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World Calibration Centre for Surface Ozone

Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

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SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, METHANE, CARBON DIOXIDE AND CARBON MONOXIDE AT THE GLOBAL GAW STATION HOHENPEISSENBERG GERMANY, JULY 2011

Submitted by

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WMO World Calibration Centre WCC-Empa

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EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The third system and performance audit at the Global GAW station Hohenpeissenberg was conducted by WCC-Empa[1] from 5 thru 7 July 2011 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Hohenpeissenberg (HPB) atmospheric research station is coordinated by the German Weather Service (DWD) under the Federal Ministry of Transport, Building and Urban Development.

Previous audits at HPB were conducted in November 1997 [*Herzog et al.*, 1997] and in June 2006 [*Zellweger et al.*, 2006].

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Stefan Gilge	DWD Hohenpeissenberg, Station Scientist
Mr. Björn Briel	DWD Hohenpeissenberg, Station Engineer
Mrs. Marita Hoffmann	DWD Hohenpeissenberg, Station Technician
Dr. Christian Plass-Duelmer	DWD Hohenpeissenberg, Head GAW / Gases Group
Dr. Wolfgang Fricke	DWD Hohenpeissenberg, Director of the HPB Observatory

This report summarises the assessment of the Hohenpeissenberg GAW station in general, as well as the surface ozone, methane, carbon dioxide and carbon monoxide measurements in particular. The assessment criteria for the ozone comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer et al.*, 2000; *Klausen et al.*, 2003].

The report is distributed to the DWD Hohenpeissenberg, QA/SAC Germany and the World Meteorological Organization in Geneva. The report 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 Hohenpeissenberg Observatory is located on an isolated mountain roughly 40 km north of Zugspitze and is part of the combined Global GAW Station Zugspitze/Schneefernerhaus - Hohenpeissenberg. The site 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 observatory is situated on top of the mountain. It has a long history of meteorological and climatological observations dating back to 1781. Access to the site is possible by road throughout the year. The station location is adequate for the intended purpose.

Station Facilities

The Hohenpeissenberg Observatory comprises laboratory and office buildings as well as facilities for visiting researchers. The air-conditioning system has been replaced after the last WCC-Empa audit. The site has all necessary infrastructures such as uninterruptable power supply and internet connection available. The Hohenpeissenberg facilities are an ideal platform for extended atmospheric research.

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

Station Management and Operation

Hohenpeissenberg is visited during weekdays by approximately 30 scientists, technical and administrational staff. The operation of the observatory and the measurements are well organised, and responsibilities are clearly defined. No change of the current practice is necessary.

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

Air Inlet Systems

The design of the air inlet systems of the permanent instrumentation is state-of-the-art and fully adequate. However, the recently installed Picarro instrument used for CH_4 and CO_2 measurement was using a provisional inlet design which is not adequate for these measurements.

> **Recommendation 2 (***, 2011)**
> *The CO_2 and CH_4 inlet needs to be moved to the uppermost possible location on the HPB Observatory. The PFA tubing that is currently used must be replaced by appropriate materials for CO_2 measurements (Dekabon, stainless steel or copper).*

Surface Ozone Measurements

The surface ozone measurements at Hohenpeissenberg were established in 1971, and instruments deploying different analytical techniques are running in parallel for ensuring highly accurate measurements.

Instrumentation. Two instruments using UV absorption technique (TEI 49C and TEI 49i) and a chemiluminescence ozone analyser (UPK 8002) are running in parallel are currently used at the station for continuous surface ozone measurements. The instrumentation is fully adequate for its intended purpose.

Standards. The station is equipped with an ozone standard (TEI49C-PS); traceability to other ozone standards apart from WCC-Empa audits has not been established. The stability of the ozone reference is regularly checked based upon calculations using the Lambert-Beer law. Calibrations are carried out every three months. It was recommended by WCC-Empa after the last audit that the pressure sensors of the instruments are checked during the calibration procedure, which is now done.

Intercomparison (Performance Audit). The ozone analyser at Hohenpeissenberg was compared against the WCC-Empa travelling standard with traceability to a Standard Reference Photometer (SRP). The results of the comparison are summarised below. The data acquired by the station data acquisition system was used for data evaluation, and no further corrections were applied. The following equations characterise the bias of the different instruments in their current states:

TEI 49C #56028-306 (BKG -0.1 ppb, SPAN 1.005) – main analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.00 ppb) / 1.002 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.69e-05 * $X_{O3}{}^2$) (1b)

TEI 49i #632519672 (BKG 0.3 ppb, SPAN 1.027) – backup analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.24 ppb) / 1.002 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.69e-05 * $X_{O3}{}^2$) (1d)

UPK 8002 #92062 (BKG 0.1 ppb, SPAN 3.75) – backup chemiluminescence analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.17 ppb) / 0.993 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.74e-05 * $X_{O3}{}^2$) (1f)

TEI 49C-PS #423807729 (BKG 0.1 ppb, SPAN 1.024) – station calibrator:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] - 0.18 ppb) / 1.001 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.65e-05 * $X_{O3}{}^2$) (1h)

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

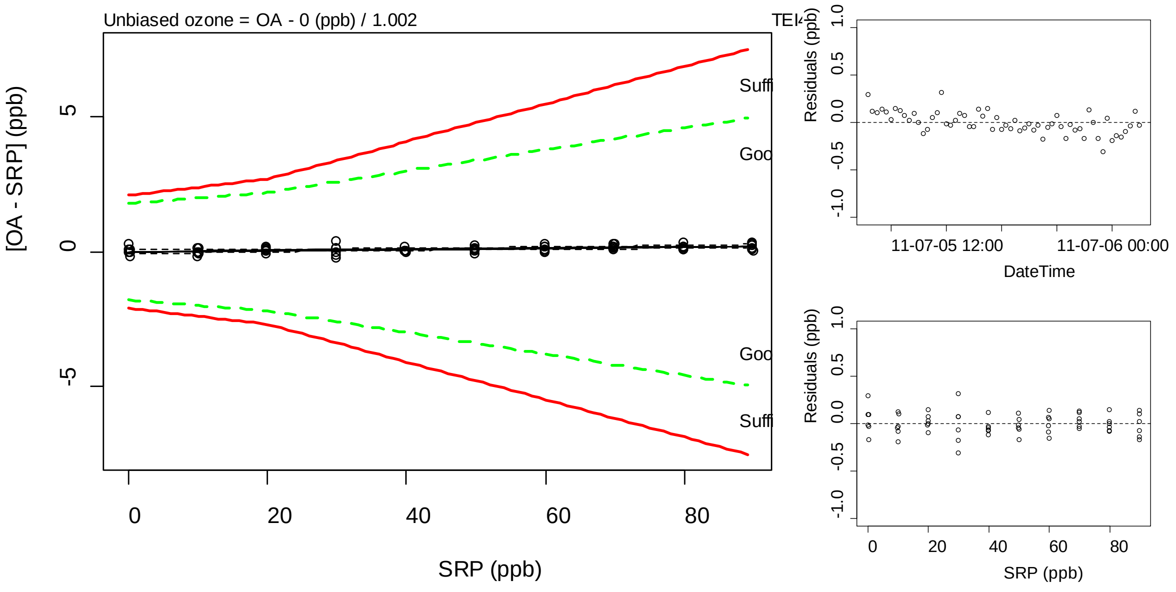

Figure 1. Left: Bias of the HPB ozone analyser (TEI 49C #56028-306) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria are delimited by green and red lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

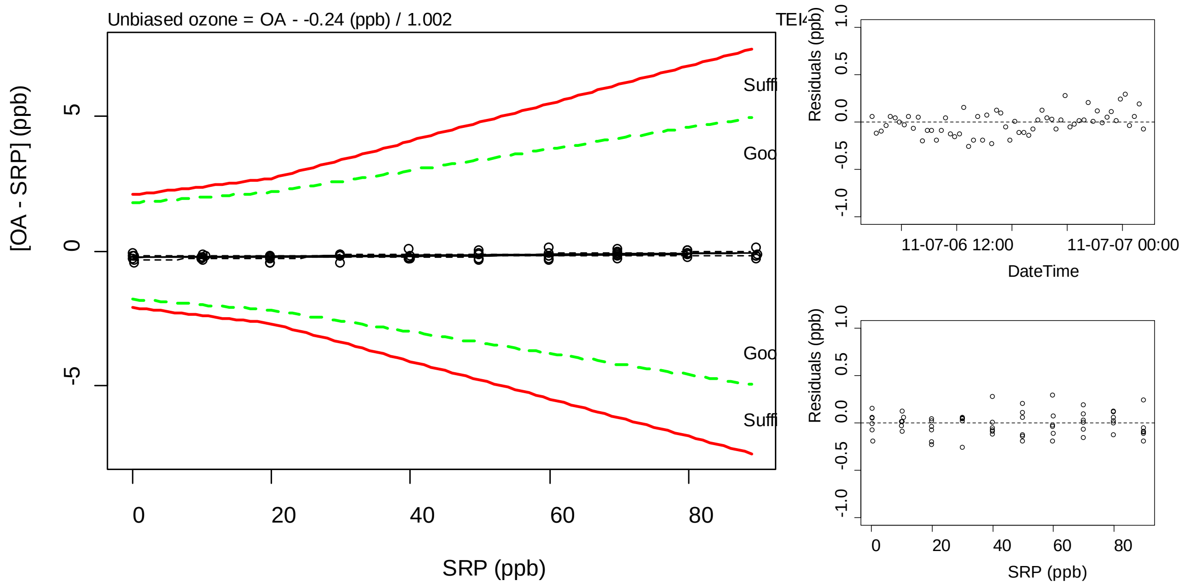

Figure 2. Same as Figure 1, for TEI 49i #632519672 backup analyser.

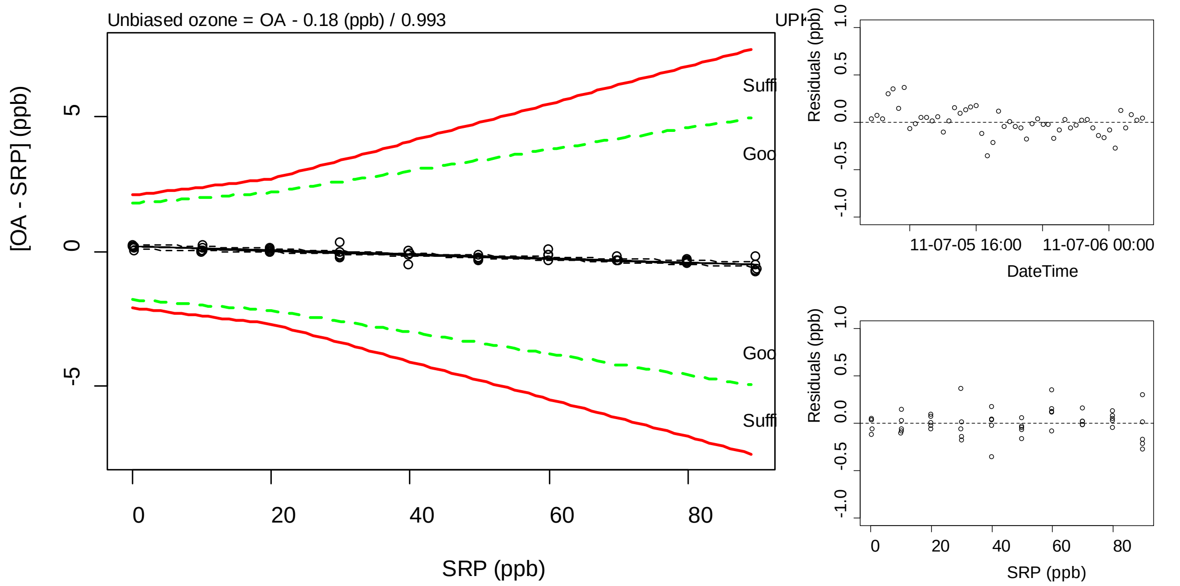

Figure 3. Same as Figure 1, for UPK 8002 #92062 backup chemiluminescence analyser.

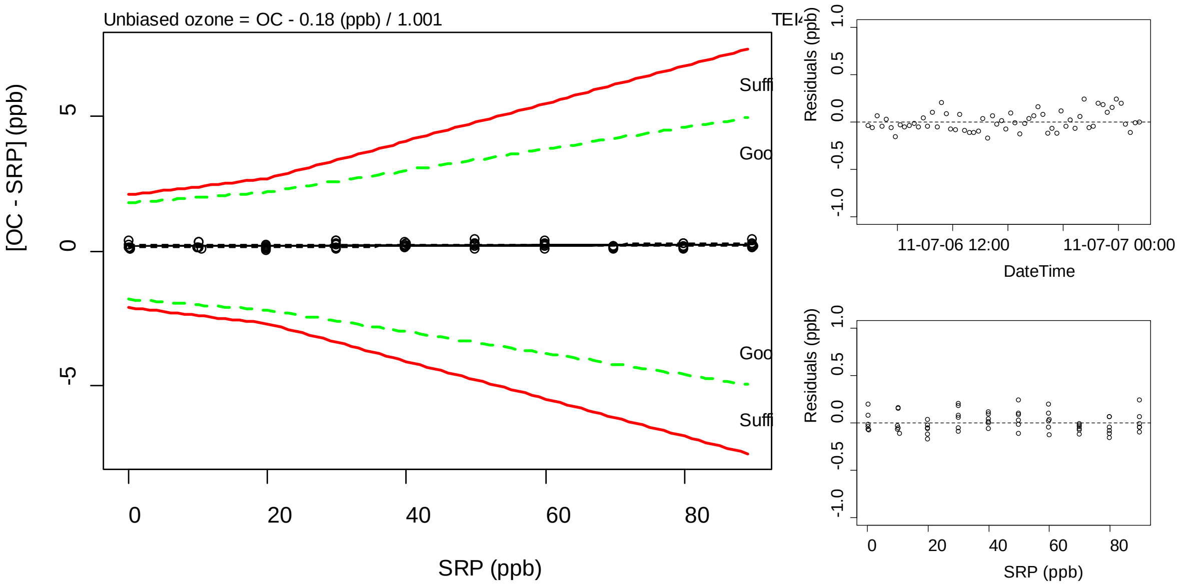

Figure 4. Same as Figure 1, for TEI 49C-PS #423807729 station calibrator.

Carbon Monoxide Measurements

Continuous measurements of CO at HPB started in January 1995, and data is available since then. No changes were made concerning the measurement setup since the last audit by WCC-Empa in 2006.

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 instrument, whereas the NDIR analyser (TEI48S) is still running as a back-up system. However, data of the TEI48S instrument was not used during the past few years, and this instrument was not assessed during this audit. The instrumentation is adequate for the intended purpose.

Standards. Commercial calibration gases (Riessner Gase, Messer and AirLiquide) with CO mole fractions of approx. 1 and 40 ppm are available at HPB. In addition, three NOAA/ESRL laboratory standards and two cylinders calibrated at the Max Planck Institute for Biogeochemistry (Jena) are available. The purchase of NOAA/ESRL standards was a recommendation of the last audit [*Zellweger et al.*, 2006], which has been fulfilled in the meantime. Adequate calibrations of the instruments are possible with these standards.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the HPB instrument with randomised carbon monoxide levels from traveling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 5 with respect to the WMO GAW Data Quality Objectives (DQOs) [*WMO*, 2010; 2011]:

Aerolaser AL5001 #142:

Unbiased CO mixing ratio:	X_{CO} (ppb) = (CO - 0.8) / 0.9875	(2a)
Remaining standard uncertainty:	u_{CO} (ppb) = sqrt (0.4 ppb^2 + 6.15e-05 * X_{CO}^2)	(2b)

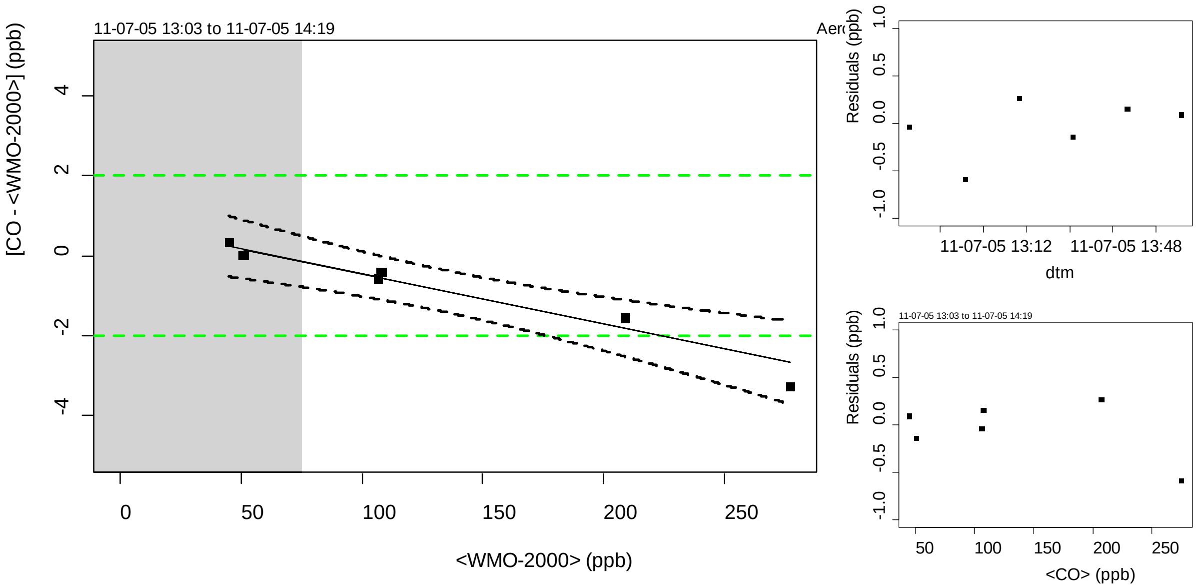

Figure 5. Left: Bias of Hohenpeissenberg Aerolaser AL5001 carbon monoxide instrument with respect to the WMO2000 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for HPB, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The above results were obtained with CO values of the WCC-Empa TS based on one specific laboratory standard on the WMO-2000 carbon monoxide scale (CA02854, see Table 16). More recently, WCC-Empa purchased additional laboratory standards from NOAA with values assigned on the WMO-2004. If these values are considered, the following results are obtained:

Aerolaser AL5001 #142:

Unbiased CO mixing ratio:	X_{CO} (ppb) = (CO - 0.8) / 1.0005	(2c)
Remaining standard uncertainty:	u_{CO} (ppb) = sqrt (0.4 ppb^2 + 6.02e-05 * X_{CO}^2)	(2d)

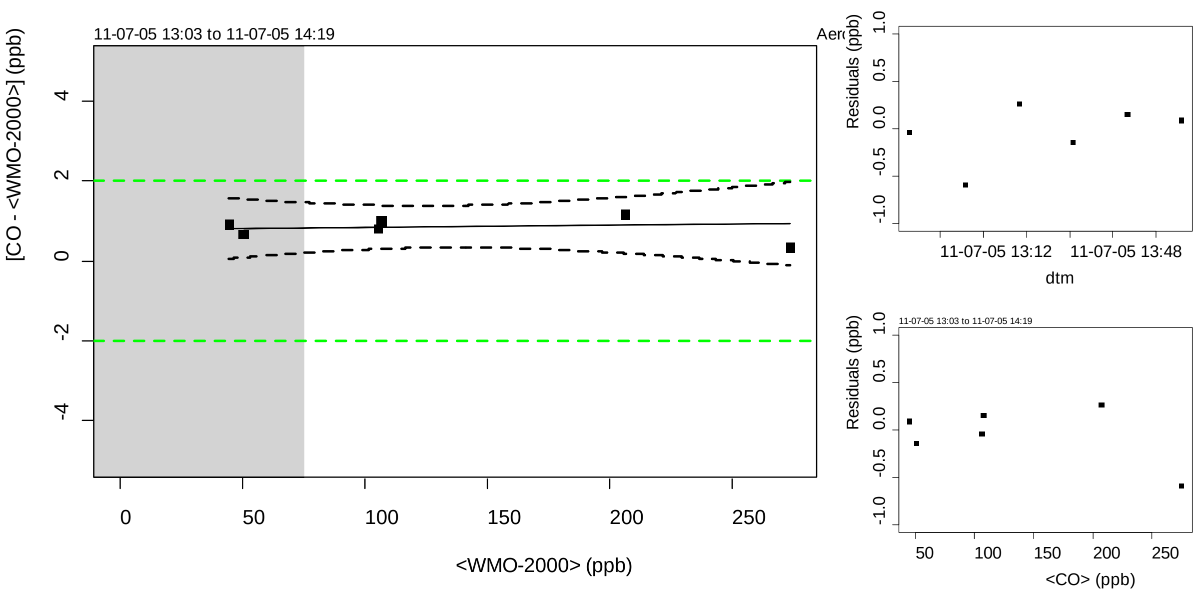

Figure 6. Same as above, with values assigned to the TS on the WMO-2004 CO scale.

Methane and Carbon Dioxide Measurements

Continuous measurements of CH_4 and CO_2 at HPB started in 2010 using a Picarro G1301 CRDS analyser. At the time of the audit, the instrument was still running using a provisional inlet system and was installed in the guest scientist laboratory on the 3rd floor of the HPB laboratory building. This location is not ideal for these measurements, and it is recommended to move the analyser to the gas laboratory on 4th floor as soon as possible.

> **Recommendation 3 (***, 2011)**
> *The Picarro instrument needs to be moved to different laboratory with an appropriate inlet system (see also recommendation 2).*

Instrumentation. A Picarro G1301 CO_2, CH_4 and H_2O analyser is available at HPB. The air is not dried, which requires a correction for dilution and spectroscopic effects. Since the instrument was running until now only on a provisional basis, such corrections have not yet been applied. The correction function was determined by WCC-Empa during the audit, and it is recommended that this function is confirmed by similar experiments by HPB staff.

> **Recommendation 4 (***, 2011)**
> *The Picarro instrument is running without drying of the sample air. This is fully adequate but requires correction for dilution and spectroscopic effects. These correction functions need to be determined by HPB staff. It is recommended to confirm the stability of the correction functions in regular intervals, e.g. 6-monthly.*

Standards. Three NOAA/ESRL laboratory standards and two cylinders calibrated at the Max Planck Institute for Biogeochemistry (Jena) are available for calibrations. Adequate calibrations are possible using these standards.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the HPB instrument with randomised carbon dioxide and methane levels from traveling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equations (3a-b for CH_4 and 4a-b for CO_2) characterise the instrument bias. The results are further illustrated in for CH_4 in Figure 7 and for CO_2 in Figure 8 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Picarro G1301 #CFADS-071:

Unbiased CH_4 mixing ratio:	X_{CH4} (ppb) = (CH_4) / 1.00016	(3a)
Remaining standard uncertainty:	u_{CH4} (ppb) = sqrt (0.1 ppb^2 + 1.16e-07 * $X_{CH4}{}^2$)	(3b)
Unbiased CO_2 mixing ratio:	X_{CO2} (ppm) = (CO_2 + 0.09) / 0.999959	(4a)
Remaining standard uncertainty:	u_{CO2} (ppm) = sqrt (0.05 ppm^2 + 1.83e-07 * $X_{CO2}{}^2$)	(4b)

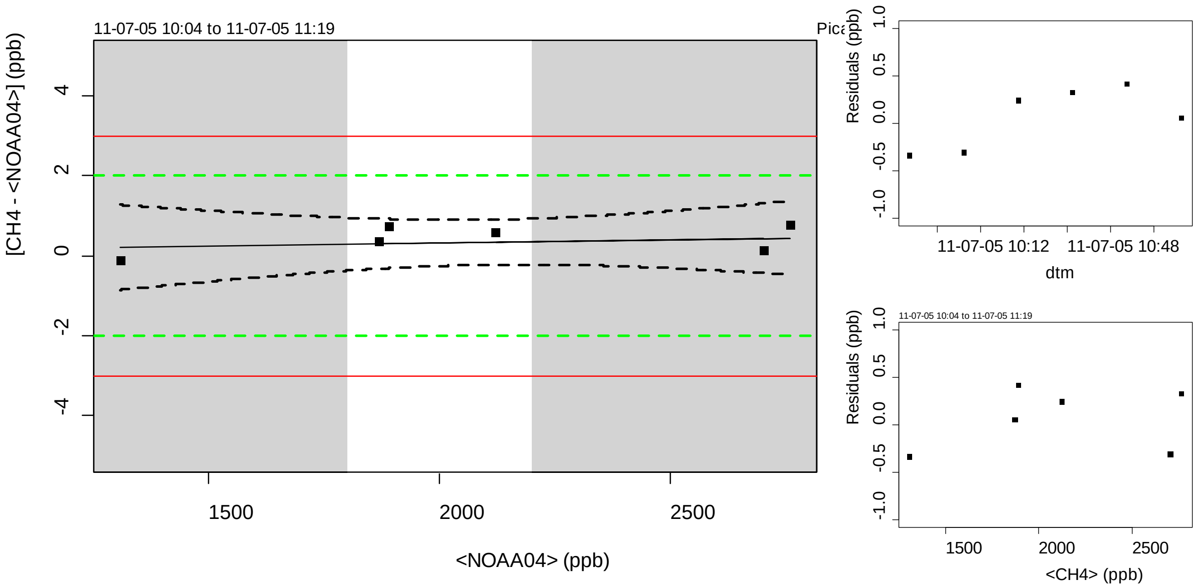

Figure 7. Left: Bias of Hohenpeissenberg Picarro G1301 methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for HPB, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

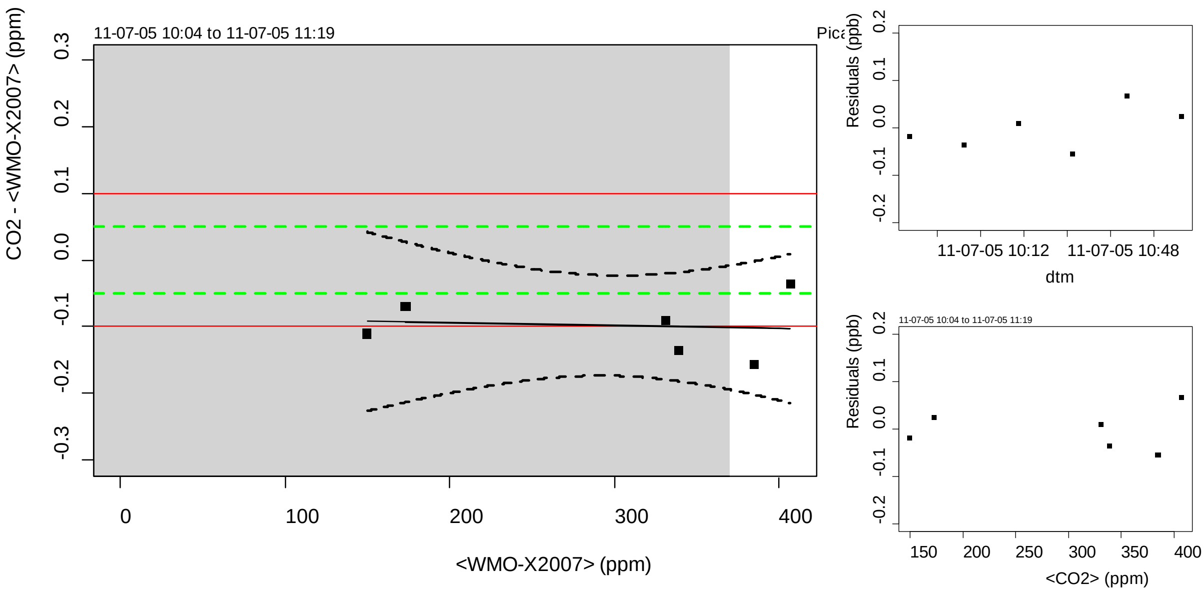

Figure 8. Left: Bias of Hohenpeissenberg Picarro G1301 carbon dioxide instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for HPB, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

Data Acquisition and Management

All instruments at HPB use a central LabView based data acquisition software. Two programmers are responsible to maintain and, if necessary, troubleshoot the system. Large monitors display the current real-time measurements and instrument status. Remote access is possible using a dongle and a key generator. All data is stored on the local server system, which is mirrored daily to the servers of the German Meteorological Service in Offenbach.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). For the parameters of the audit scope in-situ data for surface ozone and carbon monoxide (1995 – 2007) is available from WDCGG. Methane and carbon dioxide data has not yet been submitted due to the recent start of the measurements and the fact that the instrument is still running on a provisional basis.

Recommendation 5 (, 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. The delays of data submission of three or more years are too long. Submission of the Picarro data is strongly encouraged after the data has been validated.

Conclusions

The Global GAW station Hohenpeissenberg carries out a very comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the Hohenpeissenberg station an important contribution to the GAW programme. The recent addition of greenhouse gas measurements is a valuable contribution to GAW. All assessed parameters were of high quality. Continuation of the HPB measurement series and the scientific collaboration with external partners is highly recommended.

Summary Ranking of the Hohenpeissenberg GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access by road
Facilities		
Laboratory and office space	(5)	Large research facilities
Internet access	(5)	Available
Air Conditioning	(5)	Now fully operational
Power supply	(5)	Reliable, UPS
General Management and Operation		
Organisation	(5)	Well organised
Competence of staff	(5)	Highly experienced technical and scientific staff
Air Inlet System (except CH_4, CO_2)	(5)	Adequate systems
Air Inlet System (CH_4, CO_2)	(1)	Provisional inlet, not adequate (material, location)
Instrumentation		
Ozone	(5)	Up-to-date instrumentation, use of different techniques
Carbon monoxide	(5)	AL5001
Carbon dioxide and Methane	(5)	Picarro G1301
Standards		
Ozone	(4)	TEI 49C-PS, no comparisons to other references
CO, CH_4 and CO_2	(5)	NOAA and other standards, collaboration with MPI Jena
Data Management		
Data acquisition	(5)	LabView based central DAQ
Data processing	(5)	Experienced staff, scientific use of the data
Data submission	(3)	Large suite of parameters submitted but relatively long submissions delays (>3yrs)

#0: inadequate thru 5: adequate.

Dübendorf, August 2011

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

APPENDIX

Global GAW Station Hohenpeissenberg

Site description

Information about the Hohenpeissenberg GAW station can be found on the station web page (www.dwd.de/mohp), and the station is also registered in the GAW Station Information System (GAWSIS) (http://gaw.empa.ch/gawsis). No significant changes were made at the station and the surroundings since the last WCC-Empa audit.

Measurement Programme

The Hohenpeissenberg Observatory has one of the most extensive measurement programmes within GAW, and meteorological observations date back to 1781. An overview of the measurement programme and its status as of July 2011 is shown in Table 1. Refer to GAWSIS and the HPB website for more details and a complete overview of the measurement programme.

Table 1. Measurement Programme at the HPB Station (In-situ gas measurements only)

Parameter	*Current Instrument*	*Data availability (%)*		
		<12 m	*<3 y*	*Overall*
Reactive Gas				
Surface Ozone	TEI 49C, TEI 49i, UPK 8002			96
Carbon Monoxide	Aerolaser AL5001			92
VOCs (C2-C7, BTX)	GC-FID	93	86	86
NO, NO_2 and NO_x	CLD / PLC (Ecophysics) CLD / BLC (TEI42C-TL) CLD / Mo-Conv. (TEI42C-TL)			79(NO) 75(NO_2)
NO_y	CLD / Au Converter			77(NO_y)
H_2O_2 and ROOH discount. 2006	Aerolaser AL2002			54/51
SO_2	TEI43C-TL			91
H2SO4, OH radical	Chemical ionisation mass spectroscopy (CIMS)	77	82	81
PAN	GC/ECD (MeteoConsult)			86
Greenhouse Gas				
Carbon Dioxide	Picarro G1301			
Methane	Picarro G1301			
Flask sampling	NOAA/GMD flask programme			<95

Trace Gas Distributions at Hohenpeissenberg

The monthly and yearly distribution for surface ozone, carbon monoxide (both data from station analysers for 2007), methane and carbon dioxide (NOAA flask data) at Hohenpeissenberg is shown in Figure 9.

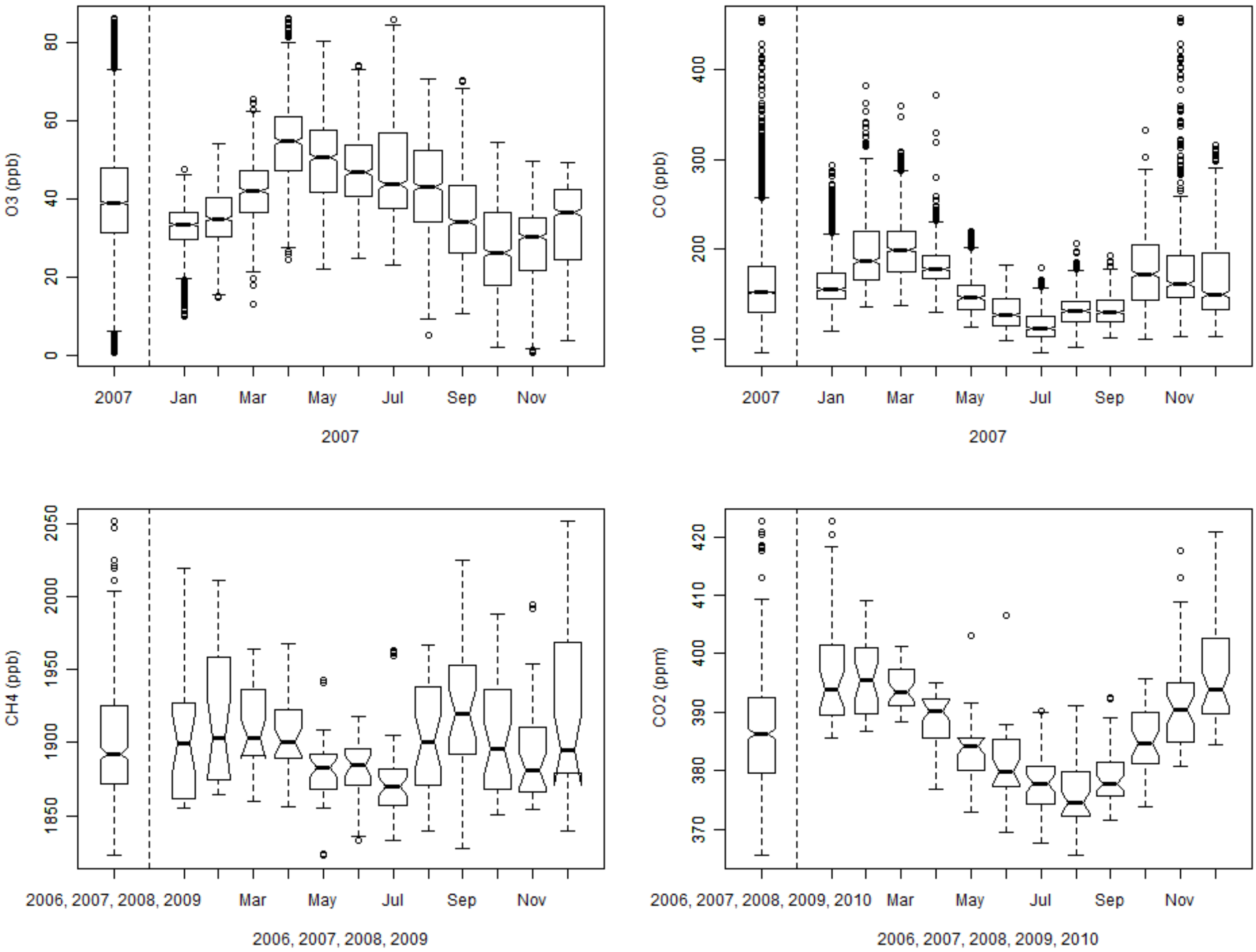

Figure 9. Yearly and monthly box plots for surface ozone surface ozone, carbon monoxide (both 2007, HPB data), methane and carbon dioxide (both NOAA flask data). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles 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 Hohenpeissenberg Observatory is run and coordinated by the German Weather Service (DWD). Approximately 50 administrative, technical and research staff are working at Hohenpeissenberg. The contact persons for the parameters of the audit scope are listed in in Table 2. Refer also to GAWSIS and the HPB website for more contact and organisational information.

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

Name	*Responsibility*
Dr. Wolfgang Fricke	Station Manager, GAW Country Contact
Dr. Christian Plass-Duelmer	Head GAW / Gases Group
Dr. Stefan Gilge	Station Scientist
Mr. Björn Briel	Station Engineer
Mrs. Marita Hoffmann	Station Technician
Mr. Reinhard-Tasso Wilhelm	Station Technician

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

Location of air intake:	The air intake is mounted on the terrace 2 m above the laboratory.
Inlet protection:	Protection against rain water / snow / insects.
Tubing / Material:	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 6-8 l min^{-1}.
Inlet filter:	PFA filter holder with Pall Zylon PFTE filters, 5µm.
Residence time:	approx. 2s

Instrumentation

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

Standards

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

Operation and Maintenance

Check for general operation:	Daily on working days (Mon – Fri).
Zero / Span check:	None.
Calibration/checks with standard:	Every 3 months, including check of pressure sensors.
Inlet filter exchange:	Every 2 weeks, more often in case of pollution episodes.
Other (cleaning, leak check etc.):	As required, usually every 6 months.

Data Acquisition and Data Transfer

The HPB station is equipped with a custom made data acquisition system based on LabView for all parameters. The DAQ acquires all metadata that are available from the instrument. Remote access is possible through the internet using a dongle (key generator). The data is acquired on a data server, which is mirrored to the DWD servers in Offenbach.

Data Treatment

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

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone from 1995 to 2007 is available from WDCGG.

Documentation

All information is entered in electronic and paper log books and checklists. A Standard Operating Procedure (SOP) has been prepared by HPB, and daily instrument check lists were available. The information was very comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison of the Ozone Analyser

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

Setup and Connections

The internal ozone generator of the WCC-Empa travelling standard was used for the generation of a randomised sequence of ozone levels ranging from 0 to 90 ppb. Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser including its inlet filter using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the station data acquisition system except for the ozone calibrator where the WCC-Empa DAQ was used.

Table 3. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
Settings	BKG = -0.2; COEFF = 1.009
Station Analyser (OA) – main instrument	
Model, S/N	TEI 49C #56028-306
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = -0.1; COEFF = 1.005
Pressure readings (torr)	Ambient 677.8, OA 678.1, no adjustments were made
Station Analyser (OA) – backup instrument	
Model, S/N	TEI 49i #632519672
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = -0.3; COEFF = 1.027
Pressure readings (torr)	Ambient 675.7, OA 676.4, no adjustments were made
Station Analyser (OA) – backup instrument, chemiluminescence	
Model, S/N	UPK 8002 #92062
Principle	Chemiluminescence
Range	0-100 ppb
Settings	BKG = 0.1; SPAN = 3.75
Pressure readings (torr)	NA
Station Calibrator (OC)	
Model, S/N	TEI 49C-PS #423807729
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = 0.1; COEFF = 1.024
Pressure readings (torr)	Ambient 675.7, OC 676.3, no adjustments were made

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison as described elsewhere *[Klausen et al., 2003]*. All results are valid for the calibration factors as given in Table 3 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary (Figures and Equations).

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main HPB ozone analyser (OA) TEI 49C #56028-306 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-07-05 10:20	1	0	0.12	0.27	0.19	0.05	0.15	NA
2011-07-05 10:40	1	40	39.99	40.00	0.10	0.10	0.01	0.00
2011-07-05 11:00	1	90	90.00	90.05	0.07	0.09	0.05	0.10
2011-07-05 11:20	1	60	60.00	60.06	0.10	0.08	0.06	0.10
2011-07-05 11:40	1	50	49.98	50.00	0.14	0.09	0.02	0.00
2011-07-05 12:00	1	20	20.01	19.91	0.21	0.12	-0.10	-0.50
2011-07-05 12:20	1	80	80.01	80.10	0.09	0.08	0.09	0.10
2011-07-05 12:40	1	10	10.11	10.10	0.41	0.12	-0.01	-0.10
2011-07-05 13:00	1	30	30.01	29.97	0.23	0.12	-0.04	-0.10
2011-07-05 13:20	1	70	69.99	69.94	0.10	0.08	-0.05	-0.10
2011-07-05 13:40	2	0	0.32	0.27	0.21	0.06	-0.05	NA
2011-07-05 14:00	2	20	19.98	19.86	0.17	0.03	-0.12	-0.60
2011-07-05 14:20	2	40	40.00	39.78	0.09	0.10	-0.22	-0.50
2011-07-05 14:40	2	90	89.99	89.86	0.12	0.09	-0.13	-0.10
2011-07-05 15:00	2	60	60.01	59.98	0.07	0.06	-0.03	0.00
2011-07-05 15:20	2	10	10.31	10.28	0.41	0.18	-0.03	-0.30
2011-07-05 15:40	2	30	29.98	30.18	0.13	0.07	0.20	0.70
2011-07-05 16:00	2	50	49.99	49.88	0.08	0.08	-0.11	-0.20
2011-07-05 16:20	2	70	70.03	69.93	0.09	0.10	-0.10	-0.10
2011-07-05 16:40	2	80	80.02	79.98	0.08	0.10	-0.04	0.00
2011-07-05 17:00	3	0	0.22	0.18	0.21	0.04	-0.04	NA
2011-07-05 17:20	3	30	30.02	29.98	0.10	0.10	-0.04	-0.10
2011-07-05 17:40	3	50	50.00	49.87	0.10	0.09	-0.13	-0.30
2011-07-05 18:00	3	10	9.96	9.78	0.16	0.08	-0.18	-1.80
2011-07-05 18:20	3	90	90.00	90.09	0.06	0.08	0.09	0.10
2011-07-05 18:40	3	60	59.99	59.97	0.12	0.09	-0.02	0.00
2011-07-05 19:00	3	20	20.01	20.03	0.12	0.08	0.02	0.10
2011-07-05 19:20	3	80	80.01	79.88	0.11	0.13	-0.13	-0.20
2011-07-05 19:40	3	70	70.00	69.98	0.15	0.12	-0.02	0.00
2011-07-05 20:00	3	40	39.97	39.80	0.09	0.06	-0.17	-0.40
2011-07-05 20:20	4	0	0.34	0.17	0.16	0.05	-0.17	NA
2011-07-05 20:40	4	40	39.96	39.79	0.04	0.08	-0.17	-0.40
2011-07-05 21:00	4	90	90.01	89.98	0.12	0.14	-0.03	0.00
2011-07-05 21:20	4	60	59.98	59.81	0.11	0.12	-0.17	-0.30
2011-07-05 21:40	4	50	50.05	49.90	0.09	0.14	-0.15	-0.30
2011-07-05 22:00	4	20	19.96	19.82	0.25	0.07	-0.14	-0.70
2011-07-05 22:20	4	80	80.00	79.86	0.10	0.11	-0.14	-0.20
2011-07-05 22:40	4	10	10.16	10.00	0.46	0.13	-0.16	-1.60
2011-07-05 23:00	4	30	30.01	29.72	0.14	0.12	-0.29	-1.00
2011-07-05 23:20	4	70	70.02	69.89	0.04	0.08	-0.13	-0.20
2011-07-05 23:40	5	0	0.25	0.09	0.14	0.05	-0.16	NA
2011-07-06 00:00	5	20	20.01	19.96	0.13	0.06	-0.05	-0.20
2011-07-06 00:20	5	40	39.97	39.82	0.12	0.11	-0.15	-0.40
2011-07-06 00:40	5	90	90.02	89.80	0.12	0.12	-0.22	-0.20
2011-07-06 01:00	5	60	59.99	59.89	0.11	0.13	-0.10	-0.20

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-07-06 01:20	5	10	10.16	9.95	0.32	0.09	-0.21	-2.10
2011-07-06 01:40	5	30	29.97	29.79	0.24	0.11	-0.18	-0.60
2011-07-06 02:00	5	50	50.05	49.78	0.10	0.08	-0.27	-0.50
2011-07-06 02:20	5	70	69.98	70.04	0.13	0.12	0.06	0.10
2011-07-06 02:40	5	80	79.99	79.92	0.10	0.09	-0.07	-0.10
2011-07-06 03:00	6	0	0.40	0.08	0.24	0.04	-0.32	NA
2011-07-06 03:20	6	30	30.03	29.61	0.19	0.13	-0.42	-1.40
2011-07-06 03:40	6	50	50.05	50.01	0.11	0.05	-0.04	-0.10
2011-07-06 04:00	6	10	10.13	9.81	0.26	0.13	-0.32	-3.20
2011-07-06 04:20	6	90	90.00	89.82	0.10	0.04	-0.18	-0.20
2011-07-06 04:40	6	60	60.00	59.76	0.12	0.09	-0.24	-0.40
2011-07-06 05:00	6	20	20.01	19.79	0.12	0.05	-0.22	-1.10
2011-07-06 05:20	6	80	80.01	79.91	0.09	0.12	-0.10	-0.10
2011-07-06 05:40	6	70	70.07	70.11	0.09	0.09	0.04	0.10
2011-07-06 06:00	6	40	40.02	39.89	0.17	0.08	-0.13	-0.30

Table 5. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the backup HPB ozone analyser (OA) TEI 49i #632519672 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-07-06 09:52	1	0	0.26	-0.07	0.12	0.07	-0.33	NA
2011-07-06 10:12	1	40	39.97	39.48	0.12	0.14	-0.49	-1.20
2011-07-06 10:32	1	90	89.99	89.56	0.13	0.08	-0.43	-0.50
2011-07-06 10:52	1	60	59.99	59.60	0.10	0.08	-0.39	-0.70
2011-07-06 11:12	1	50	50.00	49.70	0.09	0.06	-0.30	-0.60
2011-07-06 11:32	1	20	19.96	19.63	0.17	0.08	-0.33	-1.70
2011-07-06 11:52	1	80	80.01	79.66	0.09	0.08	-0.35	-0.40
2011-07-06 12:12	1	10	9.99	9.57	0.20	0.09	-0.42	-4.20
2011-07-06 12:32	1	30	30.01	29.69	0.17	0.11	-0.32	-1.10
2011-07-06 12:52	1	70	69.99	69.57	0.11	0.17	-0.42	-0.60
2011-07-06 13:12	2	0	0.36	0.02	0.14	0.04	-0.34	NA
2011-07-06 13:32	2	20	20.01	19.43	0.19	0.11	-0.58	-2.90
2011-07-06 13:52	2	40	40.00	39.54	0.17	0.10	-0.46	-1.10
2011-07-06 14:12	2	90	90.00	89.57	0.10	0.14	-0.43	-0.50
2011-07-06 14:32	2	60	59.99	59.45	0.12	0.14	-0.54	-0.90
2011-07-06 14:52	2	10	10.27	9.80	0.43	0.19	-0.47	-4.60
2011-07-06 15:12	2	30	30.06	29.73	0.14	0.08	-0.33	-1.10
2011-07-06 15:32	2	50	49.99	49.51	0.17	0.15	-0.48	-1.00
2011-07-06 15:52	2	70	70.01	69.51	0.10	0.10	-0.50	-0.70
2011-07-06 16:12	2	80	80.00	79.53	0.12	0.12	-0.47	-0.60
2011-07-06 16:32	3	0	0.21	-0.02	0.31	0.06	-0.23	NA
2011-07-06 16:52	3	30	30.03	29.40	0.21	0.15	-0.63	-2.10
2011-07-06 17:12	3	50	50.01	49.46	0.10	0.10	-0.55	-1.10
2011-07-06 17:32	3	10	10.60	10.27	0.61	0.25	-0.33	-3.10
2011-07-06 17:52	3	90	90.01	89.48	0.16	0.10	-0.53	-0.60

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-07-06 18:12	3	60	60.03	59.75	0.13	0.11	-0.28	-0.50
2011-07-06 18:32	3	20	19.99	19.38	0.20	0.12	-0.61	-3.10
2011-07-06 18:52	3	80	79.97	79.75	0.09	0.13	-0.22	-0.30
2011-07-06 19:12	3	70	70.00	69.75	0.09	0.18	-0.25	-0.40
2011-07-06 19:32	3	40	40.00	39.58	0.12	0.13	-0.42	-1.00
2011-07-06 19:52	4	0	0.40	-0.18	0.23	0.07	-0.58	NA
2011-07-06 20:12	4	40	40.02	39.66	0.12	0.08	-0.36	-0.90
2011-07-06 20:32	4	90	90.01	89.57	0.07	0.09	-0.44	-0.50
2011-07-06 20:52	4	60	60.04	59.57	0.09	0.16	-0.47	-0.80
2011-07-06 21:12	4	50	50.02	49.52	0.13	0.06	-0.50	-1.00
2011-07-06 21:32	4	20	20.01	19.56	0.20	0.06	-0.45	-2.20
2011-07-06 21:52	4	80	79.98	79.66	0.06	0.11	-0.32	-0.40
2011-07-06 22:12	4	10	10.18	9.92	0.40	0.09	-0.26	-2.60
2011-07-06 22:32	4	30	30.04	29.71	0.23	0.10	-0.33	-1.10
2011-07-06 22:52	4	70	70.00	69.68	0.09	0.09	-0.32	-0.50
2011-07-06 23:12	5	0	0.37	-0.10	0.16	0.09	-0.47	NA
2011-07-06 23:32	5	20	20.01	19.65	0.11	0.09	-0.36	-1.80
2011-07-06 23:52	5	40	39.97	39.88	0.12	0.07	-0.09	-0.20
2011-07-07 00:12	5	90	90.03	89.65	0.09	0.09	-0.38	-0.40
2011-07-07 00:32	5	60	59.99	59.61	0.10	0.12	-0.38	-0.60
2011-07-07 00:52	5	10	10.00	9.63	0.13	0.06	-0.37	-3.70
2011-07-07 01:12	5	30	29.98	29.63	0.08	0.06	-0.35	-1.20
2011-07-07 01:32	5	50	50.02	49.87	0.10	0.12	-0.15	-0.30
2011-07-07 01:52	5	70	69.99	69.64	0.11	0.10	-0.35	-0.50
2011-07-07 02:12	5	80	79.97	79.74	0.10	0.14	-0.23	-0.30
2011-07-07 02:32	6	0	0.20	-0.20	0.29	0.06	-0.40	NA
2011-07-07 02:52	6	30	30.02	29.70	0.17	0.08	-0.32	-1.10
2011-07-07 03:12	6	50	50.01	49.75	0.12	0.11	-0.26	-0.50
2011-07-07 03:32	6	10	10.15	9.78	0.46	0.14	-0.37	-3.60
2011-07-07 03:52	6	90	90.01	89.92	0.07	0.15	-0.09	-0.10
2011-07-07 04:12	6	60	59.98	59.92	0.11	0.10	-0.06	-0.10
2011-07-07 04:32	6	20	19.96	19.55	0.09	0.11	-0.41	-2.10
2011-07-07 04:52	6	80	80.01	79.72	0.07	0.08	-0.29	-0.40
2011-07-07 05:12	6	70	70.01	69.85	0.10	0.10	-0.16	-0.20
2011-07-07 05:32	6	40	40.02	39.58	0.19	0.13	-0.44	-1.10

Table 6. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the backup HPB ozone analyser (OA) UPK 8002 #92062 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-07-05 13:40	1	0	0.32	0.39	0.21	0.02	0.07	21.90
2011-07-05 14:00	1	20	19.98	19.92	0.17	0.05	-0.06	-0.30
2011-07-05 14:20	1	40	40.00	39.73	0.09	0.10	-0.27	-0.70
2011-07-05 14:40	1	90	89.99	89.56	0.12	0.10	-0.43	-0.50
2011-07-05 15:00	1	60	60.01	59.89	0.07	0.06	-0.12	-0.20

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-07-05 15:20	1	10	10.31	10.40	0.41	0.17	0.09	0.90
2011-07-05 15:40	1	30	29.98	30.13	0.13	0.08	0.15	0.50
2011-07-05 16:00	1	50	49.99	49.53	0.08	0.06	-0.46	-0.90
2011-07-05 16:20	1	70	70.03	69.46	0.09	0.07	-0.57	-0.80
2011-07-05 16:40	1	80	80.02	79.42	0.08	0.11	-0.60	-0.70
2011-07-05 17:00	2	0	0.22	0.30	0.21	0.01	0.08	NA
2011-07-05 17:20	2	30	30.02	29.81	0.10	0.07	-0.21	-0.70
2011-07-05 17:40	2	50	50.00	49.67	0.10	0.11	-0.33	-0.70
2011-07-05 18:00	2	10	9.96	9.80	0.16	0.07	-0.16	-1.60
2011-07-05 18:20	2	90	90.00	89.28	0.06	0.12	-0.72	-0.80
2011-07-05 18:40	2	60	59.99	59.66	0.12	0.09	-0.33	-0.60
2011-07-05 19:00	2	20	20.01	19.96	0.12	0.04	-0.05	-0.20
2011-07-05 19:20	2	80	80.01	79.49	0.11	0.15	-0.52	-0.60
2011-07-05 19:40	2	70	70.00	69.60	0.15	0.06	-0.40	-0.60
2011-07-05 20:00	2	40	39.97	39.84	0.09	0.09	-0.13	-0.30
2011-07-05 20:20	3	0	0.34	0.26	0.16	0.03	-0.08	NA
2011-07-05 20:40	3	40	39.96	39.30	0.04	0.09	-0.66	-1.70
2011-07-05 21:00	3	90	90.01	89.06	0.12	0.08	-0.95	-1.10
2011-07-05 21:20	3	60	59.98	59.62	0.11	0.13	-0.36	-0.60
2011-07-05 21:40	3	50	50.05	49.61	0.09	0.12	-0.44	-0.90
2011-07-05 22:00	3	20	19.96	19.83	0.25	0.07	-0.13	-0.70
2011-07-05 22:20	3	80	80.00	79.31	0.10	0.07	-0.69	-0.90
2011-07-05 22:40	3	10	10.16	10.05	0.46	0.11	-0.11	-1.10
2011-07-05 23:00	3	30	30.01	29.62	0.14	0.08	-0.39	-1.30
2011-07-05 23:20	3	70	70.02	69.44	0.04	0.08	-0.58	-0.80
2011-07-05 23:40	4	0	0.25	0.32	0.14	0.02	0.07	NA
2011-07-06 00:00	4	20	20.01	19.85	0.13	0.07	-0.16	-0.80
2011-07-06 00:20	4	40	39.97	39.64	0.12	0.15	-0.33	-0.80
2011-07-06 00:40	4	90	90.02	89.11	0.12	0.08	-0.91	-1.00
2011-07-06 01:00	4	60	59.99	59.43	0.11	0.12	-0.56	-0.90
2011-07-06 01:20	4	10	10.16	10.14	0.32	0.13	-0.02	-0.20
2011-07-06 01:40	4	30	29.97	29.69	0.24	0.12	-0.28	-0.90
2011-07-06 02:00	4	50	50.05	49.62	0.10	0.09	-0.43	-0.90
2011-07-06 02:20	4	70	69.98	69.44	0.13	0.11	-0.54	-0.80
2011-07-06 02:40	4	80	79.99	79.37	0.10	0.13	-0.62	-0.80
2011-07-06 03:00	5	0	0.40	0.37	0.24	0.02	-0.03	- NA
2011-07-06 03:20	5	30	30.03	29.67	0.19	0.09	-0.36	-1.20
2011-07-06 03:40	5	50	50.05	49.50	0.11	0.09	-0.55	-1.10
2011-07-06 04:00	5	10	10.13	10.00	0.26	0.13	-0.13	-1.30
2011-07-06 04:20	5	90	90.00	89.00	0.10	0.03	-1.00	-1.10
2011-07-06 04:40	5	60	60.00	59.65	0.12	0.08	-0.35	-0.60
2011-07-06 05:00	5	20	20.01	19.82	0.12	0.07	-0.19	-0.90
2011-07-06 05:20	5	80	80.01	79.44	0.09	0.11	-0.57	-0.70
2011-07-06 05:40	5	70	70.07	69.52	0.09	0.06	-0.55	-0.80
2011-07-06 06:00	5	40	40.02	39.76	0.17	0.10	-0.26	-0.60

Table 7. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the HPB ozone calibrator (OC) TEI 49C-PS #423807729 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2011-07-06 09:52	1	0	0.26	0.25	0.12	0.02	-0.01	NA
2011-07-06 10:12	1	40	39.97	39.92	0.12	0.10	-0.05	-0.10
2011-07-06 10:32	1	90	89.99	90.04	0.13	0.05	0.05	0.10
2011-07-06 10:52	1	60	59.99	59.95	0.10	0.10	-0.04	-0.10
2011-07-06 11:12	1	50	50.00	50.03	0.09	0.06	0.03	0.10
2011-07-06 11:32	1	20	19.96	19.93	0.17	0.05	-0.03	-0.20
2011-07-06 11:52	1	80	80.01	79.84	0.09	0.09	-0.17	-0.20
2011-07-06 12:12	1	10	9.99	9.99	0.20	0.07	0.00	0.00
2011-07-06 12:32	1	30	30.01	29.97	0.17	0.11	-0.04	-0.10
2011-07-06 12:52	1	70	69.99	69.95	0.11	0.14	-0.04	-0.10
2011-07-06 13:12	2	0	0.36	0.38	0.14	0.03	0.02	NA
2011-07-06 13:32	2	20	20.01	19.98	0.19	0.07	-0.03	-0.10
2011-07-06 13:52	2	40	40.00	40.05	0.17	0.08	0.05	0.10
2011-07-06 14:12	2	90	90.00	89.94	0.10	0.10	-0.06	-0.10
2011-07-06 14:32	2	60	59.99	60.10	0.12	0.14	0.11	0.20
2011-07-06 14:52	2	10	10.27	10.25	0.43	0.14	-0.02	-0.20
2011-07-06 15:12	2	30	30.06	30.28	0.14	0.08	0.22	0.70
2011-07-06 15:32	2	50	49.99	50.08	0.17	0.10	0.09	0.20
2011-07-06 15:52	2	70	70.01	69.93	0.10	0.12	-0.08	-0.10
2011-07-06 16:12	2	80	80.00	79.90	0.12	0.13	-0.10	-0.10
2011-07-06 16:32	3	0	0.21	0.33	0.31	0.04	0.12	NA
2011-07-06 16:52	3	30	30.03	29.96	0.21	0.16	-0.07	-0.20
2011-07-06 17:12	3	50	50.01	49.91	0.10	0.08	-0.10	-0.20
2011-07-06 17:32	3	10	10.60	10.51	0.61	0.19	-0.09	-0.80
2011-07-06 17:52	3	90	90.01	89.89	0.16	0.09	-0.12	-0.10
2011-07-06 18:12	3	60	60.03	60.07	0.13	0.12	0.04	0.10
2011-07-06 18:32	3	20	19.99	19.84	0.20	0.09	-0.15	-0.80
2011-07-06 18:52	3	80	79.97	80.03	0.09	0.14	0.06	0.10
2011-07-06 19:12	3	70	70.00	69.98	0.09	0.12	-0.02	0.00
2011-07-06 19:32	3	40	40.00	40.02	0.12	0.10	0.02	0.00
2011-07-06 19:52	4	0	0.40	0.36	0.23	0.04	-0.04	NA
2011-07-06 20:12	4	40	40.02	40.13	0.12	0.08	0.11	0.30
2011-07-06 20:32	4	90	90.01	89.99	0.07	0.08	-0.02	0.00
2011-07-06 20:52	4	60	60.04	59.91	0.09	0.09	-0.13	-0.20
2011-07-06 21:12	4	50	50.02	50.01	0.13	0.05	-0.01	0.00
2011-07-06 21:32	4	20	20.01	20.06	0.20	0.04	0.05	0.20
2011-07-06 21:52	4	80	79.98	80.04	0.06	0.07	0.06	0.10
2011-07-06 22:12	4	10	10.18	10.37	0.40	0.11	0.19	1.90
2011-07-06 22:32	4	30	30.04	30.14	0.23	0.08	0.10	0.30
2011-07-06 22:52	4	70	70.00	69.88	0.09	0.12	-0.12	-0.20
2011-07-06 23:12	5	0	0.37	0.34	0.16	0.02	-0.03	NA
2011-07-06 23:32	5	20	20.01	19.91	0.11	0.06	-0.10	-0.50
2011-07-06 23:52	5	40	39.97	40.10	0.12	0.09	0.13	0.30
2011-07-07 00:12	5	90	90.03	89.97	0.09	0.07	-0.06	-0.10
2011-07-07 00:32	5	60	59.99	60.01	0.10	0.11	0.02	0.00

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2011-07-07 00:52	5	10	10.00	9.96	0.13	0.03	-0.04	-0.40
2011-07-07 01:12	5	30	29.98	30.06	0.08	0.06	0.08	0.30
2011-07-07 01:32	5	50	50.02	50.28	0.10	0.09	0.26	0.50
2011-07-07 01:52	5	70	69.99	69.92	0.11	0.10	-0.07	-0.10
2011-07-07 02:12	5	80	79.97	79.91	0.10	0.09	-0.06	-0.10
2011-07-07 02:32	6	0	0.20	0.44	0.29	0.05	0.24	NA
2011-07-07 02:52	6	30	30.02	30.23	0.17	0.06	0.21	0.70
2011-07-07 03:12	6	50	50.01	50.12	0.12	0.06	0.11	0.20
2011-07-07 03:32	6	10	10.15	10.33	0.46	0.13	0.18	1.80
2011-07-07 03:52	6	90	90.01	90.24	0.07	0.12	0.23	0.30
2011-07-07 04:12	6	60	59.98	60.18	0.11	0.09	0.20	0.30
2011-07-07 04:32	6	20	19.96	19.96	0.09	0.06	0.00	0.00
2011-07-07 04:52	6	80	80.01	79.89	0.07	0.08	-0.12	-0.10
2011-07-07 05:12	6	70	70.01	69.99	0.10	0.04	-0.02	0.00
2011-07-07 05:32	6	40	40.02	40.03	0.19	0.14	0.01	0.00

Conclusions

The ozone measurements at Hohenpeissenberg agreed perfectly with the WCC-Empa travelling standard. The simultaneous measurements using different instruments and analytical techniques add to the very high standard of the HPB measurement. No further improvement is possible with the current measurement techniques. This level of data quality should be maintained and available data after 2007 needs to be submitted to WDCGG.

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Location of air intake: The air intake is mounted on the terrace 2 m above the laboratory.

Inlet protection: Protection against rain water / snow / insects.

Tubing / Material: Inlet is made of PFA tubing (2 m 1/8", heated to 3°C above ambient temperature, followed by approx. 2 m 1/8" PFA tubing inside the lab). Total flow is 80 ml min^{-1} in 1/8" tubing.

Inlet filter: PFA filter holder with Pall Zylon PFTE filters, 5µm.

Residence time: < 25s

Instrumentation

Hohenpeissenberg is equipped with two CO analysers, which are both running in parallel. The UV fluorescence instrument (Aerolaser AL5001) is considered the main instrument, whereas the NDIR analyser (TEI48S) is still running as a back-up system. Since data of the TEI48S instrument was not used during the past few years, this instrument was not assessed during this audit.

Standards

Commercial calibration gases (Riessner Gase, Messer and AirLiquide) with high CO mole fractions of approx., 1 and 40 ppm and three NOAA/ESRL laboratory standards are available at HPB. In addition, two cylinders calibrated at the Max Planck Institute for Biogeochemistry (Jena) are available. Table 8 gives an overview of the HPB standards.

Table 8. CO, CO_2 and CH_4 Standards available at HPB.

Cylinder ID	Type	CO (ppb)	U_{CO} (ppb)	CH_4 (ppb)	U_{CH4} (ppb)	CO_2 (ppm)	U_{CO2} (ppb)	Start of use	End of use
210	Riessner	1000	50	NA	NA	NA	NA	Nov 04	Jul 08
123	Riessner	1050	53	NA	NA	NA	NA	Jul 08	Apr 11
4887G	AirLiquide	1007	50	NA	NA	NA	NA	Apr 11	NA
A1085	Messer	40500	810	NA	NA	NA	NA	Aug 95	May 98
7596B	Messer	40800	816	NA	NA	NA	NA	May 98	Oct 01
157544	Messer	41000	820	NA	NA	NA	NA	Sep 01	Dec 03
9639C	Messer	40800	816	NA	NA	NA	NA	Oct 03	Dec 08
A7365	AirLiquide	41750	840	NA	NA	NA	NA	Sep 08	NA
CA07441	NOAA	295.70	0.21	NA	NA	NA	NA	Dec 07	NA
D780054	MPI Jena	312.06	0.48	2186.0	0.3	444.56	0.06	Oct 10	NA
D780053	MPI Jena	100.08	0.26	1647.5	0.2	361.25	0.05	Oct 10	NA
CC327218	NOAA	188.20	1.60	1811.7	NA	390.13	NA	Mar 11	NA
CC311852	NOAA	343.67	NA	1864.0	NA	391.55	NA	Mar 11	NA

Operation and Maintenance

Check for general operation:	Daily on working days (Mon – Fri). A check list is used.
Inlet filter exchange:	Every 2 weeks, more often in case of pollution episodes.
Other (cleaning, leak check etc.):	As required. Cleaning of optics by Aerolaser GmbH when analyser sensitivity drops below 20 counts/ppb.

Data Acquisition and Data Transfer

Same as for surface ozone.

Data Treatment

Data validation is carried out at HPB by the station scientist. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. One minute averages are stored and further averaged to hourly and daily means.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for carbon monoxide from 1995 to 2007 is available from WDCGG.

Documentation

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

Comparison of the Carbon Monoxide Analyser

All procedures were conducted according to the Standard Operating Procedure [WMO, 2007b] and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 17 below.

Setup and Connections

Table 12 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the HPB data acquisition system.

Table 9. Experimental details of HPB CO comparison.

Travelling standard (TS)	
WCC-Empa Traveling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 17.	
Station Analyser (AL)	
Model, S/N	Aerolaser AL5001 #142
Principle	Vacuum UV Fluorescence
Comparison procedures	
Connection	WCC-Empa TS were connected to the Aerolaser sample inlet, including the Nafion drier of the instrument. An overflow of 20 ml/min was provided using a MFC and a Valco multi position valve to choose between standards.

Results

The results of the assessment are shown in the Executive Summary (figures and equations), and the individual measurements of the TS are presented in Table 10 (WMO-2000 scale) and Table 11 (WMO-2004 scale).

Table 10. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Aerolaser AL5001 instrument with the WCC-Empa TS (WMO-2000 CO scale).

Date / Time	TS Cylinder	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(11-07-05 13:03:30)	100212_FF31496	106.83	0.39	106.25	0.37	14	-0.58	-0.54
(11-07-05 13:19:00)	110512_FB03387	277.48	1.23	274.21	0.58	13	-3.27	-1.18
(11-07-05 13:34:00)	110512_FB03350	209.08	0.79	207.52	0.55	13	-1.56	-0.75
(11-07-05 13:49:00)	100122_FA02479	50.98	0.33	50.99	0.50	13	0.01	0.02
(11-07-05 14:04:00)	080820_FA02686	108.03	0.43	107.63	0.44	13	-0.40	-0.37
(11-07-05 14:19:00)	080814_FA02488	44.99	0.34	45.31	0.48	13	0.32	0.71

Table 11. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Aerolaser AL5001 instrument with the WCC-Empa TS (WMO-2004 CO scale).

Date / Time	TS Cylinder	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(11-07-05 13:03:30)	100212_FF31496	105.44	0.38	106.25	0.37	14	0.81	0.77
(11-07-05 13:19:00)	110512_FB03387	273.87	1.21	274.21	0.58	13	0.34	0.12
(11-07-05 13:34:00)	110512_FB03350	206.36	0.78	207.52	0.55	13	1.16	0.56
(11-07-05 13:49:00)	100122_FA02479	50.32	0.33	50.99	0.50	13	0.67	1.33
(11-07-05 14:04:00)	080820_FA02686	106.63	0.42	107.63	0.44	13	1.00	0.94
(11-07-05 14:19:00)	080814_FA02488	44.41	0.34	45.31	0.48	13	0.90	2.03

Conclusions

The carbon monoxide measurements at Hohenpeissenberg agreed within the WMO GAW DQOs of 2 ppb based on the WMO-2004 CO scale. Slightly larger differences were found when the WMO-2000 CO scale was used for the assessment. In principle, these two versions of the CO scale should not significantly differ, which has been confirmed by a round robin experiment between NOAA and WCC-Empa in 2008-10. However, differences were found for laboratory standards purchased in 2010. HPB also refers to laboratory standards that were purchased very recently. These remaining uncertainties of the CO scale need further attention, and future correction of the data might become necessary.

The relative standard deviation of the multiple analysis of the TS was 0.6 % for the Aerolaser AL5001 instrument. This is comparable to other measurement techniques such as GC with HgO detectors, and significantly better compared to NDIR instruments. Therefore, the HPB instrumentation is fully adequate for CO measurements.

The audit confirmed that the HPB CO measurements comply with the WMO GAW DQOs, and the whole measurement set-up is fully adequate. No changes are required.

Methane and Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

The instrument was provisionally installed at the air conditioned laboratory for visiting scientist on the 3rd floor.

Air Inlet System

Location of air intake:	Outside wall on 3rd floor of the lab building, distance to wall approx. 1 meter, below the canopy height of the surrounding trees / forest.
Inlet protection:	Funnel as rainwater protection.
Tubing / Material:	Approx. 3 meters 1/4 inch PFA tubing to instrument, flow rate approx. 250 ml/min.
Inlet filter:	Inline particle filter inside Picarro, no external filter.
Residence time:	Approx. 10 s

The inlet is not adequate concerning materials and location. Dekabon or metal tubing should be used instead of PFA, and the inlet height should be as high as possible (above tree canopy). See Recommendations 2 and 3.

Instrumentation

A Picarro G1301 CO_2, CH_4 and H_2O analyser is available at HPB. The air is not dried, which requires a correction for dilution and spectroscopic effects. Since the instrument was running until now only on a provisional basis, such corrections have not yet been applied. The correction function was determined by WCC-Empa during the audit (see Figure 10), and it is recommended that this function is confirmed by similar experiments by HPB staff.

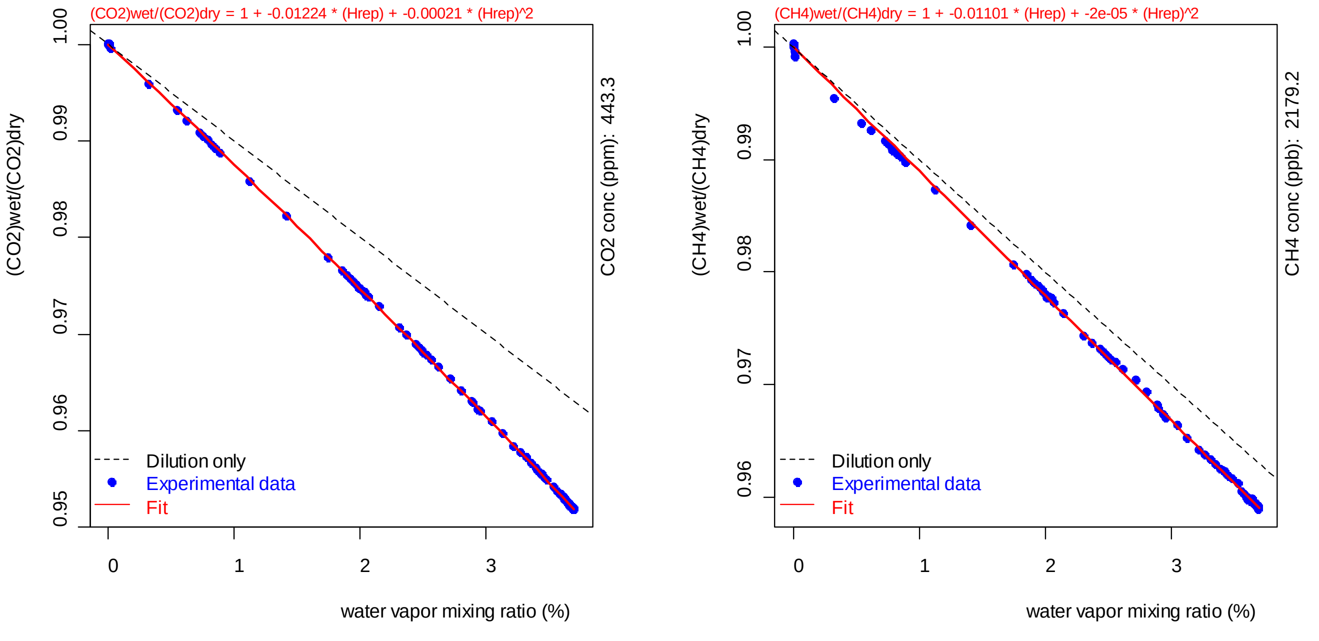

Figure 10. Quadratic fits for the HPB Picarro G1301 instrument of CO_2wet/CO_2dry and CH_4wet/CH_4dry vs. H_2O mixing ratios.

The following functions (5a-b) were obtained to compensate for the humidity interference:

$$CO_2(dry) = CO_2(wet) / (1 – 0.01224 * H_{rep} – 0.00021 * H_{rep}^2) \quad (5a)$$

$$CH_4(dry) = CH_4 (wet) / (1 – 0.01101 * H_{rep} – 1.51e\text{-}5 * H_{rep}^2) \quad (5b)$$

Where H_{rep} corresponds to the Picarro reported water mixing ratio in %

These functions are usually stable over time but should be confirmed in regular intervals. The obtained coefficients compare well to other instruments of this type [*Chen et al.*, 2010].

Standards

See Table 8 above for a list of the currently available CH_4 and CO_2 standards at HPB.

Operation and Maintenance

Check for general operation: Daily on working days (Mon – Fri).

No other regular maintenance except manual measurements of the MPI Jena standard gases have been made until now.

Data Acquisition and Data Transfer

The Picarro system was integrated in the LabView based station data acquisition system. The DAQ system of the instrument itself is also running but these data have not yet been used. Remote access is possible through the internet.

Data Treatment

Until now the Picarro data has not been evaluated.

Data Submission

Data of the Picarro instrument have not yet been submitted to the World Data Centre for Greenhouse Gases (WDCGG) due to the relative recent start of the measurements.

Documentation

All information is entered in electronic log books and checklists. The instrument manual is available at the site.

Comparison of the Picarro G1301 instrument with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure [WMO, 2007b] and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 17 below.

Setup and Connections

Table 12 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the Picarro data acquisition system.

Table 12. Experimental details of the Picarro G1301 comparison.

Travelling standard (TS)	
WCC-Empa Traveling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 17. The TS were connected to a sampling unit using 1/16 inch SS tubing with a multi position valve for cylinder selection and a MFC to control the flow rate.	
Station Analyser (OA)	
Model, S/N	Picarro G1301 #CFADS-071
Principle	CRDS
Comparison procedures	
Connection	The TS were connected to a sampling unit using 1/16 inch SS tubing. The sampling unit was custom built by WCC-Empa and consists of a multi position valve for cylinder selection and a MFC to control the flow rate.

Results

The results of the assessment are shown in the Executive Summary (figures and equations), and the individual measurements of the TS are presented in the following Tables.

Table 13. CH_4 aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Picarro G1301 instrument with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	uTS (ppb)	OA (ppb)	sd OA (ppb)	N	PIC -TS (ppb)	PIC-TS (%)
(11-07-05 10:04:30)	080814_FA02488	1309.95	0.23	1309.82	0.36	10	-0.13	-0.01
(11-07-05 10:19:30)	110512_FB03387	2704.07	0.47	2704.20	0.43	10	0.13	0.00
(11-07-05 10:34:30)	100212_FF31496	2123.03	0.37	2123.61	0.24	10	0.58	0.03
(11-07-05 10:49:30)	110512_FB03350	2761.32	0.47	2762.09	0.18	10	0.77	0.03
(11-07-05 11:04:30)	100122_FA02479	1893.25	0.34	1893.97	0.29	10	0.72	0.04
(11-07-05 11:19:30)	080820_FA02686	1871.14	0.32	1871.50	0.13	10	0.36	0.02

Table 14. CO_2 aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Picarro G1301 instrument with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	uTS (ppm)	OA (ppm)	sd OA (ppm)	N	PIC -TS (ppb)	PIC -TS (%)
(11-07-05 10:04:30)	080814_FA02488	149.82	0.04	149.71	0.03	10	-0.11	-0.07
(11-07-05 10:19:30)	110512_FB03387	339.07	0.08	338.93	0.02	10	-0.14	-0.04
(11-07-05 10:34:30)	100212_FF31496	331.12	0.08	331.03	0.02	10	-0.09	-0.03
(11-07-05 10:49:30)	110512_FB03350	384.98	0.09	384.82	0.03	10	-0.16	-0.04
(11-07-05 11:04:30)	100122_FA02479	406.98	0.09	406.94	0.02	10	-0.04	-0.01
(11-07-05 11:19:30)	080820_FA02686	172.97	0.04	172.90	0.03	10	-0.07	-0.04

Conclusions

The Picarro G1301 instrument installed at Hohenpeissenberg proved to being capable of simultaneous measurements of CH_4, CO_2, and H_2O.

For CH_4, the Picarro results were within the WMO GAW DQOs. The relative standard deviation of the multiple analysis of the TS was 0.014% based on 1-min averages. This is approx. 3 to 5 times better compared to single injections of an optimised GC/FID system. The Picarro G1301 system is therefore fully adequate for CH_4 measurements.

For CO_2, the deviation between the HPB and WCC-Empa results were slightly larger than the WMO GAW DQOs of 0.1 ppm. These DQOs are very challenging for most stations, and the differences might be due to the uncertainties of the laboratory and travelling standards. The relative standard deviation of the multiple analysis of the TS was 0.010% based on 1-min averages. This repeatability is sufficient to reach the GAW DQOs. The Picarro G1301 system is fully adequate for CO_2 measurements.

Issues with the sampling location and inlet design need to be solved. In addition, the water vapour correction must be applied, and regular re-evaluations of the water interference are necessary to demonstrate the stability of the system.

WCC-Empa Traveling Standards

Ozone

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

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

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

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 15. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 11). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in [*Klausen et al.*, 2003]).

$$X_{TS}\text{ (ppb)} = ([TS] - 0.14\text{ ppb}) / 1.001 \qquad (6a)$$

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

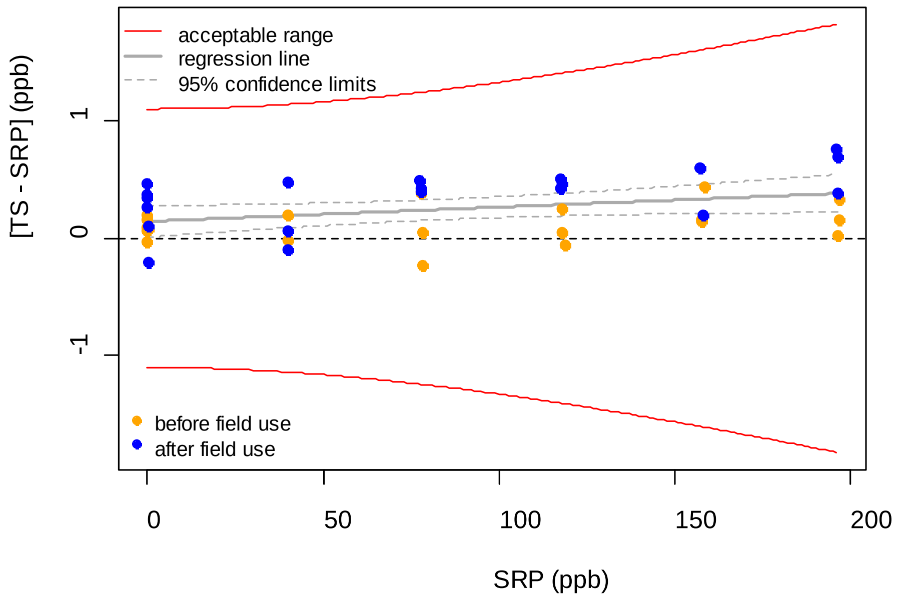

Figure 11. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2011-06-01	1	0	0.11	0.44	0.20	0.18
2011-06-01	1	80	78.48	0.11	78.25	0.15
2011-06-01	1	160	157.69	0.27	157.83	0.19
2011-06-01	1	40	40.16	0.24	40.36	0.24
2011-06-01	1	200	196.55	0.22	196.57	0.25
2011-06-01	1	120	117.91	0.38	117.96	0.20
2011-06-01	1	0	-0.09	0.35	0.00	0.15
2011-06-01	2	0	0.03	0.20	0.09	0.19
2011-06-01	2	120	118.89	0.31	118.83	0.15
2011-06-01	2	80	78.22	0.36	78.28	0.12
2011-06-01	2	160	157.65	0.19	157.81	0.20
2011-06-01	2	200	196.75	0.23	197.09	0.31
2011-06-01	2	40	40.15	0.24	40.14	0.34
2011-06-01	2	0	0.00	0.16	-0.04	0.19
2011-06-01	3	0	-0.08	0.30	0.11	0.26
2011-06-01	3	160	158.33	0.27	158.77	0.33
2011-06-01	3	40	40.18	0.21	40.38	0.28
2011-06-01	3	120	118.11	0.34	118.36	0.10
2011-06-01	3	200	196.75	0.55	196.90	0.31
2011-06-01	3	80	77.73	0.27	78.12	0.20
2011-06-01	3	0	0.03	0.29	0.20	0.14
2011-07-12	4	0	0.03	0.32	0.38	0.26
2011-07-12	4	80	77.92	0.26	78.35	0.24
2011-07-12	4	160	157.31	0.43	157.91	0.39
2011-07-12	4	120	117.78	0.27	118.25	0.15
2011-07-12	4	200	196.54	0.23	196.92	0.26
2011-07-12	4	40	39.96	0.25	39.86	0.20
2011-07-12	4	0	-0.19	0.32	0.07	0.23
2011-07-12	5	0	0.07	0.24	0.17	0.20
2011-07-12	5	40	40.04	0.40	40.10	0.21
2011-07-12	5	160	157.92	0.21	158.11	0.26
2011-07-12	5	200	196.51	0.42	197.20	0.17
2011-07-12	5	120	117.58	0.20	118.08	0.23
2011-07-12	5	80	77.20	0.37	77.69	0.21
2011-07-12	5	0	-0.22	0.14	0.15	0.15
2011-07-12	6	0	0.24	0.17	0.03	0.28
2011-07-12	6	80	77.67	0.31	78.06	0.19
2011-07-12	6	40	39.82	0.41	40.29	0.25
2011-07-12	6	160	157.18	0.22	157.79	0.23
2011-07-12	6	200	195.98	0.32	196.74	0.14
2011-07-12	6	120	117.44	0.40	117.87	0.16
2011-07-12	6	0	-0.20	0.36	0.27	0.16

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide and Methane. NOAA/ESRL was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL by way of traveling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-2000/2004 scale [Novelli, et al., 2003]

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

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

More information about the NOAA/ESRL calibration scales can be found on the GMD website (www.esrl.noaa.gov/gmd/ccl). The scales were transferred to the TS using the following instruments at WCC-Empa:

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

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

Table 16 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. For internal consistency among the available LS at WCC-Empa, new values have been assigned to the NOAA standards for some tanks. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 17, and Figure 12 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS.

Table 16. NOAA/ESRL laboratory standards at WCC-Empa.

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

*WMO-2004, #WMO-2000

Table 17. Calibration summary of the WCC-Empa travelling standards.

TS	CO	uCO	CH_4	uCH_4	CO_2	uCO_2	N_2O	uN_2O
	(ppb)	(ppb)	(ppb)	(ppb)	(ppm)	(ppm)	(ppb)	(ppb)
080814_FA02488	44.99	0.34	1309.95	0.23	149.82	0.04	129.32	NA
080820_FA02686	108.03	0.43	1871.14	0.32	172.97	0.04	131.97	NA
100122_FA02479	50.98	0.33	1893.25	0.34	406.98	0.09	305.70	0.10
100212_FF31496	106.83	0.39	2123.03	0.37	331.12	0.08	298.64	0.10
110512_FB03350	209.08	0.79	2761.32	0.47	384.98	0.09	312.80	0.10
110512_FB03387	277.48	1.23	2704.07	0.47	339.07	0.08	310.74	0.10

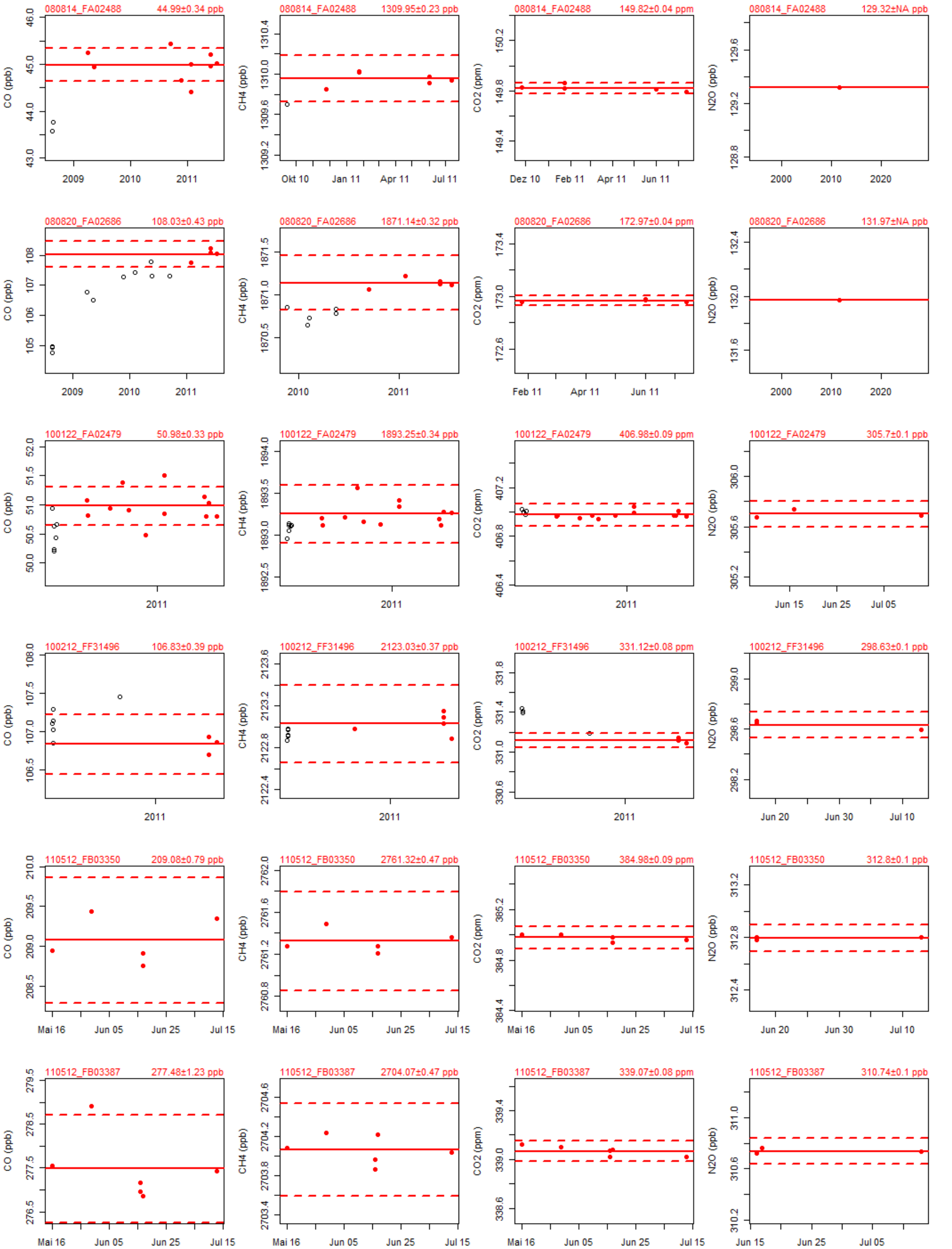

Figure 12. Results of the WCC-Empa TS calibrations. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard uncertainty and included the uncertainty of the reference scale.

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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:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.001±0.001) □ [SRP] - (0.1±0.1)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #56028-306
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = -0.1; COEFF = 1.005
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.002±0.001) □ [SRP] + (0.00±0.06)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.00 ppb) / 1.002
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.69e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments: Main ozone analyser	
1.8	Reference:	WCC-Empa Report 11/3

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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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:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.001±0.001) □ [SRP] - (0.1±0.1)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #632519672
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.3; COEFF = 1.027
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.002±0.001) □ [SRP] - (0.24±0.06)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.24 ppb) / 1.002
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.69e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments: Backup ozone analyser	
1.8	Reference:	WCC-Empa Report 11/3

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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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:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.001±0.001) □ [SRP] - (0.1±0.1)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	UPK 8002 #92062
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.1; SPAN = 3.75
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.993±0.001) □ [SRP] + (0.17±0.06)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.17 ppb) / 0.993
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.74e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments: Backup ozone analyser (chemiluminescence)	
1.8	Reference:	WCC-Empa Report 11/3

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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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:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.001±0.001) $\times$ [SRP] - (0.1±0.1)
1.6	Ozone Calibrator [OC]	
1.6.1	Model:	TEI 49C-PS #423807729
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.1; COEF = 1.024
1.6.4	Calibration at start of audit (ppb):	[OC] = (1.001±0.001) $\times$ [SRP] + (0.18±0.06)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OC] - 0.18 ppb) / 1.001
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.65e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments: Station calibrator	
1.8	Reference:	WCC-Empa Report 11/3

[OC]: Instrument readings; [SRP]: SRP readings; X_{O3}: 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:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2000 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2000 scale
1.6	Station CO Reference:	NOAA/GMD WMO-2004 laboratory standards
1.6.1	Analyser Model:	Aerolaser AL5001 #142
1.6.2	Range of calibration:	50 – 275 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9875±0.0033) X_{CO} + (0.8±0.3)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO - 0.8) / 0.9875
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (0.4 ppb^2 + 6.15e-05 * $X_{CO}{}^2$)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	Calculations based on WMO-2000 CO scale
1.8	Reference:	WCC-Empa Report 11/3

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 CO 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:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.6	Station CO Reference:	NOAA/GMD WMO-2004 laboratory standards
1.6.1	Analyser Model:	Aerolaser AL5001 #142
1.6.2	Range of calibration:	50 – 275 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.0005±0.0034) $\times$ X_{CO} + (0.8±0.3)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO - 0.8) / 1.0005
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (0.4 ppb^2 + 6.02e-05 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	Calculations based on WMO-2004 CO scale
1.8	Reference:	WCC-Empa Report 11/3

[CO]: Instrument readings; X: mixing ratios on the WMO-2004 CO scale.

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Methane 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:		Methane

1.1	Date of Audit:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station CH_4 Reference:	WS and NOAA laboratory standards (NOAA04 scale)
1.6.1	Analyser Model:	Picarro G1301 # #CFADS-071
1.6.2	Range of calibration:	1310 – 2760 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CH_4 = (1.00016±0.00007) □ X_{CH4}
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4) / 1.00016
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.1 ppb^2 + 1.16e-07 * X_{CH4}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	Instrument was calibrated based on MPI Jena working standards
1.8	Reference:	WCC-Empa Report 11/3

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

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Carbon Dioxide 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 Dioxide

1.1	Date of Audit:	2011-07-05 to 2011-07-07
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. St. Gilge , Mr. B. Briel, Mrs. M. Hoffmann
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station CO_2 Reference:	WS and NOAA laboratory standards (WMO-X2007 scale)
1.6.1	Analyser Model:	Picarro G1301 # #CFADS-071
1.6.2	Range of calibration:	150 – 407 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	CO_2 = (0.999959±0.00000) □ X_{CO2} - (0.09±0.23)
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 + 0.09) / 0.999959
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.05 ppm^2 + 1.83e-07 * X_{CO2}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	Instrument was calibrated based on MPI Jena working standards
1.8	Reference:	WCC-Empa Report 11/3

[CO_2]: Instrument readings; X: mixing ratios on the WMO-X2007 CO_2 scale.

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LIST OF ABBREVIATIONS

BKG	Background
BLC	Blue Light Converter
CCL	Central Calibration Laboratory
CLD	Chemiluminescence Detector
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DAQ	Data Acquisition System
DQO	Data Quality Objective
dtm	Date/Time
DWD	Deutscher Wetterdienst (German Weather Service)
GAWSIS	GAW Station Information System
HPB	Hohenpeissenberg
LS	Laboratory Standard
MFC	Mass Flow Controller
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
TS	Traveling Standard
UV	Ultra Violet
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard