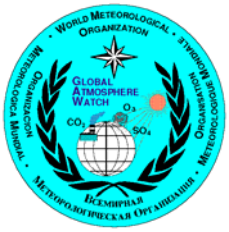

Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 06/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION HOHENPEISSENBERG

GERMANY, JUNE 2006

Submitted by

C. Zellweger, J. Klausen, B. Buchmann

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

Empa Dübendorf, Switzerland

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

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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The second system and performance audit at the Global GAW station Hohenpeissenberg (HPB) run by the German Weather Service (DWD) was conducted by WCC-Empa[1] from 20 thru 22 June 2006 in agreement with the WMO/GAW quality assurance system [*WMO*, 2001].

A previous audit at HPB was conducted in November 1997 [*Herzog, et al.*, 1997].

People present during the audit included

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Stefan Gilge	DWD, Station scientist
Mr. Reinhard-Tasso Wilhelm	DWD, Station operator
Mrs. Marita Hoffmann	DWD, Station operator

Our assessment of the station Hohenpeissenberg in general, as well as the surface ozone and carbon monoxide measurements in particular, is summarized 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 (DWD, Dr. Wolfgang Fricke) and the World Meteorological Organization in Geneva. The executive summaries will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

The Global GAW station Hohenpeissenberg is located on top of an isolated mountain 40 km north of Zugspitze. It rises 300 m above the surrounding area that is populated to an extent typical for Central Europe and partly covered with meadows (~70%) and forests (~30%). The location is adequate for the intended purpose, although the site may encounter frequent pollution episodes from nearby sources. Access to the site consists of a paved road.

Station Facilities

The Hohenpeissenberg GAW station comprises extensive laboratory and office facilities. It is an ideal platform for atmospheric research. At the time of the WCC-Empa audit however the air conditioning of the GAW laboratory was not working efficiently enough and the lab temperature exceeded 30°C. A replacement of the AC system was under way during the audit and was completed in July 2006.

Station Management and Operation

The station is permanently staffed during working days with scientists and operators. This guarantees the high level quality of the Hohenpeissenberg data. The current staff for the GAW measurements consist of two scientist and two technicians who have excellent technical and scientific expertise to operate and maintain the equipment and to work with the data.

Recommendation 1 (, on-going)**
The current station management system with responsibilities of both technical and scientific staff is regarded as optimal and should be continued.

[1] WMO/GAW GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

Air Inlet System
The design of the air inlet system is state of the art (for all parameters) and no further recommendations are made by WCC-Empa.

Surface Ozone Measurements
Instrumentation. Several ozone instruments are available at HPB. Currently two systems are continuously running, namely a TEI49C (UV absorption) and a UPK 8002 (chemiluminescence) instrument. For both instruments the analogue signal is acquired, although the data acquisition would have the capability to record the RS-232 output of the TEI49C instrument with minor modifications. The chemiluminescence instrument is only used as a back-up system in case of data loss of the main analyser. Regular inter-comparisons are made between the two instruments to ensure homogenous data sets of the two systems. The instrumentation is adequate for its intended purpose.

Recommendation 2 (*, 2006)
It should be considered to acquire the RS-232 output of the TEI49C analyser to avoid a potential bias due to D/A conversion and/or additional noise of the signal.

Standards. The station is equipped with an ozone standard (TEI49C-PS); however traceability to other ozone standards apart from WCC-Empa audits has not been established. Calibrations are carried out every three months. 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 3 (, on-going)**
The ozone standard should be compared regularly (e.g. once per year) with other ozone reference instruments which are traceable to the GAW reference, e.g. the SRP of the Umweltbundesamt (UBA) in Langen.

Recommendation 4 (, on-going)**
Pressure sensors should be checked during inter-comparisons. A bias in the pressure sensor reading with respect to a reference sensor should be eliminated.

Intercomparison (Performance Audit). The inter-comparisons extended over a period of nearly 20 hours (analysers) and 18 hours (calibrator). The raw readings of the TEI 49C instrument were corrected with a factor of 0.983 from the last inter-comparison with the station calibrator, according to the usual station method. No further corrections were applied to the UPK and the calibrator data. The results of the assessment are summarised below and are presented in Figure 1 (analysers) and Figure 2 (standard).

TEI49C #56028-306:	0 – 90 ppb good agreement	
Unbiased O3 mixing ratio (ppb)	X_{O3} (ppb) = ([OA] + 0.01 ppb) / 1.011	(1a)
UPK 8002 #92062:	0 – 90 ppb good agreement	
Unbiased O3 mixing ratio (ppb)	X_{O3} (ppb) = ([OA] – 0.21 ppb) / 1.010	(1b)
TEI49C-PS #0423807729:	0 – 90 ppb good agreement	
Unbiased O3 mixing ratio (ppb)	X_{O3} (ppb) = ([OC] – 0.01 ppb) / 1.007	(1c)

Here, [OA] represents surface ozone readings obtained from the station data acquisition (TEI49C and UPK 8002) and [OC] represent the ozone readings from the RS-232 output (TEI49C-PS).

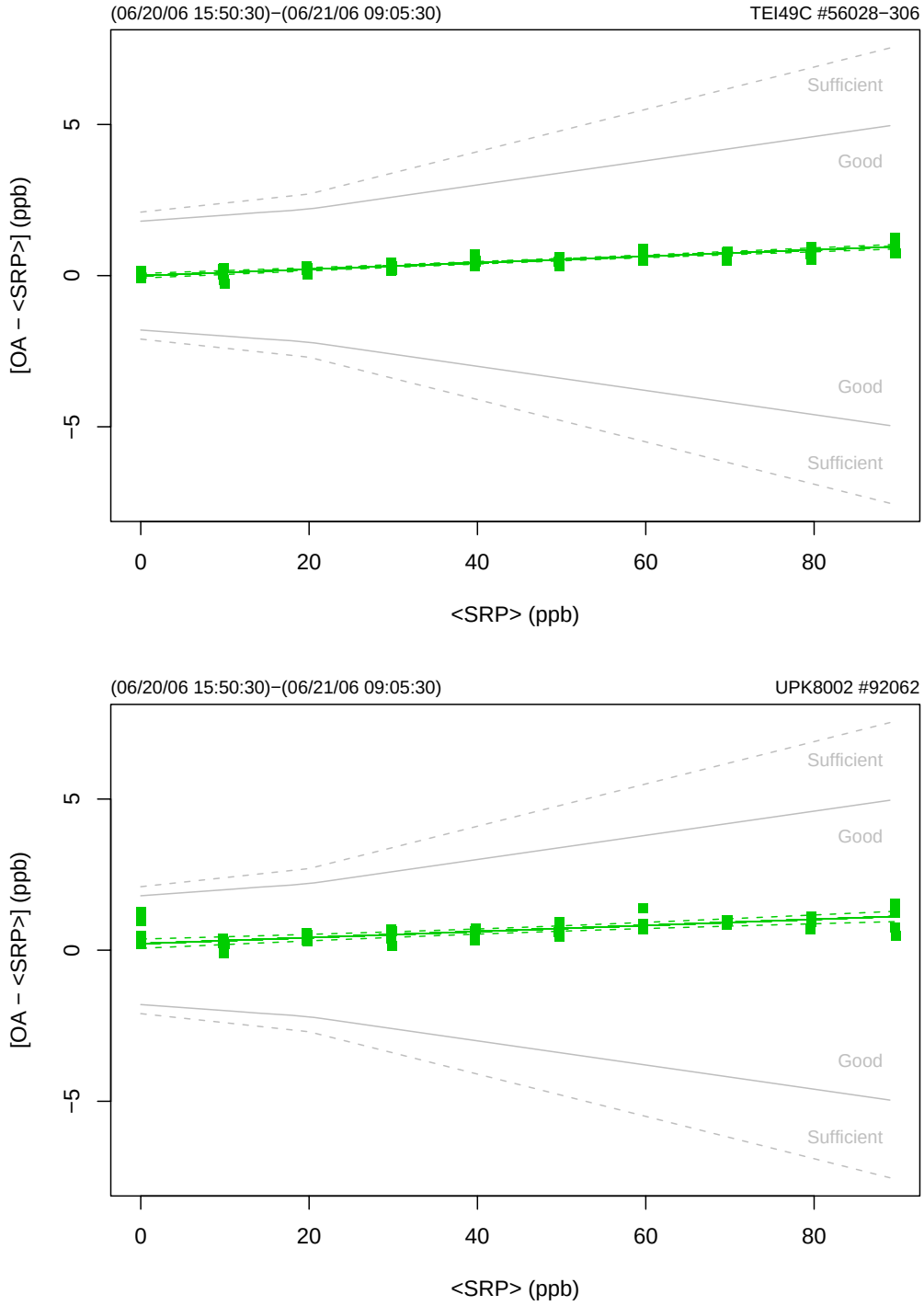

Figure 1. Bias of the Hohenpeissenberg ozone analyser with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining ‘good’ and ‘sufficient’ agreement according to GAW assessment criteria [Klausen, et al., 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.
Upper panel: TEI49C. Lower panel: UPK 8002**.**

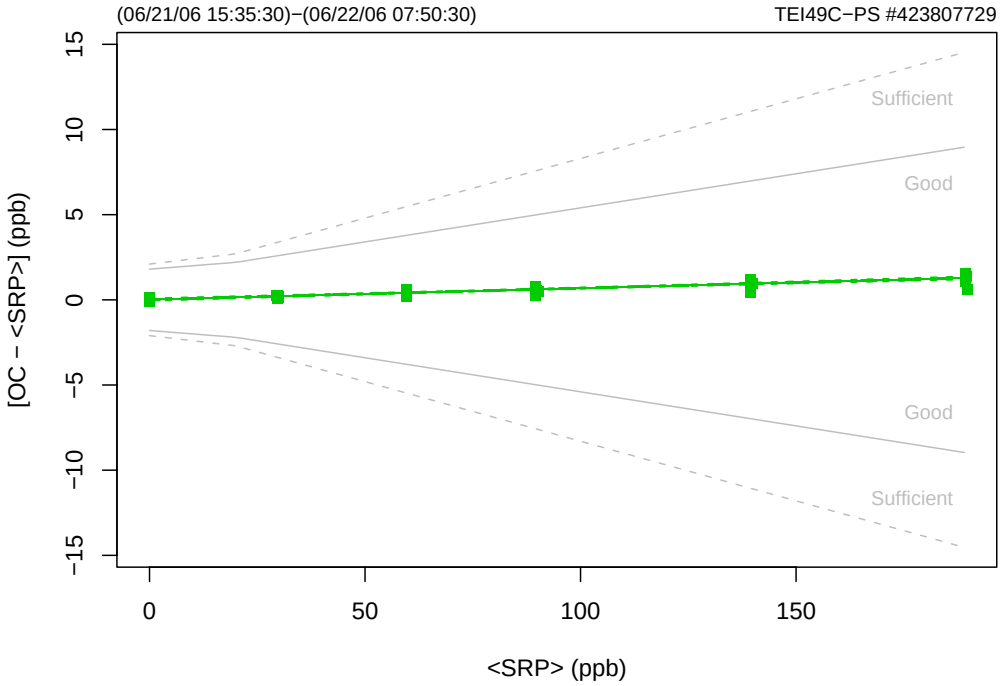

Figure 2. Bias of the Hohenpeissenberg ozone standard TEI49C-PS with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen,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

Recommendation 5 (, 2006)**
Although the inter-comparison results are well within the data quality objectives (DQO), it should be considered to correct for the remaining bias using the above equations (1a) – (1c).

Carbon Monoxide Measurements

Instrumentation. Hohenpeissenberg is currently equipped with two CO analysers, which are both running in parallel. The UV fluorescence instrument (Aerolaser AL5001) is considered the main data source, whereas the NDIR analyser (TEI48S) is running as a back-up system. The instrumentation is adequate for the intended purpose.

