high data availabilities (>90%) are expected for most parameters.

Ozone, Carbon Monoxide and Methane Distribution at Pallas

The monthly and yearly distributions of one hourly mean values for surface ozone, carbon monoxide and methane are shown in Figure 4.

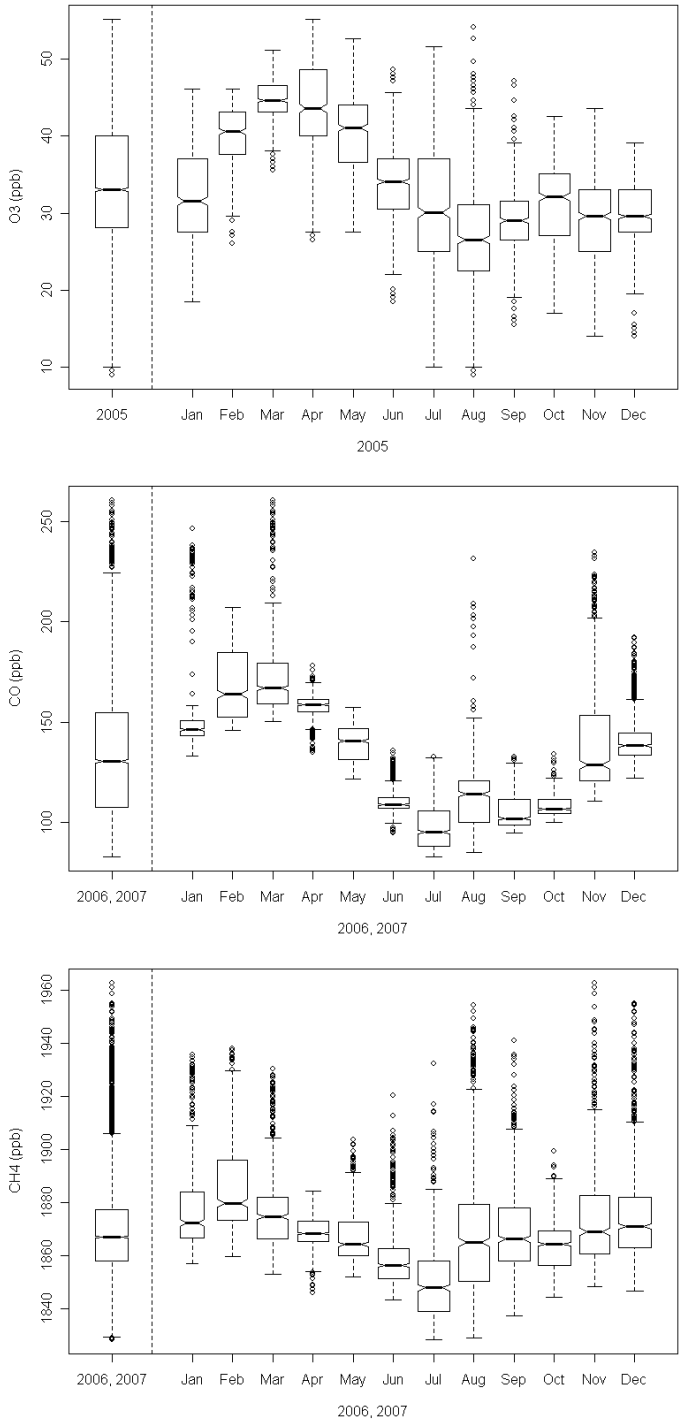

Figure 4. Yearly and monthly box plots of 1-hourly aggregates for the year for surface Ozone (upper panel, year 2005), carbon monoxide (middle panel, July 2006 thru June 2007) and methane (lower panel, July 2006 thru June 2007). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers 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 Finland are coordinated by the Finnish Meteorological institute (Director General Petteri Taalas) under the Research and Development department (Director Yrjö Viisanen). Further information about the organisation can be found on the station (http://fmigaw.fmi.fi) and FMI (www.fmi.fi) web sites.

Surface Ozone Measurements

Surface ozone measurements started in 1994 at the Pallas site, and time series are available since then. Major changes since the last audit by WCC-Empa in 2004 include the installation of a new instrument (TEI 49i), which replaces the TEI 49C analyser. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning

See previous audit report [*Zellweger, et al.*, 2003].

Air Inlet System

See previous audit report [*Zellweger, et al.*, 2003].

Instrumentation

The station is equipped with one ozone analyser (TEI 49i). Instrumental details for the ozone analysers (OA) are summarised in Table 2 below.

Standards

No ozone standard is available at the site, but 3 monthly calibrations are made with a travelling standard calibrated at FMI against SRP#37.

Operation and Maintenance

See previous audit report [*Zellweger, et al.*, 2003].

Data Acquisition and Data Transfer

A commercial system (Envidas, Envitech Ltd.) is used for data acquisition. Data is automatically transferred to FMI.

Data Treatment

Data validation is carried out at FMI using a programme of Envitech (Enview-2000). Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. Data is re-calculated using the three-monthly calibrations of the station instrument with the travelling standard.

Data Submission

Ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG) (in μgm^{-3} units).

