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

Materials Science & Technology
Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 06/2

Submitted to the

World Meteorological Organisation

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE, CARBON MONOXIDE AND METHANE

AT THE

GLOBAL GAW STATION ZUGSPITZE / SCHNEEFERNERHAUS

GERMANY, JUNE 2006

Submitted by

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ASSESSMENT AND RECOMMENDATIONS

The fourth system and performance audit at the Global GAW station Zugspitze was conducted by WCC-Empa[1] from 6 thru 9 June 2006 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007].

Previous audits at the Zugspitze GAW station were conducted in April 1996 [*Herzog, et al.*, 1996], November 1997 [*Herzog, et al.*, 1997], and February 2001 [*Zellweger, et al.*, 2001]. The station was relocated from the Zugspitze summit (Station Indices ZSP and ZGP) to the Scheefernerhaus (Station Index SFH) at 300 m lower altitude during 2001/2002. The station is jointly run by the German Weather Service (DWD) and the German Federal Environment Agency (UBA).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Ludwig Ries	UBA, Station manger
Mr. Ralph Sohmer	UBA, Station operator
Mr. Steffen Knabe	UBA, Station operator

Our assessment of the station Zugspitze 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 station manager (UBA, Dr. Ludwig Ries) and the World Meteorological Organisation 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 Schneefernerhaus observatory (2656m a.s.l.) is located on the southern slope of Zugspitze, the highest mountain of the German Alps (2964 m a.s.l.). The station was moved from the summit to Schneefernerhaus during 2001/2002. Measurements on the summit are partly ongoing but are not longer considered as part of the GAW programme. Further information is available in GAWSIS (www.empa.ch/gaw/gawsis).

The location is adequate for the intended purpose. Access to the site is possible by cable car and cog railway.

Recommendation 1 (, on-going)**
The move from the summit to the new location created different data series. Comparability of the measurements between the two sites should be investigated and published.

Recommendation 2 (, on-going)**
Data that is still acquired at the summit should be submitted to the corresponding data centres because it potentially provides valuable information of the differences between the two locations.

[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.

Station Facilities
The Schneefernerhaus 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 permanently staffed during working days with scientists, engineers and operators. This guarantees the high level quality of the Zugspitze data. The current staff for the GAW measurements consists of one scientist and two technicians who have excellent technical and scientific expertise to operate and maintain the equipment and to work with the data. One engineer position was vacant at the time of the audit, but was filled in 2007.

> **Recommendation 3 (**, on-going)**
> *The current station management system with responsibilities of both technical and scientific staff is regarded as optimal and should be continued. Vacant positions should be filled.*

Air Inlet System
The overall design of the air inlet system is state of the art (for all parameters) and adequate for its intended purpose. However, an ozone loss of approximately 0.5% was found in the sample line between the instrument and the manifold.

> **Recommendation 4 (***, 2006)**
> *The sample line between the ozone analyser and the manifold including the selection valve for zero air should carefully be checked for ozone loss. Some of the fittings are stainless steel which is not adequate for ozone inlet systems. Critical parts need to be replaced immediately. (Done after the audit).*

Surface Ozone Measurements
Instrumentation. One TEI 49C ozone instrument is available at the SFH station. The instrumentation is adequate for its intended purpose.

Standards. The station is equipped with an ozone standard (TEI49C-PS) which is calibrated against the ozone standard of UBA (SRP#29) on a yearly basis. Calibrations are carried out every three months and the data of the analyser is corrected based on these calibrations. The pressure sensors are usually not checked during the calibration procedure, but the pressure sensor of the ozone standard was found to agree well with the station reference pressure.

> **Recommendation 5 (**, on-going)**
> *Pressure sensors should be checked during inter-comparisons. A bias in the pressure sensor reading should be adjusted to a reference pressure sensor.*

Intercomparison (Performance Audit). The inter-comparisons extended over a period of approximately 13 hours (analyser) and 6 hours (calibrator). The raw readings of the TEI 49C instrument were corrected with a factor of 0.9887 and an offset of -0.06 ppb based on the last inter-comparison with the station calibrator, according to the usual station method. No further corrections were applied to the calibrator data. The results of the assessment are summarised below and are presented in Figure 1 (analyser with inlet filter) and Figure 2 (standard).

TEI49C #65220-347: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.04 ppb) / 0.9832 (1a)

TEI49C-PS #58686-319: 0 – 190 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OC] + 0.00 ppb) / 0.9855 (1b)

Here, [OA] represents surface ozone readings obtained from the station data acquisition and [OC] represents surface ozone readings obtained from the RS-232 output.

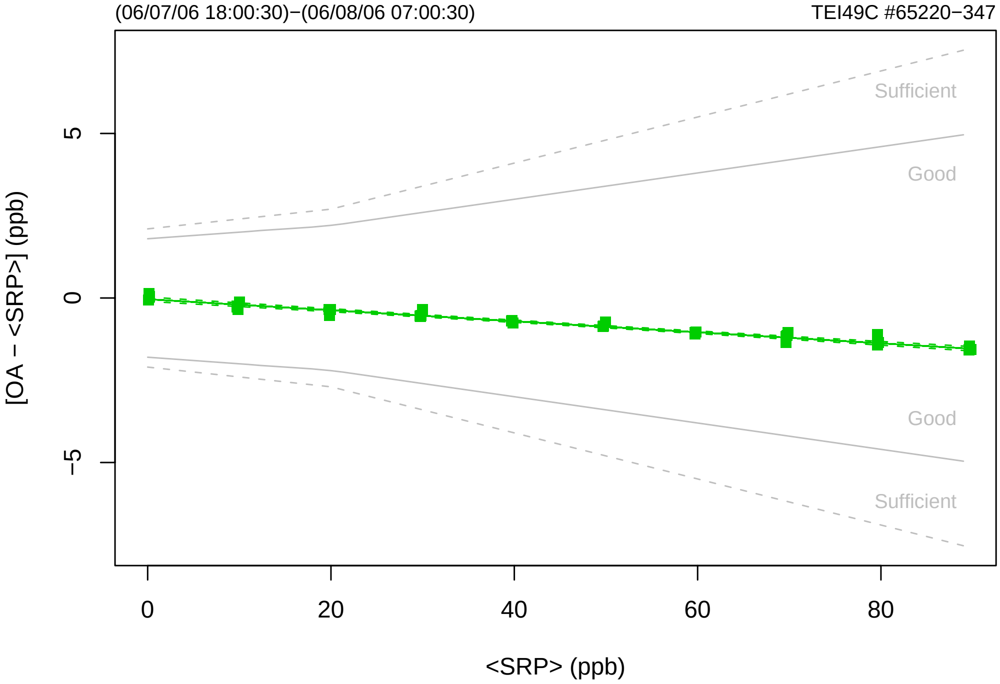

Figure 1. Bias of the Zugspitze ozone analyser with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen, et al., 2003] are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

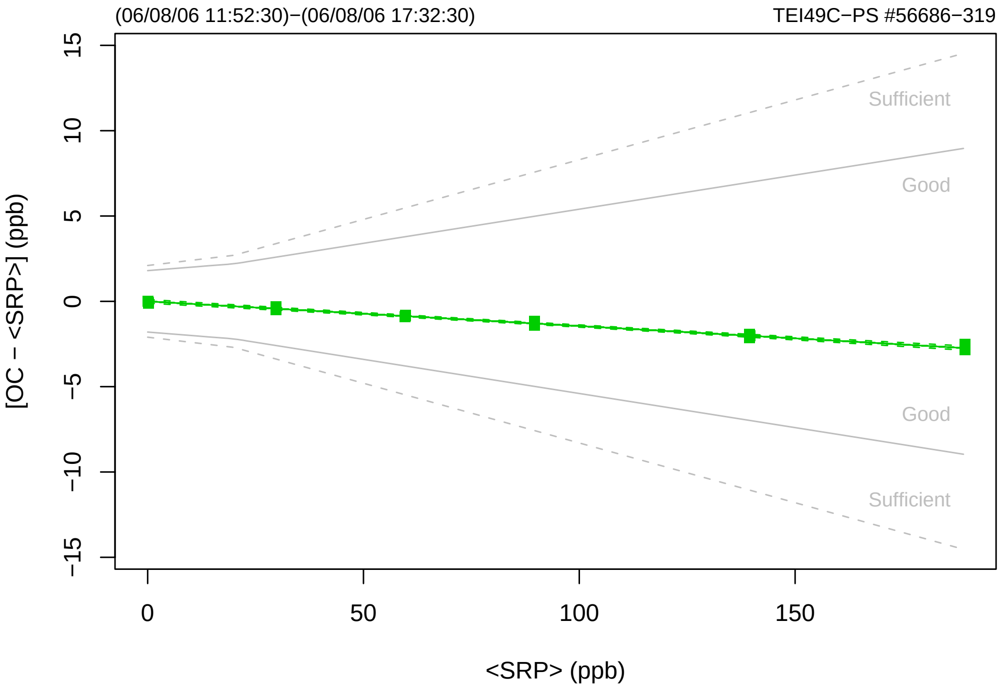

Figure 2. Bias of the Zugspitze ozone standard TEI49C-PS with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen, et al., 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Recommendation 6 (, 2007)**
Although the inter-comparison results are well within the data quality objectives (DQO) of the GAW programme, it should be considered to correct the bias of the ozone calibrator using equation (1b). The correction for the station analyser should then be made using the bias corrected data of the OC / OA inter-comparisons.

Recommendation 7 (, 2007)**
It is recommended to re-calibrate the ozone standard (OC) against SRP#29 of UBA (Langen). The calibration settings should be changed to minimise the bias between the OC and SRP#29. This has not been accomplished during previous OC – SRP inter-comparisons.

Carbon Monoxide Measurements

Instrumentation. Zugspitze is currently equipped with three CO analysers, which are all running in parallel. One of the UV fluorescence instruments (Aerolaser AL5002) is considered as the main data source, whereas the NDIR analyser (TEI48C-TL) and the second UV fluorescence instrument (Aerolaser AL5001) are running as back-up systems. The second Aerolaser instrument is property of UBA. In the framework of the cooperation with IMK-IFU it will be installed at the summit for approx. one year to allow for a better inter-comparison with Schneefernerhaus CO data. The instrumentation is adequate for the intended purpose.

Standards. Currently 8 standards in the concentration range 100 – 500 ppb are available. The Aerolaser and the TEI 48C-TL instruments are calibrated with a working standard (Messer, CO in synthetic air). With this equipment, adequate calibration of the carbon monoxide measurements is possible. Calibrations are carried out automatically.

Recommendation 8 (, 2007)**
It is recommended to use NOAA/GMD the carbon monoxide standards to calibrate working standards to establish a link of the SFH CO measurements to the GAW reference (WMO-2000 carbon monoxide scale).

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instruments with randomised carbon monoxide concentrations from a dilution system as well as direct inter-comparisons with travelling standards (only Aerolaser instruments).The following equations characterise the instrument bias (cf. Figure 3 - Figure 5):

Assessment with WCC-Empa dilution system:

Aerolaser AL5001:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = (CO – 2.2) / 0.956 (2a)

Aerolaser AL5002:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = (CO – 1.2) / 0.953 (2b)

TEI48C-TL:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = (CO + 2.8) / 1.004 (2c)

Assessment with WCC-Empa travelling standards:

Aerolaser AL5001:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = (CO + 1.2) / 0.968 (2d)

Aerolaser AL5002:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = (CO + 3.4) / 0.987 (2e)

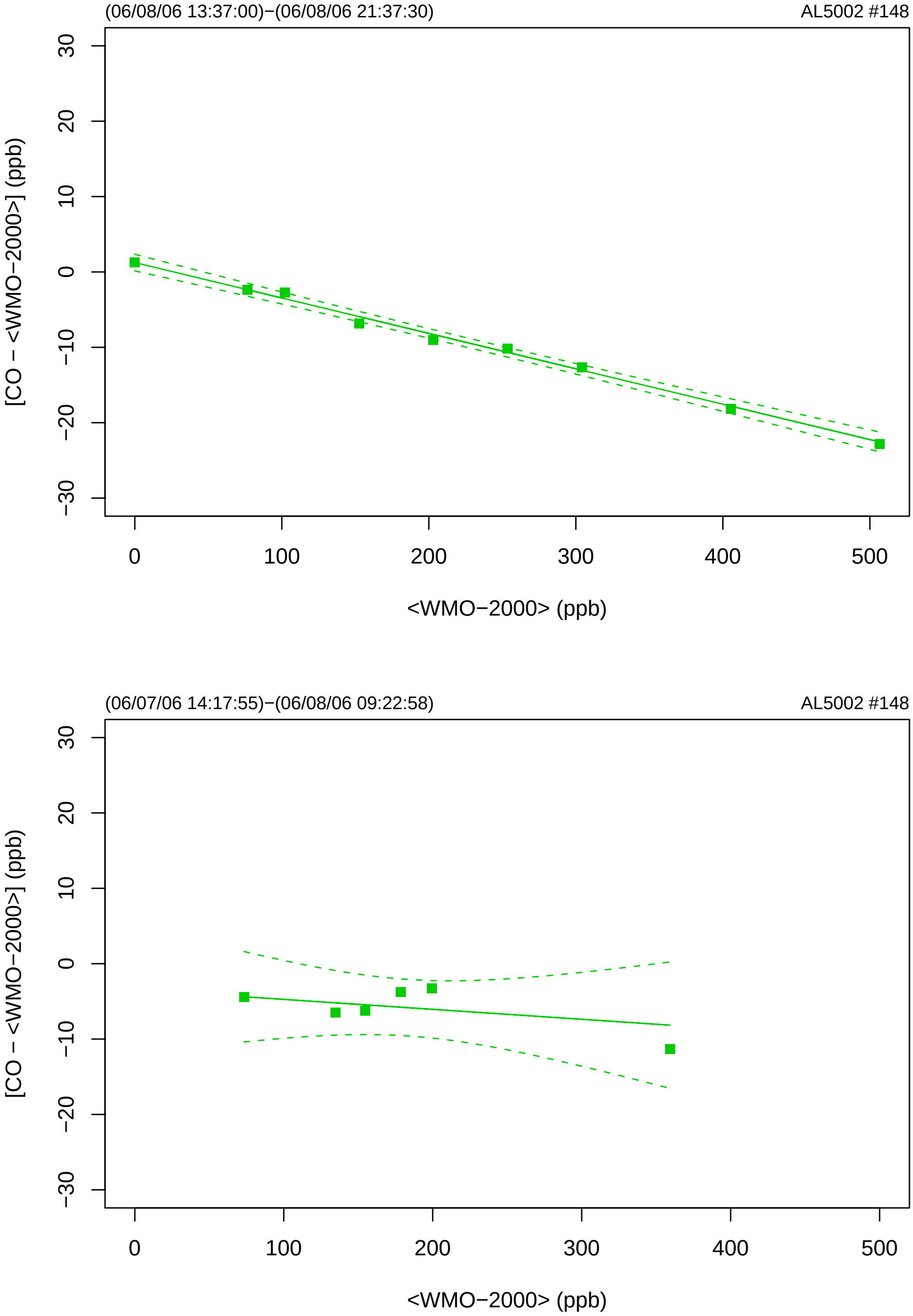

Figure 3. Bias of the Zugspitze back-up carbon monoxide analyser (Aerolaser AL5002) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Upper panel: Assessment with the dilution system. Lower Panel: Assessment with travelling standards.

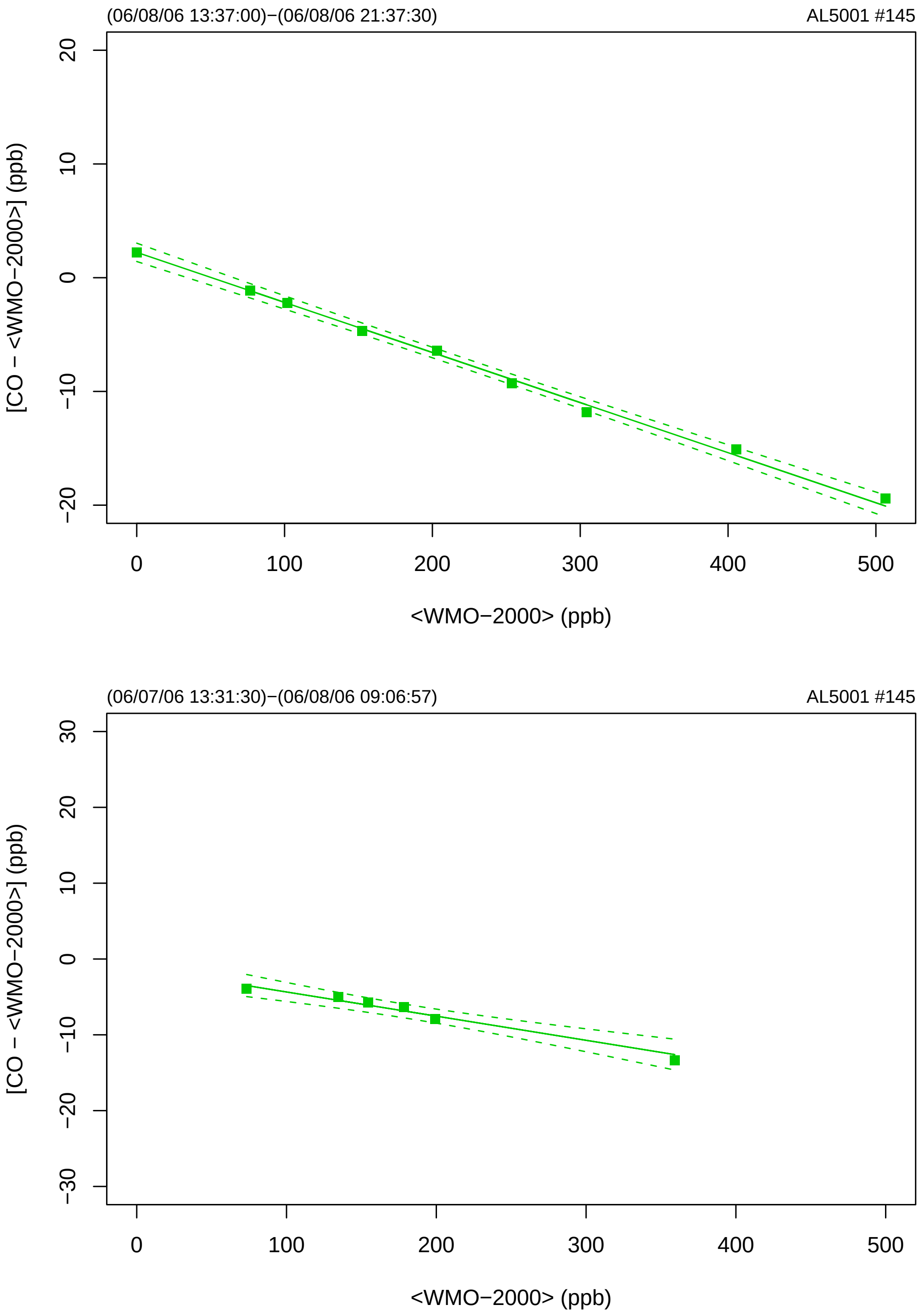

Figure 4. Bias of the main carbon monoxide analyser (AL5002) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Upper panel: Assessment with the dilution system. Lower Panel: Assessment with travelling standards.

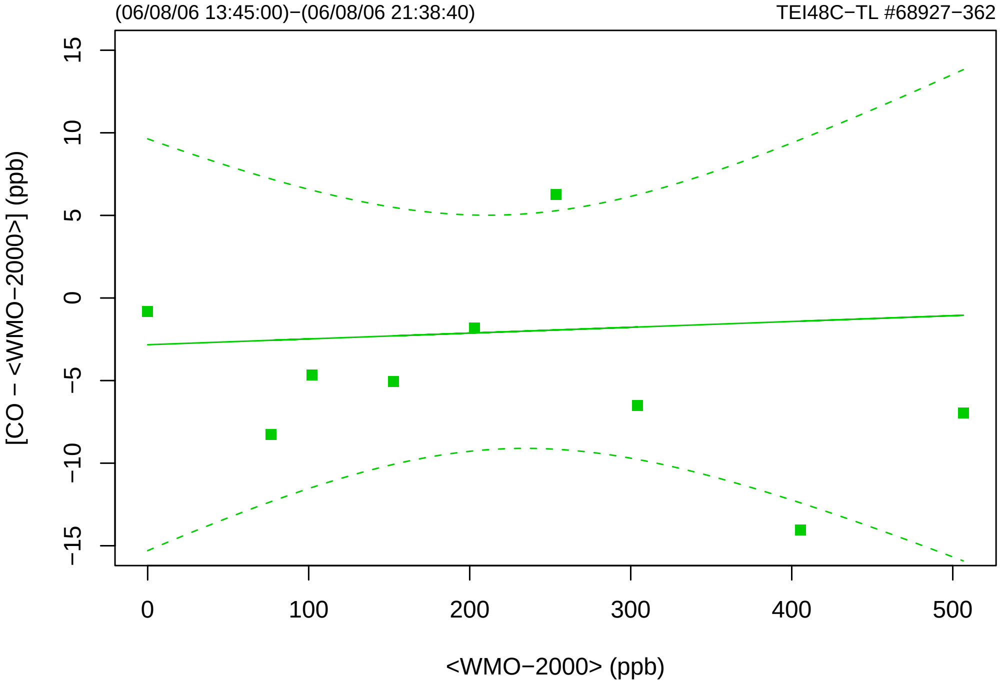

Figure 5. Bias of the Zugspitze back-up carbon monoxide analyser (TEI48C-TL) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

It can be seen from Figure 3 and Figure 4 that the assessment resulted in a slightly different bias for the inter-comparison with dilution unit and the travelling standards, respectively. Uncertainties and noise are higher for the assessment with the travelling standards. This can be explained by the shorter inter-comparison duration as well as automatic instrument calibrations during the experiment. Furthermore, the assessment with the TS was made using the calibration port of the Aerolaser, whereas the sample port was used for the evaluation with the dilution system. A difference was also observed when the TS were analysed on the sample port, which was tested with a few standards.

Recommendation 9 (, 2007)**
The inter-comparisons with the dilution unit and the WCC-Empa cylinders showed differences for the Aerolaser AL5001 instrument. Part of these differences potentially originates from an effect of the Nafion dryer. The effect of the Nafion dryer on the measurements should further be assessed.

Recommendation 10 (3, immediately)**
The frequency of the automatic calibrations of the Aerolaser system (every 15 hours) is potentially to long to account for zero and sensitivity drift. It is recommended to reduce the interval to 3 hours (done after the audit).

Methane Measurements

Instrumentation. The SFH station is equipped with a HP6890 GC/FID/ECD system for the measurements of CH_4, CO_2, SF_6 and N_2O. The system was installed in collaboration with the University Heidelberg (Ingeborg Levin Group) [*Bader*, 2001]. The instrumentation is adequate for the intended purpose and shows a good reproducibility for multiple injections of a gas sample.

Standards. Currently two standards are used for the calibration of the methane instrument. Both standards were obtained from a local calibration gas supplier (Deuste-Steininger GmbH) and were calibrated against the CMDL83 methane scale at the regional GAW station Schauinsland. With this equipment, adequate calibration of the methane measurements is possible.

Recommendation 11 (*, 2007)
It is recommended to use the methane standards purchased from NOAA/GMD to establish a direct link of the SFH methane measurements to the GAW reference.

Recommendation 12 (, 2007)**
All methane measurements should be reported on the NOAA04 CH_4 scale.

Intercomparison (Performance Audit). The inter-comparison involved repeated measurements of WCC-Empa travelling standards with the SFH instrument. The following equation characterises the instrument bias (cf. Figure 6):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 0.98601 (3)

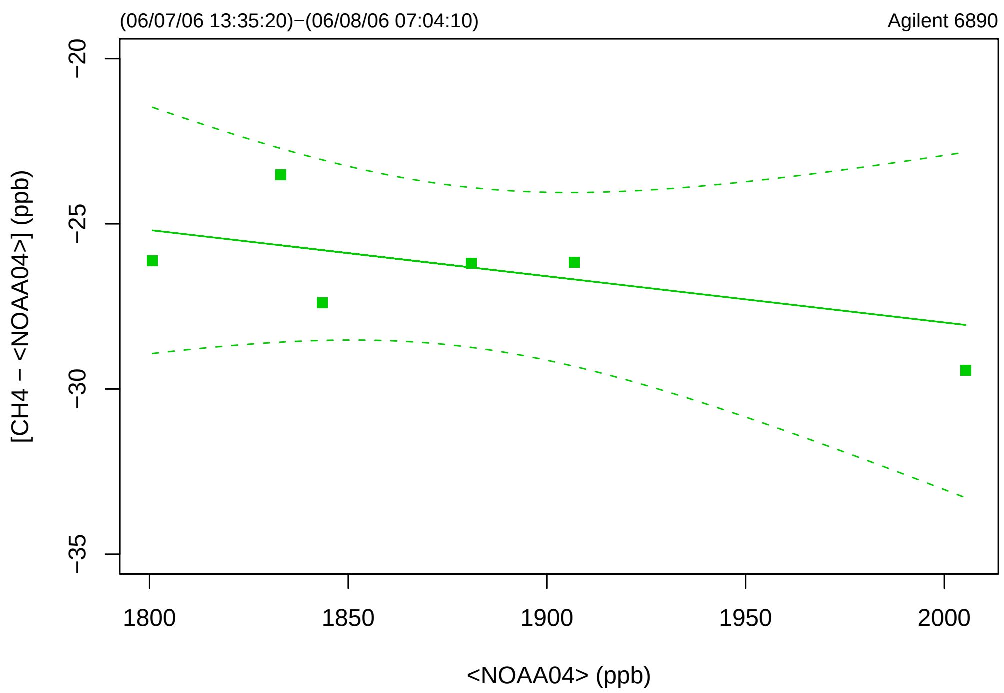

Figure 6. Bias of the Zugspitze methane GC (HP 6890 Series) with respect to the NOAA04 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

The lower findings of 1.4% can be explained by the scale difference. Based on the NOAA04 scale the difference reduces to 0.16%, which is within the measurement uncertainty. All GAW data should be reported on the NOAA04 methane scale.

Data Acquisition and Management

Different data acquisition systems are currently in use at the SFH station. For all “monitor” type instruments DAQAS (www.daqas.com) is used. DAQAS was jointly programmed by the SFH station manager in collaboration with external partners. One minute data is stored for further analysis. Remote access to all instruments is possible, and the data is backed up in regular intervals. Currently data of the Aerolaser instruments is still acquired on the ALXXX software (Aerolaser GmbH), but implementation to DAQAS is planned for the near future. The gas chromatograph (greenhouse gases) uses HPChemStation.

Data Submission

Data submission was delayed during the past few years due to the move from the summit to SFH. At the time of the audit, methane was available for 2002/03 at WDCGG. Ozone and methane data until the end of 2005 were submitted shortly after the audit. It was noticed that ozone data was submitted in μgm^{-3} units (20°C), without information about the reference pressure. The methane data was submitted without information about the version of the calibration scale. Carbon monoxide data have not yet been submitted, but submission is planned for the near future.

Recommendation 11 (, 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 12 (, ongoing)**

All data must be submitted in mole fraction units.

Recommendation 13 (, ongoing)**

Data submission must include information about the reference scale, including the scale version.

Conclusions

The Global GAW station Zugspitze comprises an extensive suite of ongoing measurements. All assessed measurements were of high quality. For some parameters longer time series exist from the summit platform. It is important to have long enough temporal overlap between the two sites to gather information about the characteristics of the two locations.

Summary Ranking of Zugspitze Station

System Audit	Adequacy#	Comment
Access	(5)	
Facilities		
Laboratory and office space	(5)	
Air Conditioning	(5)	
Power supply	(5)	
General Management and Operation		
Organisation	(4)	
Competence of staff	(5)	
Air Inlet System	(3)	Ozone loss in sample line
Instrumentation		
Ozone	(5)	
Carbon monoxide	(5)	
Methane	(5)	
Aerosol parameters*	(5)	Comprehensive suite of measurements
Reactive gas other than CO*	(5)	
Reactive gas other than CH_4*	(5)	
Meteo*	(5)	
Standards		
Ozone	(4)	Re-calibration recommended
Carbon monoxide	(4)	No direct link to NOAA/GMD
Methane	(3)	Link to NOAA/GMD via Schauinsland; CMDL83 scale.
Data Management		
Data acquisition	(5)	
Data processing	(5)	
Data submission	(4)	

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

Dübendorf, March 2007

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APPENDIX

Global GAW Station Zugspitze

Site description

Information about the Zugspitze GAW station is available on the internet and the station is also registered in GAWSIS.

Links: www.umweltbundesamt.de/uba-info-daten/daten/gaw/aktivitaeten.htm
www.schneefernerhaus.de
www.empa.ch/gaw/gawsis

Measurement Programme

The measurement programme of Zugspitze (SFH and ZUG platforms) is shown in Table 1. Some of the measurements were re-located from the summit to Schneefernerhaus. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the SFH / ZUG Station

Parameter	Current Instrument	Data Coverage (%)		
		<12 m	<3 y	Overall
Aerosol				
Multiwavelength optical depth	Filter Radiometry			
Number concentration	CPC			
Number size distribution	DMA	>90%	>90%	>90%
Ozone				
Surface ozone	TEI49C	>90%	>90%	>90%
Reactive Gas				
VOCs (C_2-C_7, BTX)	GC-FID (Flasks)	>90%	>90%	>90%
Carbon monoxide	Aerolaser AL5001 / 5002	>90%	>90%	>90%
NO, NO_x	Ecophysics CLD / PLC	>90%	>90%	>90%
NO_y	CLD / Au Converter			
SO_2	TEI43C-TL			
Greenhouse Gas				
CFCs	GC-MS			
CH_4	GC-FID (HP 6890 Series)	>90%	>90%	>90%
CO_2	NDIR	>90%	>90%	>90%
N_2O	GC-ECD (HP 6890 Series)	>90%	>90%	>90%
SF_6	GC-ECD (HP 6890 Series)	>90%	>90%	>90%
Solar radiation				
Global irradiance	Pyranometer			
Radio Nuclide				
Beryllium Be-7	Filter (γ spectrometry)			
CO_2 (C-14)	Filter (β spectrometry)			
Krypton Kr-85	GC / β counter			
Radon Rn-222	PIPS (Canberra) α counter			
Ancillary Measurements				
Meteo (PTU, wind speed and direction)				

Ozone, Carbon Monoxide and Methane Distribution at Zugspitze

The monthly and yearly distributions of one hourly mean values for surface ozone (2005, SFH), carbon monoxide (2001, ZUG) and methane (2005, SFH) are shown in Figure 5. Data was obtained from WDCGG.

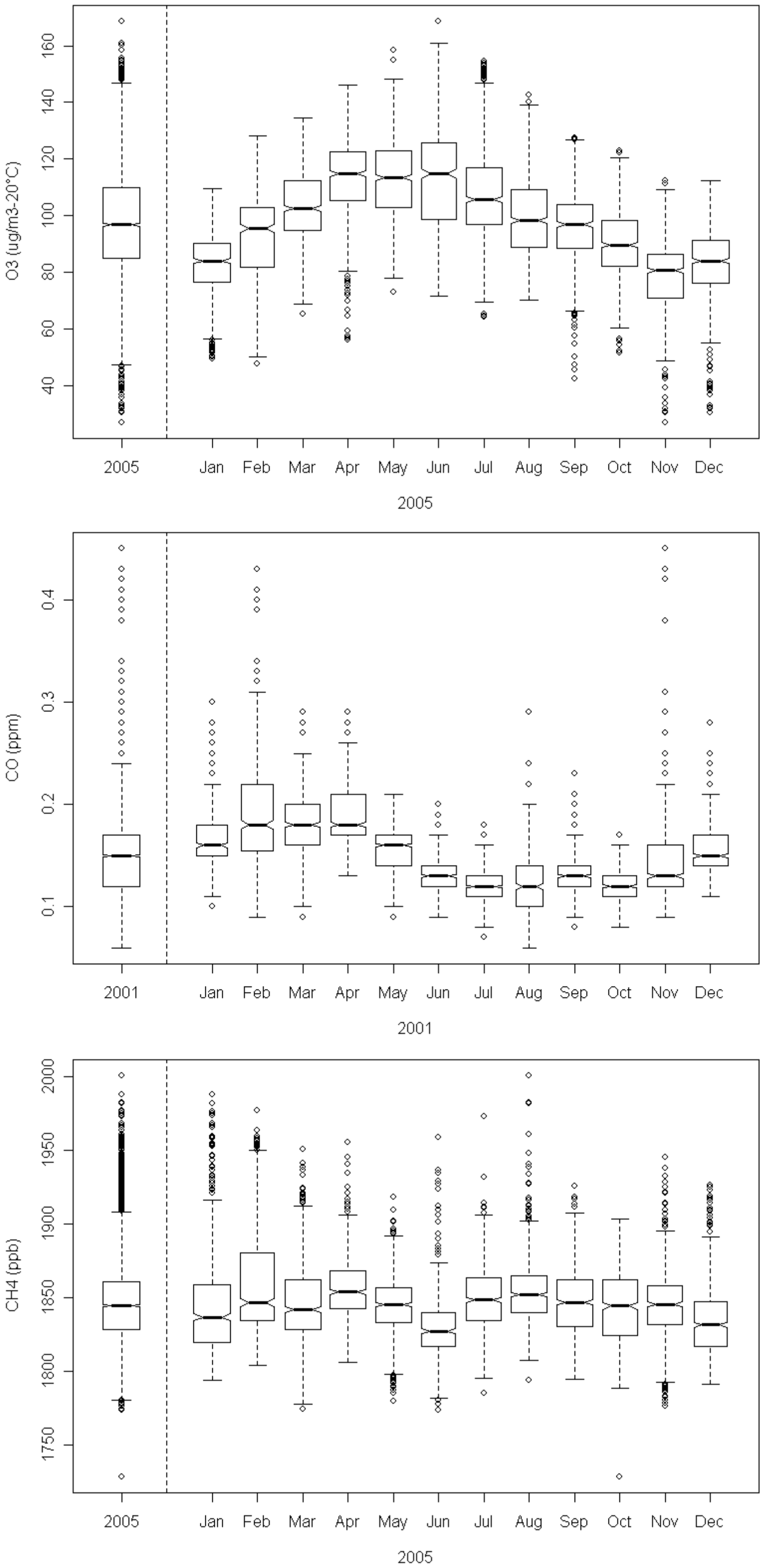


Figure 7. Yearly and Monthly Box Plots of 1-hourly aggregates for the year 2004 for surface ozone, carbon monoxide and methane (lower panel). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside 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 at SFH are jointly operated by the Umweltbundesamt (UBA) and the German Weather Service (DWD). The parameters of the scope of WCC-Empa are run by UBA. An Organisational chart of UBA is shown in Figure 8.

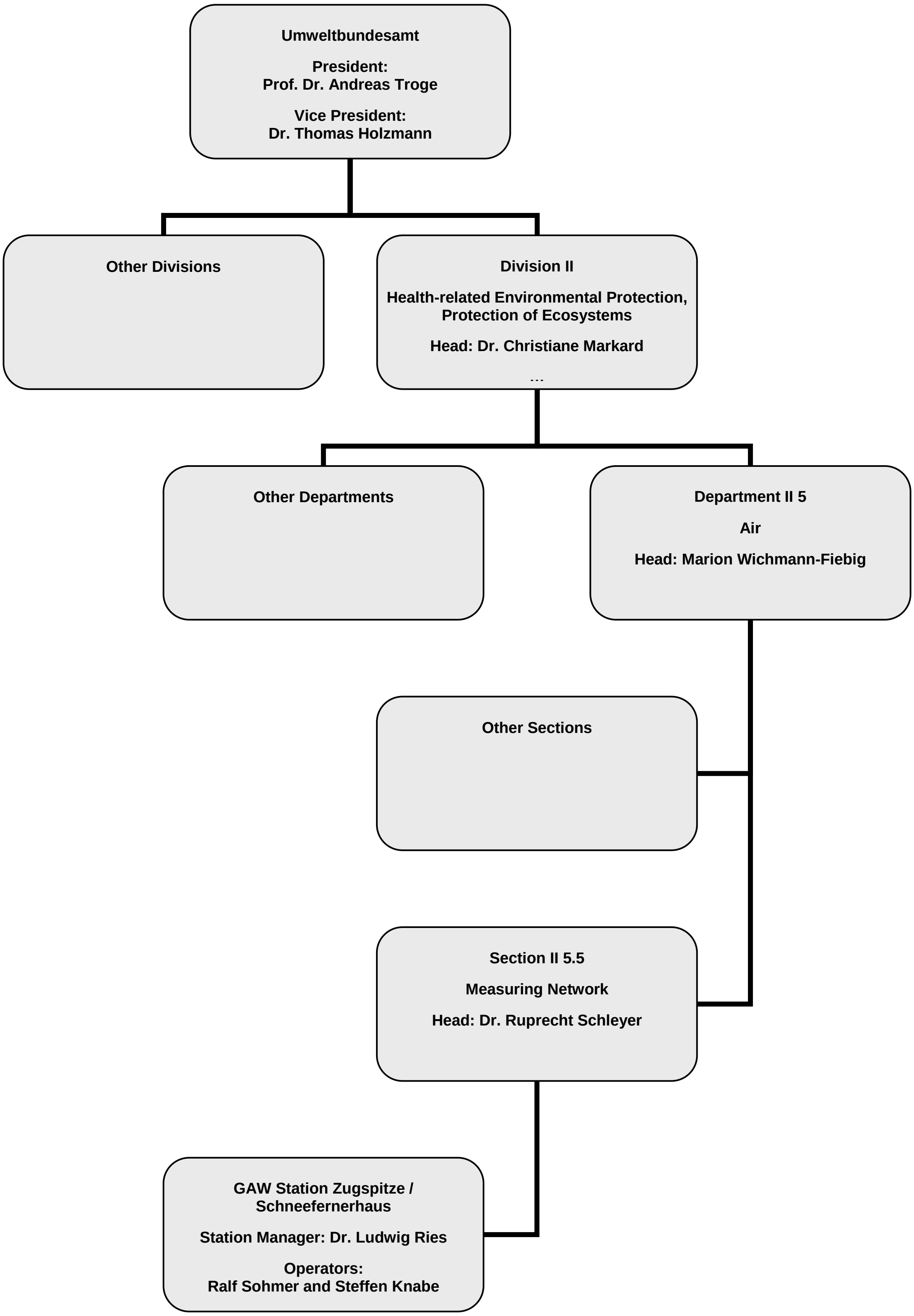


Figure 8. Organisation of UBA GAW activities at Zugspitze as of June 2006.

Surface Ozone Measurements

The instrumentation and set-up remained basically the same with the exception of the data acquisition since the last WCC-Empa audit in 2001. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-a].

Monitoring Set-up and Procedures

Air Conditioning
The laboratory is air conditioned and all instruments are protected from sunlight.

Air Inlet System
The air intake has been described in the last audit report [*Zellweger, et al.*, 2001]. It was found that some connecting materials in the inlet tubing cause an ozone loss of approximately 0.5% (cf. recommendation 4). The residence time is estimated to be approximately 5 s.

Instrumentation
The surface ozone monitoring equipment has been described in the last audit report [*Zellweger, et al.*, 2001]. Instrumental details for the ozone analysers (OA) are summarised in Table 2 below.

Standards
The station has been equipped with a TEI49C-PS ozone calibrator which is yearly inter-compared to the ozone reference standards of UBA Langen. Instrumental details for the ozone calibrator (OC) are summarised in Table 2 below.

Operation and Maintenance
No changes since the last audit [*Zellweger, et al.*, 2001].

Data Acquisition and Data Transfer
The ozone measurements were integrated into the DAQAS data acquisition system. DAQAS (Data Acquisition and Quality Assurance System) has been developed in the frame of a R&D project funded by UBA and is freely available for use within the GAW programme (www.daqas.com).

Data Treatment
All data are quality controlled using the DAQAS system. DAQAS provides comprehensive tools for data evaluation and quality control.

Data Submission
Data is submitted to the GAW World Data Centre for Surface Ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG).

Documentation
All events related to ozone measurements are logged in the DAQAS system. All information was found to be comprehensive and up-to-date. The instrument manuals are available at the site.

Inter-Comparison of Ozone Analyzer and Calibrator

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 the transfer standard with the station analysers and the station standard. The data used for the evaluation was recorded by the WCC-Empa data acquisition system. Data of the TEI49C was corrected for its bias according the usual station method using the calibration factor (0.9887) and the offset (-0.057 ppb) from the last inter-comparison with the station standard. No further corrections were applied to the SFH TEI49C-PS standard.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.011
Ozone analyzer (OA)	Model, S/N	TEI 49C #65220-347
	Principle	UV absorption
	Range	0-1000 ppb
	Settings	BKG = 0.0; COEFF = 1.000
Ozone standard (OC)	Model, S/N	TEI 49C-PS #58686-319
	Principle	UV absorption
	Range	0-1000 ppb
	Settings	BKG = 0.0; COEFF = 1.007
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. 2.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA / OC
Data acquisition	TS, OA, OC	One minute aggregates from digital output of WCC-Empa data acquisition (custom designed LabView programme)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	740.5 (WCC-Empa reference)
	TS	742.5, adjusted to 740.5 (555.5 mmHg)
	OA	735.1 (not adjusted because the instrument was calibrated without adjustment of the pressure sensor)
	OC	740.4 (not adjusted)
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90 (OA) 0, 30, 60, 90, 140, 190 (OC)
Duration per level (min)		20
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		OA: 4 runs (7 thru 8 June, 2006) OC: 3 runs (8 June, 2006)

Results

Each ozone level was applied for 20 minutes, and the last 10 one-minute averages were aggregated. The results are shown in Table 3 (OA) and Table 4 (OC). 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 analysers (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 SFH main ozone analyzer (OA) TEI 49C #65220-347 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-07 18:05	1	0	0.41	0.25	0	0.13	0.04
2006-06-07 18:25	1	30	30.21	29.63	0	0.10	0.06
2006-06-07 18:45	1	50	50.18	49.19	0	0.13	0.05
2006-06-07 19:05	1	20	20.19	19.62	0	0.10	0.04
2006-06-07 19:25	1	70	70.13	68.81	0	0.11	0.07
2006-06-07 19:45	1	90	90.13	88.27	0	0.05	0.05
2006-06-07 20:05	1	10	10.21	9.87	0	0.15	0.05
2006-06-07 20:25	1	40	40.10	39.10	0	0.08	0.02
2006-06-07 20:45	1	80	79.99	78.36	0	0.07	0.07
2006-06-07 21:05	1	60	60.07	58.77	0	0.06	0.06
2006-06-07 21:25	2	0	0.35	0.28	0	0.14	0.03
2006-06-07 21:45	2	50	50.00	48.89	0	0.09	0.04
2006-06-07 22:05	2	70	70.00	68.58	0	0.09	0.05
2006-06-07 22:25	2	90	89.96	88.21	0	0.07	0.07
2006-06-07 22:45	2	30	30.04	29.28	0	0.10	0.08
2006-06-07 23:05	2	10	9.94	9.49	0	0.23	0.08
2006-06-07 23:25	2	80	79.91	78.51	0	0.12	0.07
2006-06-07 23:45	2	20	20.05	19.30	0	0.14	0.09
2006-06-08 00:05	2	40	39.92	38.99	0	0.09	0.03
2006-06-08 00:25	2	60	59.97	58.63	0	0.10	0.07
2006-06-08 00:45	3	0	0.37	0.17	0	0.08	0.04
2006-06-08 01:05	3	20	19.98	19.41	0	0.09	0.07
2006-06-08 01:25	3	10	9.97	9.48	0	0.11	0.03
2006-06-08 01:45	3	90	89.89	88.02	0	0.07	0.05
2006-06-08 02:05	3	60	59.99	58.67	0	0.12	0.08
2006-06-08 02:25	3	50	49.95	48.83	0	0.10	0.06
2006-06-08 02:45	3	80	79.91	78.21	0	0.11	0.04
2006-06-08 03:05	3	70	69.94	68.49	0	0.08	0.06
2006-06-08 03:25	3	30	29.99	29.20	0	0.12	0.05
2006-06-08 03:45	3	40	39.96	39.03	0	0.09	0.05
2006-06-08 04:05	4	0	0.27	0.01	0	0.08	0.03
2006-06-08 04:25	4	30	29.97	29.19	0	0.10	0.03
2006-06-08 04:45	4	50	49.94	48.82	0	0.10	0.06
2006-06-08 05:05	4	20	20.03	19.41	0	0.09	0.06
2006-06-08 05:25	4	70	69.93	68.30	0	0.07	0.05
2006-06-08 05:45	4	90	89.92	88.06	0	0.08	0.04
2006-06-08 06:05	4	10	10.07	9.51	0	0.08	0.06
2006-06-08 06:25	4	40	39.97	39.04	0	0.09	0.03
2006-06-08 06:45	4	80	79.92	78.23	0	0.08	0.07
2006-06-08 07:05	4	60	59.96	58.60	0	0.04	0.05

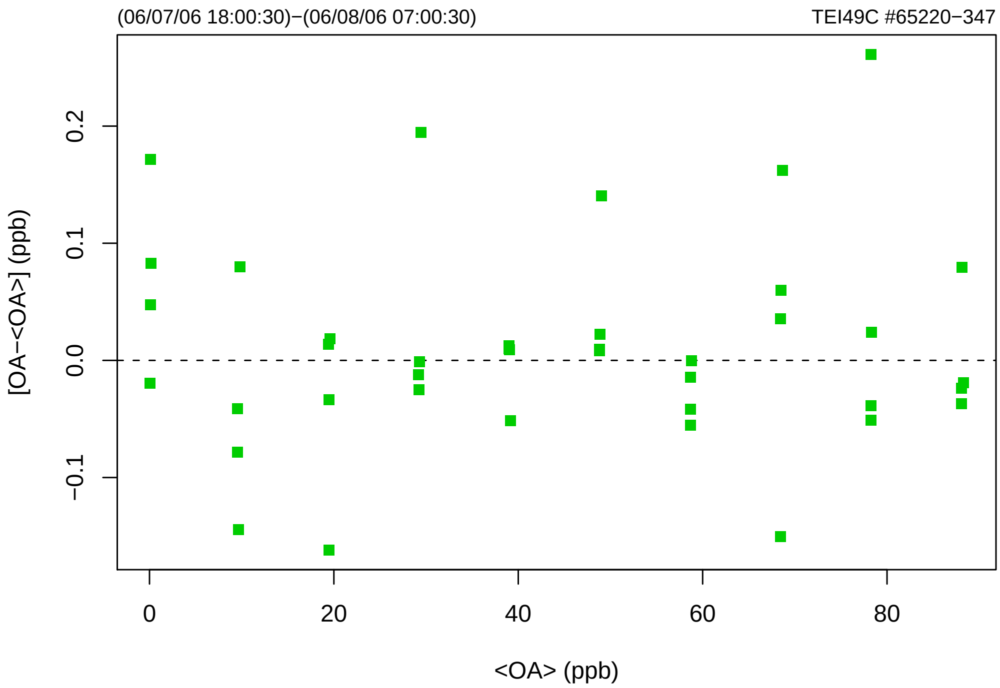
[#]0: valid data; 1: invalid data.

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the SFH ozone calibrator (OC) TEI 49C-PS # 58686-319 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OC (ppb)	Flag[#]	sdTS (ppb)	sdOC (ppb)
2006-06-08 11:57	1	0	0.33	0.13	0	0.17	0.04
2006-06-08 12:17	1	30	29.93	29.35	0	0.09	0.04
2006-06-08 12:37	1	60	59.91	58.74	0	0.09	0.04
2006-06-08 12:57	1	140	139.77	137.49	0	0.14	0.04
2006-06-08 13:17	1	190	189.78	186.54	0	0.05	0.06
2006-06-08 13:37	1	90	89.91	88.45	0	0.09	0.06
2006-06-08 13:57	2	0	0.38	0.09	0	0.12	0.03
2006-06-08 14:17	2	190	189.78	186.61	0	0.13	0.04
2006-06-08 14:37	2	30	30.00	29.28	0	0.13	0.04
2006-06-08 14:57	2	60	59.95	58.88	0	0.09	0.06
2006-06-08 15:17	2	140	139.86	137.50	0	0.05	0.03
2006-06-08 15:37	2	90	89.96	88.27	0	0.07	0.05
2006-06-08 15:57	3	0	0.39	0.10	0	0.10	0.04
2006-06-08 16:17	3	90	89.89	88.35	0	0.12	0.06
2006-06-08 16:37	3	30	29.96	29.42	0	0.12	0.03
2006-06-08 16:57	3	140	139.78	137.29	0	0.06	0.07
2006-06-08 17:17	3	60	59.96	58.86	0	0.05	0.04
2006-06-08 17:37	3	190	189.78	186.87	0	0.10	0.05

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

Figure 9 - Figure 10 show the regression residuals of the ozone analysers and the ozone calibrator with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.



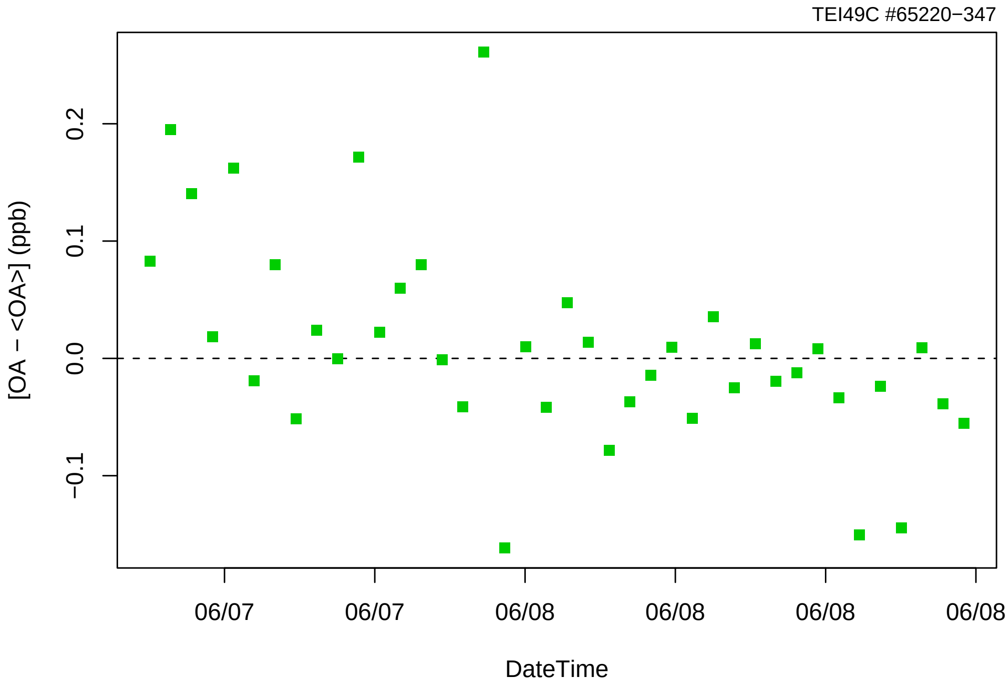
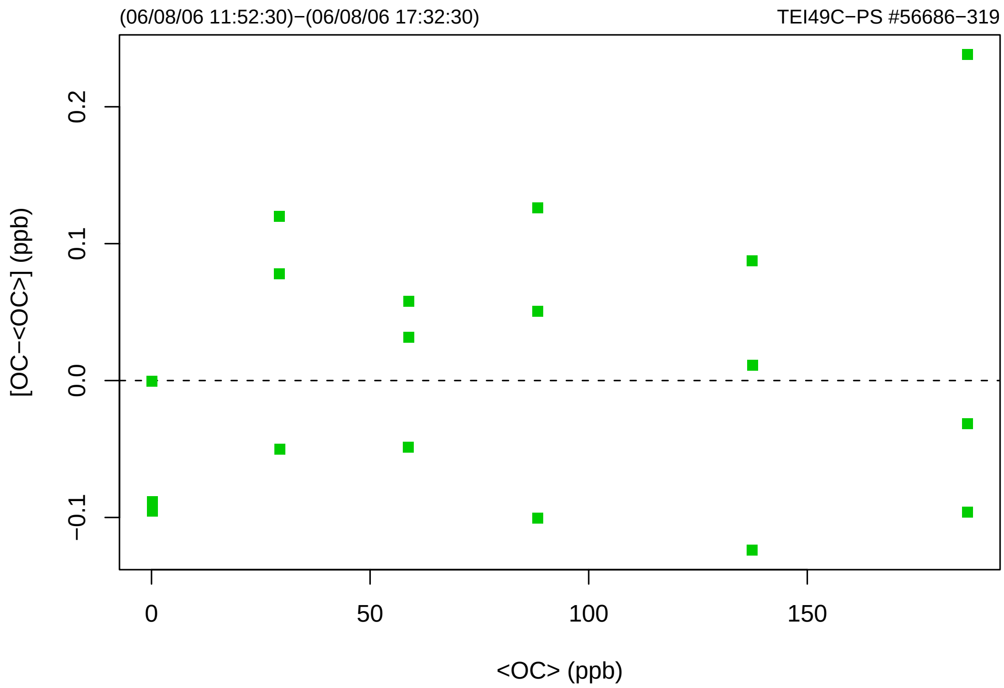


Figure 9. Regression residuals of the main SFH ozone analyser (OA) as a function of concentration (upper panel) and time (lower panel).



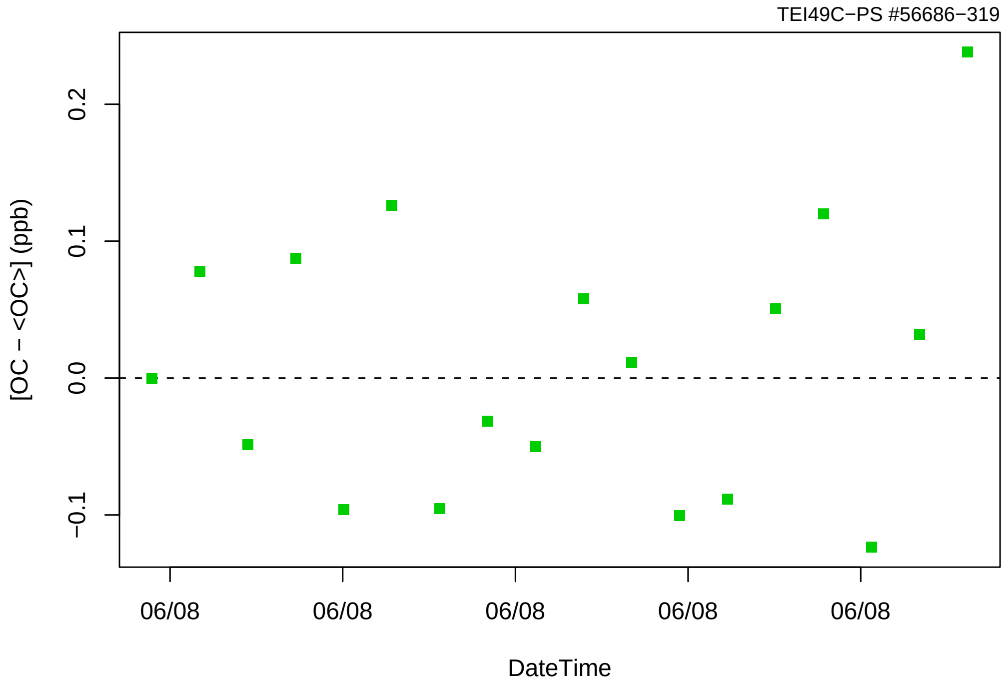


Figure 10. Regression residuals of the SFH ozone calibrator (OC) as a function of concentration (upper panel) and time (lower panel).

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 49C:

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.04\ ppb) / 0.9832}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.28\ ppb^2 + 2.68e\text{-}05 * X_{O3}^2)} \qquad (1a)$$

TEI 49C-PS

$$\mathbf{X_{O3}\ (ppb) = ([OC] + 0.00\ ppb) / 0.9855}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.28\ ppb^2 + 2.67e\text{-}05 * X_{O3}^2)} \qquad (1b)$$

Changes Made to Instrument

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

Conclusions

The findings of this audit demonstrate good agreement between SFH ozone measurements and WCC-Empa, with SFH results consistently being approximately 1.5% lower compared to WCC-Empa. In addition to this difference an ozone loss of approximately 0.5% was observed in the connection between the manifold and the instrument. Therefore data should be corrected (cf. recommendations 6 and 7) and the connection of the instrument to the manifold should be re-designed (cf. recommendation 4).

Carbon Monoxide Measurements

Carbon monoxide measurements were moved from the summit to SFH in 2002. Changes since the last WCC-Empa audit in 2001 are mainly the installation of two UV-Fluorescence instruments (Aerolaser AL5001 and AL5002) and a new NDIR analyser (TEI48C-TL). The NDIR analyser is running as a back-up system only. The GC/RGD-2 and TEI48C-TL systems remained at the summit and are currently still running, but data are no longer submitted to WDCGG.

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

Monitoring Set-up and Procedures

Air Conditioning

The laboratory is air conditioned and all instruments are protected from sunlight.

Air Inlet System

The carbon monoxide instruments are also connected to the manifold described in the previous audit report [*Zellweger, et al.*, 2001]. The Aerolaser instruments are connected with a common 1 m ¼” PTFE tubing and share an inlet filter. After the filter each instrument is connected with 0.3 m ¼” PTFE tubing to the external Nafion drier. The TEI48C analyser is also connected with a total of approx. 2 m ¼” PTFE tubing including valves for calibration gases and external zeros. The automatic zero checks are made using an additional 3-way valve and a Sofnocat trap. Residence times are estimated to be approximately 5 s (TEI 48C-TL) and 8 s (AL5001 and AL5002).

Instrumentation

The SFH station is currently equipped with one NDIR (TEI48C-TL) and two UV-Fluorescence (Aerolaser AL5001 and AL5002) carbon monoxide analysers. One of the Aerolaser systems (AL5001) will be lent to IMK-IFU for approximately one year to obtain additional CO data from the summit. Instrumental details are listed in Table 7 below.

Standards and Calibration

The station is equipped with a working standard (Messer) and several laboratory standards (Deuste Steininger). The concentration of the working standard is assigned using the laboratory standards. The laboratory standards were calibrated using a set of NOAA/GMD standards from an informal inter-comparison experiment in December 2004. The Aerolaser instruments are automatically calibrated every 15 hours (zero/span) using the working standard. The TEI48C is switching between zero and ambient air measurements every ten minutes to account for zero drift, and weekly span calibrations with the working standard are performed manually. Table 5 gives details of the cylinders currently available at the station.

Table 5. Carbon monoxide standards available at SFH station

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Messer, #7356B working standard	1030±21 ppb, CO in synthetic air	2004-12	SFH	2005-01	cont.
Deuste Steininger, #2104C, lab standard	253.0±5.1 ppb, CO in synthetic air	2004-12	SFH	2003-05	cont.
Deuste Steininger, #20484, lab standard	105.4±2.1 ppb, CO in synthetic air	2004-12	SFH	2003-05	cont.
Deuste Steininger, #936A, lab standard	574.4±11.5 ppb, CO in synthetic air	2004-12	SFH	2003-12	cont.
Deuste Steininger, #R661A, lab standard	268.1±5.4 ppb, CO in synthetic air	2004-12	SFH	2003-11	cont.
Deuste Steininger, #1876B, lab standard	525.1±10.5 ppb, CO in synthetic air	2004-12	SFH	2005-01	cont.
Deuste Steininger, #3442A, lab standard	281.4±5.6 ppb, CO in synthetic air	2004-12	SFH	2005-01	cont.
Deuste Steininger, #0532C, lab standard	153.1±3.1 ppb, CO in synthetic air	2004-12	SFH	2004-08	cont.
Deuste Steininger, #1609, lab standard	140.3±2.9 ppb, CO in synthetic air	2004-12	SFH	2005-04	cont.

Operation and Maintenance

The instruments are daily checked for general operation whenever the station is visited (usually on 5 days per week). The inlet filter is replaced at least every 2 weeks. Manual calibrations are done once per week (TEI 48C-TL). The optical system of the TEI 48C-TL is checked every 6 months and cleaned when necessary. Cleaning of the Aerolaser optical systems is made by Aerolaser GmbH when the sensitivity is lower than 20 counts/ppb.

Data Acquisition and Data Transfer

TEI48C-TL: DAQAS (see ozone); implementation of the Aerolaser instruments into DAQAS is planned. Currently the ALXXX software (Aerolaser GmbH) is used to acquire Aerolaser data.

Data Treatment

Data of both instruments is regularly checked for consistency with time series plots.
TEI 48C-TL: Corrections are applied to the data based on the weekly calibrations. The values of the automatic zero checks are used to apply a zero correction with a moving time window. The average zero reading during a 10-minute zero check is subtracted from the following 10-minute ambient data. This results in one CO value every twenty minutes, which is further averaged to one hourly and daily means.

AL5001:
No corrections of the data are necessary. One minute averages are stored and further averaged to one hourly and daily means.

Data Submission

Data of the SFH platform have not yet been submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG), but submission is planned. Data of the summit platform is available until the end of 2001, but submission is discontinued because these data are not considered GAW data since the start of the measurements at SFH.

Documentation

Electronic checklists, instrument and station log books were available, sufficiently comprehensive and up-to-date. The instrument manuals are available at the site. In addition daily check lists are filled in on working days and are weekly discussed with the station manger.

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 6 (TS) and Table 7 (dilution system) below.

Setup and Connections

The Aerolaser analysers were inter-compared by direct measurements of travelling standards. Details of this experiment are shown in Table 6. In addition, all analysers were also inter-compared using a dilution system, and the experimental setup is shown in Table 7. The data used for the evaluation was recorded by the SFH data acquisition system, and only corrections according to the usual station methods were applied. These corrections included a zero compensation (TEI 48C-TL).

Table 6. Experimental details of the carbon monoxide inter-comparison with travelling standards.

Travelling standard (TS)	WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)	Level / Cylinder / Reference / St. Uncert. 1 / FF31496 / 73.41 / 0.69 2 / 041109_FA01467 / 134.68 / 0.83 3 / 041109_0627B / 154.58 / 0.82 4 / 050415_FA02466 / 178.54 / 1.21 5 / 030703_FA01477 / 199.38 / 1.00 6 / 050701_FA02505 / 359.22 / 1.82
Field instrument (Model, S/N)	See Table 7 below (only Aerolaser instruments)
Connection of TS to field instrument	Calibration gas port of Aerolaser
Data Acquisition	1-minute aggregates from SFH data acquisition
Duration per level (min)	Variable, between 14 and 32 min
Sequence of levels	Randomised sequence
Runs	1 run (7-8 June, 2006)

Table 7. Experimental details of the carbon monoxide inter-comparison with the dilution system (all analysers).

Travelling standard (TS)		One cylinder (051010_FA02474, 9952.4±48.9 ppb in synthetic air) and a zero-air generator (silica gel - inlet filter 5 μm - metal bellow pump – Purafil- Sofnocat - outlet filter 5 μm) custom-built by WCC-Empa, in combination with a dilution system (Breitfuss, MGM)	
Levels (ppb)		Level / Reference / St.Uncertainty 1 / 0.00 / 0.03 2 / 76.31 / 0.38 3 / 101.57 / 0.50 4 / 152.04 / 0.75 5 / 202.22 / 1.00 6 / 252.79 / 1.25 7 / 303.22 / 1.50 8 / 403.93 / 2.00 9 / 504.74 / 2.50	
Field instruments	Model, S/N	TEI 48C-TL #68927-362	AL5001 #145 AL5002 #148
	Principle	NDIR, Gas Filter Correlation Technique	Vacuum UV-Fluorescence
	Modification	None	None
	Range	1 ppm	10 ppm
	Settings	BKG 4.487 ppm COEFF 1.092	NA (frequent calibrations); Typical conditions during the audit: AL5001 Sens 84 counts/ppb Zero 4200 counts AL5002 Sens 135 counts/ppb Zero 3500 counts
Connection of TS to field instrument		Sample inlet including inlet filter	
Data Acquisition		1-minute aggregates from SFH data acquisition	
Duration per level (min)		60; TEI 48C-TL: Automatic zero checks every 15 min	
Sequence of levels		Randomised fixed sequence	
Runs		1 run (8 June, 2006)	

NA: Not applicable

Results

Inter-comparison with the dilution system

Each carbon monoxide level was applied for 60 minutes, which resulted in a maximum of 60 useable 1' averages per level and run for the AL5001, and 4 usable 5' averages for the TEI 48C-TL instrument. These were corrected for zero-drift (TEI 48C-TL) and further aggregated by level before use in the assessment (cf. Table 8, AL5001, Table 9, AL5002, and Table 10, TEI 48C-TL).

Table 8. CO aggregates computed from 1' averages for each level during the inter-comparison of the SFH AL5001 analyzer with the WCC-Empa transfer standard (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	AL5001 CO (ppb)	sdCO (ppb)	No. 1' av.
(06/08/06 13:37:00)	0.00	0.03	2.23	0.30	55
(06/08/06 14:38:30)	101.95	0.33	99.75	0.30	58
(06/08/06 15:38:30)	76.60	0.25	75.46	0.38	58
(06/08/06 16:38:30)	253.74	0.82	244.46	0.69	58
(06/08/06 17:38:30)	304.35	0.99	292.55	0.69	58
(06/08/06 18:38:30)	152.61	0.50	147.91	0.53	58
(06/08/06 19:40:48)	202.98	0.66	196.57	0.54	45
(06/08/06 20:38:00)	506.63	1.64	487.22	0.98	57
(06/08/06 21:37:30)	405.45	1.31	390.37	0.67	56

Table 9. CO aggregates computed from 1' averages for each level during the inter-comparison of the SFH AL5002 analyzer with the WCC-Empa transfer standard (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	AL5002 CO (ppb)	sdCO (ppb)	No. 1' av.
(06/08/06 13:37:00)	0.00	0.03	1.24	0.07	55
(06/08/06 14:38:30)	101.95	0.33	99.21	0.30	58
(06/08/06 15:38:30)	76.60	0.25	74.25	0.23	58
(06/08/06 16:38:30)	253.74	0.82	243.54	0.38	58
(06/08/06 17:38:30)	304.35	0.99	291.69	0.38	58
(06/08/06 18:38:30)	152.61	0.50	145.77	0.30	58
(06/08/06 19:40:48)	202.98	0.66	193.97	0.27	45
(06/08/06 20:38:00)	506.63	1.64	483.78	0.60	57
(06/08/06 21:37:30)	405.45	1.31	387.26	0.52	56

Table 10. CO aggregates computed from 10' averages for each level during the inter-comparison of the SFH TEI 48C-TL analyzer with the WCC-Empa transfer standard (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	TEI 48C-TL CO (ppb)	sdCO (ppb)	No. 5' av.
(06/08/06 13:37:00)	0.00	0.03	-0.82	6.26	5
(06/08/06 14:38:30)	101.95	0.33	97.30	8.85	3
(06/08/06 15:38:30)	76.60	0.25	68.33	3.17	3
(06/08/06 16:38:30)	253.74	0.82	259.99	3.03	3
(06/08/06 17:38:30)	304.35	0.99	297.85	6.90	4
(06/08/06 18:38:30)	152.61	0.50	147.56	9.72	4
(06/08/06 19:40:48)	202.98	0.66	201.17	0.07	2
(06/08/06 20:38:00)	506.63	1.64	499.67	4.88	4
(06/08/06 21:37:30)	405.45	1.31	391.41	13.79	3

Figure 11 (AL5001), Figure 12 (AL5002) and Figure 13 (TEI48C-TL) show the regression residuals plotted against time and concentration. The absence of concentration dependences (upper panels) in the residuals indicates linearity of the instrument. The absence of temporal trends (lower panels) indicates stable instrument conditions.

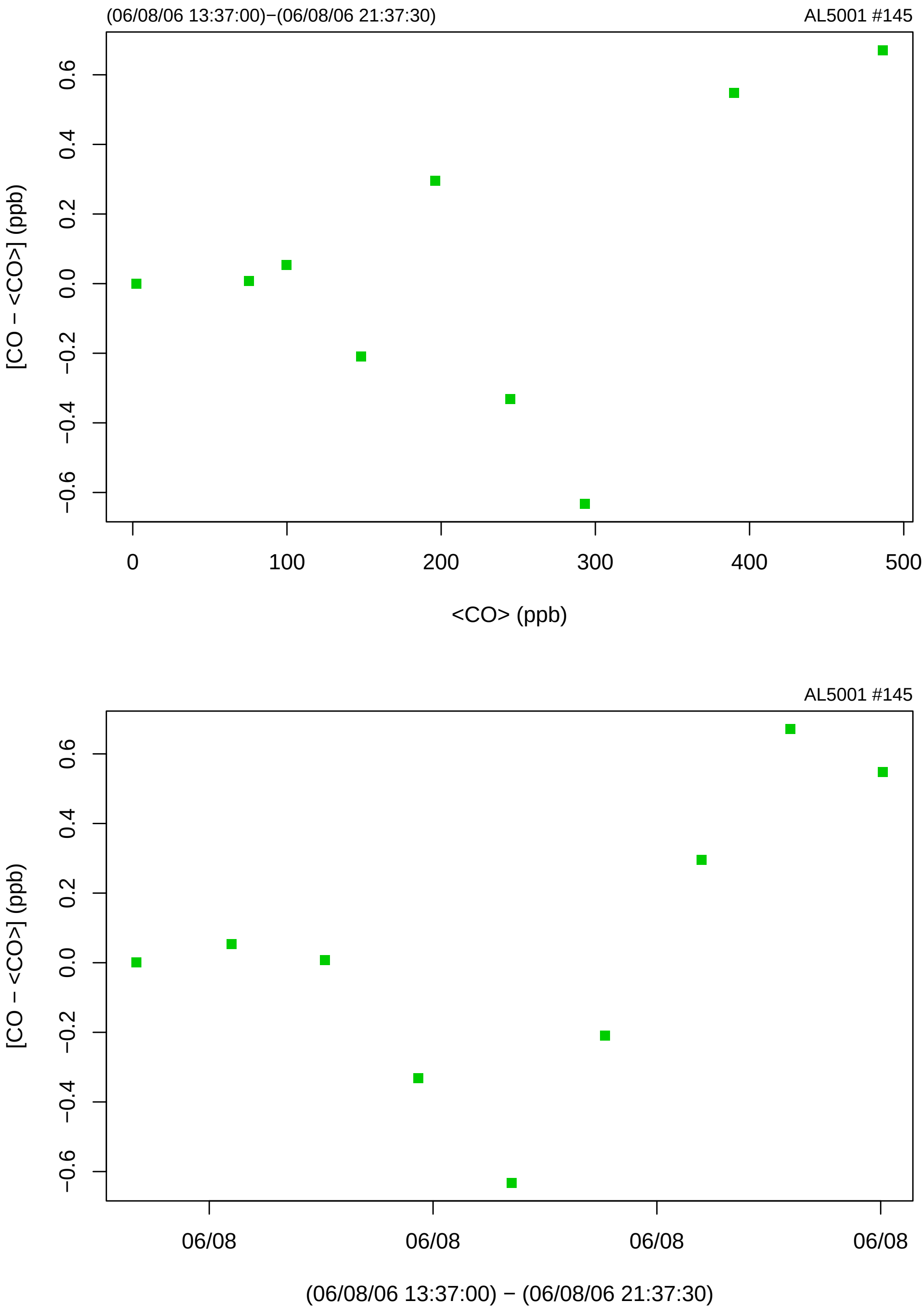


Figure 11. Regression residuals of the SFH AL5001 carbon monoxide analyser. Points represent averages of valid 1'-aggregates. Upper panel: concentration dependence; Lower panel: time dependence.

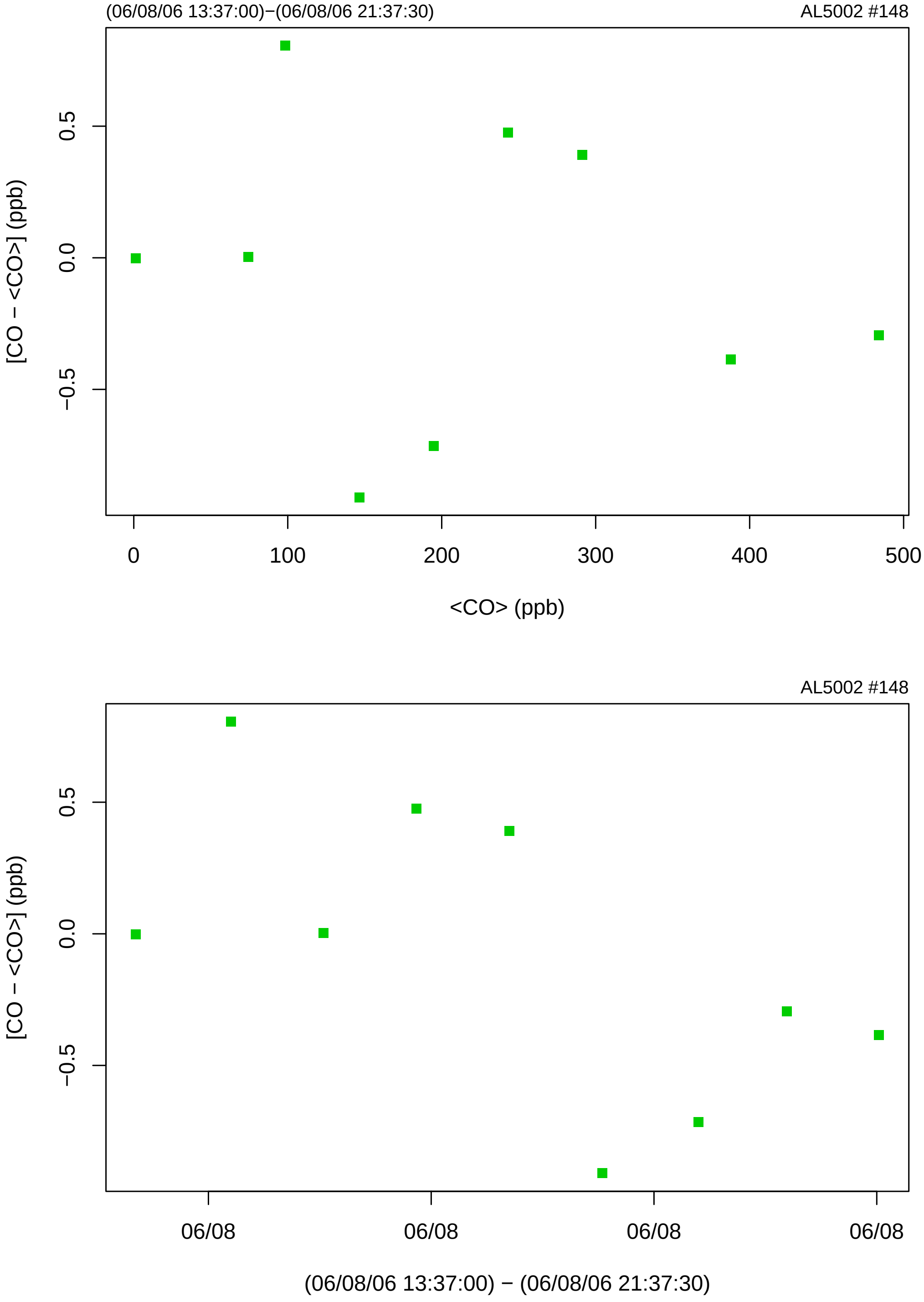


Figure 12. Regression residuals of the SFH AL5002 carbon monoxide analyser. Points represent averages of valid 1'-aggregates. Upper panel: concentration dependence; Lower panel: time dependence.

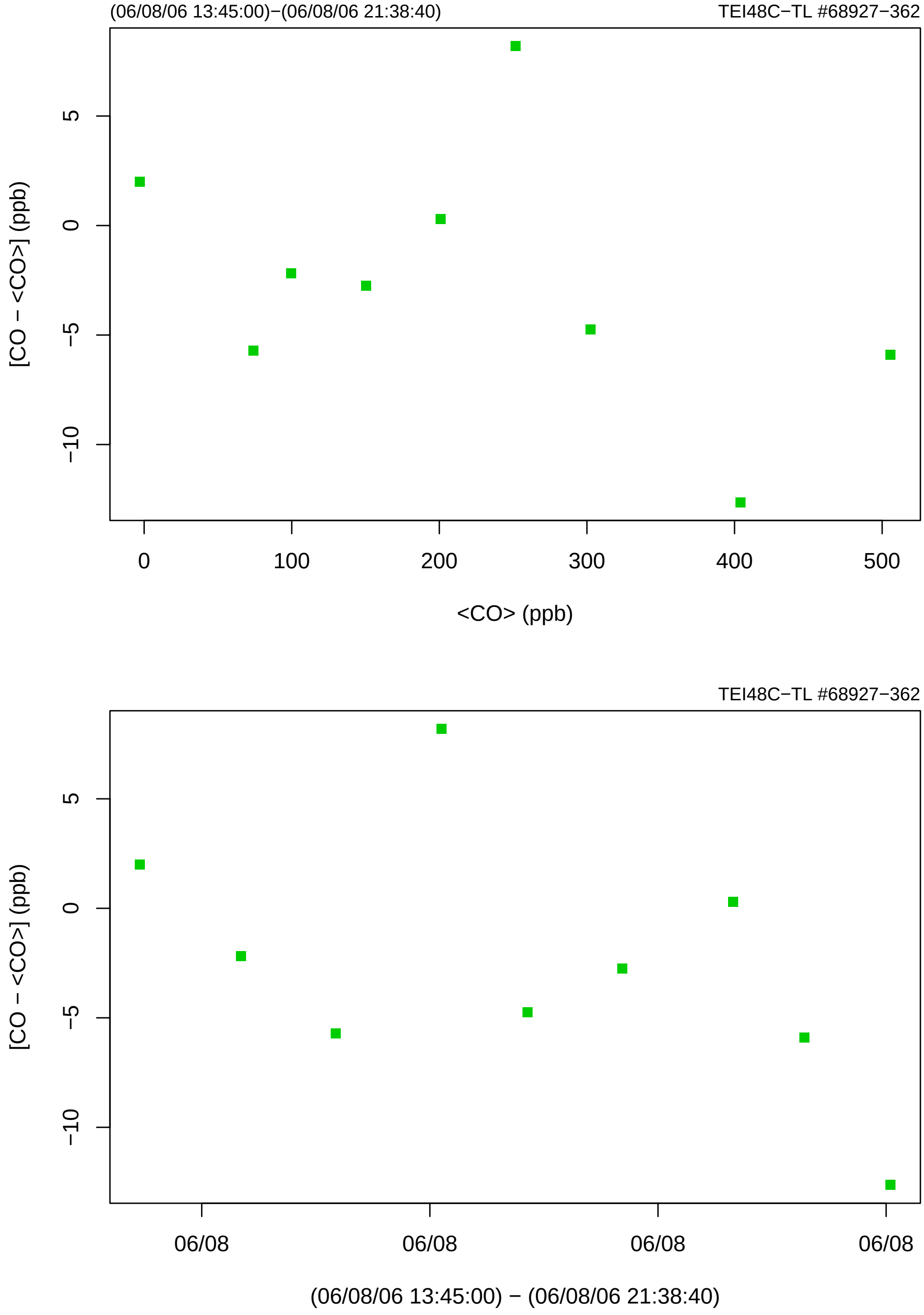


Figure 13. Regression residuals of the SFH TEI 48C-TL carbon monoxide analyser. Points represent averages of valid 5'-aggregates. Upper panel: time dependence; Lower panel: Concentration dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the SFH CO analysers X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the 1' (Aerolaser) and the zero corrected 5' (TEI48C-TL) inter-comparison data using the following equations:

AL5001:

X_{CO} (ppb) = (CO – 2.2) / 0.956

u_{CO} (ppb) = sqrt(0.2 ppb^2 + 2.84e-05 * X_{CO}^2) (2a)

AL5002:

X_{CO} (ppb) = (CO – 1.2) / 0.953

u_{CO} (ppb) = =sqrt(0.4 ppb^2 + 2.85e-05 * X_{CO}^2) (2b)

TEI48C-TL:

X_{CO} (ppb) = (CO + 2.8) / 1.004

u_{CO} (ppb) = sqrt(45.0 ppb^2 + 6.72e-05 * X_{CO}^2) (2c)

The estimate of the remaining standard uncertainty u_{CO} based on instrument noise and a linear concentration dependent contribution of 0.5%. Furthermore an uncertainty contribution of 3 ppb was assumed due to imperfect zero correction (TEI48C-TL only).

Inter-comparison with travelling standards

Direct measurements with WCC-Empa travelling standards were made with the Aerolaser analysers. Each cylinder was measured between 14 and 32 minutes, which resulted in a maximum of 32 useable 1' averages per level and run. These were further aggregated by level before use in the assessment (cf. Table 11 and Table 12).

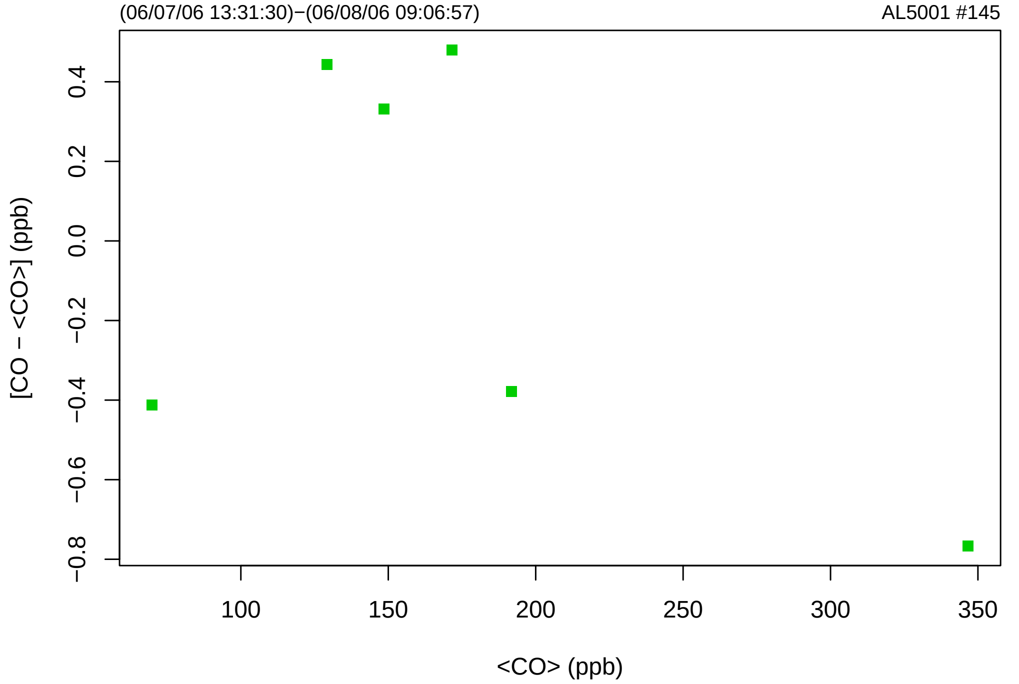
Table 11. CO aggregates computed from 1' averages for each level during the inter-comparison of the SFH AL5001 analyser with WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS Identification	TS (ppb)	sdTS (ppb)	AL5001 CO (ppb)	sdCO (ppb)	No. 1' av.
(06/07/06 13:31:30)	030703_FA01477	199.38	1.00	191.49	0.96	32
(06/07/06 15:30:27)	041109_FA01467	134.68	0.83	129.67	0.45	20
(06/07/06 16:20:44)	041109_0627B	154.58	0.82	148.82	0.43	15
(06/08/06 07:50:30)	FF31496	73.41	0.69	69.50	0.41	14
(06/08/06 08:21:29)	050701_FA02505	359.22	1.82	345.84	0.62	27
(06/08/06 09:06:57)	050415_FA02466	178.54	1.21	172.17	0.67	23

Table 12. CO aggregates computed from 1' averages for each level during the inter-comparison of the SFH AL5002 analyser with WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS Identification	TS (ppb)	sdTS (ppb)	AL5002 CO (ppb)	sdCO (ppb)	No. 1' av.
(06/07/06 14:17:55)	030703_FA01477	199.38	1.00	196.10	1.10	30
(06/07/06 15:55:10)	041109_FA01467	134.68	0.83	128.18	0.38	23
(06/07/06 16:11:39)	041109_0627B	154.58	0.82	148.36	0.25	18
(06/08/06 08:00:53)	FF31496	73.41	0.69	68.99	0.55	18
(06/08/06 08:41:32)	050701_FA02505	359.22	1.82	347.86	0.85	32
(06/08/06 09:22:58)	050415_FA02466	178.54	1.21	174.80	0.55	30

Figure 14 (AL5001) and Figure 15 (AL5002) show the regression residuals plotted against time and concentration. The absence of concentration dependence (upper panel) in the residuals indicates linearity of the instrument. The absence of a temporal trend (lower panel) indicates stable instrument conditions.



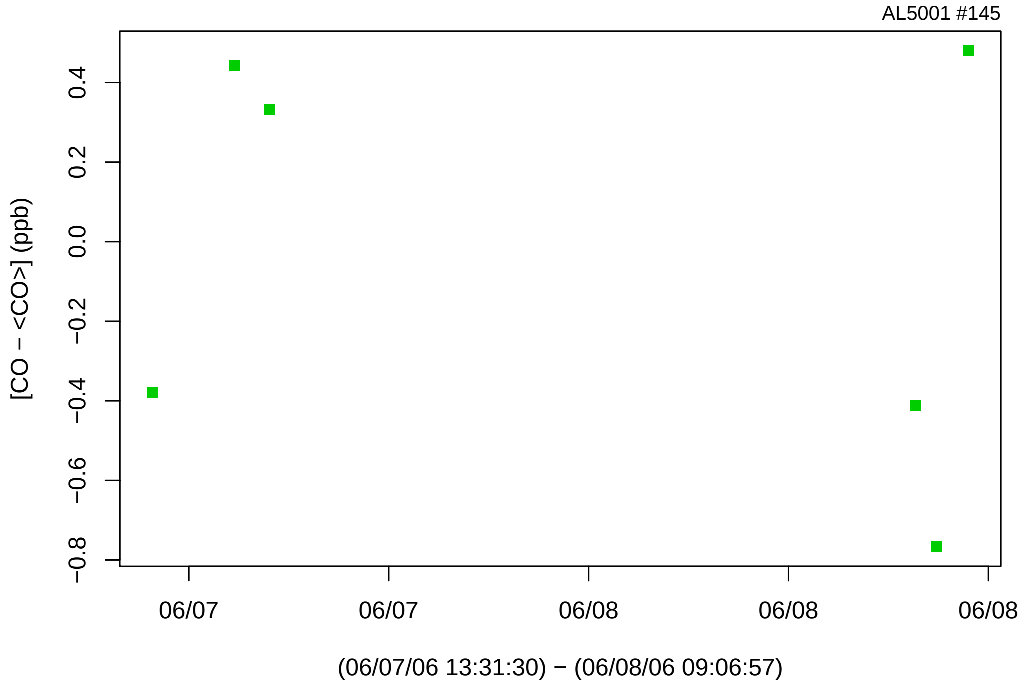


Figure 14. Regression residuals of the SFH AL5001 carbon monoxide analyser based on the inter-comparison with travelling standards. Points represent averages of valid 1'-aggregates. Upper panel: time dependence; Lower panel: Concentration dependence.

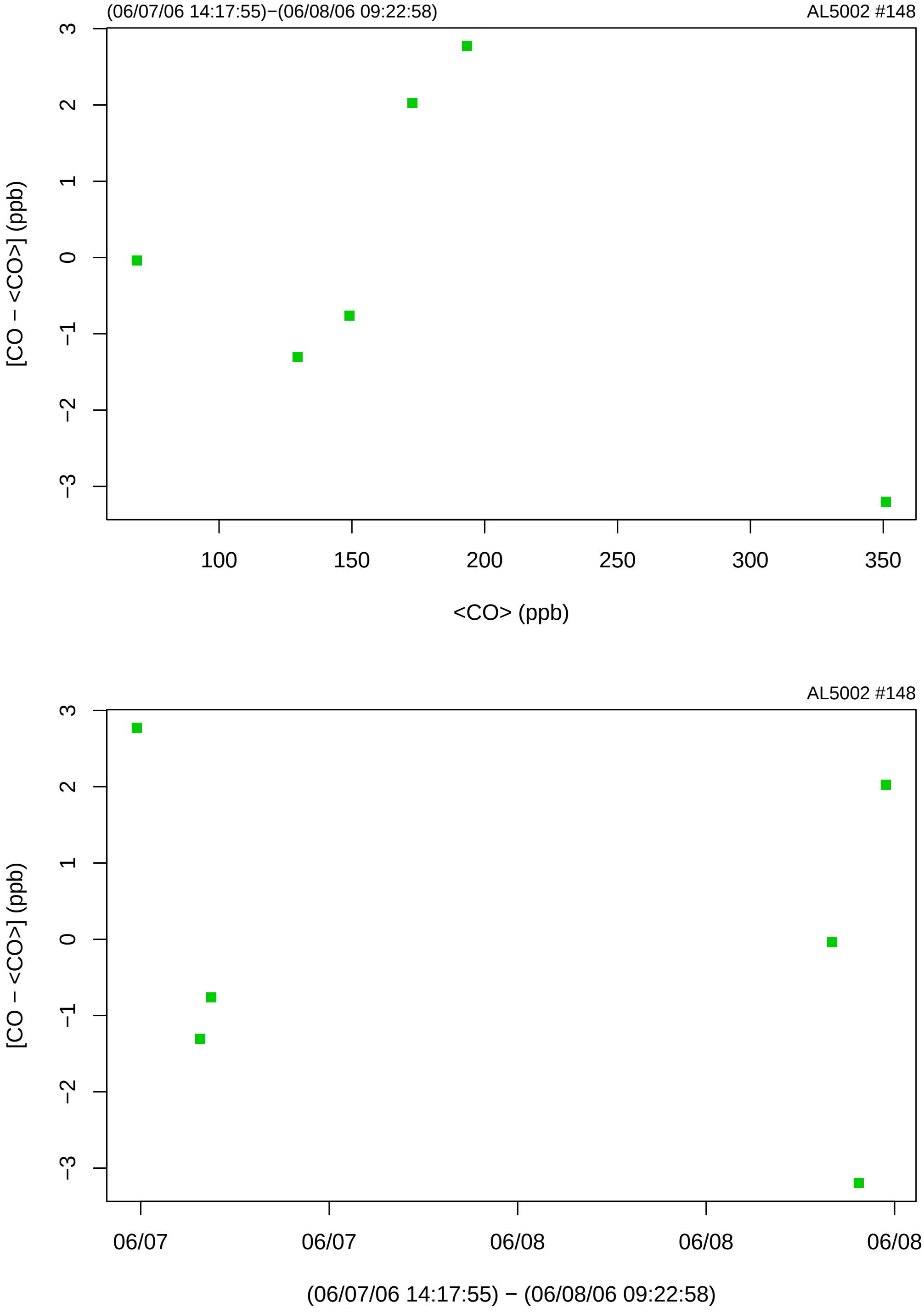


Figure 15. Regression residuals of the SFH AL5002 carbon monoxide analyser based on the inter-comparison with travelling standards. Points represent averages of valid 1'-aggregates. Upper panel: time dependence; Lower panel: Concentration dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the Aerolaser analysers X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the 1' inter-comparison data using equation

AL5001:

$$X_{CO}\ (ppb) = (CO + 1.2) / 0.968$$

$$u_{CO}\ (ppb) = sqrt(2.2\ ppb^2 + 3.34e\text{-}05 * X_{CO}^2) \qquad (2d)$$

AL5002:

$$X_{CO}\ (ppb) = (CO + 3.4) / 0.987$$

$$u_{CO}\ (ppb) = sqrt(7.0\ ppb^2 + 3.73e\text{-}05 * X_{CO}^2) \qquad (2e)$$

The estimation of the remaining standard uncertainty u_{CO} was done in analogy to (2a-b).

Discussion

In general, good results were obtained during the inter-comparisons of the SFH carbon monoxide analysers when compared to WCC-Empa travelling standards. The results of the comparison with the dilution unit were used for the final assessment, because of the following reasons:

- These experiments were made using the sample inlet of the Aerolaser system.
- Each level was applied for a longer time period when compared to the inter-comparison with the TS.

The following discussion addresses a few issues that were found during the inter-comparisons.

Aerolaser AL5001 and AL5002:

A slight difference was observed between the inter-comparison with the dilution unit and the WCC-Empa cylinders. The difference can be explained as follows:

- The Nafion dryer was found to influence the measurements during the inter-comparison with the WCC-Empa cylinders. All values had an offset of approx. 1-2 ppb when the Nafion dryer was in use. The reason could not be found during the audit, and the effect of the Nafion dryer should further be assessed.
- Both Aerolaser instruments were calibrated several times during the inter-comparison with the TS. The sensitivity and zero of the AL5002 showed significant changes between the calibrations, whereas AL5001 changed only slightly. This resulted in a lower reproducibility of the AL5002 instrument.

TEI48C-TL:

The agreement between the TEI48C-TL and WCC-Empa was good, but with a relative large remaining uncertainty. However, this level of uncertainty is expected for an NDIR instrument.

Changes made to the instrument

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

Conclusions

All carbon monoxide analysers were found to operate well within the limits of the instrument specifications. Small remaining differences could be explained by an effect of the Nafion dryer during the experiment, which needs to be further assessed.

Methane Measurements

Methane measurements were moved from the summit to SFH in 2001, after the last audit by WCC-Empa. The methane GC described in the previous audit report [*Zellweger, et al.*, 2001] remained at the summit site. The installation of the new methane GC at SFH was done in analogy and with support of the Carbon Cycle Group of the University of Heidelberg. The instrument has two detectors (FID and ECD) and is designed to measure simultaneously CH_4, CO_2, N_2O and SF_6. The old GC system remained at the summit; data of this system are no longer submitted to WDCGG.

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
The methane GC is also connected to the manifold described in the previous audit report [*Zellweger, et al.*, 2001]. The GC is connected to the manifold with 2 m ¼” stainless steel tubing. A metal below pump is used to flush the inlet line with 2 l/min. An inlet filter is mounted after the pump, and the air is dried with a cold trap (-40°C). The residence time is estimated to be approximately 10 s.

Instrumentation
The analytical system for methane is based of an HP 6890 Series GC equipped with two detectors (FID and ECD) and a methanizer. Simultaneous measurements of CH_4, CO_2, N_2O and SF_6 are made. Instrumental details are listed in Table 14 below.

Standards and Calibration
The standard methane scale, to which the SFH CH_4 measurements are referenced, is based on standards obtained from Deuste Steininger GmbH. Calibration of these standards is done at the Regional GAW station Schauinsland against NOAA/GMD laboratory standards (currently still CMDL83 methane scale [*Dlugokencky, et al.*, 2005]). Table 5 shows details of the cylinders currently available at the station.

Calibration of the instrument is performed using the working and the target standards. Injections are made every five minutes. The working standard is injected after two injections of ambient air, and the target gas is injected three times every 6 hours. Peak area is used for data evaluation.

Table 13. Methane standards at the SFH station (from Deuste Steininger, calibrated at Schauinsland against NOAA/GMD CMDL83 standards)

Manufacturer, S/N, Use	CH_4 Content (ppb in air)	In service	
		From	To
4699B working standard	1733.4	2000-01-01	2001-12-03
2849A target	1836.8	2000-01-01	2001-12-03
4699B target	1733.4	2001-12-03	2002-07-29
2849A working standard	1836.8	2001-12-03	2002-07-29
2849A target	1836.8	2002-07-29	2002-12-05
4945 working standard	1864.7	2002-07-29	2003-05-23
5043 target	1862.8	2002-12-05	2003-05-23
5043 working standard	1862.8	2003-05-23	2004-07-01

4945 target	1864.7	2003-05-23	2004-05-06
5720 target	1870	2004-05-06	2004-07-01
5720 working standard	1870	2004-07-01	2004-12-20
5043 target	1862.8	2004-07-01	2004-12-01
4945B target	1831.2	2004-12-01	2004-12-20
4945B working standard	1831.2	2004-12-20	2006-04-06
2849B working standard	1836.8	2006-04-06	Cont.
5720 target	1870	2004-12-20	Cont.

Operation and Maintenance
The system is checked for general operation whenever the station is visited. Instrument parameters such as baseline value and noise, gas pressures and cold trap are checked and noted in a (daily) check list. Data of the previous day(s) is inspected. The calibration of the system is checked every two weeks using the data of the automatic injections of working standard and target gases.

Data Acquisition and Data Transfer
Data acquisition is made using HPChemStation (Rev. A.06.03 [509]) software. Peak area is used for data analysis. Reports are generated automatically and are further processed with custom made software (Visual Basic, programmed by University of Heidelberg).

Data Treatment
Data is visually inspected. If questionable data is observed the data evaluation and peak integration is re-checked. Valid data is further aggregated to half hourly averages.
The HP Chemstation software produces report (.txt) and binary files containing the chromatograms. Data of these files is extracted using a custom made Visual Basic (VB) programme (config.exe), which produces a file containing meta information (sample ports, names). A further VB programme (Probenfiles_erzeugen.exe) is then used to extract all relevant information of the report and the config files to produce a data file with date and concentrations (DDMMYY.ch4. DDMMYY.co2.etc). These files are further processed using the GC organizer (also VB) to 30 minute averages. A further check with the half hourly values is then made using the programme “QWERT”; information of the log files is added and data is flagged (valid and invalid, with comments about the reason for invalid data).

Data Submission
Methane data of SFH was for the first time submitted after the audit in September 2006 and covers the time period from 2002 (start of measurements) until end of 2005. Hourly, daily and monthly data without further ancillary data is available from WDCGG. Data refers to NOAA/GMD, but the scale version is not specified in the data file. Submission is planned to continue in regular (yearly) intervals.

Documentation
Hand-written instrument specific check lists, instrument manuals and an instrument specific standard operating procedure are available at the site. The check lists are sufficiently comprehensive and up-to-date.

Inter-Comparison of Methane 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 standard to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 21 and Table 22 below.

Setup and Connections

Table 14 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 SFH data acquisition system, and no further corrections were applied.

Table 14. Experimental details of the methane inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 030703_FA01477 / 1800.7 / 1.1 2 / 050701_FA02505 / 1833.0 / 0.5 3 / FF31496 / 1843.4 / 1.2 4 / 041109_0627B / 1881.0 / 0.9 5 / 041109_FA01467 / 1906.9 / 0.6 6 / 050415_FA02466 / 2005.4 / 2.1
Field instrument	Model, S/N	HP 6890 Series
	Principle	GC / FID Detector
	Sample loop	15 ml
	Column	Packed fused silica: Haysep (80/100 mesh) length 12 ft, diameter 3/16”
	Carrier gas	N_2 99.9999%
	Temperatures	Column: 80°C, FID 250°C, Methanizer 375°C
	Instrument specials	A few seconds before injection, the flow through the loop is stopped to equilibrate pressure.
Connection of TS to field instrument		TS were connected to the sample selection valve of the SFH system
Data Acquisition		HPChemStation GC control software; peak height was used for data evaluation
Number of injections		Each TS was injected between 15 and 20 times; these injections were aggregated for further analysis.
Sequence of levels		Randomised sequence
Runs		1 run (7 thru 8 June, 2006)

Results

Each TS was injected between 15 and 20 times, which resulted in a maximum of 20 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 15).

Table 15. CH_4 aggregates computed from single injections (mean and standard deviation of mean) for each level during the inter-comparison of the SFH methane analyzer with the WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	CH_4 (ppb)	sdCH_4 (ppb)	No. of inj.
(06/07/06 13:35:20)	1843.44	1.18	1816.04	0.66	15
(06/07/06 16:39:00)	2005.39	2.06	1975.96	0.67	20
(06/07/06 20:11:46)	1833.00	0.54	1809.49	0.91	17
(06/08/06 00:39:00)	1880.97	0.85	1854.77	1.07	17
(06/08/06 03:48:27)	1800.74	1.06	1774.63	0.51	18
(06/08/06 07:04:10)	1906.88	0.61	1880.71	0.94	20

Figure 16 shows the regression residuals of the HP 6890 Series plotted against time and concentration. The absence of a temporal trend (upper panel) indicates stable instrument conditions. The absence of concentration dependence (lower pane) indicates linearity of the instrument.

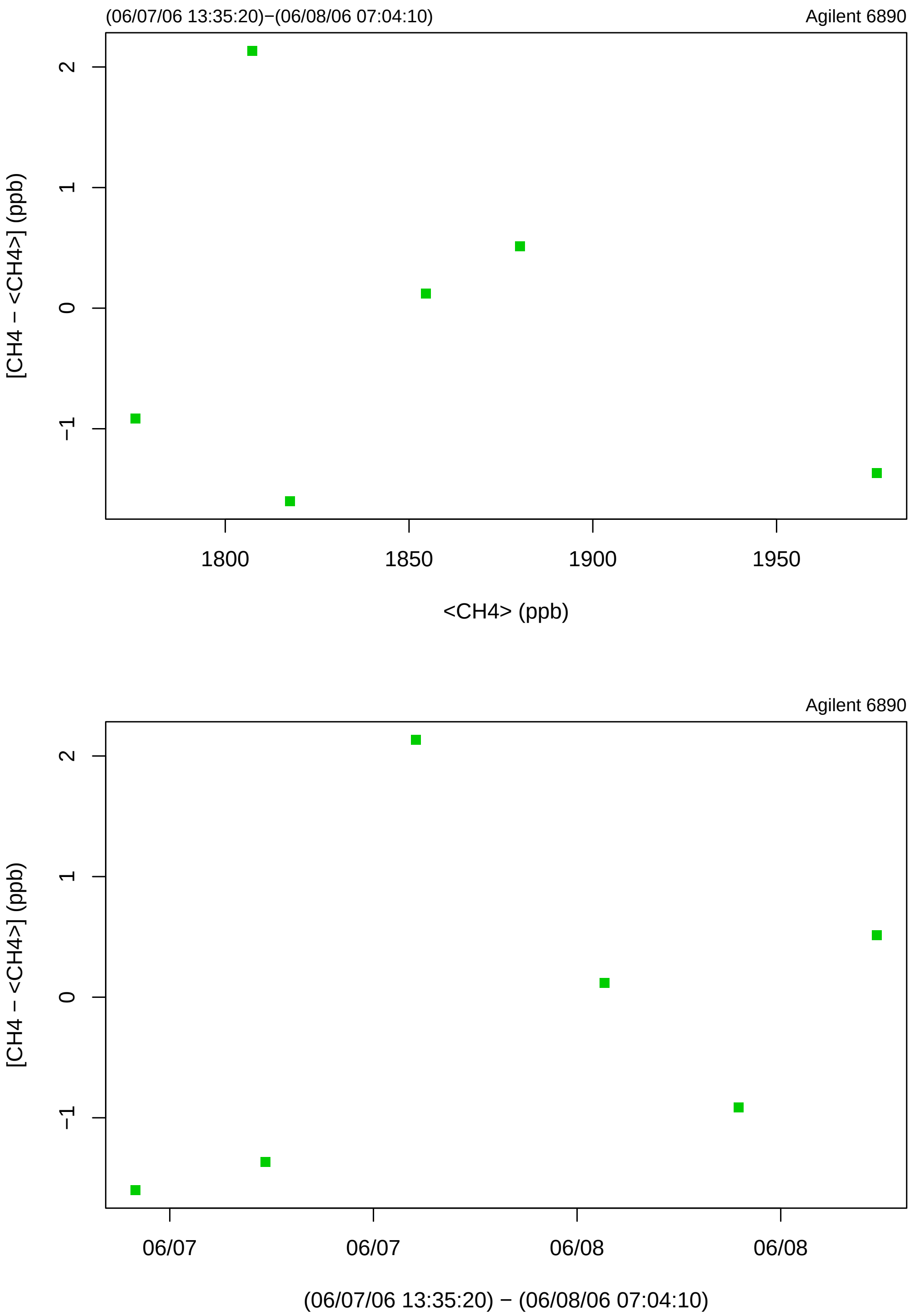


Figure 16. Regression residuals of the SFH methane GC. Points represent averages of valid single injections. Upper panel: concentration dependence; Lower panel: time dependence.

Based on these inter-comparison results, unbiased methane volume mixing ratios of the HP 6890 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).

$$\mathbf{X_{CH4}\ (ppb) = (CH_4) / 0.98601}$$
$$\mathbf{u_{CH4}\ (ppb) = sqrt(2.0\ ppb^2 + 1.24e\text{-}07 * X_{CH4}^2)} \qquad (3)$$

Conclusions

The significant deviation (cf. Figure 6) between SFH and WCC-Empa can be explained by different scale versions (SFH: CMDL83, WCC-Empa: NOAA04). When SHF results are converted to NOAA04 scale, the agreement is better than 0.3%, with SFH values being on average 0.18% lower compared to WCC-Empa. 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 SFH GC was good, with an average standard deviation of 0.04% (15-20 injections). This value is comparable to the best GC/FID systems at GAW stations. Therefore no further technical recommendations are made by WCC-Empa.

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 16, the inter-comparison data is given in Table 17.

Table 16. 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 = -0.2; 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 the audit (16 May, 2006) 3 runs after the audit (26 June, 2006)

Table 17. Five-minute aggregates computed from 10 valid 30-second values for the intercomparison of the Standard Reference Photometer (SRP) with the WCC-Empa transfer standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2006-05-16	1	0	-0.15	0.26	0.03	0.09
2006-05-16	1	90	91.93	0.4	92.17	0.06
2006-05-16	1	190	192.25	0.36	192.57	0.17
2006-05-16	1	30	32.2	0.35	32.15	0.14
2006-05-16	1	140	142.36	0.43	142.8	0.07
2006-05-16	1	60	61.18	0.32	61.63	0.13
2006-05-16	1	0	-0.17	0.23	0.1	0.09
2006-05-16	2	0	-0.15	0.33	0.16	0.05
2006-05-16	2	90	91.96	0.31	92.35	0.04
2006-05-16	2	190	192.01	0.49	192.73	0.14
2006-05-16	2	30	32.36	0.38	32.57	0.07
2006-05-16	2	140	142.26	0.32	142.78	0.04
2006-05-16	2	60	61.27	0.46	61.51	0.12
2006-05-16	2	0	-0.15	0.24	0.12	0.06
2006-05-16	3	0	-0.25	0.48	0.12	0.09
2006-05-16	3	30	32.18	0.37	32.4	0.12
2006-05-16	3	140	142.15	0.27	142.67	0.07
2006-05-16	3	60	60.87	0.33	61.43	0.11
2006-05-16	3	90	91.85	0.3	92.1	0.11
2006-05-16	3	190	191.73	0.38	192.32	0.15
2006-05-16	3	0	0.06	0.27	0.1	0.12
2006-06-26	4	0	-0.08	0.29	0.15	0.1
2006-06-26	4	90	89.48	0.26	89.34	0.17
2006-06-26	4	190	188.62	0.48	188.53	0.19
2006-06-26	4	60	59.49	0.25	59.44	0.06
2006-06-26	4	140	139.83	0.28	139.78	0.11
2006-06-26	4	30	31.43	0.24	31.57	0.09
2006-06-26	4	0	0	0.41	0.14	0.07
2006-06-26	5	0	0.16	0.19	0.24	0.12
2006-06-26	5	30	31.3	0.38	31.38	0.09
2006-06-26	5	190	189.35	0.44	189.58	0.24
2006-06-26	5	90	90.2	0.27	90.58	0.09
2006-06-26	5	140	140.43	0.17	140.7	0.24
2006-06-26	5	60	59.79	0.38	60.14	0.06
2006-06-26	5	0	-0.1	0.36	0.25	0.05
2006-06-26	6	0	0.11	0.31	0.15	0.07
2006-06-26	6	90	90.01	0.27	90.38	0.09
2006-06-26	6	190	189.36	0.26	190.09	0.15
2006-06-26	6	30	31.6	0.28	32	0.11
2006-06-26	6	140	140.26	0.28	140.69	0.05
2006-06-26	6	60	59.95	0.3	60.2	0.05
2006-06-26	6	0	-0.13	0.26	0.25	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 17). 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]).

$$\mathbf{X_{TS}\ (ppb) = ([TS] - 0.20\ ppb) / 1.0011}$$

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

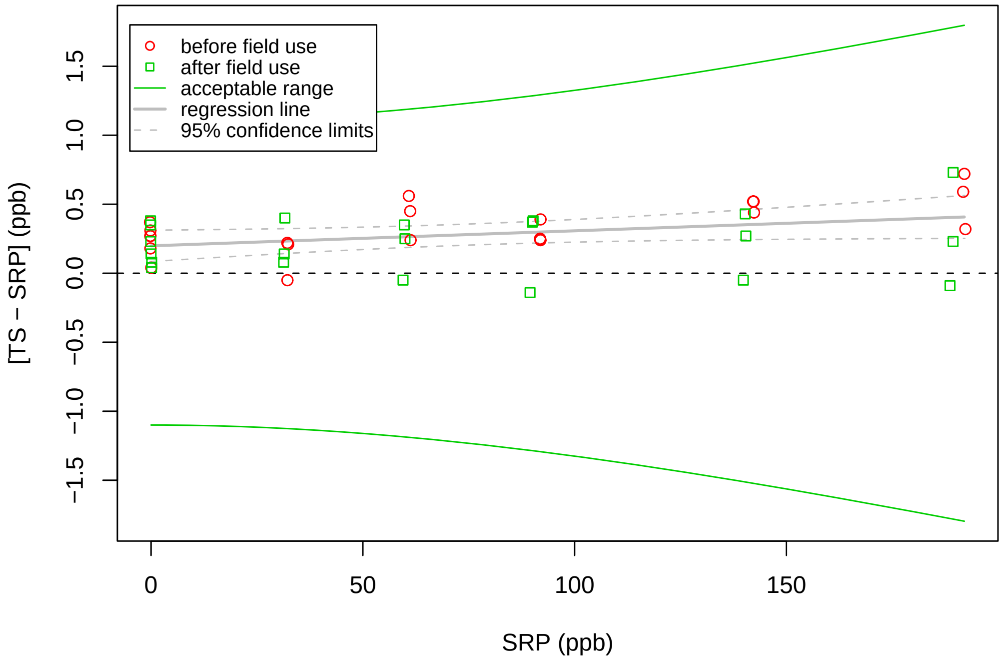


Figure 17. Deviations between transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 AL5001 vacuum-fluorescence analyzer (Aerolaser), an instrument with high precision and proven linearity. Details are given in Table 18 - Table 20.

Table 18. 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)		Dilution unit: zero air (1) and a high concentration carbon monoxide cylinder (2), in combination with a dilution unit (3) and Carbon monoxide cylinders for direct inter-comparisons. (cf. Table 20)
(1) Zero air supply		Ambient air – Silicagel drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		051010_FA02474, 9952.4±48.9 ppb in synthetic air.
(3) Dilution unit		Breitfuss MGM #2262/91/1. The levels used were calibrated before and after the field inter-comparison against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851).
Connection between instruments		Ca. 2 meter 6 mm Sertoflex tubing (dilution unit). Ca. 2 meter 1/8" stainless steel tubing (cylinders).
Data acquisition		Aerolaser 1-min averages
Levels (ppb)		Dilution unit: 0, 75, 100, 150, 200, 250, 300, 400, 500 Cylinders: cf. Table 20
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 19. Calibration of the Breitfuss dilution system and carbon monoxide mixing ratios at different levels determined with WCC-Empa reference before and after the audit.

Date	Mass Flow Controller MFC 1 (mL min^{-1})		Mass Flow Controller MFC 2 (mL min^{-1})		Carbon Monoxide Mixing Ratio (ppb)	
	Set	**Measured#**	**Set**	**Measured**	**Calc.**	**Measured#**
2006-05-10	1800.0	1789.5 ± 1.0	0.000	0.000 ± 0.005	0.0	0.3 ± 0.6
2006-05-10	1782.0	1773.0 ± 1.0	18.000	18.252 ± 0.015	101.4	101.7 ± 0.7
2006-05-10	1786.5	1777.5 ± 0.3	13.500	13.719 ± 0.011	76.2	76.9 ± 1.8
2006-05-10	1755.0	1746.1 ± 0.2	45.000	45.470 ± 0.017	252.6	253.2 ± 2.1
2006-05-10	1746.0	1737.5 ± 0.2	54.000	54.553 ± 0.011	0.0	305.4 ± 1.7
2006-05-10	1773.0	1764.5 ± 0.2	27.000	27.331 ± 0.013	151.8	152.0 ± 0.8
2006-05-10	1764.0	1755.9 ± 0.2	36.000	36.403 ± 0.013	202.1	202.7 ± 1.4
2006-05-10	1710.0	1700.8 ± 0.3	90.000	90.817 ± 0.016	504.5	505.6 ± 2.6
2006-05-10	1728.0	1719.3 ± 0.2	72.000	72.664 ± 0.013	403.6	402.8 ± 1.1
2006-06-28	1800.0	1791.3 ± 1.1	0.000	0.000 ± 0.005	0.0	0.2 ± 0.1
2006-06-28	1782.0	1776.6 ± 0.5	18.000	18.343 ± 0.011	101.7	102.8 ± 0.3
2006-06-28	1786.5	1781.5 ± 0.8	13.500	13.806 ± 0.009	76.5	77.3 ± 0.2
2006-06-28	1755.0	1749.4 ± 0.5	45.000	45.625 ± 0.012	253.0	255.4 ± 0.5
2006-06-28	1746.0	1740.7 ± 0.3	54.000	54.746 ± 0.010	303.5	305.5 ± 0.3
2006-06-28	1773.0	1767.9 ± 0.2	27.000	27.452 ± 0.009	152.2	153.7 ± 0.3
2006-06-28	1764.0	1759.0 ± 0.3	36.000	36.542 ± 0.011	202.5	204.2 ± 0.2
2006-06-28	1710.0	1704.0 ± 0.2	90.000	91.122 ± 0.008	505.2	508.1 ± 0.5
2006-06-28	1728.0	1722.5 ± 0.2	72.000	72.927 ± 0.011	404.2	406.4 ± 0.4

#Average±sd (n =10)

Table 20. Calibration of the carbon monoxide travelling standards with the WCC-Empa reference before and after the audit.

Date	2006-03-22	2006-05-03	2006-06-27
Cylinder identification	CO (ppb)#	CO (ppb)#	CO (ppb)#
050701_FA02505		359.42 ± 1.54	359.02 ± 0.44
FF31496	73.00 ± 0.90		73.82 ± 0.15
041109_FA01467		134.33 ± 1.16	135.02 ± 0.25
050415_FA02466		177.96 ± 1.37	179.11 ± 0.29
030703_FA01477		199.46 ± 1.25	199.29 ± 0.27
041109_0627B		154.76 ± 0.95	154.39 ± 0.22

#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 21). 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 22.

Table 21. NOAA/GMD 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 22. Calibration of the methane travelling standards with the WCC-Empa reference before and after the audit.

Date	2006-04-28	2006-05-02	2006-06-26
Cylinder identification	CH_4 (ppb)#	CH_4 (ppb)#	CH_4 (ppb)#
030703_FA01477		1801.5 ± 0.7	1800.0 ± 1.6
050701_FA02505	1832.7 ± 0.9		1832.3 ± 1.2
FF31496	1842.6 ± 0.9		1844.3 ± 1.7
041109_0627B		1881.5 ± 1.6	1880.4 ± 1.4
041109_FA01467		1907.3 ± 1.3	1906.5 ± 1.4
050415_FA02466	2004.0 ± 1.4		2006.8 ± 0.9

#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 (SFH)

0.1	Station Name:	Zugspitze - Schneefernerhaus
0.2	GAW ID:	SFH
0.3	Coordinates/Elevation:	47.412°N, 10.982°E (2650 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	6 – 9 June, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. L. Ries, R. Sohmer, S. Knabe
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):	[TS] = (1.0011±0.0010) × [SRP] + (0.20±0.09)
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49C # 65220-347
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG: 0.0 COEF: 1.000
1.5.4	Calibration at start of audit (ppb):	[OA] = (0.983±0.000) × [SRP] - (0.04±0.05)
1.5.5	Unbiased ozone mixing ratio at start of audit (ppb):	X = ([OA] + 0.04) / 0.983
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.69e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio after audit (ppb):	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	Values of OA were corrected based on the inter-comparison with the station standard: $OA_{corr.}$ = 0.9887 x OA - 0.057 ppb
1.7	Reference:	WCC-Empa Report 06/2

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

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Carbon Monoxide Audit Executive Summary (SFH)

0.1	Station Name:	Zugspitze - Schneefernerhaus
0.2	GAW ID:	SFH
0.3	Coordinates/Elevation:	47.412°N, 10.982°E (2650 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	6 – 9 June, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. L. Ries, R. Sohmer, S. Knabe
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	051010_FA02474, 9952.4±48.9 ppb (α=0.05)
1.4.2	Zero Air:	Ambient Air, Purafil, Sofnocat, filter (WCC-Empa)
1.4.3	Dilution unit:	Breitfuss MGM #2262/91
1.4.4	Range of calibration:	0 – 500 ppb
1.5	CO analyzer [CA]	
1.5.1	Model:	Aerolaser AL5002 S/N 148
1.5.2	Range of calibration:	0 – 500 ppb
1.5.3	Coefficients at start of audit	not applicable
1.5.4	Calibration at start of audit (ppb):	CO = (0.953±0.001) $\times$ X + (1.2±0.0)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO – 1.2) / 0.953
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (0.4\ ppb^2 + 2.85e\text{-}05 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.6	Comments:	Main station CO instrument
1.7	Reference:	WCC-Empa Report 06/2

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

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Methane Audit Executive Summary (SFH)

0.1	Station Name:	Zugspitze - Schneefernerhaus
0.2	GAW ID:	SFH
0.3	Coordinates/Elevation:	47.412°N, 10.982°E (2650 m a.s.l)
Parameter:		Methane

1.1	Date of Audit:	6 – 9 June, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. L. Ries, R. Sohmer, S. Knabe
1.3	CH_4 Reference:	NOAA04
1.4	CH_4 Transfer Standard [TS]	
1.4.1	CH_4 Cylinders:	030703_FA01477, 1800.7±1.1 ppb 050701_FA02505, 1833.0±0.5 ppb FF31496, 1843.4±1.2 ppb 041109_0627B, 1881.0±0.9 ppb 041109_FA01467, 1906.9±0.6 ppb 050415_FA02466, 2005.4±2.1 ppb
1.5	CH_4 analyzer [CA]	
1.5.1	Model:	HP 6890 Series
1.5.2	Range of calibration:	1800 –2005 ppb
1.5.3	Coefficients at start of audit	not applicable
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (0.98601 \pm 0.00033) \times X$
1.5.5	Unbiased CH_4mixing ratio (ppb) at start of audit:	$X = CH_4 / 0.98601$
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (2.0\ ppb^2 + 1.24e\text{-}07 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CH_4 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 06/2

[CH_4]: Instrument readings; X: mixing ratios on the NOAA04 CH_4 scale.

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