Standards. The station is currently equipped with a dilution unit and one carbon monoxide cylinder in the high ppm range (43.3 ppm), as well as one carbon monoxide cylinder at the 1 ppm level (0.97 ppm). These standards were purchased from Messer Germany and Riessner Gase and have been inter-compared to NOAA/GMD standards during an informal round robin in 2006. With this equipment, adequate calibration of the carbon monoxide measurements is possible; however the possibility of direct link to the NOAA/GMD WMO-2000 carbon monoxide scale would be preferable. Calibrations are carried out manually.

Recommendation 6 (, 2006)**
It is recommended to purchase carbon monoxide standards directly from NOAA/GMD to establish a direct link of the HPB CO measurements to the GAW reference (WMO-2000 carbon monoxide scale).

Recommendation 7 (, 2006)**
It should be considered to perform instrument calibrations automatically at regular intervals. In principle this should be simple with the AL5001 instrument, however the automatic calibration routine of this particular instrument is subject to frequent failures. The instrument needs to be repaired.

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 (AL5001 only). Two levels at 400 ppb and 500 ppb CO were excluded from the assessment of the Aerolaser instrument because of excessive noise. These results are only presented in the Appendix.

No formal data quality objectives have been established for CO. The following equations characterise the instrument bias (cf. Figure 3 and Figure 4):

Assessment with WCC-Empa dilution system:

Aerolaser AL5001:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] - 0.7 ppb)/ 0.994 (2a)

TEI48S:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 1.2 ppb) / 1.004 (2b)

Assessment with WCC-Empa travelling standards:

Aerolaser AL5001:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] - 1.6 ppb)/ 1.003 (2c)

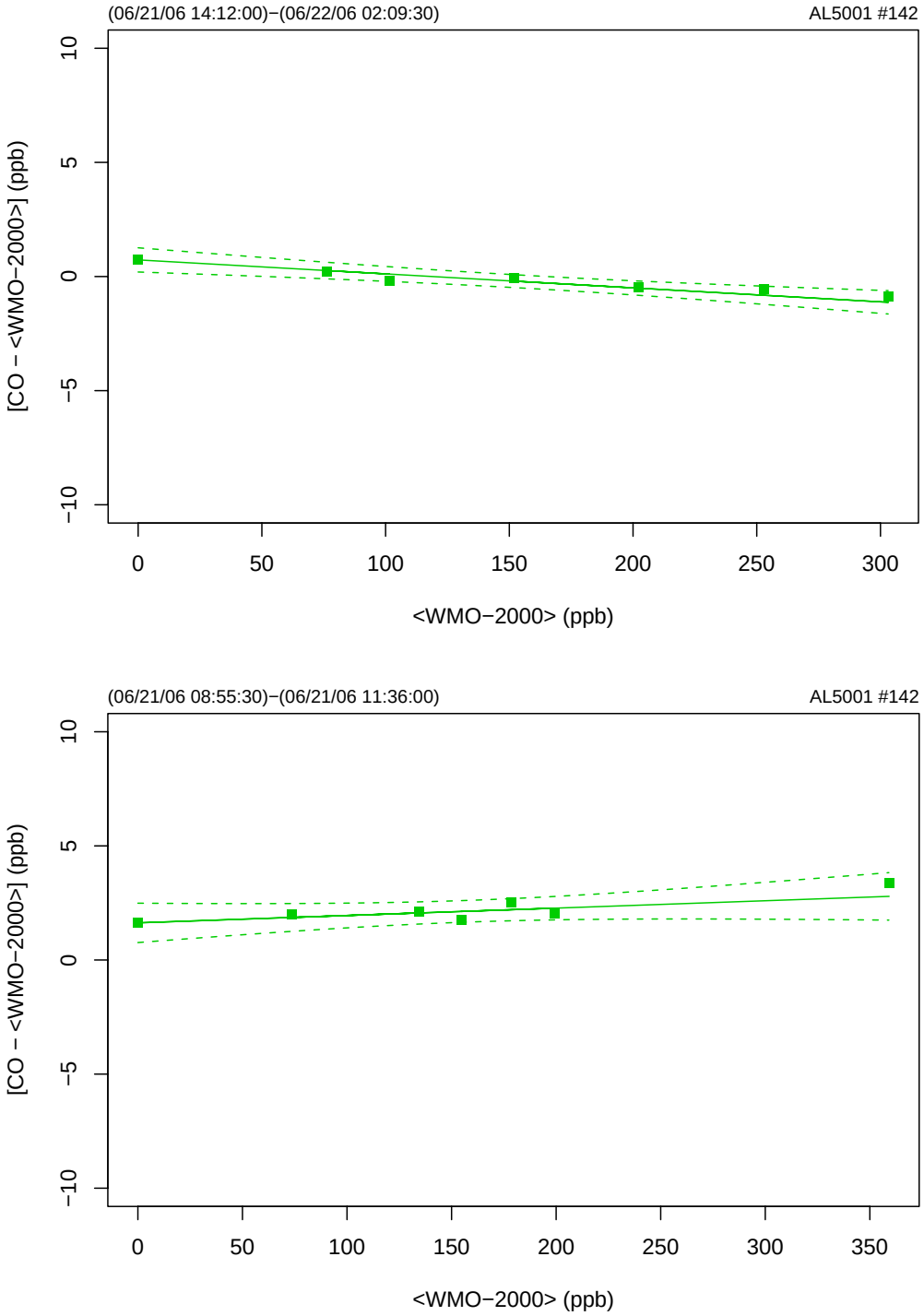

Figure 3. Bias of the Hohenpeissenberg main carbon monoxide analyser (Aerolaser AL5001) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Upper panel: Assessment with the dilution system. Lower Panel: Assessment with travelling standards.

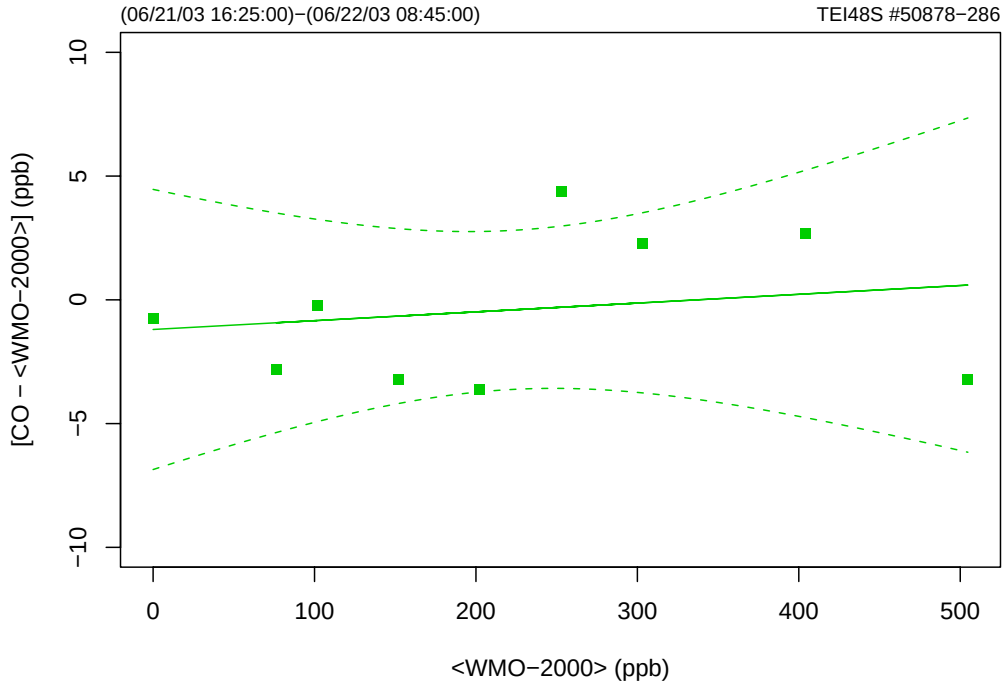

Figure 4. Bias of the Hohenpeissenberg back-up carbon monoxide analyser (TEI48S) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Recommendation 8 (, 2006)**
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 the Nafion dryer. The effect of the Nafion dryer on the measurements should further be assessed.

Data Acquisition and Management

Data of the HPB station are acquired on a custom built data acquisition system (MAUS - Measurement and Unit controlled System). MAUS has user configurable interfaces which can handle both analogue and serial input signals. One minute data is stored for further analysis. Remote access to all instruments is possible, and the data is backed up at regular intervals.

Data Submission

All parameters within the scope of WCC-Empa were submitted to the World Data Centre for Greenhouse Gases. The records are complete and data are usually submitted within a maximum of one year after completion of the measurements.

Conclusions

The Global GAW station Hohenpeissenberg comprises an extensive suite of ongoing measurements. The combination of long time series with the large number of measured parameters makes the HPB station an important contribution to the GAW programme. All assessed measurements were of high quality. Careful data evaluation is however needed due to the influence of local and regional pollution sources.

Summary Ranking of Hohenpeissenberg Station

System Audit	Adequacy[#]	Comment
Access	(5)	
Facilities		
Laboratory and office space	(5)	
Air Conditioning	(5)	Replaced after the audit
Power supply	(5)	
General Management and Operation		
Organisation	(5)	
Competence of staff	(5)	
Air Inlet System	(5)	
Instrumentation		
Ozone	(5)	Also column measurements
Carbon monoxide	(5)	
Aerosol parameters*	(5)	Comprehensive suite of measurements
Reactive gas other than CO*	(5)	
Precipitation chemistry*	(5)	
Meteo*	(5)	Observations since 1781
Standards		
Ozone	(4)	No comparisons to other standards; evaluation with Lambert Beer law.
Carbon monoxide	(4)	No direct link to NOAA/GMD
Data Management		
Data acquisition	(4)	
Data processing	(5)	
Data submission	(5)	

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

Dübendorf, June 2006

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

APPENDIX

Global GAW Station Hohenpeissenberg

Site description

The Hohenpeissenberg GAW station has been described in detail elsewhere, e.g. [*Mannschreck, et al.*, 2004] (cf. www.dwd.de/en/FundE/Observator/MOHP/MOHP.htm for a list of publications) and the station is also registered in GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Programme

The observatory Hohenpeissenberg has a long history of meteorological measurements dating back to 1781 and comprises today an extensive suite of observations of the atmosphere. The status of the programme as of June 2006 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the HPB Station

Parameter	Current Instrument	Data Coverage (%)		
		<12 m	<3 y	Overall
Aerosol				
Major comp. (size fract.)	Multistage impactor			
Major inorg. comp. (coarse)	Filter sampling			
Light absorption coefficient and Single scattering albedo (SSA)	MAAP and Aethalometer (SSA calculated)			
Light scattering coefficient	Nephelometer			
Mass concentration (TSP)	Continuous gravimetry			
Multiwavelength optical depth	Filter Radiometry			
Number concentration	CPC (>3nm and >11nm)			
Number size distribution	OPC (Las-X)			
Ozone				
Surface ozone	UV absorption (TEI49C), chemiluminescence (UPK 8002), wet chemical method (KI)	99	99	99
Total column ozone	Brewer, Dobson and Microtops			
Vertical ozone profile	Brewer-Mast Sonde			
Vertical ozone profile	Lidar			
Reactive Gas				
VOCs (C2-C7, BTX)	GC-FID / GEMS / SCHIED			
Carbon monoxide	UV resonance fluorescence (AL5001) and NDIR (TEI48)	98	98	98
NO, NO2 and NOx	CLD / PLC (Ecophysics) CLD / BLC (TEI42C-TL) CLD / Mo-Conv. (TEI42C-TL)	97/88/88	98/95/95	98/95/95
NOy	CLD / Au Converter	94	94	94
H2O2 and ROOH	Enzyme Catalysed Fluorescence (ECF) (Aerolaser AL2002)	45/45	59/56	58/52
SO2	TEI43C-TL	99	98	98
H2SO4 and OH radical	Cimetidine (CIM) method			
PAN	GC/ECD (MeteoConsult)	71	69	62
Solar radiation				
Diffuse / global irradiance	Pyranometer			
UV Spectral	Brewer			
jNO2 und jO(1D)	Filter radiometer and Brewer			
Aerosol Optical Depth	PFR			
Precipitation Chemistry				
Electric conductivity and pH				
Inorganic ions	IC (Dionex)			
Trace metals	ICP-MS			
Radio Nuclide				
Radon	Tracerlab WLM-Plus/ASF200			
Ancillary Measurements				
Meteo (15 parameters)				

Missing data availability: no data coverage information was available at the time of the audit.

Ozone and Carbon Monoxide Distribution at Hohenpeissenberg

The monthly and yearly distributions of one hourly mean values for surface ozone and carbon monoxide for the year 2004 are shown in Figure 5.

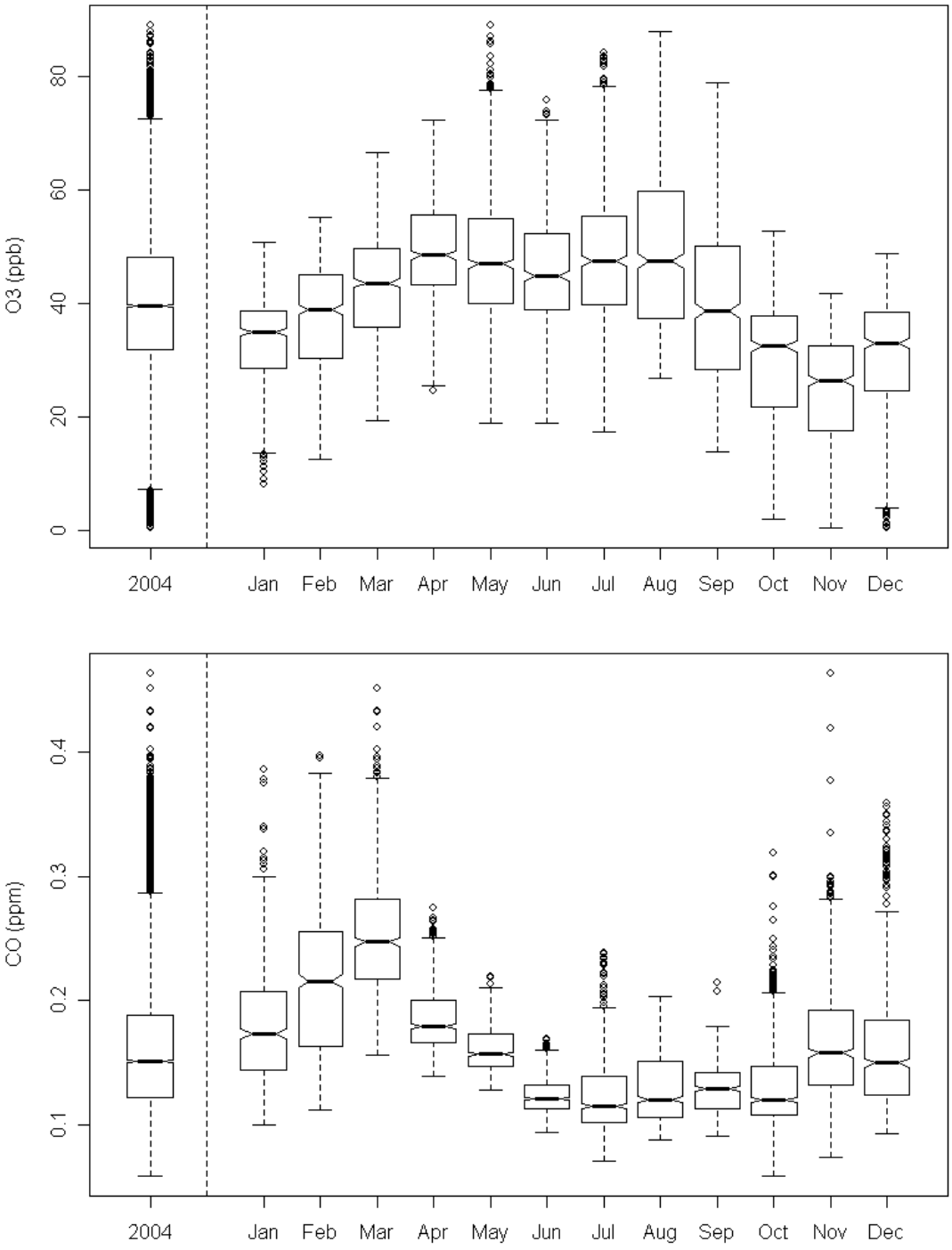

Figure 5. Yearly and Monthly Box Plots of 1-hourly aggregates for the year 2004 for Surface Ozone (upper panel) and Carbon Monoxide (lower panel). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organization and Contact Persons

The GAW activities are organised under the Meteorological Observatory Hohenpeissenberg and are directed by the GAW Country Contact Dr. Wolfgang Fricke (Figure 6). The observatory is run by the German Weather Service (DWD).

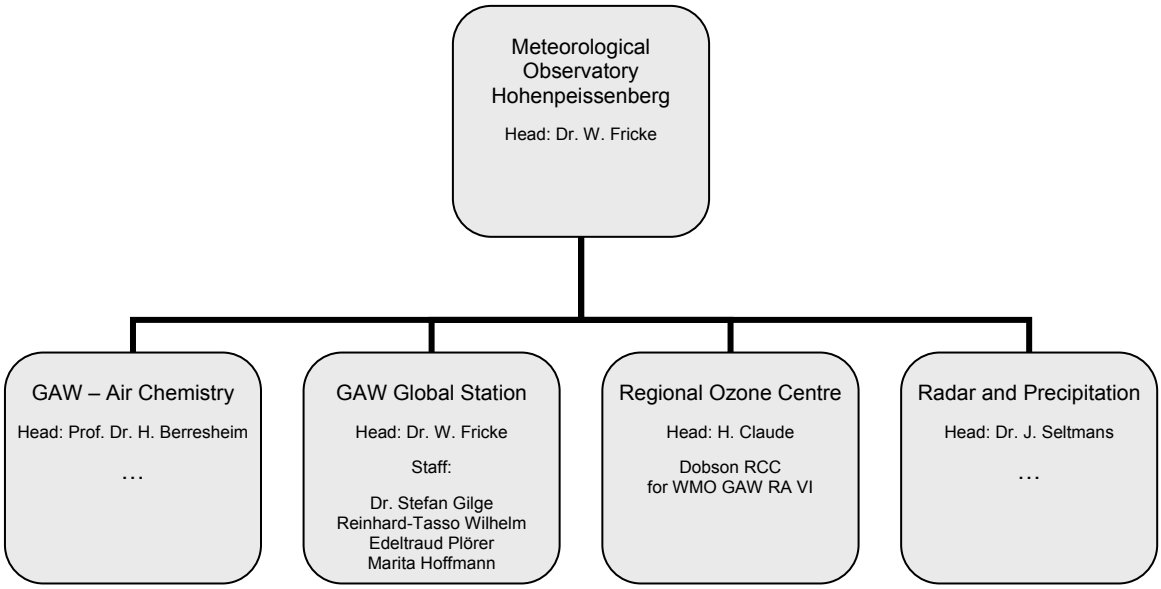

Figure 6. Organization of GAW Activities at Hohenpeissenberg as of June 2006.

Surface Ozone Measurements

Significant changes were made since the last WCC-Empa audit in 1997. The instrumentation remained basically the same, but a new ozone calibrator was purchased. All instruments are installed in a new laboratory with a new inlet system. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-a].

Monitoring Set-up and Procedures

Air Conditioning

The laboratory station is air conditioned (23°C), but the air conditioning system was not efficiently working during the audit. Room temperature exceeded 30°C. Replacement of the AC system is planned (cf. recommendation 2).

Air Inlet System

The air intake is mounted on the terrace 2 m above the laboratory. The inlet is made of PFA tubing (2 m 3/8", heated to 3°C above ambient temperature, followed by approx. 3 m 1/4" PFA tubing). Total flow is 3 l min^{-1}. Both ozone instruments and the SO_2 and CO instruments are connected to this inlet. All instruments are protected by Teflon filters. All materials used are adequate, and the residence time is estimated to be approximately 4 s.

Instrumentation

The surface ozone monitoring equipment has been described in the last audit report [*Herzog, et al.*, 1997]. 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 however is not regularly inter-compared to other ozone reference standards. Instrumental details for the ozone calibrator (OC) are summarised in Table 2 below. Analyser and calibrator are checked twice per year by calculating the ozone mixing ratios according to Lambert-Beer's-Law.

Operation and Maintenance
The instruments are checked for general operation whenever the station is visited (usually Monday to Friday). The inlet filter is replaced every two weeks, and in case of pollution episodes earlier. An inter-comparison with the ozone standard is done every three months.

Data Acquisition and Data Transfer
The analogue outputs of the ozone analysers are connected to the data acquisition system (MAUS) that stores one minute averages. Remote access to the data is possible through the internet.

Data Treatment
Data is regularly checked for consistency with time series plots. Corrections are applied to the data based on the inter-comparisons with the ozone standard every three months. Valid one minute data is then further averaged to one hourly and daily means.

Data Submission
Data is submitted to the GAW World Data Centre for Surface Ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG), usually with a maximum delay of one year.

Documentation
Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. All information is available as paper copies but is entered into an electronic data base as well. The instrument manuals are available at the site.

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

Setup and Connections
Table 2 details the experimental setup during the inter-comparison of transfer standard with the station analysers and the station standard. The data used for the evaluation was recorded by both WCC-Empa and Hohenpeissenberg data acquisition systems as indicated. Data of the HPB data acquisition system (HPB analysers) was used for the evaluation of the results. Data of the TEI49C was corrected according the usual station method using the calibration factor (0.973) from the last inter-comparison with the station standard. No further corrections were applied to the UPK instrument and the HPB 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
Main ozone analyzer (OA)	Model, S/N	TEI 49C #56028-306
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.4; COEFF = 1.020
Back-up ozone analyzer (OA)	Model, S/N	UPK 8002 #92062
	Principle	Chemiluminescence
	Range	0-100 ppb
	Settings	ZERO = 0.12 ; SPAN = 4.18
Ozone standard (OC)	Model, S/N	TEI 49C-PS #0423807729
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = -0.1; COEFF = 1.024
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 and station standard OC	One minute aggregates from digital output (custom designed LabView programme)
	Analysers OA	One minute aggregates from analogue output (MAUS)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	907.3 (Station reference)
	TS	901.4, adjusted to 907.3 (680.6 mmHg)
	TEI 49C	896.8 (not adjusted because the instrument was calibrated without adjustment of the pressure sensor)
	UPK	NA (no pressure sensor)
	TEI49 C-PS	905.6 (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)		15
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		OA: 8 runs (20 thru 21 June, 2006) OC: 12 runs (21 thru 22 June, 2006)

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 (main analyser OA), Table 4 (back-up analyser OA) and Table 5 (standard 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 analyser (OA) and ozone standard (OC) 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 HPB main ozone analyzer (OA) TEI 49C #56028-306 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-20 13:25	1	0	0.23	0.42	0	0.15	0.19
2006-06-20 13:40	1	20	19.71	20.06	0	0.11	0.11
2006-06-20 13:55	1	40	39.79	40.20	0	0.10	0.18
2006-06-20 14:10	1	50	49.88	50.40	0	0.09	0.19
2006-06-20 14:25	1	10	9.94	10.06	0	0.13	0.18
2006-06-20 14:40	1	90	89.89	90.74	0	0.05	0.11
2006-06-20 14:55	1	70	69.93	70.70	0	0.09	0.27
2006-06-20 15:10	1	30	30.00	30.25	0	0.07	0.19
2006-06-20 15:25	1	60	59.95	60.55	0	0.07	0.10
2006-06-20 15:40	1	80	79.95	80.63	0	0.09	0.48
2006-06-20 15:55	2	0	0.25	0.21	0	0.09	0.15
2006-06-20 16:10	2	90	89.92	90.88	0	0.08	0.17
2006-06-20 16:25	2	30	29.99	30.20	0	0.13	0.21
2006-06-20 16:40	2	10	10.06	10.09	0	0.10	0.10
2006-06-20 16:55	2	40	39.96	40.43	0	0.11	0.13
2006-06-20 17:10	2	80	79.93	80.51	0	0.05	0.15
2006-06-20 17:25	2	60	59.98	60.46	0	0.05	0.18
2006-06-20 17:40	2	20	20.06	20.10	0	0.07	0.20
2006-06-20 17:55	2	50	49.98	50.35	0	0.10	0.18
2006-06-20 18:10	2	70	69.93	70.33	0	0.08	0.40
2006-06-20 18:25	3	0	0.27	0.07	0	0.06	0.14
2006-06-20 18:40	3	10	10.02	9.87	0	0.09	0.19
2006-06-20 18:55	3	80	79.91	80.59	0	0.08	0.19
2006-06-20 19:10	3	60	59.96	60.35	0	0.08	0.15
2006-06-20 19:25	3	40	40.01	40.26	0	0.11	0.21
2006-06-20 19:40	3	50	49.99	50.29	0	0.04	0.18
2006-06-20 19:55	3	70	69.95	70.43	0	0.07	0.15
2006-06-20 20:10	3	20	20.07	19.96	0	0.11	0.12
2006-06-20 20:25	3	30	29.98	30.09	0	0.10	0.13
2006-06-20 20:40	3	90	89.91	90.47	0	0.08	0.52
2006-06-20 20:55	4	0	0.23	0.13	0	0.09	0.32
2006-06-20 21:10	4	20	19.98	20.08	0	0.10	0.15
2006-06-20 21:25	4	40	39.98	40.23	0	0.08	0.10
2006-06-20 21:40	4	50	49.97	50.26	0	0.14	0.13
2006-06-20 21:55	4	10	9.96	9.81	0	0.23	0.29
2006-06-20 22:10	4	90	89.94	90.70	0	0.09	0.21
2006-06-20 22:25	4	70	70.00	70.53	0	0.08	0.15
2006-06-20 22:40	4	30	30.03	29.97	0	0.11	0.23
2006-06-20 22:55	4	60	59.95	60.58	0	0.09	0.14
2006-06-20 23:10	4	80	79.93	80.48	0	0.09	0.49
2006-06-20 23:25	5	0	0.25	0.16	0	0.05	0.51
2006-06-20 23:40	5	90	89.91	90.70	0	0.10	0.30
2006-06-20 23:55	5	30	30.00	30.12	0	0.12	0.24

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-21 00:10	5	10	9.95	9.94	0	0.20	0.25
2006-06-21 00:25	5	40	39.97	40.08	0	0.07	0.24
2006-06-21 00:40	5	80	79.91	80.33	0	0.08	0.23
2006-06-21 00:55	5	60	59.98	60.21	0	0.07	0.21
2006-06-21 01:10	5	20	20.02	19.93	0	0.10	0.20
2006-06-21 01:25	5	50	49.98	50.04	0	0.07	0.24
2006-06-21 01:40	5	70	69.93	70.14	0	0.06	0.40
2006-06-21 01:55	6	0	0.27	-0.02	0	0.06	0.18
2006-06-21 02:10	6	10	10.25	9.78	0	0.54	0.39
2006-06-21 02:25	6	80	79.91	80.32	0	0.06	0.33
2006-06-21 02:40	6	60	59.95	60.27	0	0.07	0.26
2006-06-21 02:55	6	40	39.99	40.21	0	0.09	0.15
2006-06-21 03:10	6	50	49.97	50.15	0	0.09	0.26
2006-06-21 03:25	6	70	69.92	70.18	0	0.08	0.23
2006-06-21 03:40	6	20	20.02	19.84	0	0.08	0.16
2006-06-21 03:55	6	30	30.01	29.97	0	0.12	0.19
2006-06-21 04:10	6	90	89.91	90.34	0	0.06	0.62
2006-06-21 04:25	7	0	0.23	0.05	0	0.09	0.46
2006-06-21 04:40	7	20	19.96	20.02	0	0.08	0.18
2006-06-21 04:55	7	40	39.95	40.03	0	0.09	0.18
2006-06-21 05:10	7	50	49.94	50.19	0	0.10	0.15
2006-06-21 05:25	7	10	9.95	9.77	0	0.27	0.18
2006-06-21 05:40	7	90	89.90	90.56	0	0.08	0.25
2006-06-21 05:55	7	70	69.95	70.36	0	0.07	0.19
2006-06-21 06:10	7	30	30.06	30.13	0	0.09	0.21
2006-06-21 06:25	7	60	59.99	60.30	0	0.10	0.15
2006-06-21 06:40	7	80	79.96	80.20	0	0.07	0.68
2006-06-21 06:55	8	0	0.23	-0.01	0	0.05	0.14
2006-06-21 07:10	8	90	90.03	90.48	0	0.06	0.15
2006-06-21 07:25	8	30	30.12	30.07	0	0.11	0.19
2006-06-21 07:40	8	10	10.09	9.74	0	0.07	0.15
2006-06-21 07:55	8	40	39.93	40.11	0	0.09	0.06
2006-06-21 08:10	8	80	79.87	80.29	0	0.10	0.16
2006-06-21 08:25	8	60	59.89	60.11	0	0.08	0.21
2006-06-21 08:40	8	20	19.97	19.94	0	0.11	0.17
2006-06-21 08:55	8	50	49.92	50.12	0	0.11	0.17
2006-06-21 09:10	8	70	69.90	70.39	0	0.06	0.27

[#]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 HPB back-up ozone analyzer (OA) UPK 8002 # 92062 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-20 13:25	1	0	0.23	0.47	0	0.15	0.09
2006-06-20 13:40	1	20	19.71	19.89	0	0.11	0.16
2006-06-20 13:55	1	40	39.79	39.89	0	0.10	0.19
2006-06-20 14:10	1	50	49.88	50.10	0	0.09	0.20
2006-06-20 14:25	1	10	9.94	10.11	0	0.13	0.46
2006-06-20 14:40	1	90	89.89	90.51	0	0.05	0.27
2006-06-20 14:55	1	70	69.93	70.29	0	0.09	0.29
2006-06-20 15:10	1	30	30.00	30.15	0	0.07	0.27
2006-06-20 15:25	1	60	59.95	60.31	0	0.07	0.27
2006-06-20 15:40	1	80	79.95	79.76	0	0.09	2.81
2006-06-20 15:55	2	0	0.25	0.51	0	0.09	0.67
2006-06-20 16:10	2	90	89.92	90.37	0	0.08	0.65

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-20 16:25	2	30	29.99	30.13	0	0.13	0.16
2006-06-20 16:40	2	10	10.06	10.11	0	0.10	0.15
2006-06-20 16:55	2	40	39.96	40.27	0	0.11	0.34
2006-06-20 17:10	2	80	79.93	80.59	0	0.05	0.45
2006-06-20 17:25	2	60	59.98	60.51	0	0.05	0.24
2006-06-20 17:40	2	20	20.06	20.34	0	0.07	0.21
2006-06-20 17:55	2	50	49.98	50.17	0	0.10	0.24
2006-06-20 18:10	2	70	69.93	69.60	0	0.08	2.15
2006-06-20 18:25	3	0	0.27	0.34	0	0.06	0.05
2006-06-20 18:40	3	10	10.02	10.08	0	0.09	0.45
2006-06-20 18:55	3	80	79.91	80.62	0	0.08	0.40
2006-06-20 19:10	3	60	59.96	60.57	0	0.08	0.19
2006-06-20 19:25	3	40	40.01	40.47	0	0.11	0.19
2006-06-20 19:40	3	50	49.99	50.62	0	0.04	0.19
2006-06-20 19:55	3	70	69.95	70.53	0	0.07	0.58
2006-06-20 20:10	3	20	20.07	20.13	0	0.11	0.24
2006-06-20 20:25	3	30	29.98	30.39	0	0.10	0.36
2006-06-20 20:40	3	90	89.91	90.04	0	0.08	2.84
2006-06-20 20:55	4	0	0.23	1.06	0	0.09	2.16
2006-06-20 21:10	4	20	19.98	20.29	0	0.10	0.19
2006-06-20 21:25	4	40	39.98	40.29	0	0.08	0.20
2006-06-20 21:40	4	50	49.97	50.33	0	0.14	0.38
2006-06-20 21:55	4	10	9.96	10.15	0	0.23	0.56
2006-06-20 22:10	4	90	89.94	91.17	0	0.09	0.43
2006-06-20 22:25	4	70	70.00	70.72	0	0.08	0.36
2006-06-20 22:40	4	30	30.03	30.31	0	0.11	0.27
2006-06-20 22:55	4	60	59.95	61.08	0	0.09	0.27
2006-06-20 23:10	4	80	79.93	80.29	0	0.09	2.64
2006-06-20 23:25	5	0	0.25	1.31	0	0.05	3.05
2006-06-20 23:40	5	90	89.91	91.08	0	0.10	0.75
2006-06-20 23:55	5	30	30.00	30.43	0	0.12	0.26
2006-06-21 00:10	5	10	9.95	9.97	0	0.20	0.26
2006-06-21 00:25	5	40	39.97	40.35	0	0.07	0.42
2006-06-21 00:40	5	80	79.91	80.74	0	0.08	0.39
2006-06-21 00:55	5	60	59.98	60.51	0	0.07	0.42
2006-06-21 01:10	5	20	20.02	20.21	0	0.10	0.12
2006-06-21 01:25	5	50	49.98	50.42	0	0.07	0.11
2006-06-21 01:40	5	70	69.93	69.77	0	0.06	2.52
2006-06-21 01:55	6	0	0.27	0.31	0	0.06	0.07
2006-06-21 02:10	6	10	10.25	10.24	0	0.54	0.47
2006-06-21 02:25	6	80	79.91	80.67	0	0.06	0.29
2006-06-21 02:40	6	60	59.95	60.56	0	0.07	0.35
2006-06-21 02:55	6	40	39.99	40.47	0	0.09	0.25
2006-06-21 03:10	6	50	49.97	50.65	0	0.09	0.29
2006-06-21 03:25	6	70	69.92	70.56	0	0.08	0.50
2006-06-21 03:40	6	20	20.02	20.20	0	0.08	0.08
2006-06-21 03:55	6	30	30.01	30.48	0	0.12	0.50
2006-06-21 04:10	6	90	89.91	90.03	0	0.06	3.22
2006-06-21 04:25	7	0	0.23	0.98	0	0.09	1.98
2006-06-21 04:40	7	20	19.96	20.31	0	0.08	0.16
2006-06-21 04:55	7	40	39.95	40.25	0	0.09	0.20
2006-06-21 05:10	7	50	49.94	50.14	0	0.10	0.50
2006-06-21 05:25	7	10	9.95	10.02	0	0.27	0.70
2006-06-21 05:40	7	90	89.90	90.85	0	0.08	0.33
2006-06-21 05:55	7	70	69.95	70.66	0	0.07	0.46

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-21 06:10	7	30	30.06	30.45	0	0.09	0.24
2006-06-21 06:25	7	60	59.99	60.54	0	0.10	0.38
2006-06-21 06:40	7	80	79.96	80.00	0	0.07	3.03
2006-06-21 06:55	8	0	0.23	0.24	0	0.05	0.08
2006-06-21 07:10	8	90	90.03	90.21	0	0.06	0.54
2006-06-21 07:25	8	30	30.12	30.02	0	0.11	0.18
2006-06-21 07:40	8	10	10.09	9.79	0	0.07	0.20
2006-06-21 07:55	8	40	39.93	40.01	0	0.09	0.48
2006-06-21 08:10	8	80	79.87	80.28	0	0.10	0.55
2006-06-21 08:25	8	60	59.89	60.33	0	0.08	0.23
2006-06-21 08:40	8	20	19.97	20.07	0	0.11	0.13
2006-06-21 08:55	8	50	49.92	50.27	0	0.11	0.21
2006-06-21 09:10	8	70	69.90	70.47	0	0.06	0.33

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

Table 5. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the HPB ozone calibrator (OC) TEI 49C-PS # 0423807729 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OC (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-21 14:10	1	0	0.24	0.08	0	0.10	0.26
2006-06-21 14:25	1	30	29.84	29.69	0	0.15	0.20
2006-06-21 14:40	1	90	89.85	89.95	0	0.05	0.16
2006-06-21 14:55	1	140	139.78	140.11	0	0.07	0.23
2006-06-21 15:10	1	60	59.94	60.04	0	0.10	0.14
2006-06-21 15:25	1	190	189.73	190.29	0	0.09	0.15
2006-06-21 15:40	2	0	0.22	0.02	0	0.08	0.27
2006-06-21 15:55	2	30	29.94	29.98	0	0.07	0.19
2006-06-21 16:10	2	60	59.91	59.95	0	0.07	0.13
2006-06-21 16:25	2	190	189.71	190.38	0	0.05	0.26
2006-06-21 16:40	2	140	139.82	140.21	0	0.06	0.11
2006-06-21 16:55	2	90	89.98	90.25	0	0.07	0.17
2006-06-21 17:10	3	0	0.19	0.07	0	0.08	0.13
2006-06-21 17:25	3	190	189.75	190.46	0	0.06	0.17
2006-06-21 17:40	3	30	30.07	30.03	0	0.11	0.17
2006-06-21 17:55	3	90	89.92	90.25	0	0.03	0.13
2006-06-21 18:10	3	60	59.89	60.12	0	0.08	0.14
2006-06-21 18:25	3	140	139.78	140.23	0	0.09	0.33
2006-06-21 18:40	4	0	0.24	-0.04	0	0.11	0.12
2006-06-21 18:55	4	30	29.70	29.71	0	0.44	0.27
2006-06-21 19:10	4	90	89.85	90.14	0	0.08	0.14
2006-06-21 19:25	4	140	139.76	140.39	0	0.08	0.31
2006-06-21 19:40	4	60	59.92	60.09	0	0.07	0.11
2006-06-21 19:55	4	190	189.74	190.55	0	0.06	0.21
2006-06-21 20:10	5	0	0.20	0.04	0	0.08	0.16
2006-06-21 20:25	5	30	29.90	29.84	0	0.15	0.15
2006-06-21 20:40	5	60	59.94	60.17	0	0.09	0.17
2006-06-21 20:55	5	190	189.74	190.69	0	0.07	0.14
2006-06-21 21:10	5	140	139.87	140.44	0	0.07	0.20
2006-06-21 21:25	5	90	89.94	90.29	0	0.05	0.22
2006-06-21 21:40	6	0	0.27	0.16	0	0.13	0.15
2006-06-21 21:55	6	190	189.74	190.51	0	0.07	0.26
2006-06-21 22:10	6	30	30.00	29.95	0	0.07	0.10
2006-06-21 22:25	6	90	89.91	90.37	0	0.10	0.17
2006-06-21 22:40	6	60	59.94	60.06	0	0.09	0.17
2006-06-21 22:55	6	140	139.77	140.32	0	0.08	0.18

DateTime (UTC+1)	Run	Level	TS (ppb)	OC (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2006-06-21 23:10	7	0	0.21	0.00	0	0.10	0.19
2006-06-21 23:25	7	30	30.00	30.01	0	0.11	0.18
2006-06-21 23:40	7	90	89.91	90.40	0	0.06	0.23
2006-06-21 23:55	7	140	139.85	140.57	0	0.08	0.20
2006-06-22 00:10	7	60	59.97	60.20	0	0.07	0.19
2006-06-22 00:25	7	190	189.79	190.74	0	0.06	0.25
2006-06-22 00:40	8	0	0.28	-0.03	0	0.08	0.12
2006-06-22 00:55	8	30	29.98	29.98	0	0.11	0.20
2006-06-22 01:10	8	60	59.94	60.13	0	0.06	0.14
2006-06-22 01:25	8	190	189.74	190.70	0	0.08	0.21
2006-06-22 01:40	8	140	139.88	140.62	0	0.04	0.11
2006-06-22 01:55	8	90	89.96	90.42	0	0.06	0.18
2006-06-22 02:10	9	0	0.26	0.03	0	0.09	0.12
2006-06-22 02:25	9	190	189.74	190.81	0	0.07	0.16
2006-06-22 02:40	9	30	30.02	30.05	0	0.08	0.09
2006-06-22 02:55	9	90	89.92	90.39	0	0.09	0.10
2006-06-22 03:10	9	60	59.96	60.31	0	0.11	0.18
2006-06-22 03:25	9	140	139.82	140.65	0	0.10	0.14
2006-06-22 03:40	10	0	0.24	0.03	0	0.12	0.19
2006-06-22 03:55	10	30	29.97	29.84	0	0.08	0.21
2006-06-22 04:10	10	90	89.93	90.36	0	0.09	0.15
2006-06-22 04:25	10	140	139.80	140.63	0	0.08	0.12
2006-06-22 04:40	10	60	59.96	60.19	0	0.04	0.19
2006-06-22 04:55	10	190	189.79	190.93	0	0.05	0.17
2006-06-22 05:10	11	0	0.24	0.01	0	0.07	0.19
2006-06-22 05:25	11	30	29.96	29.99	0	0.08	0.19
2006-06-22 05:40	11	60	59.93	60.13	0	0.10	0.18
2006-06-22 05:55	11	190	189.84	190.80	0	0.20	0.33
2006-06-22 06:10	11	140	140.29	140.88	0	0.07	0.19
2006-06-22 06:25	11	90	90.48	90.67	0	0.11	0.22
2006-06-22 06:40	12	0	0.20	0.14	0	0.07	0.09
2006-06-22 06:55	12	190	190.18	190.36	0	0.13	0.21
2006-06-22 07:10	12	30	30.25	30.15	0	0.12	0.09
2006-06-22 07:25	12	90	89.96	89.90	0	0.07	0.16
2006-06-22 07:40	12	60	59.95	59.89	0	0.06	0.12
2006-06-22 07:55	12	140	139.83	139.92	0	0.11	0.17

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

Figure 7 - Figure 9 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.

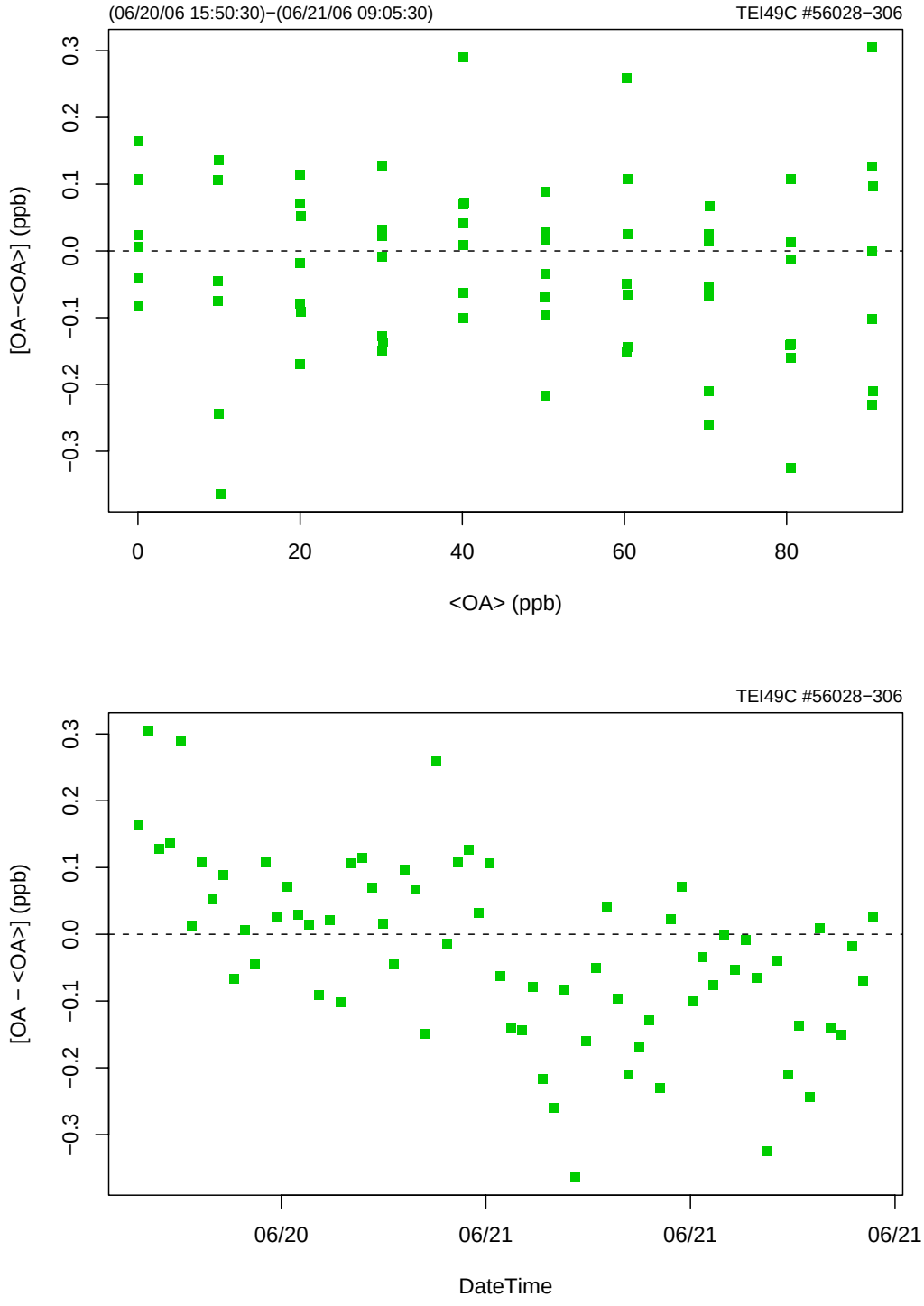

Figure 7. Regression residuals of the main HPB ozone analyser (TEI 49C) as a function of concentration (upper panel) and time (lower panel).

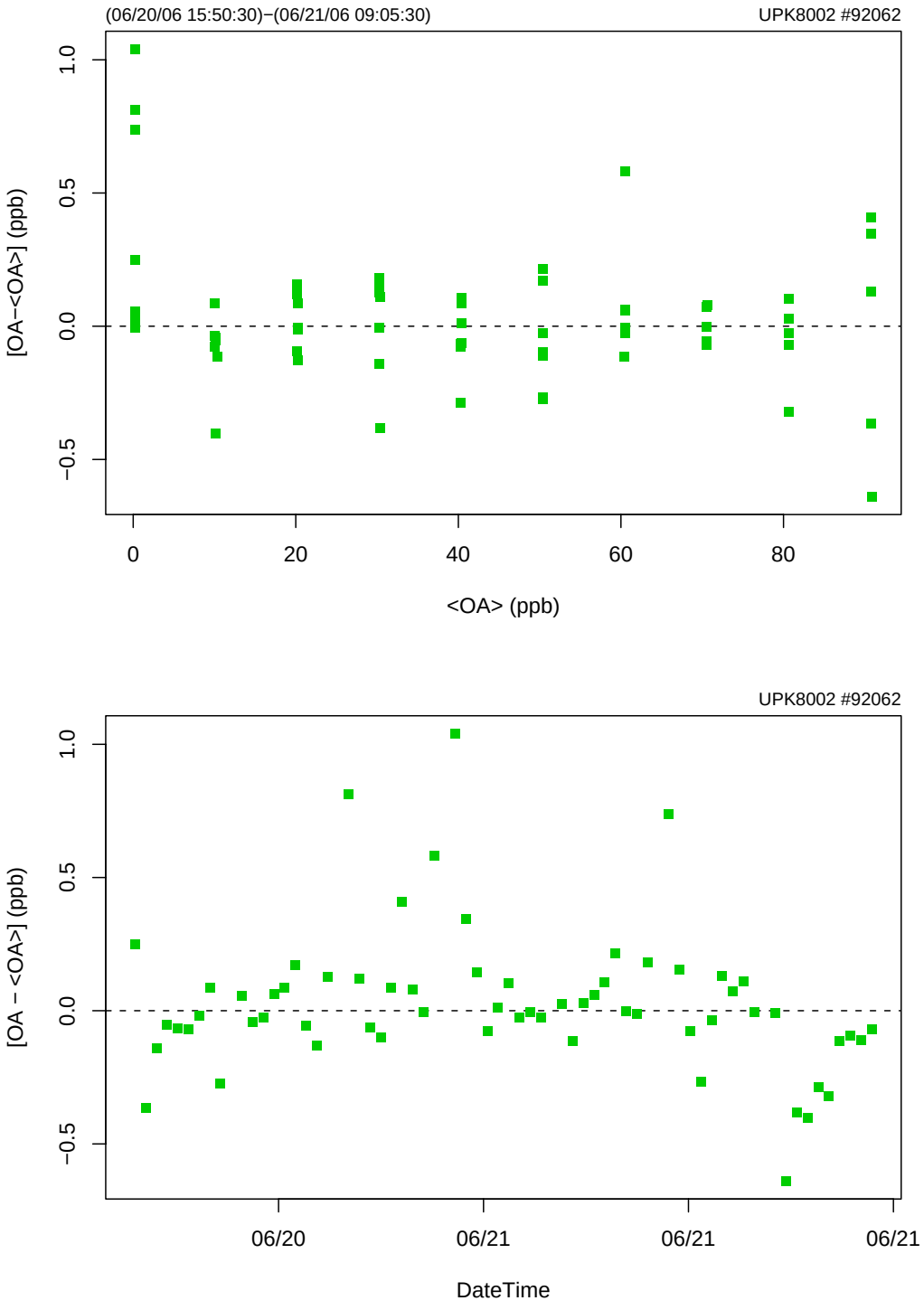

Figure 8. Regression residuals of the back-up HPB ozone analyser (UPK 8002) as a function of concentration (upper panel) and time (lower panel).

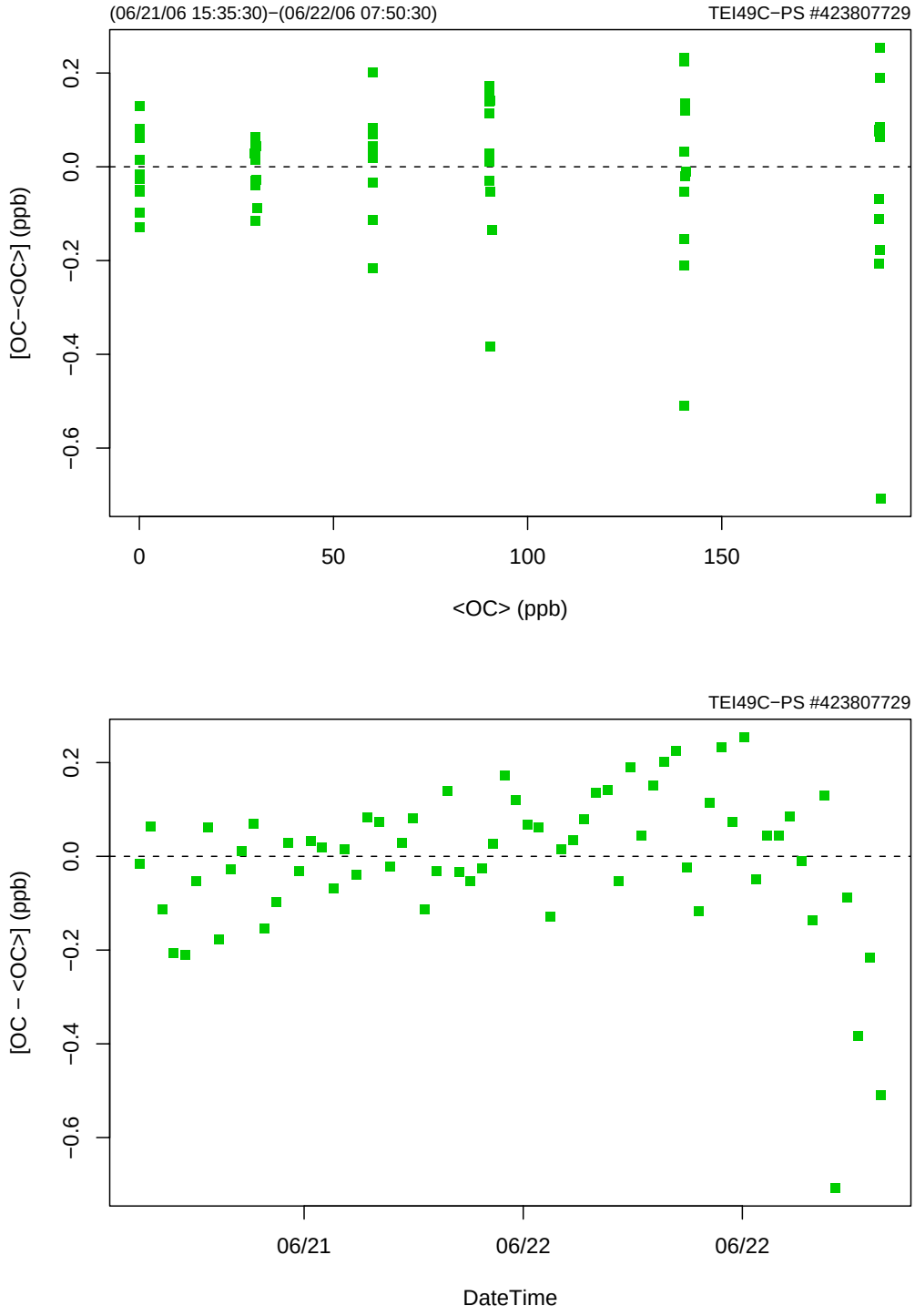

Figure 9. Regression residuals of the HPB ozone calibrator (TEI 49C-PS) as a function of concentration (upper panel) and time (lower panel).

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:

$$X_{O3}\ (ppb) = ([OA] + 0.01\ ppb) / 1.011$$

$$u_{O3}\ (ppb) = sqrt(0.27\ ppb^2 + 2.55e\text{-}05 * X_{O3}^2) \quad (1a)$$

UPK

$$X_{O3}\ (ppb) = ([OA] - 0.21\ ppb) / 1.010$$

$$u_{O3}\ (ppb) = sqrt(0.32\ ppb^2 + 2.55e\text{-}05 * X_{O3}^2) \quad (1b)$$

TEI49C-PS

$$X_{O3}\ (ppb) = ([OC] - 0.01\ ppb) / 1.007$$

$$u_{O3}\ (ppb) = sqrt(0.29\ ppb^2 + 2.57e\text{-}05 * X_{O3}^2) \quad (1c)$$

Changes Made to Instrument

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

Conclusions

The findings of this audit demonstrate good agreement between HPB ozone measurements and WCC-Empa, with HPB results consistently being approximately 1% higher compared to WCC-Empa. Therefore only minor and mainly technical recommendations are proposed by WCC-Empa.

Carbon Monoxide Measurements

Significant changes were made since the last WCC-Empa audit in 1997. All instruments were installed in a new laboratory with a new inlet system. The NDIR analyser was complemented by a UV-Fluorescence instrument and is running since then as a back-up system only. 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 air inlet system is identical to the one for surface ozone as described above for the NDIR instrument. The UV-Fluorescence instrument has its own 1/8" inlet tubing with a total length of approximately 4 m (same inlet location as for the other instruments). Residence times were estimated to be 4 s (TEI 48S) and 9 s (AL5001).

Instrumentation

The HPB station is equipped with two carbon monoxide analysers. The system which was originally installed in 1995 (NDIR, TEI 48S) was replaced in 2004 by an Aerolaser AL5001 and is now running as a back-up system. The TEI 48S instrument was modified [*Parrish, et al.*, 1994] to achieve better precision and lower detection limits. Instrumental details are listed in Table 8 below.

Standards and Calibration

The station is equipped with one cylinder in the 1000 ppb range for direct calibration of the Aerolaser AL5001 instrument, and a dilution system based on a higher concentration standard and mass flow controllers for manual span checks of the TEI 48S system. Table 6 gives details of the cylinders currently available at the station. The instruments are currently calibrated in daily (AL5001) and weekly (TEI 48S) intervals. Once per month the Aerolaser system is used to check the dilution unit to establish a link between the two calibration systems. Calibrations are started manually for both systems, and the NDIR system switch between zero and ambient air

measurements every ten minutes to account for zero drift. Ambient data are corrected using the zero values of the automatic zero bracketing the measurement data.

Table 6. Carbon monoxide standards available at HPB station

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Riessner Gase, #210 Direct use	1000±50 ppb, CO 99.9% in synthetic air 99.999% 970 ppb assigned by HPB based on NOAA/GMD standards	2004/2006	HPB	2004-09	continues
Messer, #9639C Dilution unit	43300±866 ppb, CO 99.997% in synthetic air 99.999%		Messer		continues

Operation and Maintenance

The instruments are checked for general operation whenever the station is visited (usually every weekday). The inlet filter is replaced at least every 2 weeks. Manual calibrations are started every working day (AL5001) and once per week (TEI 48S). The optical system of the TEI 48S is checked every 6 months and cleaned when necessary. The AL5001 optical system is cleaned by Aerolaser GmbH when the sensitivity is lower than 20 counts/ppb.

Data Acquisition and Data Transfer

The analogue (TEI 48S) and the RS-232 (AL5001) output are connected to the data acquisition system (MAUS) that stores one minute averages. Remote access to the data is possible through the internet.

Data Treatment

Data of both instruments is regularly checked for consistency with time series plots.
TEI 48S:
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. The average zero reading of the last five minutes of the 10-minute zero check before and the first five minutes of the 10-minute zero check after the 10 minute ambient measurement is subtracted from the 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 except a correction factor for the calibration gas. Currently all values a multiplied by 0.97 because the calibration standard was assigned 970 ppb CO instead of the 1000 ppb of the certificate. One minute averages are stored and further averaged to one hourly and daily means.

Data Submission

Data is submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG), usually with a maximum delay of one year.

Documentation

Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. All information is available as paper copies but is entered into an electronic data base as well. The instrument manuals are available at the site.

Inter-Comparison of Carbon Monoxide Analysers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation-b] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 8 (dilution system) and Table 7 (WCC-Empa cylinders) below.

Setup and Connections

The AL5001 analyser was inter-compared by direct measurements of travelling standards. Details of this experiment are shown in Table 7. In addition, both analysers were also inter-compared using a dilution system, and the experimental setup is shown in Table 8. The data used for the evaluation was recorded by the HPB data acquisition system, and only corrections according to the usual station methods were applied. These corrections included a zero compensation (TEI 48S) and a correction of the bias of the calibration standard (AL5001). Two levels at 400 ppb and 500 ppb CO were excluded in the data evaluation of the AL5001 instrument due to excessive noise. The reason could not further be assessed; the laboratory temperature was exceeding 30°C during this experiment. However, it seems relatively unlikely that this caused the additional instrument noise.

Table 7. 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)
Field instrument (Model, S/N)	See Table 8 below (only AL5001)
Connection of TS to field instrument	Sample inlet including inlet filters
Data Acquisition	1-minute aggregates from HPB data acquisition
Levels (ppb)	Level Cylinder Reference St. Uncert. 1 Zero Air 0.00 0.50 2 FF31496 73.41 0.69 3 041109_FA01467 134.68 0.83 4 041109_0627B 154.58 0.82 5 050415_FA02466 178.54 1.21 6 030703_FA01477 199.38 1.00 7 050701_FA02505 359.22 1.82
Duration per level (min)	Variable, between 17 and 36 min
Sequence of levels	Randomised sequence
Runs	1 run (21 June, 2006)

Table 8. Experimental details of the carbon monoxide inter-comparison with the dilution system (both 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)	
Field instruments	Model, S/N	TEI 48S #50878-286	AL5001 #142
	Principle	NDIR, Gas Filter Correlation Technique	Vacuum UV-Fluorescence
	Modification	See [*Parrish, et al.*, 1994]	None
	Range	1 ppm	10 ppm
	Settings	Zero = 192; SPAN = 980	NA (frequent calibrations); Typical conditions during the audit: Sens 74.7 counts/ppb, Zero 4670 counts
	Pressure Sensor	710 mmHg (946.4 hPa); Station ref. 904.8 hPa; no adjustments were made	NA
Connection of TS to field instrument		Sample inlet including inlet filters	
Data Acquisition		1-minute aggregates from HPB data acquisition	
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	
Duration per level (min)		120; TEI 48S: Automatic zero checks every 10 min Level 8 and 9 were not used for the assessment of the AL5001 analyser.	
Sequence of levels		Randomised fixed sequence	
Runs		1 run (21 thru 22 June, 2006)	

NA: Not applicable

Results

Inter-comparison with the dilution system

Each carbon monoxide level was applied for 120 minutes, which resulted in a maximum of 120 useable 1' averages per level and run for the AL5001, and 6 usable 10' averages for the TEI 48S instrument. These were corrected for zero-drift (TEI 48S) and further aggregated by level before use in the assessment (cf. Table 9, AL5001, and Table 10, TEI 48S).

Table 9. CO aggregates computed from 1' averages for each level during the inter-comparison of the HPB 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.
(06/06/21 14:12:00)	0.00	0.03	0.73	0.29	119
(06/06/21 16:12:00)	101.57	0.50	101.40	0.29	119
(06/06/21 18:11:30)	76.31	0.38	76.54	0.38	118
(06/06/21 20:11:00)	252.79	1.25	252.23	0.45	119
(06/06/21 22:10:30)	303.22	1.50	302.35	0.51	118
(06/06/22 00:10:25)	152.04	0.75	151.99	0.53	116
(06/06/22 02:09:30)	202.22	1.00	201.76	0.43	118
(06/06/22 04:09:00)	504.74	2.50	500.21*	0.70*	119
(06/06/22 06:07:00)	403.93	2.00	406.88*	6.54*	115

* Not used in the assessment due to large deviations and high noise.

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

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	TEI 48S CO (ppb)	sdCO (ppb)	No. 10' av.
(06/06/21 16:25:00)	101.57	0.50	101.33	2.50	6
(06/06/21 18:25:00)	76.31	0.38	73.50	2.43	6
(06/06/21 20:25:00)	252.79	1.25	257.17	2.79	6
(06/06/21 22:25:00)	303.22	1.50	305.50	4.68	6
(06/22/03 00:25:00)	152.04	0.75	148.83	4.75	6
(06/22/03 02:15:00)	202.22	1.00	198.60	2.61	5
(06/22/03 04:25:00)	504.74	2.50	501.50	4.18	6
(06/22/03 06:15:00)	403.93	2.00	406.60	4.72	5
(06/22/03 08:45:00)	0.00	0.03	-0.75	1.49	8

Figure 10 shows the regression residuals of the AL5001 plotted against time and concentration. 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. However, the last two measurements at higher concentrations show significantly larger residuals to the linear regression and were not used in the evaluation of the inter-comparison result. These values were obtained in the morning of 22 June, when the air-conditioning of the laboratory was no longer working and indoor temperature exceeded 32°C.

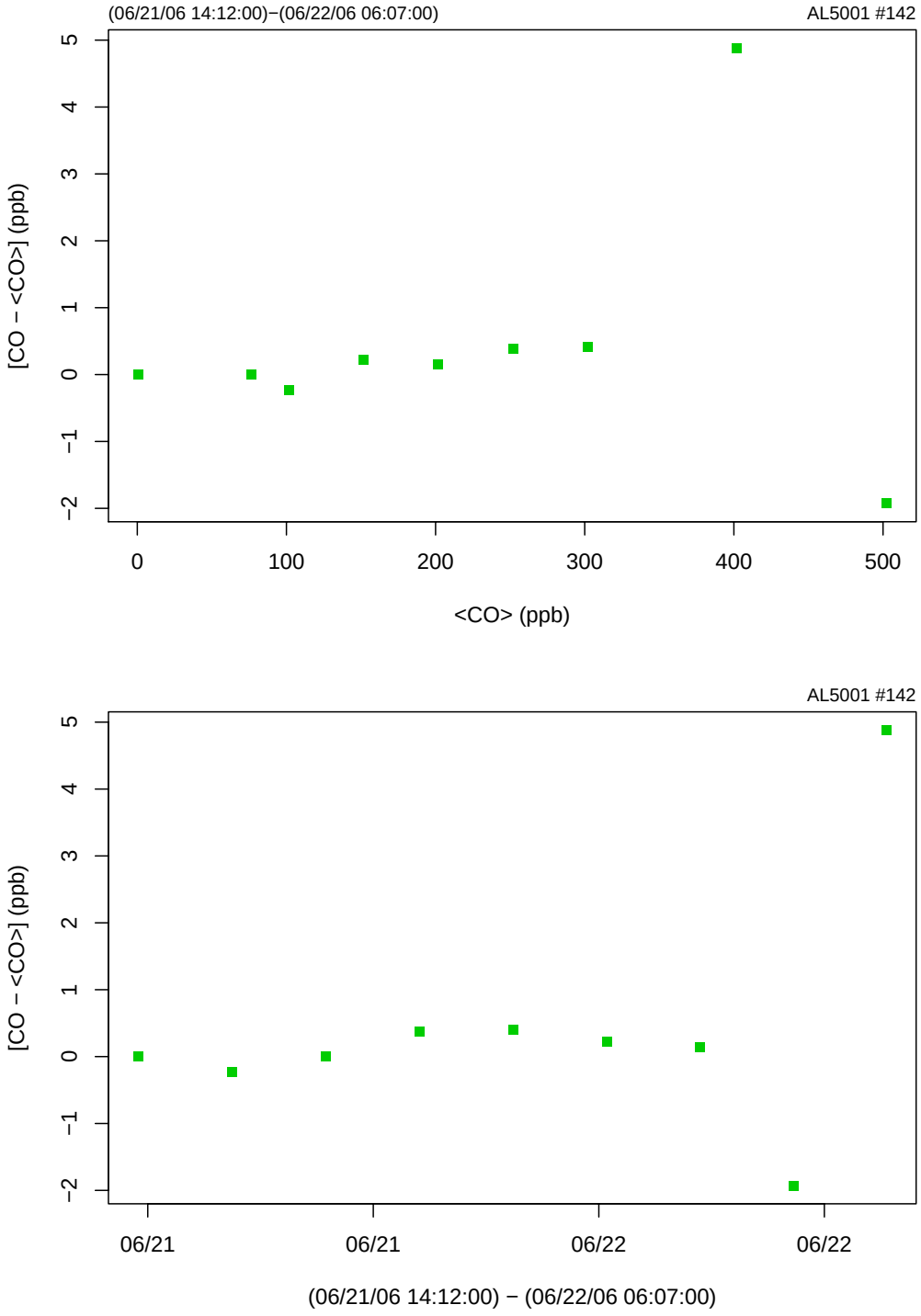

Figure 10. Regression residuals of the HPB AL5001 carbon monoxide analyser. Points represent averages of valid 1'-aggregates. Upper panel: concentration dependence; Lower panel: time dependence.

Based on these inter-comparison results (excluding levels at 400 ppb and 500 ppb CO), unbiased carbon monoxide volume mixing ratios of the AL5001 analyser X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the 1' inter-comparison data using equation

X_{CO} (ppb) = ([CO] - 0.7 ppb)/ 0.994

u_{CO} (ppb) = =sqrt(1.1 ppb^2 + 5.01e-06 * X_{CO}^2) (2a)

Figure 11 shows the regression residuals of the TEI 48S plotted against time and concentration. 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.

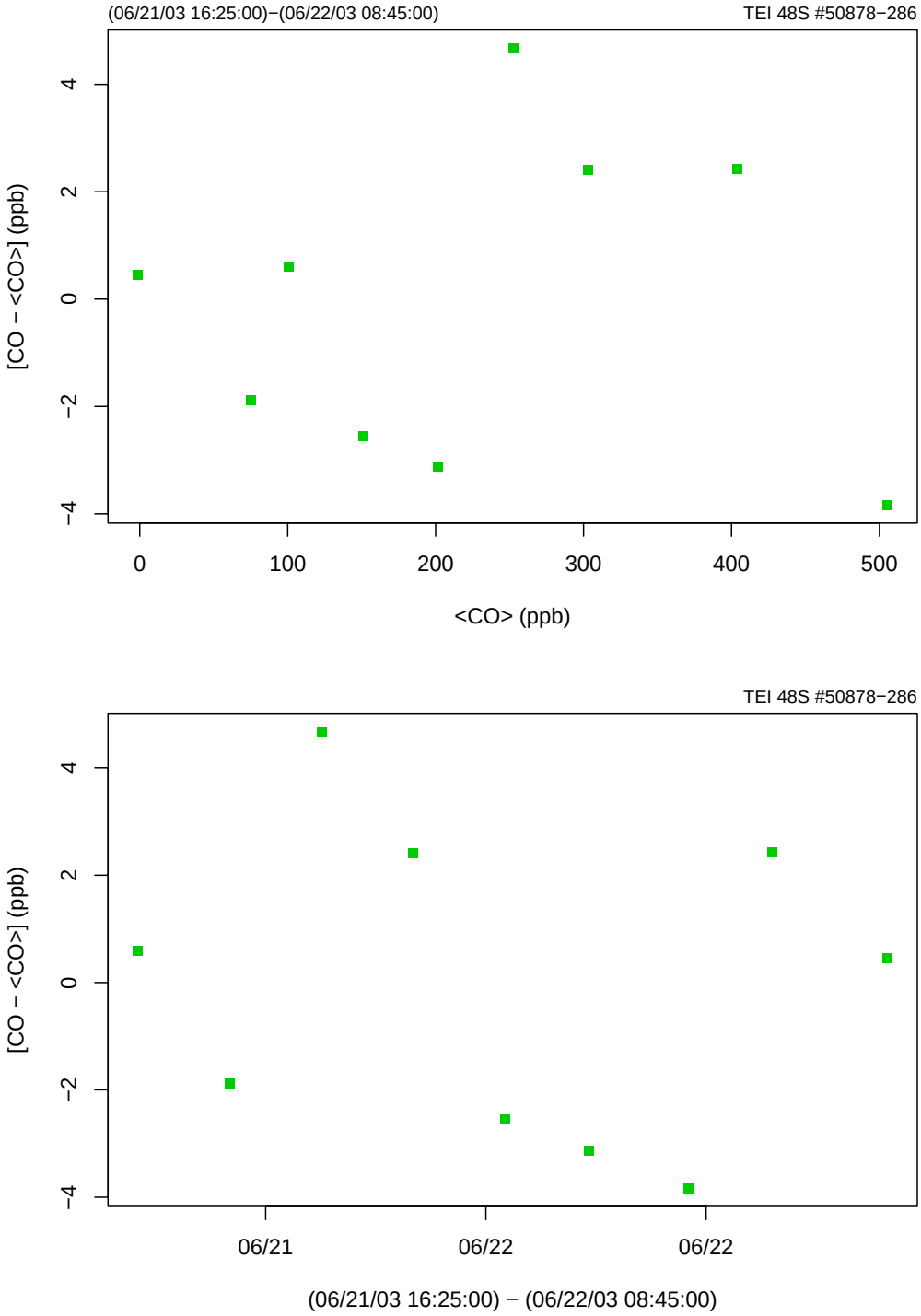

Figure 11. Regression residuals of the HPB TEI 48S carbon monoxide analyser. Points represent averages of valid 10'-aggregates. Upper panel: concentration dependence; Lower panel: time dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the TEI 48S analyser X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the zero corrected 10' inter-comparison data using equation

$$\mathbf{X_{CO}\ (ppb) = ([CO] + 1.2\ ppb) / 1.004}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(61.4\ ppb^2 + 6.93e\text{-}05 * X_{CO}^2)} \quad (2b)$$

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 1 ppb was assumed due to imperfect zero correction.

Inter-comparison with travelling standards

Direct measurements with WCC-Empa travelling standards were made with the AL5001 analyser. Each cylinder was measured between 17 and 36 minutes, which resulted in a maximum of 36 useable 1' averages per level and run. These were further aggregated by level before use in the assessment (cf. Table 11).

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

Date Time (UTC+1)	TS Identification	TS (ppb)	sdTS (ppb)	AL5001 CO (ppb)	sdCO (ppb)	No. 1' av.
(06/21/06 08:55:30)	050701_FA02505	359.22	1.82	362.60	0.49	16
(06/21/06 09:16:30)	FF31496	73.41	0.68	75.43	0.36	16
(06/21/06 09:39:30)	041109_FA01467	134.68	0.83	136.78	0.43	16
(06/21/06 10:25:30)	Zero Air (HPB)	0.00	0.50	1.64	0.27	12
(06/21/06 10:51:00)	050415_FA02466	178.54	1.21	181.08	0.92	33
(06/21/06 11:17:30)	030703_FA01477	199.38	1.00	201.43	0.41	16
(06/21/06 11:36:00)	041109_0627B	154.58	0.82	156.32	0.37	17

Figure 12 shows the regression residuals of the AL5001 plotted against time and concentration. 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.

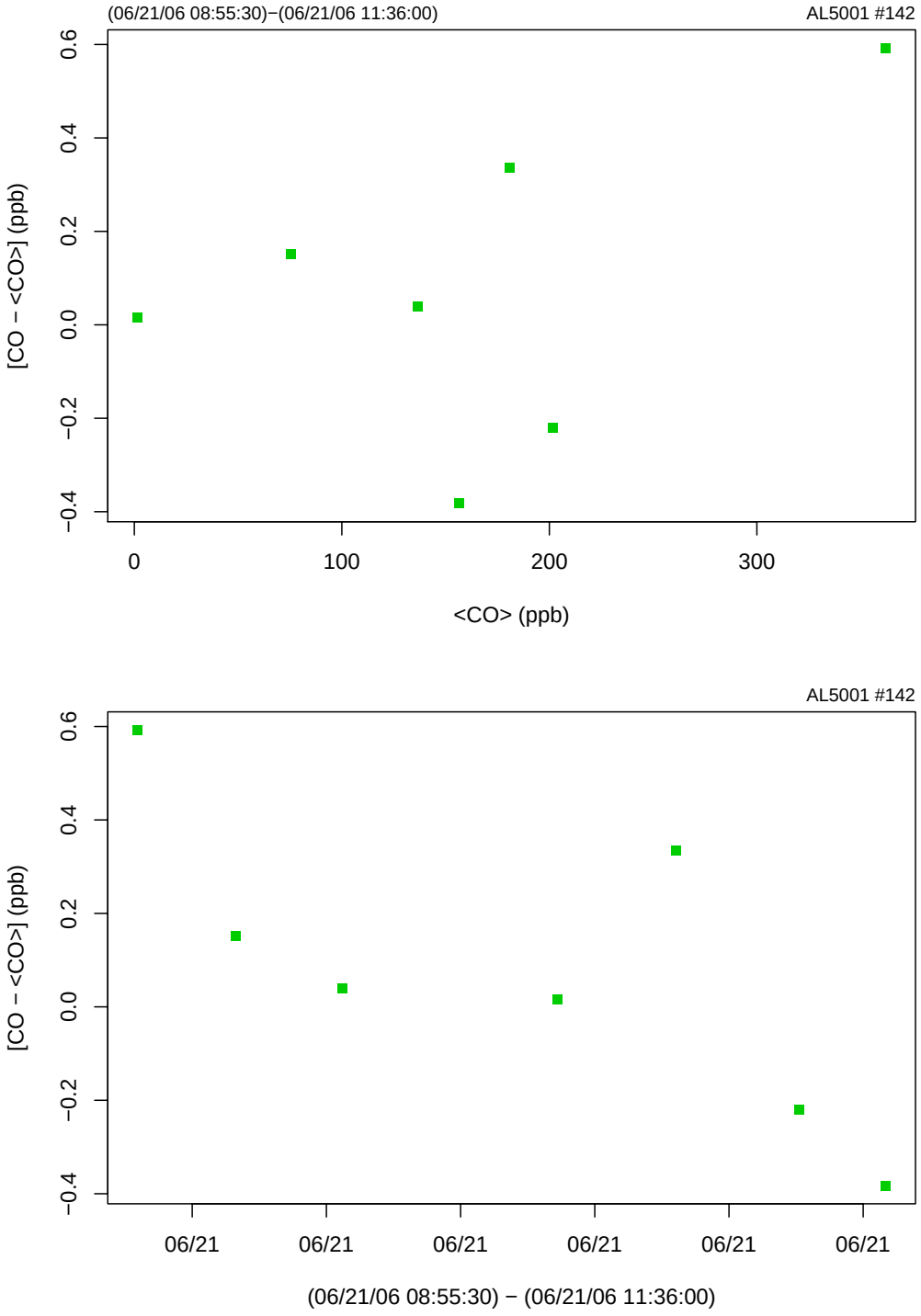

Figure 12. Regression residuals of the HPB AL5001 carbon monoxide analyser based on the inter-comparison with travelling standards. Points represent averages of valid 1'-aggregates. Upper panel: concentration dependence; Lower panel: time dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the AL5001 analyser X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the 1' inter-comparison data using equation

$$\mathbf{X_{CO}\ (ppb) = ([CO] - 1.6\ ppb)/\ 1.003}$$

$$\mathbf{u_{CO}\ (ppb) = =sqrt(1.3\ ppb^2 + 1.17e\text{-}05 * X_{CO}^2)} \quad (2c)$$

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

Discussion

In general, good results were obtained during the inter-comparisons of the HPB carbon monoxide analysers when compared to WCC-Empa travelling standards. The following discussion addresses a few issues that were found during the inter-comparisons.

Aerolaser AL5001:

A slight difference was observed between the inter-comparison with the dilution unit and the WCC-Empa cylinders (equations 2a and 2c). 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 be further assessed.
- The offset was also observed during the inter-comparison with the dilution unit, but was less pronounced. Furthermore, the last two levels (higher concentrations) showed significantly increased residuals and noise. A possible explanation is due the fact that the air-conditioning was not working during these two levels and room temperature exceeded 30°C. The data was not excluded from the analysis because the influence on the linear regression is only small.

TEI48S:

The agreement between the TEI48S and WCC-Empa was good, but with a relatively 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

Both 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.

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 summarized in Table 12, the inter-comparison data is given in Table 13.

Table 12. 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 shipment of TS (16 May, 2006) 3 runs after return of TS (26 June, 2006)

Table 13. Five-minute aggregates computed from 10 valid 30-second values for the inter-comparison of the Standard Reference Photometer (SRP) with the WCC-Empa transfer standard (TS).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2006-05-16	1	0	-0.15	0.26	0.03	0.09
2006-05-16	1	90	91.93	0.40	92.17	0.06
2006-05-16	1	190	192.25	0.36	192.57	0.17
2006-05-16	1	30	32.20	0.35	32.15	0.14
2006-05-16	1	140	142.36	0.43	142.80	0.07
2006-05-16	1	60	61.18	0.32	61.63	0.13
2006-05-16	1	0	-0.17	0.23	0.10	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	32.40	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	0.30	92.10	0.11
2006-05-16	3	190	191.73	0.38	192.32	0.15
2006-05-16	3	0	0.06	0.27	0.10	0.12
2006-06-26	4	0	-0.08	0.29	0.15	0.10
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	0.00	0.41	0.14	0.07
2006-06-26	5	0	0.16	0.19	0.24	0.12
2006-06-26	5	30	31.30	0.38	31.38	0.09
2006-06-26	5	190	189.35	0.44	189.58	0.24
2006-06-26	5	90	90.20	0.27	90.58	0.09
2006-06-26	5	140	140.43	0.17	140.70	0.24
2006-06-26	5	60	59.79	0.38	60.14	0.06
2006-06-26	5	0	-0.10	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	31.60	0.28	32.00	0.11
2006-06-26	6	140	140.26	0.28	140.69	0.05
2006-06-26	6	60	59.95	0.30	60.20	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 13). 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]).

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

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

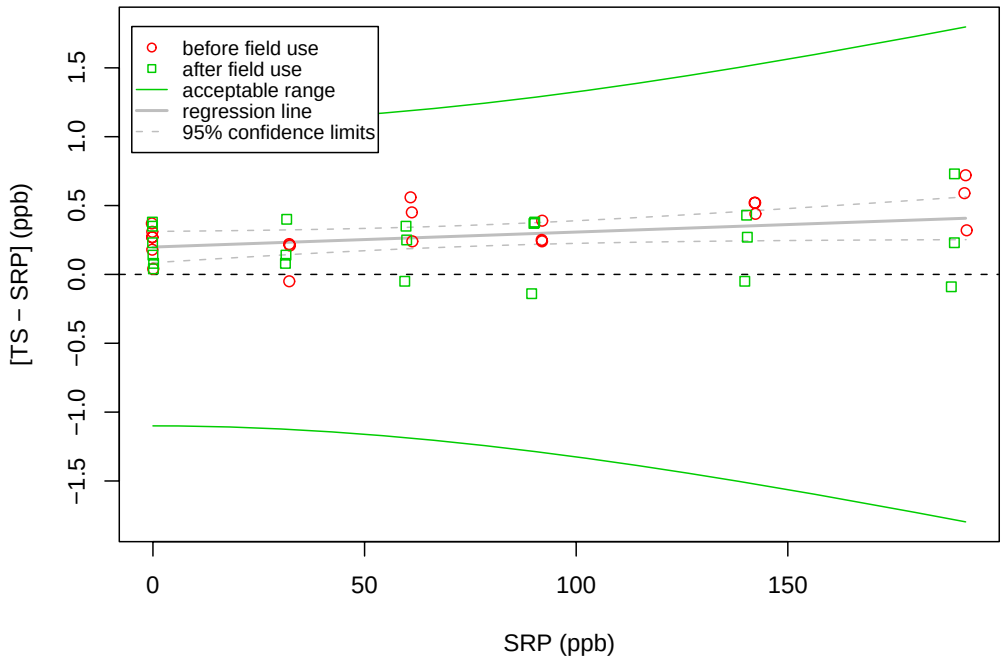

Figure 13. Deviations between transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 14 - Table 16.

Table 14. 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 15)
(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 15
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 15. Calibration of the Breitfuss dilution system and carbon monoxide mixing ratios at different levels determined with WCC-Empa reference before and after the audit.

	Mass Flow Controller MFC 1 (mL min^{-1})		Mass Flow Controller MFC 2 (mL min^{-1})		Carbon Monoxide Mixing Ratio (ppb)	
Date	**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 16. 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)

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Ozone Audit Executive Summary (HPB)

0.1	Station Name:	Hohenpeissenberg
0.2	GAW ID:	HPB
0.3	Coordinates/Elevation:	47.800°N, 11.017°E (985 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	20 – 21 June, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. S. Gilge, R.-T. Wilhelm
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):	$(1.0010\pm0.0010) \times [SRP] + (0.20\pm0.09)$
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49C #56028-306
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG: 0.4 COEF: 1.020
1.5.4	Calibration at start of audit (ppb):	$[OA] = (1.011\pm0.000) \times [SRP] - (0.01\pm0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] + 0.01) / 1.011$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.55e\text{-}5 \times X^2)^{1/2}$
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 06/3

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

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Carbon Monoxide Audit Executive Summary (HPB)

0.1	Station Name:	Hohenpeissenberg
0.2	GAW ID:	HPB
0.3	Coordinates/Elevation:	47.800°N, 11.017°E (985 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	21 – 22 June, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. S. Gilge, R.-T. Wilhelm
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 AL5001 S/N 142
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):	$CO = (0.995 \pm 0.002) \times X + (0.7 \pm 0.0)$
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 0.7) / 0.995$
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (3.2\ ppb^2 + 2.93e\text{-}05 \times X^2)^{1/2}$
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:	
1.7	Reference:	WCC-Empa Report 06/3

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

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