Documentation

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

Inter-Comparison of Ozone Analyser

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included inter-comparisons of the travelling 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 the transfer standard with the station analyser. The data used for the evaluation was recorded by both WCC-Empa and Pallas data acquisition systems as indicated. In addition, data of the PAL instrument was downloaded using the TEI iPort software. No further corrections were applied to the data.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.4; COEFF = 1.012
Ozone analyser (OA)	Model, S/N	TEI 49i #619917500
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.3; COEFF = 1.037
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	One minute aggregates from digital output (custom de-signed LabView programme)
	Analyser OA	TEI iPort software and station DAQ
Pressure readings at beginning of inter-comparison (hPa)	Ambient	934.0 (Station reference)
	TS	934.0
	TEI 49C	932.6 (not adjustments were made)
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90
Duration per level (min)		15
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		9 runs (6 thru 7 September, 2007)

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. The results are shown in

Table 3. 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.

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the PAL ozone analyser (OA) TEI 49i #619917500 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2007-09-06 10:05	1	0	0.17	0.07	0	0.14	0.03
2007-09-06 10:20	1	30	29.65	29.76	0	0.17	0.10
2007-09-06 10:35	1	60	59.79	59.58	0	0.16	0.07
2007-09-06 10:50	1	40	39.90	39.64	0	0.18	0.11
2007-09-06 11:05	1	90	89.82	89.38	0	0.10	0.03
2007-09-06 11:20	1	50	49.86	49.66	0	0.29	0.08
2007-09-06 11:35	1	10	10.01	9.97	0	0.14	0.09
2007-09-06 11:50	1	20	19.77	19.82	0	0.39	0.11
2007-09-06 12:05	1	80	79.83	79.75	0	0.20	0.09
2007-09-06 12:20	1	70	69.92	69.72	0	0.24	0.06
2007-09-06 12:35	2	0	0.10	-0.09	0	0.20	0.03
2007-09-06 12:50	2	40	39.98	39.78	0	0.26	0.06
2007-09-06 13:05	2	70	69.88	69.63	0	0.21	0.07
2007-09-06 13:20	2	30	29.92	29.62	0	0.20	0.07
2007-09-06 13:35	2	90	89.89	89.41	0	0.17	0.04
2007-09-06 13:50	2	20	20.04	19.86	0	0.21	0.05
2007-09-06 14:05	2	10	9.90	9.78	0	0.26	0.04
2007-09-06 14:20	2	60	59.86	59.58	0	0.16	0.03
2007-09-06 14:35	2	50	49.88	49.59	0	0.14	0.05
2007-09-06 14:50	2	80	79.89	79.54	0	0.19	0.03
2007-09-06 15:05	3	0	0.10	-0.19	0	0.20	0.03
2007-09-06 15:20	3	90	89.89	89.60	0	0.24	0.03
2007-09-06 15:35	3	70	69.92	69.70	0	0.17	0.07
2007-09-06 15:50	3	40	39.94	39.72	0	0.21	0.05
2007-09-06 16:05	3	50	49.93	49.59	0	0.17	0.06
2007-09-06 16:20	3	20	19.88	19.70	0	0.29	0.04
2007-09-06 16:35	3	30	29.93	29.79	0	0.20	0.06
2007-09-06 16:50	3	60	59.93	59.66	0	0.19	0.07
2007-09-06 17:05	3	10	10.16	10.01	0	0.21	0.08
2007-09-06 17:20	3	80	79.88	79.47	0	0.21	0.10
2007-09-06 17:35	4	0	0.05	-0.07	0	0.17	0.03
2007-09-06 17:50	4	30	29.75	29.64	0	0.42	0.11
2007-09-06 18:05	4	60	59.88	59.51	0	0.21	0.10
2007-09-06 18:20	4	40	39.95	39.46	0	0.26	0.06
2007-09-06 18:35	4	90	89.90	89.45	0	0.12	0.03
2007-09-06 18:50	4	50	49.98	49.56	0	0.20	0.10
2007-09-06 19:05	4	10	10.07	10.08	0	0.18	0.13
2007-09-06 19:20	4	20	19.93	19.64	0	0.18	0.08
2007-09-06 19:35	4	80	79.87	79.40	0	0.20	0.10
2007-09-06 19:50	4	70	69.91	69.52	0	0.21	0.09
2007-09-06 20:05	5	0	0.01	-0.23	0	0.23	0.04
2007-09-06 20:20	5	40	39.94	39.54	0	0.18	0.06
2007-09-06 20:35	5	70	69.90	69.40	0	0.14	0.07
2007-09-06 20:50	5	30	30.01	29.64	0	0.20	0.10
2007-09-06 21:05	5	90	89.88	89.48	0	0.14	0.09
2007-09-06 21:20	5	20	20.06	19.69	0	0.24	0.11
2007-09-06 21:35	5	10	10.16	10.11	0	0.26	0.09
2007-09-06 21:50	5	60	59.92	59.60	0	0.17	0.11
2007-09-06 22:05	5	50	49.94	49.52	0	0.11	0.13
2007-09-06 22:20	5	80	79.92	79.52	0	0.19	0.10

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2007-09-06 22:35	6	0	-0.03	-0.24	0	0.14	0.04
2007-09-06 22:50	6	90	89.88	89.61	0	0.12	0.08
2007-09-06 23:05	6	70	69.93	69.53	0	0.13	0.11
2007-09-06 23:20	6	40	39.94	39.66	0	0.17	0.08
2007-09-06 23:35	6	50	49.93	49.76	0	0.14	0.17
2007-09-06 23:50	6	20	19.82	19.51	0	0.41	0.09
2007-09-07 00:05	6	30	29.93	29.57	0	0.15	0.12
2007-09-07 00:20	6	60	59.94	59.65	0	0.12	0.10
2007-09-07 00:35	6	10	8.88	8.86	0	1.43	0.44
2007-09-07 00:50	6	80	79.90	79.56	0	0.11	0.11
2007-09-07 01:05	7	0	0.04	-0.28	0	0.16	0.03
2007-09-07 01:20	7	30	29.93	29.27	0	0.14	0.14
2007-09-07 01:35	7	60	59.91	59.49	0	0.16	0.08
2007-09-07 01:50	7	40	39.97	39.57	0	0.26	0.07
2007-09-07 02:05	7	90	89.89	89.66	0	0.10	0.07
2007-09-07 02:20	7	50	49.94	49.69	0	0.10	0.09
2007-09-07 02:35	7	10	9.75	9.51	0	0.68	0.14
2007-09-07 02:50	7	20	20.02	19.67	0	0.24	0.07
2007-09-07 03:05	7	80	79.89	79.51	0	0.13	0.11
2007-09-07 03:20	7	70	69.92	69.49	0	0.10	0.10
2007-09-07 03:35	8	0	0.01	-0.27	0	0.11	0.06
2007-09-07 03:50	8	40	39.94	39.46	0	0.20	0.12
2007-09-07 04:05	8	70	69.91	69.65	0	0.20	0.07
2007-09-07 04:20	8	30	29.95	29.58	0	0.17	0.10
2007-09-07 04:35	8	90	89.92	89.64	0	0.15	0.06
2007-09-07 04:50	8	20	20.07	19.52	0	0.19	0.10
2007-09-07 05:05	8	10	8.66	8.58	0	1.32	0.49
2007-09-07 05:20	8	60	59.92	59.73	0	0.20	0.12
2007-09-07 05:35	8	50	49.93	49.61	0	0.17	0.12
2007-09-07 05:50	8	80	79.90	79.66	0	0.18	0.08
2007-09-07 06:05	9	0	-0.03	-0.28	0	0.13	0.03
2007-09-07 06:20	9	90	89.89	89.69	0	0.15	0.08
2007-09-07 06:35	9	70	69.93	69.79	0	0.18	0.12
2007-09-07 06:50	9	40	39.96	39.76	0	0.15	0.07
2007-09-07 07:05	9	50	49.95	49.69	0	0.12	0.09
2007-09-07 07:20	9	20	20.04	19.88	0	0.14	0.09
2007-09-07 07:35	9	30	29.90	29.63	0	0.16	0.08
2007-09-07 07:50	9	60	59.91	59.44	0	0.12	0.06
2007-09-07 08:05	9	10	9.74	9.60	0	0.68	0.18
2007-09-07 08:20	9	80	79.90	79.76	0	0.13	0.05

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

Figure 5 shows the regression residuals of the ozone analyser with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

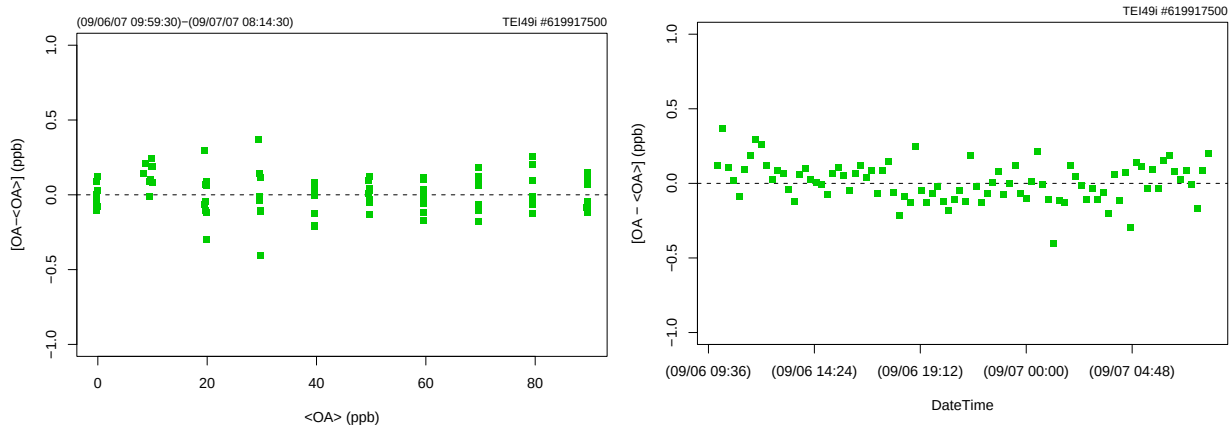

Figure 5. Regression residuals of the PAL ozone analyser (TEI 49i) as a function of concentration (left panel) and time (right panel).

Based on these inter-comparison results, unbiased ozone volume mixing ratios 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 49i #619917500:

$$X_{O3}\ (\text{ppb}) = ([\text{OA}] + 0.25\ \text{ppb}) / 1.001$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.29\ \text{ppb}^2 + 2.59\text{e-}05 * X_{O3}^2) \qquad (1)$$

Conclusions

The findings of this audit demonstrate good agreement between PAL ozone measurements and WCC-Empa. Therefore no further recommendations are proposed by WCC-Empa except that data should be submitted in mole fraction units to WDCGG.

Carbon Monoxide Measurements

Major changes since the last audit by WCC-Empa include the installation of a new carbon monoxide instrument. This was recommended by WCC-Empa after the audit in 2003. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

See previous audit report [*Zellweger, et al.*, 2003].

Air Inlet System

The air inlet system and manifold is identical as for the surface ozone measurements, and has been described in [*Zellweger, et al.*, 2003]. From the manifold the instrument is connected as follows:

- approx. 6 m 1/8" stainless steel tubing
- cold trap -27°C
- approx. 2 m 1/8" stainless steel tubing
- KNF N035AT18 pump, pressure control, distribution of air to CO/CH_4/N_2O/SF_6, H_2 and CO_2 inst.
- Flow rate to pump 3 l min^{-1}, after pump 550 ml min^{-1}
- approx. 8 m 1/8" stainless steel tubing to instrument

Overall residence time is approximately 2 seconds.

Instrumentation

Pallas is equipped with an Agilent 6890N GC-FID/ECD system for simultaneous measurements of CH_4, CO, SF_6 and N_2O. The GC system was built in analogy to the systems used by Environment Canada (Group of Doug Worthy).

Standards and Calibration

The carbon monoxide instrument is calibrated using a working standard (pressurised air). The working standard is calibrated at the site using the laboratory standards. Table 4 gives details of the cylinders currently available at the station.

Injections are made every 7.5 minutes, alternating between working standard and ambient air. Two bracketing working standard injections are used to calculate the ambient data.

Table 4. Carbon monoxide standards available at the PAL station

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
NOAA/ESRL CA06212 laboratory standard	63.3 ppb CO[1] 70.0 ppb CO[2]	2004	NOAA/ESRL	2004	2005.
NOAA/ESRL CA06177 laboratory standard	63.3 ppb CO[1] 72.1 ppb CO[2]	2004	NOAA/ESRL	2004	cont.
NOAA/ESRL CA06249 laboratory standard	145.1 ppb CO[1] 151.2 ppb CO[2]	2004	NOAA/ESRL	2004	cont.
NOAA/ESRL CA06206 laboratory standard	231.0 ppb CO[1] 231.8 ppb CO[2]	2004	NOAA/ESRL	2004	cont.
AGA 5661338 target gas	288.7 ppb CO	2007	PAL	2007	cont.

[1] WMO-88 carbon monoxide scale, RGA-3 instrument at NOAA/ESRL
[2] WMO-2000 carbon monoxide scale, VURF instrument at NOAA/ESRL

Operation and Maintenance

The system is checked for general operation each working day. Remote access is possible, and instrument parameters and chromatograms are frequently checked. The working standard is calibrated against the laboratory standards 4 to 5 times per year. A zero check using CO free air (Sofnocat) is performed in irregular intervals.

Data Acquisition and Data Transfer

The entire instrument is controlled by a Linux based PC using multiple RS-232 serial data ports and a custom made GC control software written in Python. The software controls the Agilent 6890N GC including all the electrically actuated Valco valves.

Data Treatment

Final concentrations are calculated using the peak heights of the working standard injections. A drift correction is applied to the working standard concentration in case of a recognisable drift. Raw and final data are stored.

Data Submission

Carbon monoxide data have not yet is submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG).

Documentation

All information is entered in electronic log books. The log book entries were comprehensive and up-to-date. Instrument manuals are available at the site.

Inter-Comparison of the Carbon Monoxide Analyser

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] 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 are given in Table 5 below.

Setup and Connections

The Agilent 6890N instrument was inter-compared by direct measurements of travelling standards. Details of this experiment are shown in Table 5. The data used for the evaluation was recorded by the PAL data acquisition system.

Table 5. 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 / 040719_0653B / 85.85 / 0.50 2 / 050419-1 FA02482 / 107.54 / 0.60 3 / 050419_FA02479 / 121.22 / 0.75 4 / 050415_FA02476 / 142.82 / 0.74 5 / 050415_FA02466 / 180.97 / 0.95 6 / 060602_0646B / 221.94 / 1.11 7 / 050701_FA02505 / 360.29 / 1.90
Field instrument	Model, S/N	Agilent 6890N, S/N US 1021700
	Principle	GC with FID Detector / Methanizer Pre-column: Mole sieve 5Å 80/100, 1.1m, 3/16" o.d. Analytical column: Unibeads 1S 60/80, 4 ft, 1/8" o.d. Carrier: N_2 6.0 - Mole sieve Column temp. 90°C, Detector temp. 170°C Sample loop 10 ml Sample air dried to dew point -27°C
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Duration per level (min)		Injections every 15 min; total 9-11 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (6-7 September, 2007)

Results

The GC system was inter-compared using WCC-Empa travelling standards. Each level was injected between 9 and 11 times. This resulted in a maximum of 11 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 6).

Table 6. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the PAL GC with WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	PAL CO (ppb)	sdCO (ppb)	No. of inj.
2007-09-06 15:05	050419_FA02479	121.22	0.75	119.19	0.49	11
2007-09-06 18:05	050701_FA02505	360.29	1.90	353.24	1.16	11
2007-09-06 21:05	050419-1 FA02482	107.54	0.60	105.57	1.16	11
2007-09-07 00:05	050415_FA02476	142.82	0.74	139.82	1.02	11
2007-09-07 06:20	060602_0646B	221.94	1.11	216.51	0.75	9
2007-09-07 06:12	040719_0653B	85.85	0.50	84.22	1.02	10
2007-09-07 09:05	050415_FA02466	180.97	0.95	177.52	1.18	11

Figure 6 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. The absence of concentration dependence (upper panel) in the residuals indicates linearity of the instrument.

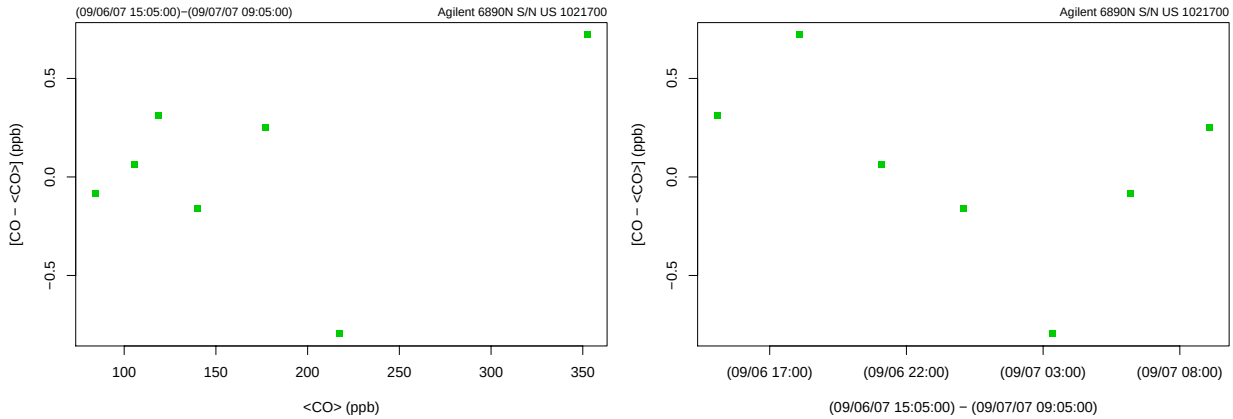

Figure 6. Regression residuals of the PAL RGA-3 based on the inter-comparison with travelling standards. Points represent averages of valid single injections. Left panel: mole fraction dependence; Right panel: time dependence.

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).

$$X_{CO}\ (\text{ppb}) = ([CO] - 0.4\ \text{ppb}) / 0.977$$

$$u_{CO}\ (\text{ppb}) = \text{sqrt}\ (1.6\ \text{ppb}^2 + 5.51\text{e-}05 * X_{CO}^2) \qquad (2)$$

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 Pallas CO instrument was working well, however, the inter-comparison revealed a difference of approximately 2% between PAL and WCC-Empa. These differences are most likely due to differences in the laboratory standards. Re-calibration of the standards at NOAA/ESRL is recommended.

Methane Measurements

Methane measurements started at PAL in 2004 with the installation of a GC-FID system for the simultaneous measurement of CO, CH_4, SF_6 and N_2O.

All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Identical as for carbon monoxide (same instrument).

Standards and Calibration

The standard methane scale, to which the PAL CH_4 measurements are referenced, is based on standards obtained from NOAA/ESRL. Table 7 shows details of the cylinders currently available at the station.

Calibration of the instrument is performed using the working standard. Injections are made every 7.5 minutes, alternating between sample and standard. Peak height is used for data evaluation.

Table 7. Methane standards available at Pallas

Manufacturer, S/N, Use	**CH_4 Content (ppb)**	**Calibration**		**In service**	
		Date	**By**	**From**	**To**
NOAA/ESRL CA06212 laboratory standard	1866.5 ppb CH_4 [*] 1889.6 ppb CH_4 [#]	2004	NOAA/ESRL	2004	2005.
NOAA/ESRL CA06177 laboratory standard	1791.1 ppb CH_4 [*] 1813.3 ppb CH_4 [#]	2004	NOAA/ESRL	2004	cont.
NOAA/ESRL CA06249 laboratory standard	1923.0 ppb CH_4 [*] 1946.8 ppb CH_4 [#]	2004	NOAA/ESRL	2004	cont.
NOAA/ESRL CA06206 laboratory standard	1972.5 ppb CH_4 [*] 1997.0 ppb CH_4 [#]	2004	NOAA/ESRL	2004	cont.
AGA 5661338 target gas	1855.9 ppb CH_4 [#]	2007	PAL	2007	cont.

[*] CMDL-83 methane scale
[#] NOAA-04 methane scale

Data Submission

Methane data have not yet been submitted to WDCGG.

Inter-Comparison of Methane Analysers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] 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 are given in Table 8 below.

Setup and Connections

Table 8 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 PAL data acquisition system, and no further corrections were applied.

Table 8. Experimental details of the methane inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 050419_FA02482 / 1776.93 / 0.16 2 / 050701_FA02505 / 1832.81 / 0.59 3 / 060602_0646B / 1835.87 / 0.26 4 / 040719_0653B / 1848.84 / 0.31 5 / 050419_FA02479 / 1880.49 / 0.33 6 / 050415_FA02476 / 1966.07 / 0.44 7 / 050415_FA02466 / 2006.47 / 0.89
Field instrument	Model, S/N	AGILENT 6890N, S/N US 1021700
Connection of TS to field instrument		TS were connected to the sample selection valve of the PAL system
Data Acquisition		Station data acquisition
Number of injections		Injections every 15 min; total 11-12 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (6 thru 7 September, 2007)

Results

Each TS was injected between 11 or 12 times, which resulted in a maximum of 12 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 9).

Table 9. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the inter-comparison of the PAL methane analyser with the WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS (ppb)	uTS (ppb)	CH_4 (ppb)	uCH_4 (ppb)	No. of inj.
2007-09-06 15:05	1880.49	0.33	1881.30	0.96	12
2007-09-06 18:05	1832.81	0.59	1834.16	1.05	12
2007-09-06 21:05	1776.94	0.16	1778.39	1.07	11
2007-09-07 00:05	1966.07	0.44	1966.18	1.22	11
2007-09-07 06:20	1835.87	0.26	1835.96	0.99	12
2007-09-07 06:12	1848.84	0.31	1849.17	1.01	12
2007-09-07 09:05	2006.47	0.89	2005.71	1.02	12

Figure 7 shows the regression residuals of the AGILENT 6890N Series GC plotted against time and concentration. The absence of a temporal trend (upper panel) indicates stable instrument conditions. The absence of concentration dependence (lower panel) indicates linearity of the instrument.

Based on the inter-comparison results, unbiased methane volume mixing ratios of the AGILENT 6890N Series analyser 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).

$$X_{CH4}\ (\text{ppb}) = (CH_4) / 1.0002$$

$$u_{CH4}\ (\text{ppb}) = \text{sqrt}\ (1.1\ \text{ppb}^2 + 4.11\text{e-}08 * X_{CH4}^2) \quad (3)$$

Conclusions

No significant deviations between Pallas 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 Pallas GC was good, with an average standard deviation of 0.06% (11-12 injections). This value is comparable to the best GC-FID systems at GAW stations. Therefore no further technical recommendations are made by WCC-Empa.

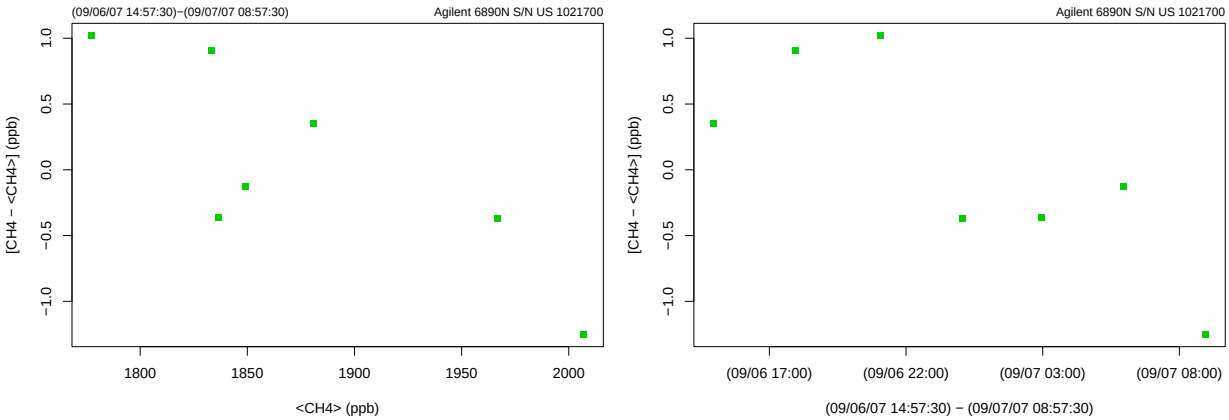

Figure 7. Regression residuals of the PAL methane GC. Points represent averages of valid single injections. Left panel: concentration dependence; Right panel: time dependence.

WCC-Empa Travelling Standards

Ozone

The WCC-Empa travelling 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 10, the inter-comparison data is given in Table 11.

Table 10. Experimental details of the inter-comparison of travelling standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Travelling standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.4; COEFF = 1.012
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 (27 July, 2007) 3 runs after return of TS (31 October, 2007)

Table 11. Five-minute aggregates computed from 10 valid 30-second values for the inter-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)
2007-07-27	1	0	0.08	0.53	-0.08	0.07
2007-07-27	1	90	86.66	0.40	86.35	0.11
2007-07-27	1	190	179.60	0.24	179.75	0.17
2007-07-27	1	30	30.65	0.36	30.62	0.07
2007-07-27	1	140	133.91	0.36	133.76	0.18
2007-07-27	1	60	57.02	0.52	57.22	0.06
2007-07-27	1	0	0.02	0.46	-0.10	0.06
2007-07-27	2	0	-0.10	0.62	-0.01	0.07
2007-07-27	2	30	30.09	0.43	29.84	0.11
2007-07-27	2	140	132.89	0.37	132.51	0.12
2007-07-27	2	60	56.94	0.45	56.80	0.12
2007-07-27	2	90	85.39	0.31	85.12	0.08
2007-07-27	2	190	177.89	0.29	177.56	0.15
2007-07-27	2	0	-0.13	0.38	0.04	0.08
2007-07-27	3	0	-0.06	0.23	-0.02	0.12
2007-07-27	3	90	85.44	0.21	85.25	0.12
2007-07-27	3	190	177.92	0.24	177.91	0.13
2007-07-27	3	140	132.54	0.30	132.47	0.13
2007-07-27	3	30	30.46	0.34	30.36	0.13
2007-07-27	3	60	56.45	0.66	56.80	0.10
2007-07-27	3	0	0.24	0.23	0.05	0.08
2007-10-31	4	0	-0.04	0.18	-0.16	0.07
2007-10-31	4	90	85.99	0.19	86.42	0.12
2007-10-31	4	190	173.94	0.39	174.71	0.36
2007-10-31	4	140	130.61	0.13	131.21	0.12
2007-10-31	4	30	28.32	0.10	28.45	0.12
2007-10-31	4	60	55.44	0.10	55.80	0.07
2007-10-31	4	0	0.00	0.24	-0.04	0.11
2007-10-31	5	0	-0.18	0.22	-0.08	0.12
2007-10-31	5	60	55.41	0.19	55.66	0.13
2007-10-31	5	190	173.14	0.38	174.24	0.38
2007-10-31	5	90	85.76	0.12	86.24	0.06
2007-10-31	5	30	28.30	0.20	28.40	0.07
2007-10-31	5	140	130.12	0.30	130.93	0.31
2007-10-31	5	0	0.11	0.17	0.01	0.07
2007-10-31	6	0	0.06	0.15	-0.14	0.12
2007-10-31	6	190	173.09	0.40	174.28	0.36
2007-10-31	6	140	129.81	0.18	130.68	0.13
2007-10-31	6	30	28.38	0.16	28.25	0.11
2007-10-31	6	60	55.24	0.27	55.59	0.09
2007-10-31	6	90	85.33	0.16	85.81	0.08
2007-10-31	6	0	-0.05	0.25	-0.09	0.09

[#]the level is only indicative.

The travelling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 8). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (equation 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [*Klausen, et al.*, 2003]).

$$X_{TS}\ (\text{ppb}) = ([TS] - 0.04\ \text{ppb}) / 1.0023$$

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

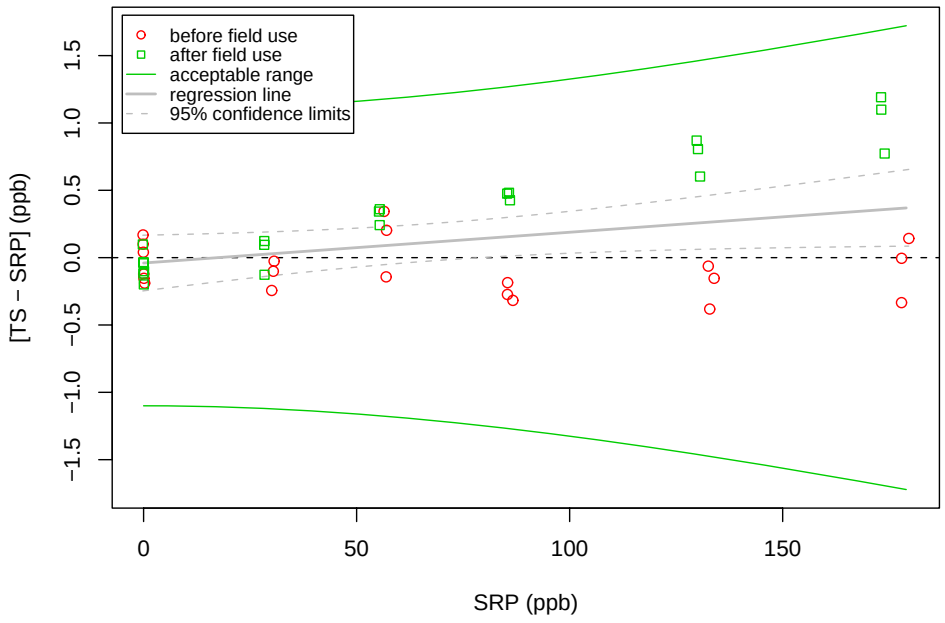

Figure 8. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 12 and Table 13.

Table 12. 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 one specific cylinders, 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 13)
Connection between instruments		Ca. 2 meter 1/8” stainless steel tubing (cylinders).
Levels (ppb)		85 – 360 ppb cf. Table 13
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 13. Calibration of the carbon monoxide travelling standards with the WCC-Empa reference before and after the audit.

Date	2007-06-13			2007-09-25		
Cylinder identification	CO (ppb)#			CO (ppb)#		
040719_0653B	85.68	±	0.37	86.03	±	0.48
050419-1 FA02482	107.35	±	0.46	107.73	±	0.35
050419_FA02479	120.91	±	0.47	121.54	±	0.56
050415_FA02476	142.95	±	0.47	142.69	±	0.73
050415_FA02466	180.77	±	0.62	181.17	±	0.59
060602_0646B	221.96	±	0.89	221.92	±	0.87
050701_FA02505	359.87	±	1.26	360.72	±	0.99

Average±sd (n = approx. 100)

No significant drift was observed over the period of the audit.

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 14). 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 15.

Table *14*. NOAA/ESRL CH4 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 15. Calibration of the methane travelling standards with the WCC-Empa reference before and after the audit (Average mole fraction in ppb ± sd (n = 10)).

Cylinder	040719_0653B	050415_FA02476	050415_FA02466	050419_FA02482	050419_FA02479	050701_FA02505	060602_0646B
2006-08-07	1848.3±1.0	NA	NA	NA	NA	1831.1±1.4	NA
2006-11-22	NA	NA	NA	1777.1±1.6	1880.8±1.9	1832.2±1.7	NA
2007-04-13	NA	NA	NA	1776.9±1.4	1879.5±0.7	NA	NA
2007-06-14	1848.8±1.1	1966.5±1.2	2005.6±1.1	1776.5±0.9	1880.7±0.9	1833.8±1.1	1836.0±1.1
2007-07-05	NA	NA	NA	NA	NA	NA	1835.4±1.4
2007-09-25	1849.4±1.5	1965.6±1.3	2007.4±1.9	1777.2±0.7	1881.0±0.7	1833.2±1.2	1836.3±1.0

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Ozone Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.974°N 24.116°E (560 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	6 – 7 September, 2007
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Juha Hatakka, Heikki Lättilä, Eero Yliniemi
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):	(1.0023±0.0010) × [SRP] - (0.04±0.13)
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49i #619917500
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.3 ppb, SPAN 1.037
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.001±0.000) × [SRP] - (0.25±0.05)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] + 0.25) / 1.001
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.29\ ppb^2 + 2.59e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 07/3

[OA]: Instrument readings; [SRP]: SRP readings; X: mixing ratios on SRP scale

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Carbon Monoxide Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.974°N 24.116°E (560 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	6 – 7 September, 2007	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Station staff involved in audit:	Juha Hatakka	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	040719_0653B	85.85±0.50 ppb
		050419_FA02482	107.54±0.60 ppb
		050419_FA02479	121.22±0.75 ppb
		050415_FA02476	142.82±0.74 ppb
		050415_FA02466	180.97±0.95 ppb
		060602_0646B	221.94±1.11 ppb
		050701_FA02505	360.29±1.90 ppb
1.5	CO analyzer [CA]		
1.5.1	Model:	AGILENT 6890N S/N US 1021700	
1.5.2	Range of calibration:	0 – 400 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	$CO = (0.977 \pm 0.005) \times X + (0.4 \pm 0.8)$	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 0.4) / 0.977$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (1.5\ ppb^2 + 5.51e\text{-}05 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	BKG -8.900 SPAN 1.062	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CO mixing ratio (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 07/3	

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 CO scale.

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Methane Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.974°N 24.116°E (560 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	6 – 7 September, 2007	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Station staff involved in audit:	Juha Hatakka	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	040719_0653B	1776.93±0.16 ppb
		050419_FA02482	1832.81±0.59 ppb
		050419_FA02479	1835.87±0.26 ppb
		050415_FA02476	1848.84±0.31 ppb
		050415_FA02466	1880.49±0.33 ppb
		060602_0646B	1966.07±0.44 ppb
		050701_FA02505	2006.47±0.89 ppb
1.5	CH_4 analyzer [CA]		
1.5.1	Model:	Agilent 6890N S/N US 1021700	
1.5.2	Range of calibration:	1775 –2010 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.0002 \pm 0.0001) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.0002$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (1.1\ ppb^2 + 4.11e\text{-}08 \times X^2)^{1/2}$	
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 07/3	

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

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LIST OF ABBREVIATIONS

a.s.l.	above sea level
CCL	Central Calibration Laboratory
DAQ	Data Acquisition System
GAW	Global Atmosphere Watch
GC	Gas Chromatograph
FMI	Finnish Meteorological Institute
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyser
PAL	Pallas GAW Station
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Travelling Standard
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation