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

Materials Science & Technology

Laboratory for Air Pollution and
Environmental Technology

WCC-Empa REPORT 06/4

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World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE, CARBON MONOXIDE AND METHANE

AT THE

GLOBAL GAW STATION JUNGFRAUJOCH

SWITZERLAND, JULY 2006

Submitted by

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

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ASSESSMENT AND RECOMMENDATIONS

The second system and performance audit at the Global GAW station Jungfraujoch (JFJ) was conducted by WCC-Empa[1] from 25 thru 27 July 2006 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007]. The JFJ observatory is operated by the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG). GAW measurements are carried out by Empa (mainly gaseous parameters) as a joint project with the Federal Office for the Environment (FOEN). Other institutes active at JFJ include the Paul Scherrer Institute (PSI) (mainly aerosol parameters) and MeteoSwiss (meteorological parameters). In addition, campaign based measurements are frequently performed. Furthermore JFJ has one of the longest solar absorption FTIR spectra measurements run by the Institut de Géophysique et d'Astrophysique (Liège, Belgium).

The first audit at JFJ was conducted in January 1999 [*Herzog, et al.*, 1999].

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Dr. Hans-Eckhard Scheel	IMK-IFU, WCC-N_2O
Dr. Martin Steinbacher	Empa Dübendorf, Station scientist

Our assessment of the station Jungfraujoch in general, as well as the surface ozone, carbon monoxide and methane 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 head Swiss Air Pollution Monitoring Network (NABEL) (Empa, Dr. Christoph Hüglin) 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 high alpine research station Jungfraujoch (3580 m) is situated on a mountain saddle between Jungfrau and Mönch. The station is located in the centre of Europe and is surrounded by highly industrialized regions. This special geographical situation offers the opportunity to monitor background concentrations but also to investigate the transport of anthropogenic pollutants from the boundary layer to the free troposphere. The site is all year round accessible by train. Further information is available in GAWSIS (www.empa.ch/gaw/gawsis).

Station Facilities

The Jungfraujoch GAW station comprises several laboratory rooms; most of the available space is occupied by permanent measurements, but some additional space may be used for campaign based experiments. Due to its location it is an ideal platform for atmospheric research.

Recommendation 1 (, 2007)**
The air-conditioning system is not able to maintain a stable laboratory temperature. WCC-Empa recommends to upgrade or replace the current AC system..

[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 based on mutual agreement.

Station Management and Operation

The station is permanently staffed with custodians. Basic maintenance work is done by the custodians. The site is regularly visited by station operators or scientists for maintenance and calibrations.

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. A TEI49C (UV absorption) instrument is used for surface ozone measurements. The instrumentation is adequate for its intended purpose.

Standards. The Swiss National Air Pollution Monitoring Network (NABEL) is equipped with two ozone standards (TEI49C-PS). Traceability of these standards to the GAW reference is ensured by at least half-yearly calibrations against the ozone reference (SRP#15) of WCC-Empa. On-site calibrations are carried out every three months.

Intercomparison (Performance Audit). The inter-comparisons extended over a period of 10 hours, and no further corrections were applied to the analyser data. The result of the assessment is summarised below and are presented in Figure 1.

TEI49C #0532213860: 0 – 90 ppb good agreement

Unbiased O3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.16 ppb) / 1.005 (1)

Here, [OA] represents surface ozone readings obtained from the station data acquisition (TEI49C).

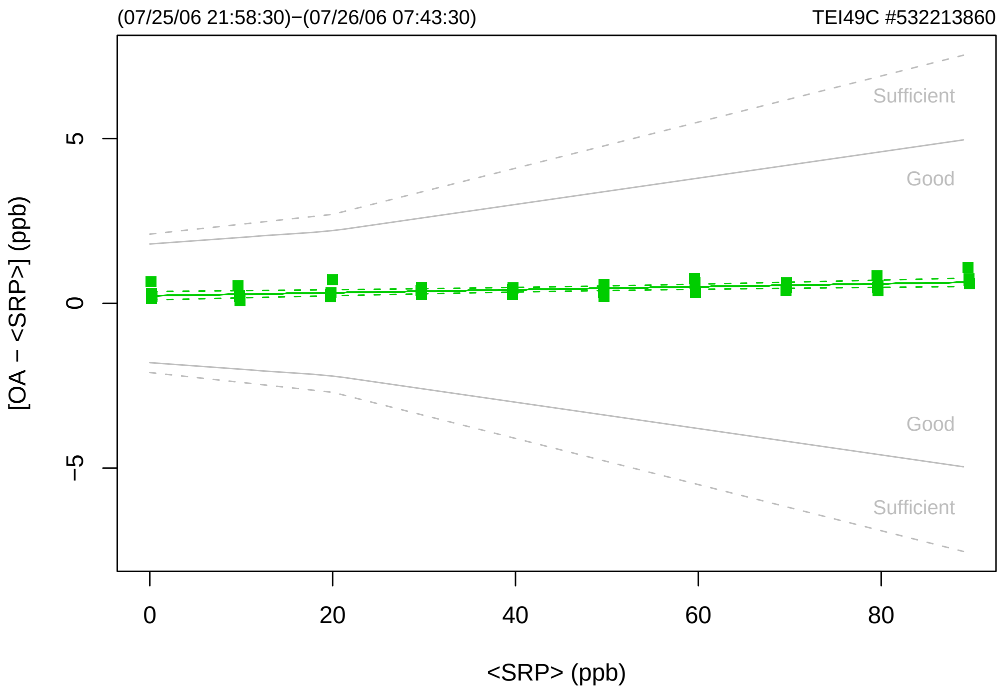

Figure 1. Bias of the Jungfraujoch ozone analyser with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining ‘good’ and ‘sufficient’ agreement according to GAW assessment criteria [Klausen, et al., 2003]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

Carbon Monoxide Measurements

Instrumentation. Jungfraujoch is currently equipped with three CO analysers, which are all running in parallel. Two techniques (NDIR and GC-FID) are running within the NABEL network; The GC/HgO instrument is used mainly for H_2 measurements, and CO data of this analyser is not routinely evaluated. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with two carbon monoxide standards. One standard (ppm level) is used for the calibration of the NDIR instrument; the other standard (ppb level) is used as a working standard of the GC-FID system. The ppm standard is calibrated against NIST at the NABEL calibration laboratory; the ppb standard is calibrated against NOAA/GMD WMO-2000 carbon monoxide scale at the calibration laboratory of WCC-Empa. With this equipment, adequate calibration of the carbon monoxide measurements is possible, though a direct link to the CCL with laboratory standards obtained from NOAA/GMD would be preferable. Calibrations of the NDIR system are carried out manually approximately every three weeks; however, zero checks are made automatically every 49 hours and are used for the correction of a zero offset.

> **Recommendation 2 (***, 2007)**
> *It should be considered to link the Jungfraujoch measurements directly to the CCL with laboratory standards from NOAA/GMD. Access to such standards is possible through WCC-Empa for CO and CH_4, but not for N_2O and SF_6. This recommendation is made for all variables of the GC-FID instrument.*
>
> **Recommendation 3 (**, 2007)**
> *WCC-Empa recommends to review the current procedure of the zero offset correction. It is encouraged to evaluate the significance of the zero offset before a correction is applied.*

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instruments with randomised carbon monoxide concentrations from a dilution system (NDIR) and from travelling standards (GC-FID). The following equations characterise the instrument bias (cf. Figure 2 and Figure 3):

Assessment with WCC-Empa travelling standards:

Agilent 6890 GC-FID:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 2.5 ppb) / 0.983 (2a)

Assessment with WCC-Empa dilution system:

Horiba APMA-360:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 1.8 ppb) / 1.008 (2b)

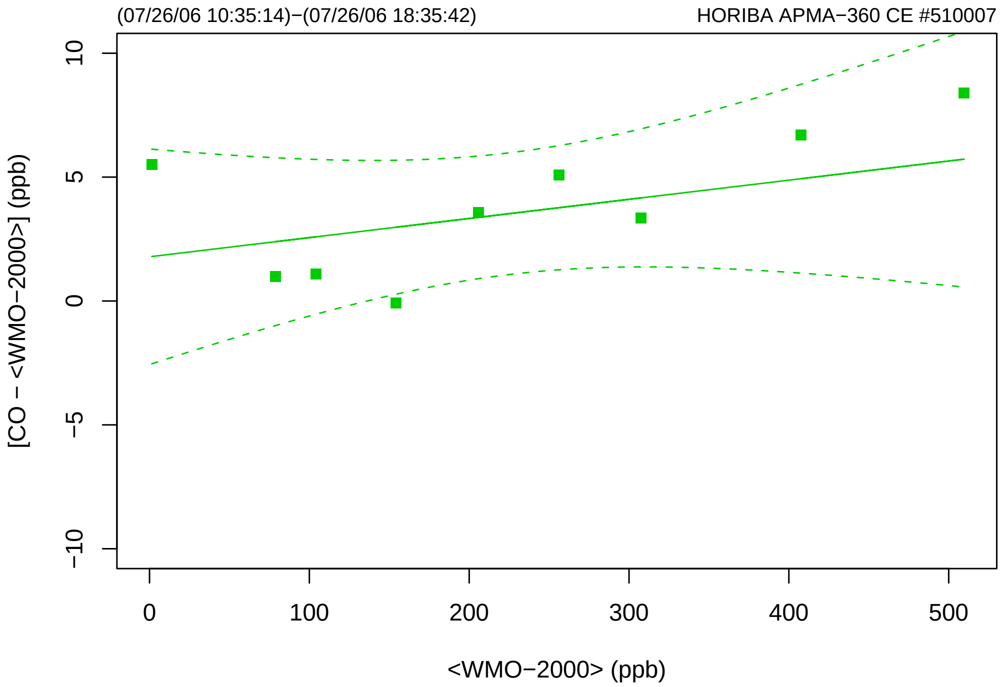

Figure 2. Bias of the Jungfraujoch NDIR carbon monoxide analyser (Horiba APMA-360) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

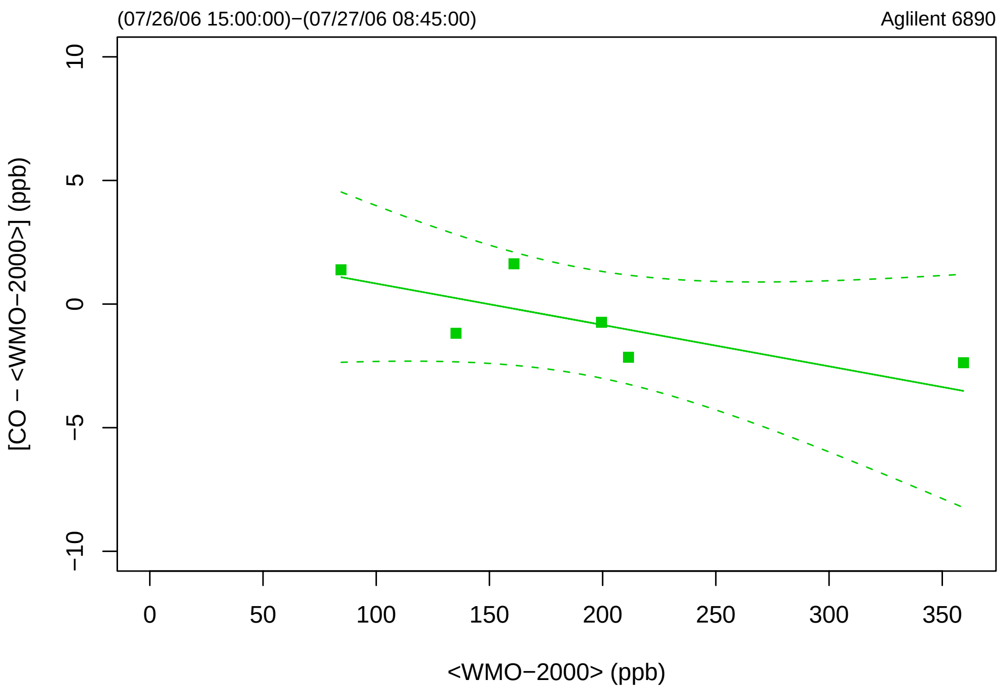

Figure 3. Bias of the Jungfraujoch GC-FID system (Agilent 6890) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Methane Measurements

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

Standards. One working standard is used for the calibration of the JFJ GC system. The working standards are calibrated against the NOAA04 methane scale at WCC-Empa before and after field use. The working standards are filled by Empa and contain whole natural air, usually from Dübendorf. With this equipment, adequate calibration of the methane measurements is possible.

Intercomparison (Performance Audit). The inter-comparison involved repeated measurements of WCC-Empa travelling standards with the JFJ instrument. The following equations characterise the instrument bias (cf. Figure 4):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 1.00115 (3)

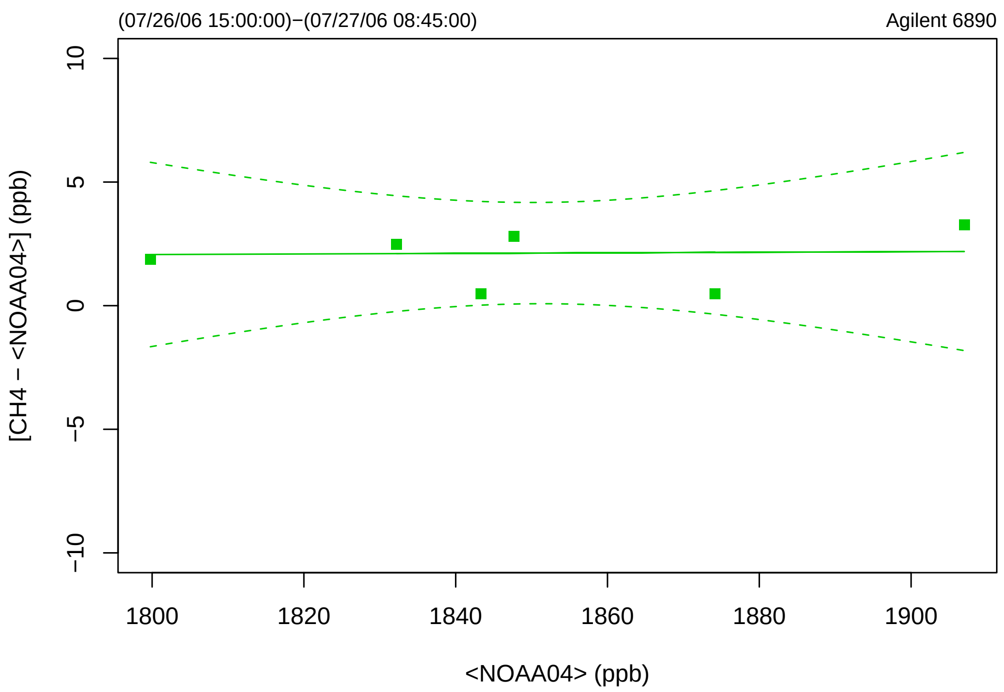

Figure 4. Bias of the Jungfraujoch methane GC (AGILENT 6890 Series) with respect to the NOAA04 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Data Acquisition and Management

Montior instruments: The JFJ station is equipped with a data acquisition PC with programmes from Breitfuss GmbH (EasyComp, Anacomp4 and Anavis Version 20040430). Data is automatically transferred to FOEN and Empa. Data validation is carried out at Empa, and the final data is stored in a data base at FOEN. 10 minutes raw data are stored and are available for further analysis. One minute raw data are also stored for 3 months, but are automatically deleted afterwards. More information on the NABEL data acquisition can be found in [*Empa*, 2005] and on the Breitfuss web site (www.breitfuss.de).

GC instrument: The entire instrument is under the control of a Linux based PC using multiple RS-232 serial data ports and control software written at Scripps Institution of Oceanography (SIO). This includes all the electrically actuated Valco valves and the Agilent 6890 GC. This software has been developed for the Agage network (http://agage.eas.gatech.edu).

Data Submission

Data are regularly (yearly) submitted to the World Data Centre for Greenhouse Gases (WDCGG). At the time of the audit methane data was not yet available at WDCGG, but submission is planned. The records are complete and include ancillary meteorological data.

> **Recommendation 3 (**, 2007)**
> *Data of the GC-FID system (CO, CH_4, N_2O, SF_6) as well as VOC data should be submitted to WDCGG.*

Conclusions

The Global GAW station Jungfraujoch comprises an extensive suite of ongoing measurements. The combination of long time series with the large number of measured parameters makes the JFJ station an important contribution to the GAW programme. All assessed measurements were of high quality.

Summary Ranking of Jungfraujoch Station

System Audit	Adequacy#	Comment
Access	(5)	
Facilities		
Laboratory and office space	(5)	
Air Conditioning	(3)	Lab temperature not stable
Power supply	(5)	
General Management and Operation		
Organisation	(5)	
Competence of staff	(5)	
Air Inlet System	(5)	
Instrumentation		
Ozone	(5)	
Carbon monoxide	(4)	
Aerosol parameters*	(5)	Comprehensive suite of measurements
Reactive gas other than CO*	(5)	
Meteo*	(5)	
Standards		
Ozone	(4)	Calibrations every 6 months
Carbon monoxide	(4)	Linked to CCL only through WCC-Empa
Data Management		
Data acquisition	(5)	
Data processing	(5)	
Data submission	(4)	Data is only partly submitted

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

Dübendorf, January 2007

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

APPENDIX

Global GAW Station Jungfraujoch

Site description

The Jungfraujoch GAW station has been described in detail elsewhere, e.g. [*Zellweger, et al.*, 2003] (cf. http://www.ifjungo.ch/publications for a list of publications) and the station is also registered in GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Programme

The observatory Jungfraujoch has a long research history dating back to the 1920's and comprises today an extensive suite of observations of the atmosphere. The status of the programme as of July 2006 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the JFJ Station

Parameter	Current Instrument	Data Coverage (%)		
		<12 m	<3 y	Overall
Aerosol				
Major inorg. comp. (coarse)	Filter sampling / IC			
Light absorption coefficient	Filter and light attenuation (Aethalometer)			
Light scattering coefficient	Nephelometer			
Mass concentration (TSP, PM10, PM1)	Filter sampling / gravimetry / β-ray attenuation			
Multiwavelength optical depth	Filter Radiometry			
Number concentration	CPC			
Ozone				
Surface ozone	UV absorption (TEI49C)	97	94	94
Reactive Gas				
CO	NDIR (Horiba APMA-360) and GC-FID (Agilent 6890)	NDIR: 97 FID: 91	NDIR: 94 FID: 86	NDIR: 62 NA
NO, NO_2 and NO_x	CLD / PLC (Ecophysics)	NO: 71 NO_x: 68	NO: 77 NO_x: 75	NO: 81 NO_x: 78
NO_y	CLD / Au Converter	70	77	76
SO_2	TEI43C-TL	96	NA	NA
Greenhouse Gas				
N_2O	GC-ECD (Agilent 6890)	72	79	NA
CH4	GC-FID (Agilent 6890)	91	87	NA
SF_6	GC-ECD (Agilent 6890) and GC-MS	72	76	NA
VOCs, CFCs, HFCs, HCFCs	GC-MS	74	68	
Solar radiation				
Global irradiance	Pyranometer (global broadband)			
Direct irradiance	Pyrheliometer (direct broadband)			
UV Spectral	UV photometry			
UV Broadband	Sunphotometry/Filter Radiometry			
Precipitation Chemistry				
Electric conductivity and pH				
Inorganic ions	IC (Dionex)			
Trace metals	ICP-MS			
Radio Nuclide				
Radon				
Beryllium [Be-7]	Filter sampling + gamma spectrometry			
Ancillary Measurements				
Meteo (complete set of parameters)		63-100	88-100	95-99

Missing data availability: no data coverage information was available at the time of the audit.
NA: Not applicable

Ozone, Carbon Monoxide and Methane Distribution at Jungfraujoch

The monthly and yearly distributions of one hourly mean values for surface ozone, carbon monoxide and methane for the year 2005 are shown in Figure 5.

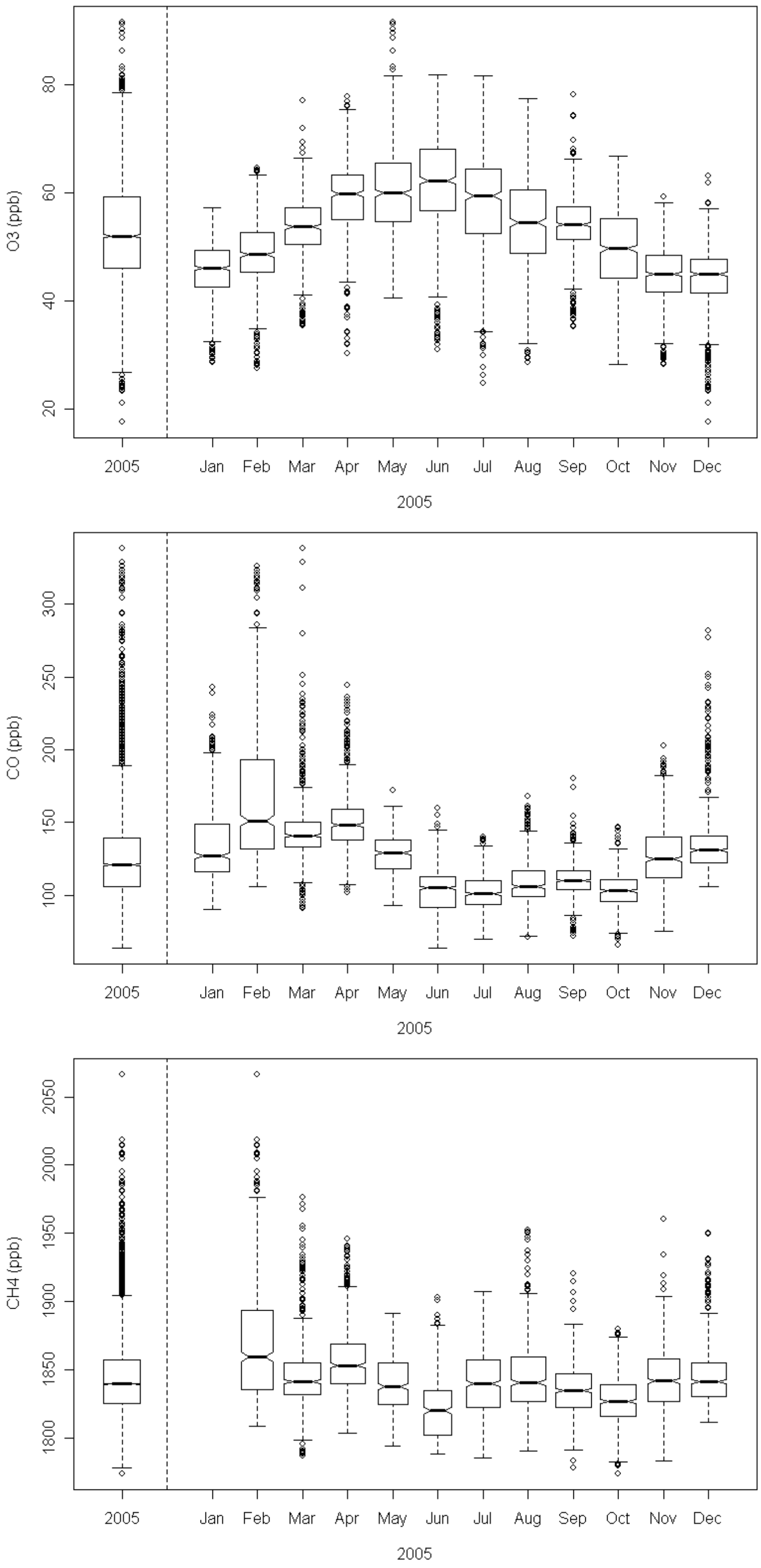

Figure 5. Yearly and Monthly Box Plots of 1-hourly aggregates for the year 2005 for Surface Ozone (upper panel), Carbon Monoxide (middle panel) and Methane (lower panel). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organisation and Contact Persons

Different national and international partners are involved in the GAW activities at JFJ. The measurements of the scope of WCC-Empa are made by Empa as a joint project with the Air Pollution Control and Non-Ionizing-Radiation Division, Section Air Quality Management of the Federal Office for the Environment (FOEN). All institutes involved in Swiss GAW activities meet in a biannual meeting co-ordinated by MeteoSwiss for information exchange. The observatory is managed by the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG).

Surface Ozone Measurements

The ozone measurements were already described in the previous audit report [*Herzog, et al.*, 1999]. The instrumentation and operations remained basically the same. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-a].

Monitoring Set-up and Procedures

Air Conditioning

The laboratory is air conditioned, but the air conditioning system was often not able to reach a stable laboratory temperature. Laboratory temperature varies between 20 and 25°C, but periods with more than 30°C and fast temperature changes occur during periods with measurement campaigns (cf. Recommendation 2).

Air Inlet System

The air intake is mounted on the terrace above the laboratory. The inlet is made of stainless steel with an inner diameter of 8 cm and a total length of 3.1 m. The air flow through this part is 50 $m^3 h^{-1}$, and a heating system provides a constant gas temperature of approx. 12°C. The glass manifold (length approx. 3 m, id. 4 cm) is connected to the inlet with PTFE tubing (length approx. 5 m, id. 2.2 cm). The flow rate through the manifold is approx. 100 l/min. All materials used are adequate, and the residence time is estimated to be below 5 seconds in the whole inlet system (of which approx. 1 second in the stainless steel part).

Instrumentation

The surface ozone monitoring equipment has been described in the last audit report [*Herzog, et al.*, 1999]. Instrumental details for the ozone analyser (OA) currently available at the station are summarised in Table 2 below.

Standards

The NABEL network has two TEI 49C-PS ozone calibrators, which are used for the calibration of the ozone analysers at the NABEL sites. A calibration is performed usually every three months, but at least twice per year. The TEI 49C-PS instruments are calibrated against the SRP#15 of WCC-Empa every 3 to 6 months.

Operation and Maintenance

The instrument is remotely checked for general operation during working days. The inlet filter is replaced every one to two months, and in case of pollution episodes earlier. An inter-comparison with one of the NABEL ozone standards is done every three to six months.

Data Acquisition and Data Transfer

The digital output of the ozone analyser is connected to the data acquisition system (Breitfuss EasyComp, Anacomp4 and Anavis Version 20040430). Data is automatically transferred to FOEN and Empa. More information on the data acquisition system can be found in [*Empa*, 2005] and on the Breitfuss web site (www.breitfuss.de).

Data Treatment

Data validation is carried out at Empa, and the final data is stored in a data base at FOEN. Validated 10 minute averages are available for further analysis. One minute raw data are also stored for 3 months, but are automatically deleted afterwards. Data is monthly validated using the log file information and time series plots.

Data Submission

Ozone 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

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

Inter-Comparison of Ozone Analyser

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 analyser. The data used for the evaluation was recorded by both WCC-Empa and Jungfraujoch data acquisition systems as indicated. Data of the JFJ data acquisition system was used for the evaluation of the results. No further corrections were applied to the data.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.011
Ozone analyser (OA)	Model, S/N	TEI 49C #0532213860
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; 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. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS	One minute aggregates from digital output (custom designed LabView programme)
	Analyser OA	Station Data Acquisition (Breitfuss)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	668.4 (Station reference)
	TS	670.6, adjusted to 668.4 (501.4 mmHg)
	TEI 49C	668.4 (not adjustments were necessary)
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90 (OA)
Duration per level (min)		15
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		3 runs (25 thru 26 July, 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. These aggregates were used in the assessment of the inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results refer to the calibration factors as given in Table 2 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the JFJ ozone analyser (OA) TEI 49C #0532213860 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
2006-07-26 00:33	1	0	0.34	0.48	0	0.08	0.07
2006-07-26 00:48	1	90	89.86	90.35	0	0.14	0.07
2006-07-26 01:03	1	30	29.91	29.98	0	0.11	0.08
2006-07-26 01:18	1	60	59.88	60.29	0	0.14	0.05
2006-07-26 01:33	1	40	39.93	40.16	0	0.11	0.06
2006-07-26 01:48	1	50	49.90	50.09	0	0.09	0.05
2006-07-26 02:03	1	80	79.87	80.16	0	0.10	0.05
2006-07-26 02:18	1	10	9.98	10.02	0	0.28	0.10
2006-07-26 02:33	1	20	20.03	20.16	0	0.10	0.06
2006-07-26 02:48	1	70	69.85	70.13	0	0.10	0.04
2006-07-26 03:03	2	0	0.43	0.46	0	0.14	0.08
2006-07-26 03:18	2	30	29.89	30.05	0	0.08	0.06
2006-07-26 03:33	2	60	59.87	60.26	0	0.09	0.06
2006-07-26 03:48	2	90	89.87	90.30	0	0.06	0.04
2006-07-26 04:03	2	20	19.98	20.06	0	0.13	0.07
2006-07-26 04:18	2	40	39.91	40.18	0	0.09	0.11
2006-07-26 04:33	2	80	79.89	80.03	0	0.11	0.12
2006-07-26 04:48	2	10	10.01	10.04	0	0.17	0.07
2006-07-26 05:03	2	50	49.89	49.88	0	0.07	0.05
2006-07-26 05:18	2	70	69.89	70.15	0	0.10	0.06
2006-07-26 05:33	3	0	0.35	0.33	0	0.08	0.05
2006-07-26 05:48	3	90	89.89	90.25	0	0.06	0.07
2006-07-26 06:03	3	10	10.04	9.94	0	0.14	0.06
2006-07-26 06:18	3	80	79.84	80.10	0	0.09	0.08
2006-07-26 06:33	3	60	59.88	60.00	0	0.11	0.09
2006-07-26 06:48	3	20	19.94	19.96	0	0.10	0.03
2006-07-26 07:03	3	30	29.87	30.07	0	0.13	0.07
2006-07-26 07:18	3	40	39.87	39.94	0	0.09	0.06
2006-07-26 07:33	3	70	69.83	70.01	0	0.08	0.04
2006-07-26 07:48	3	50	49.86	49.98	0	0.11	0.06

#0: valid data; 1: invalid data.

Figure 6 shows the regression residuals of the ozone analyser with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

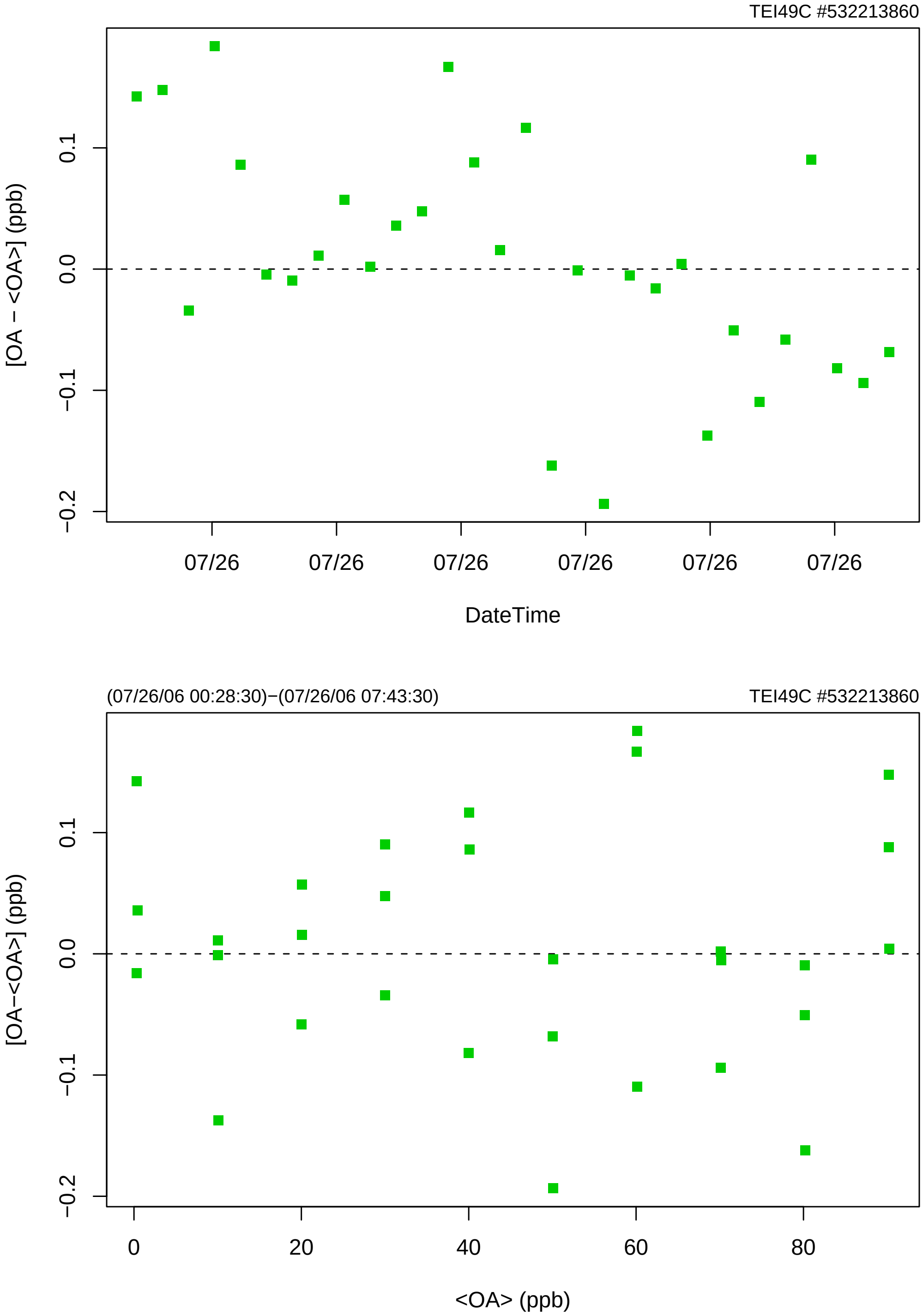

Figure 6. Regression residuals of the JFJ ozone analyser (TEI 49C) as a function of time (upper panel) and concentration (lower panel).

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 #0532213860:

$$X_{O3}\ (ppb) = ([OA] - 0.16\ ppb) / 1.005$$
$$u_{O3}\ (ppb) = sqrt(0.27\ ppb^2 + 2.68e-05 * X_{O3}^2) \quad (1)$$

Changes Made to Instrument

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

Conclusions

The findings of this audit demonstrate good agreement between JFJ ozone measurements and WCC-Empa. Therefore no further recommendations are proposed by WCC-Empa.

Carbon Monoxide Measurements

The changes since the last WCC-Empa audit include the installation of a GC-FID system for the simultaneous measurement of CO, CH_4, SF_6 and N_2O in 2005. Otherwise the instrumentation for carbon monoxide measurements remained basically the same with a Horiba APMA NDIR monitor. This instrument is periodically replaced by another instrument of the same type (approximately every two years), and instruments not in use are serviced and calibrated before the next use. Instruments are decommissioned after approx. seven years of use in the national air pollution monitoring network.

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. The NDIR instrument is connected to the manifold with approx. 3 m PTFE tubing. The residence times is estimated to be 4 s. The GC-FID system is also connected to the manifold with approx. 4 m stainless steel tubing (1/8” OD). A KNF Neuberger pump with a flow rate of approximately 1 l/min supplies air to the instrument. A pressure relief valve releases the excess air right in front off the gas selector valve. The flow through the sampling loops is controlled to 40 ml/min using a mass flow controller (Bronkhorst). The loops are mounted in an isolated housing on top of the GC oven to reduce temperature fluctuations. A 10-port gas selector valve allows to alternately measuring ambient air and standard samples. Residence time is estimated to be less than 4s.

Instrumentation

The JFJ station is permanently equipped with two carbon monoxide measurement systems. In addition to the NDIR analyser a GC-FID system was installed in 2005, and both instruments are running in parallel since then. Instrumental details are listed in Table 5 and Table 6 below. Currently CO is also measured with an RGA-3 instrument, however the main purpose of this system is hydrogen measurements.

Standards and Calibration

Each of the carbon monoxide instruments is equipped with its own working standard. These working standards are calibrated at Empa before use, and a check for drift is done before the cylinder reaches the lower pressure limit (approx. 5 bar for ppm standards, and 30 bar for ppb standards). Peak height is used for data evaluation (GC-FID).

Table 4 gives details of the cylinders currently available at the station. The instruments are currently calibrated in daily (GC-FID) and monthly (NDIR) intervals. For the NDIR system calibrations are made manually, and additional automatic zero checks are made every 49 hours to account for zero drift. Ambient data are corrected using the zero values of the automatic zero check, usually with monthly averages.

Table 4. Carbon monoxide standards available at JFJ station

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Messer Schweiz #7127 NDIR working standard	2.13 ppm CO 99.997% in nitrogen 99.999%	02-08-27 06-04-26	Empa, against NIST SRM*	2005-02	2006-01
Messer Schweiz #68874 NDIR working standard	2.02 ppm CO 99.997% in nitrogen 99.999%	05-04-13 06-12-04	Empa, against NIST SRM*	2006-01	2006-10
Messer Schweiz #66959 NDIR working standard	2.02 ppm CO 99.997% in nitrogen 99.999%		Empa, against NIST SRM*	2006-10	cont.
Real air standard 030701WS_CA04549 GC-FID working standard	300.9 ppb CO in whole air	04-12-16 05-07-20	WCC-Empa, against WMO-2000	2005-02	2005-07
Real air standard CC106830 GC-FID working standard	172.9 ppb CO in whole air (initial), 182.3 ppb (after use); standard subject to drift	05-07-15 06-05-17	WCC-Empa, against WMO-2000	2005-07	2006-04
Real air standard 050701_CA06439 GC-FID working standard	438.8 ppb CO in whole air	05-10-06	WCC-Empa, against WMO-2000	2006-04	cont.

* NIST SRM was linked to WMO-2000 scale at WCC-Empa

Operation and Maintenance

The station is visited approximately every three weeks; the ongoing maintenance work is done during these visits (e.g. manual calibrations and checks, filter changes etc.). All instruments are remotely monitored for operation and errors; in case of an instrument failure the house keeper is contacted for a first diagnosis; the station is visited when the problem cannot be solved remotely.

Data Acquisition and Data Transfer

NDIR instrument: The JFJ station is equipped with a data acquisition PC with programmes from Breitfuss GmbH (EasyComp, Anacomp4 and Anavis Version 20040430). Data is automatically transferred to FOEN and Empa. Data validation is carried out at Empa, and the final data is stored in a data base at FOEN. Validated 10 minute averages are available for further analysis. One minute raw data are also stored for 3 months, but are automatically deleted afterwards. More information on the NABEL data acquisition can be found in [*Empa*, 2005] and on the Breitfuss web site (www.breitfuss.de).

GC instrument: The entire instrument is under the control of a Linux based PC using multiple RS-232 serial data ports and control software written at Scripps Institution of Oceanography (SIO). This includes all the electrically actuated Valco valves and the Agilent 6890 GC. This software has been developed for the Agage network (http://agage.eas.gatech.edu).

Data Treatment

Data of both instruments is regularly checked for consistency with time series plots.
NDIR analyser:
The values of the automatic zero checks are used to apply a zero correction. This is usually done by aggregating the zero checks to monthly averages; these averages are then used for a correction of the data. However, linear interpolation is used between zero checks when a significant drift is recognisable.
GC-FID:
Final concentrations are calculated using the injections of the working standard. A drift correction is applied to the working standard concentration in case of a recognisable drift; however, this is normally not necessary. Raw and final data are stored.

Data Submission

Data of the NDIR instrument 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. Data of the GC-FID instrument have not been submitted.

Documentation

Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. All information is entered into an electronic data base. 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 5 (WCC-Empa cylinders) and Table 6 (dilution system) below.

Setup and Connections

The GC-FID instrument was inter-compared by direct measurements of travelling standards. Details of this experiment are shown in Table 5. The NDIR analyser was inter-compared using the WCC-Empa reference instrument and a dilution system, and the experimental setup is shown in Table 6. The data used for the evaluation was recorded by the JFJ data acquisition system, and only corrections according to the usual station methods were applied. These corrections included a zero compensation of the NDIR instrument of -2 ppb based on the automatic zero checks.

Table 5. Experimental details of the carbon monoxide inter-comparison with travelling standards.

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 040719_ 0653B / 84.55 / 0.56 2 / 041109_FA01467 / 135.21 / 0.73 3 / FF30491 / 160.92 / 0.80 4 / 030703_FA01477 / 199.44 / 1.02 5 / 060602_0664B / 211.45 / 1.10 6 / 050701_FA02505 / 359.36 / 1.86
Field instrument	Model, S/N	Agilent 6890
	Principle	GC-FID with methanizer, ECD (SF_6 and N_2O) -Ni catalyst heated to 375°C and flushed with H_2. -FID columns: Unibeads 1S and Molecular Sieve 5Å -ECD columns: Hayesep Q -FID carrier gas: N_2 (5.0 with Alltech nitrogen purifier) -ECD carrier gas: 5% CH_4 (4.5) in Ar (5.0) -H_2 generated with Schmidlin H_2 generator -Flow through loop. 40 ml/min, stopped before injection -10-port selection valve for standard and sample inj.
Connection of TS to field instrument		Spare port of the 10-port selection valve
Data Acquisition		Station data acquisition
Duration per level (min)		One injection per hour; total 7-9 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (26-27 July, 2006)

Table 6. Experimental details of the carbon monoxide inter-comparison with the dilution system (NDIR analyser).

Travelling standard (TS)		One cylinder (051010_FA02474, 10000±50 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); The reference concentration produced with the MGM was measured with the WCC-Empa reference instrument Aerolaser AL5001, which was calibrated with a WMO-2000 traceable standard during the inter-comparison (050825_CA06490 352.5 ppb CO in air).
Levels (ppb)		Level / Reference / St.Uncertainty 1 / 1.43 / 0.50 2 / 78.70 / 0.50 3 / 104.19 / 0.52 4 / 154.36 / 0.77 5 / 205.92 / 1.03 6 / 256.08 / 1.28 7 / 307.55 / 1.54 8 / 407.52 / 2.04 9 / 509.67 / 2.55
Field instrument	Model, S/N	HORIBA APMA-360 CE #510007
	Principle	NDIR, Cross Flow Modulation Technique
	Range	1 ppm
	Settings	Zero = -5; SPAN = 1.075
Connection of TS to field instrument		Sample line including inlet filter
Data Acquisition		1 min averages form station data acquisition (NDIR) and Aerolaser ALXXX data acquisition (WCC-Empa reference)
Duration per level (min)		60
Sequence of levels		Randomised fixed sequence
Runs		1 run (26 July, 2006)

Results

GC-FID system

The GC-FID system was audited using WCC-Empa travelling standards. One injection per hour was made for each standard, which resulted in a maximum of 9 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 7).

Table 7. CO aggregates computed from single injections for each level during the inter-comparison of the JFJ Agilent 6890 GC-FID with WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS Identification	TS	sdTS	Agilent 6890	sd	No. of inj.
		(ppb)	(ppb)	(ppb)	(ppb)	
(07/26/06 15:00:00)	041109_FA01467	135.21	0.73	134.02	4.39	7
(07/26/06 16:39:17)	040719_ 0653B	84.55	0.56	85.93	2.12	7
(07/27/06 00:04:00)	060602_0664B	211.45	1.10	209.30	3.36	9
(07/27/06 00:34:00)	030703_FA01477	199.44	1.02	198.70	3.51	9
(07/27/06 08:15:00)	FF30491	160.92	0.80	162.55	5.50	7
(07/27/06 08:45:00)	050701_FA02505	359.36	1.86	357.00	4.79	7

Figure 7 shows the regression residuals of the GC-FID instrument 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, though a small remaining non-linearity can not be excluded at low concentrations.

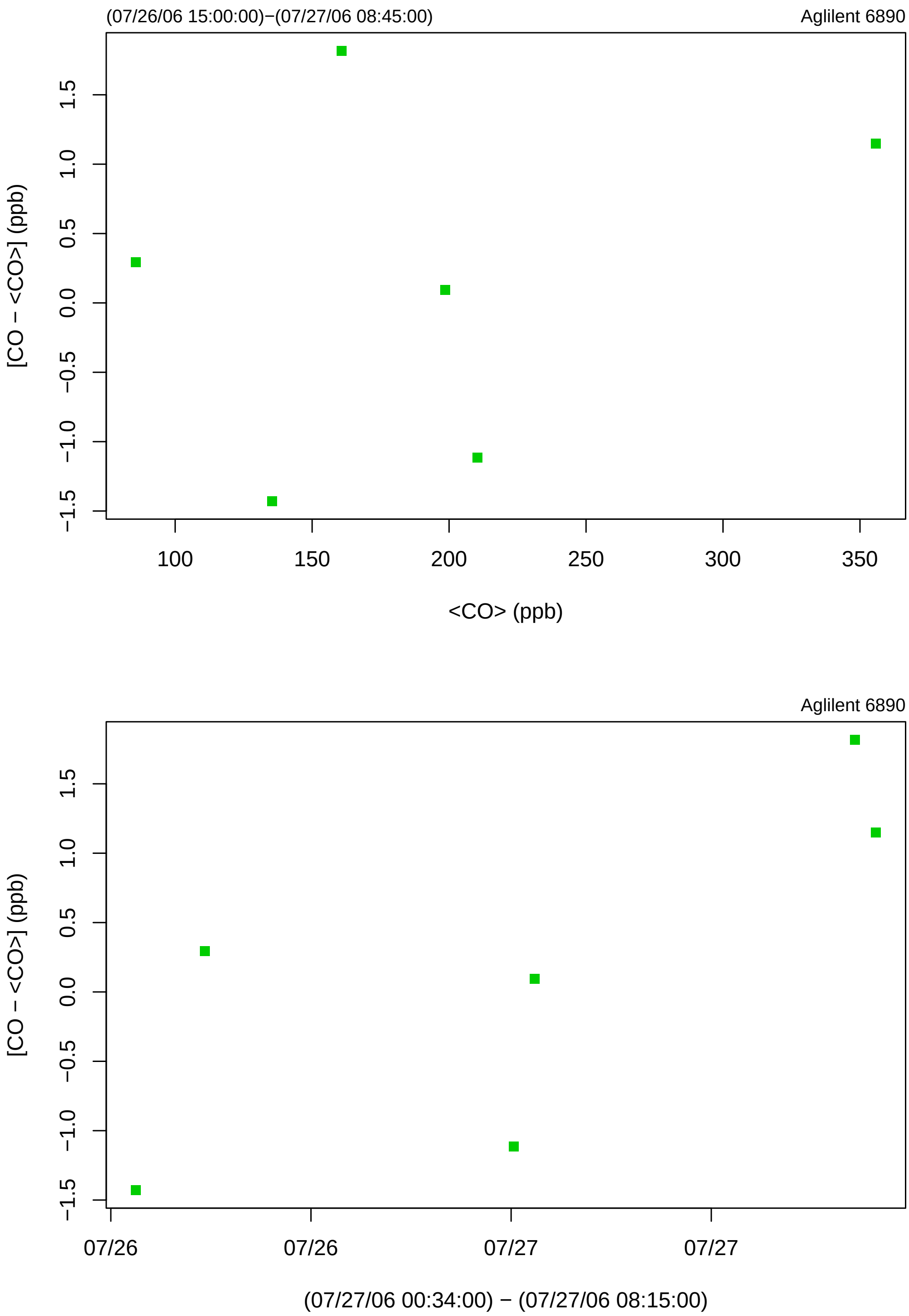

Figure 7. Regression residuals of the JFJ Agilent 6890 GC based on the inter-comparison with travelling standards. Points represent averages of valid single injections. Upper panel: concentration dependence; Lower panel: time dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the Agilent 6890 GC-FID system X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed from the 1' inter-comparison data using equation

$$\mathbf{X_{CO}\ (ppb) = ([CO] - 2.5\ ppb) / 0.983}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(4.2\ ppb^2 + 1.04e\text{-}04 * X_{CO}^2)} \qquad (2a)$$

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

Changes made to the instrument

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

NDIR instrument

Each carbon monoxide level was applied for 60 minutes, which resulted in a maximum of 60 useable 1' averages per level and run. These were corrected for zero-drift (-2ppb) and further aggregated by level before use in the assessment (cf. Table 8).

Table 8. CO aggregates computed from 1' averages for each level during the inter-comparison of the JFJ Horiba APMA-360 carbon monoxide analyser with the WCC-Empa transfer standard (TS).

Date Time (UTC+1)	TS Aerlaser AL5001 (ppb)	sdTS (ppb)	Horiba APMA-360 CO (ppb)	sdCO (ppb)	No. 1' av.
(07/26/06 10:35:14)	1.43	0.50	6.94	9.09	52
(07/26/06 11:35:36)	104.19	0.52	105.27	9.77	48
(07/26/06 12:33:22)	78.70	0.50	79.69	9.37	52
(07/26/06 13:32:59)	256.08	1.28	261.17	8.36	52
(07/26/06 14:32:00)	307.55	1.54	310.90	9.50	51
(07/26/06 15:33:30)	154.36	0.77	154.29	8.46	56
(07/26/06 16:34:30)	205.92	1.03	209.50	8.31	56
(07/26/06 17:36:00)	509.67	2.55	518.08	7.72	53
(07/26/06 18:35:42)	407.52	2.04	414.23	8.74	53

Figure 8 shows the regression residuals of the Horiba APMA-360 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.

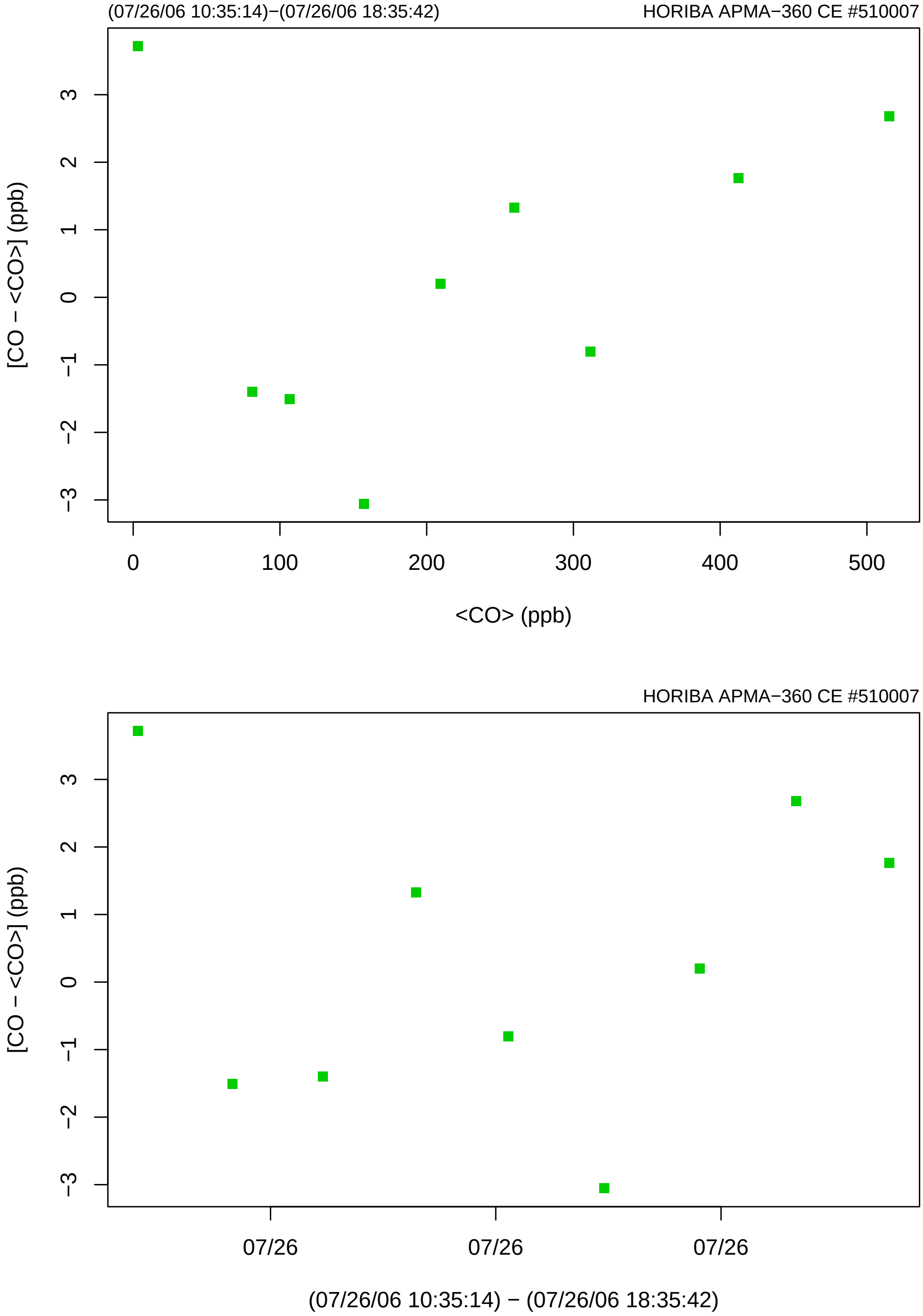

Figure 8. Regression residuals of the JFJ Horiba APMA-360 carbon monoxide analyser. Points represent averages of valid 1'-aggregates. Upper panel: concentration dependence; Lower panel: time dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios of the Horiba APMA-360 analyser X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} for a 5-min average value can be computed from the 1' inter-comparison data using equation

$$\mathbf{X_{CO}\ (ppb) = ([CO] - 1.8\ ppb) / 1.008}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(14.6\ ppb^2 + 4.21e\text{-}05 * X_{CO}^2)} \qquad (2a)$$

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

Conclusions

Both carbon monoxide analysers were found to operate well within the limits of the instrument specifications. However, the zero offset correction of the NDIR instrument adds additional uncertainty to the data.

Methane Measurements

Methane measurements started at JFJ in 2005 with the installation of a GC-FID system for the simultaneous measurement of CO, CH_4, SF_6 and N_2O.

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

Monitoring Set-up and Procedures

See above (carbon monoxide GC-FID measurements).

Standards and Calibration

The standard methane scale, to which the JFJ CH_4 measurements are referenced, is based on standards obtained from NOAA/GMD. Calibration of the station standards (working standards) is done at WCC-Empa against NOAA/GMD standards (NOAA04methane scale [*Dlugokencky, et al.*, 2005]). Table 9 shows details of the cylinders currently available at the station.

Calibration of the instrument is performed using the working standard. Injections are made every 15 minutes, alternating between sample and standard. Peak height is used for data evaluation.

Table 9. Methane standards available at JFJ station

Manufacturer, S/N, Use	CH_4 Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Real air standard 030701WS_CA04549 GC-FID working standard	1857.3 ppb CH_4 in whole air	04-01-22 04-07-15	WCC-Empa, against WMO-2000	2005-02	2005-07
Real air standard CC106830 GC-FID working standard	1861.6 ppb CH_4 in whole air	05-07-15 06-05-17	WCC-Empa, against NOAA04	2005-07	2006-04
Real air standard 050701_CA06439 GC-FID working standard	1838.0 ppb CH_4 in whole air	05-07-15	WCC-Empa, against NOAA04	2006-04	cont.

Data Submission
Methane data of JFJ have not yet been submitted to WDCGG.

Inter-Comparison of Methane Analysers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation-b] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standard to the WMO/GAW Reference Standard at NOAA/ESRL-GMD are given in Table 10 below.

Setup and Connections
Table 10 shows details of the experimental setup during the inter-comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the JFJ data acquisition system, and no further corrections were applied.

Table 10. Experimental details of the methane inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 030703_FA01477 / 1799.77 / 0.46 2 / 050701_FA02505 / 1832.20 / 1.61 3 / FF30491 / 1843.35 / 1.30 4 / 040719_0653B / 1847.71 / 0.91 5 / 060602_0664B / 1874.19 / 1.07 6 / 041109_FA01467 / 1907.01 / 0.77
Field instrument	Model, S/N	AGILENT 6890 Series, see Table 5
Connection of TS to field instrument		TS were connected to the sample selection valve of the JFJ system
Data Acquisition		Station data acquisition
Number of injections		One injection per hour; total 7-9 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (26 thru 27 July, 2006)

Results

Each TS was injected between 7 and 9 times, which resulted in a maximum of 20 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 11).

Table 11. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the inter-comparison of the JFJ methane analyser with the WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS (ppb)	uTS (ppb)	CH_4 (ppb)	uCH_4 (ppb)	No. of inj.
(07/26/06 15:00:00)	1907.01	0.77	1910.27	3.55	7
(07/26/06 16:39:17)	1847.71	0.91	1850.51	4.29	7
(07/27/06 00:04:00)	1874.19	1.07	1874.66	2.58	9
(07/27/06 00:34:00)	1799.77	0.46	1801.64	4.11	9
(07/27/06 08:15:00)	1843.35	1.30	1843.84	2.12	7
(07/27/06 08:45:00)	1832.20	1.61	1834.67	3.36	7

Figure 9 shows the regression residuals of the AGILENT 6890 Series GC plotted against time and concentration. The absence of a temporal trend (upper panel) indicates stable instrument conditions. The absence of concentration dependence (lower pane) indicates linearity of the instrument.

Based on these inter-comparison results, unbiased methane volume mixing ratios of the AGILENT 6890 Series analyser X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed from the single injection inter-comparison data using equation (3).

$$X_{CH4}\ (ppb) = (CH_4) / 1.00115$$
$$u_{CH4}\ (ppb) = sqrt(1.4\ ppb^2 + 7.82e\text{-}08 * X_{CH4}^2) \quad (3)$$

Conclusions

No significant deviations between JFJ and WCC-Empa were found. The good result of the inter-comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. The repeatability of the JFJ GC was good, with an average standard deviation of 0.07% (7-9 injections). This value is comparable to the best GC-FID systems at GAW stations. Therefore no further technical recommendations are made by WCC-Empa.

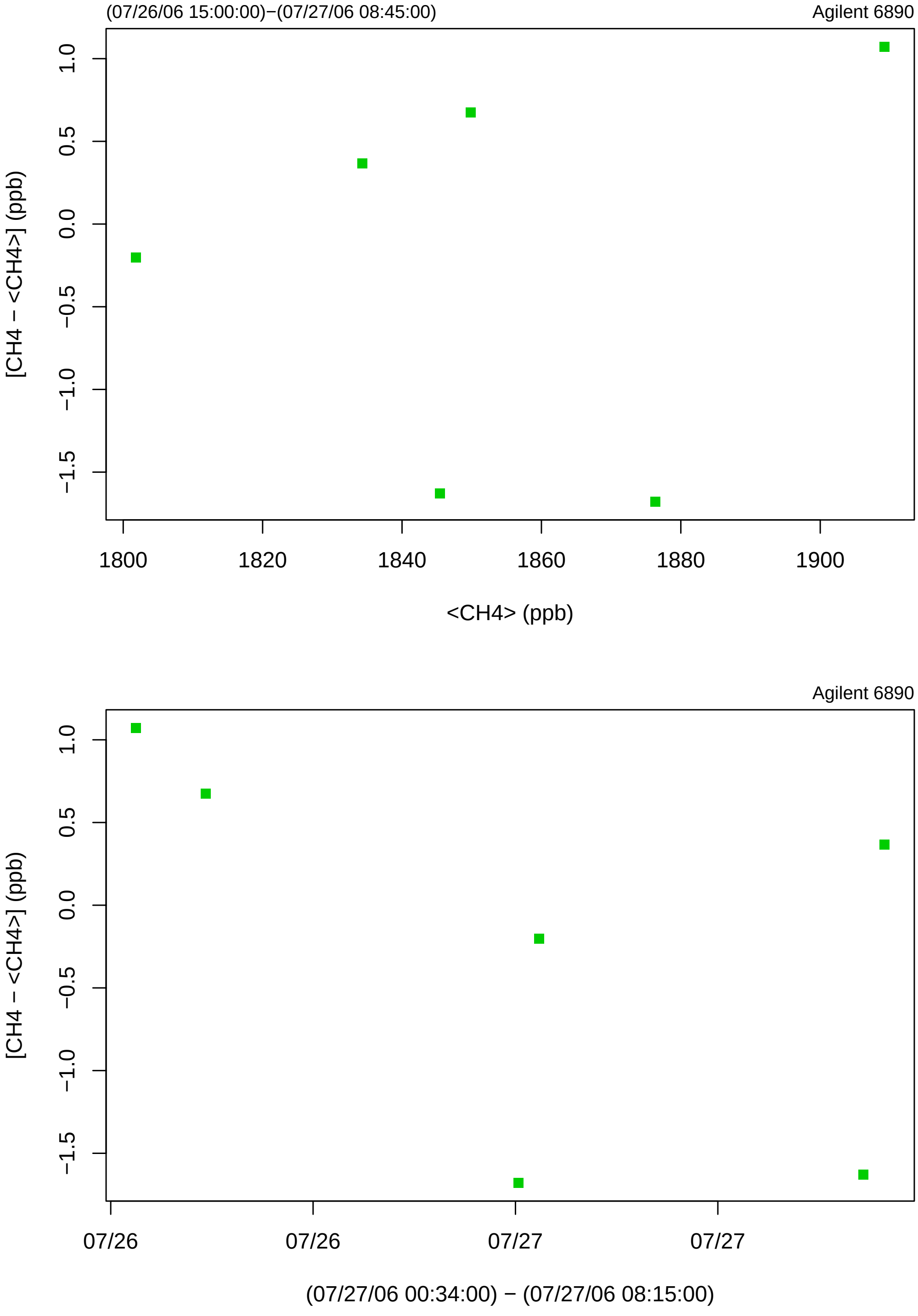

Figure 9. Regression residuals of the JFJ methane GC. Points represent averages of valid single injections. Upper panel: concentration dependence; Lower panel: time dependence.

WCC-Empa Transfer Standards

Ozone

The WCC-Empa transfer standard (TS) was compared with the Standard Reference Photometer before and after use during the field audit. Details of these inter-comparisons at the Empa calibration laboratory are 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 (26 June, 2006) 3 runs after return of TS (4 August, 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)
2006-06-26	1	0.0	-0.1	0.3	0.2	0.1
2006-06-26	1	140.0	89.5	0.3	89.3	0.2
2006-06-26	1	90.0	188.6	0.5	188.5	0.2
2006-06-26	1	30.0	59.5	0.3	59.4	0.1
2006-06-26	1	190.0	139.8	0.3	139.8	0.1
2006-06-26	1	60.0	31.4	0.2	31.6	0.1
2006-06-26	1	0.0	0.0	0.4	0.1	0.1
2006-06-26	2	0.0	0.2	0.2	0.2	0.1
2006-06-26	2	90.0	31.3	0.4	31.4	0.1
2006-06-26	2	190.0	189.4	0.4	189.6	0.2
2006-06-26	2	60.0	90.2	0.3	90.6	0.1
2006-06-26	2	140.0	140.4	0.2	140.7	0.2
2006-06-26	2	30.0	59.8	0.4	60.1	0.1
2006-06-26	2	0.0	-0.1	0.4	0.3	0.1
2006-06-26	3	0.0	0.1	0.3	0.2	0.1
2006-06-26	3	30.0	90.0	0.3	90.4	0.1
2006-06-26	3	190.0	189.4	0.3	190.1	0.2
2006-06-26	3	90.0	31.6	0.3	32.0	0.1
2006-06-26	3	140.0	140.3	0.3	140.7	0.1
2006-06-26	3	60.0	60.0	0.3	60.2	0.1
2006-06-26	3	0.0	-0.1	0.3	0.3	0.1
2006-08-04	4	0.0	-0.1	0.3	0.1	0.1
2006-08-04	4	140.0	138.3	0.4	138.3	0.1
2006-08-04	4	90.0	88.8	0.5	89.1	0.1
2006-08-04	4	30.0	31.1	0.3	31.3	0.1
2006-08-04	4	190.0	187.6	0.3	187.8	0.2
2006-08-04	4	60.0	59.3	0.4	59.7	0.1
2006-08-04	4	0.0	0.0	0.3	0.2	0.1
2006-08-04	5	0.0	0.2	0.2	0.1	0.1
2006-08-04	5	90.0	89.7	0.6	89.9	0.1
2006-08-04	5	190.0	188.6	0.3	189.0	0.2
2006-08-04	5	60.0	60.0	0.3	60.2	0.1
2006-08-04	5	140.0	139.8	0.3	140.3	0.1
2006-08-04	5	30.0	31.6	0.3	31.9	0.1
2006-08-04	5	0.0	-0.1	0.5	0.2	0.1
2006-08-04	6	0.0	0.0	0.3	0.2	0.1
2006-08-04	6	30.0	31.6	0.2	31.7	0.1
2006-08-04	6	190.0	188.8	0.3	189.3	0.1
2006-08-04	6	90.0	90.4	0.3	90.7	0.1
2006-08-04	6	140.0	140.0	0.4	140.7	0.1
2006-08-04	6	60.0	60.3	0.4	60.4	0.1
2006-08-04	6	0.0	0.2	0.2	0.2	0.1

#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 10). 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]).

$$X_{TS}\ (ppb) = ([TS] - 0.17\ ppb) / 1.0008$$

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

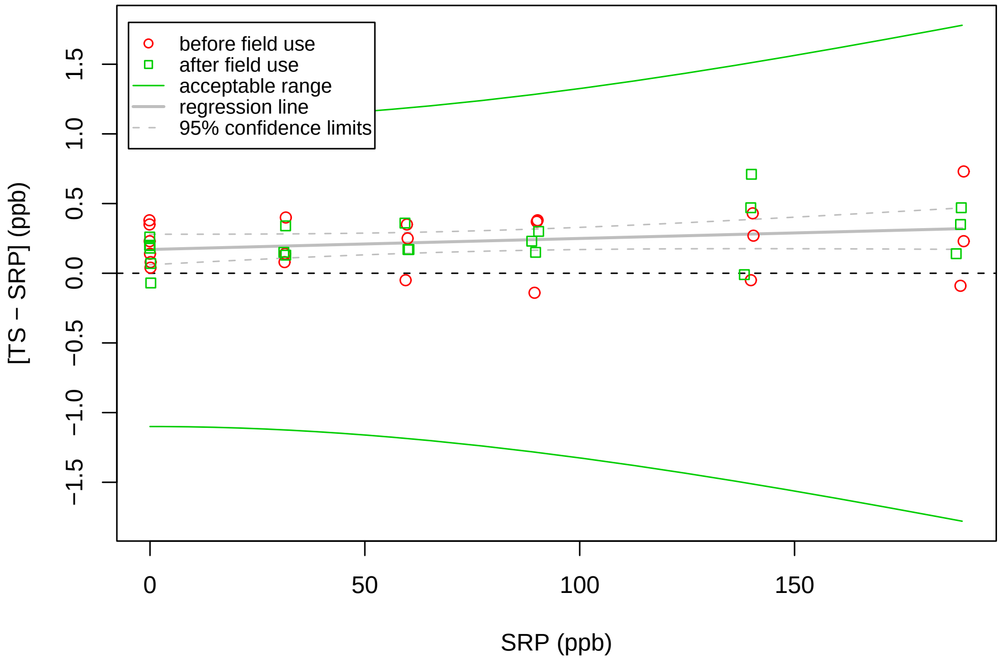

Figure 10. Deviations between transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly inter-compared with the CCL by way of travelling standards. The scale was transferred to the travelling standard using an Aerolaser AL5001 vacuum-fluorescence analyser, an instrument with high precision and proven linearity. Details are given in Table 14 - Table 15.

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 CO cylinder (2), in combination with a dilution unit (3) and the AL5001 reference analyser (4) and Carbon monoxide cylinders for direct inter-comparisons. (cf. Table 5)
(1) Zero air supply		Ambient air – Silicagel drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		051010_FA02474, 10000±50 ppb in synthetic air.
(3) Dilution unit		Breitfuss MGM #2262/91/1.
(4) Reference analyser		Aerolaser AL5001 S/N 117
Connection between instruments		Ca. 2 meter 6 mm Sertoflex tubing (dilution unit). Ca. 2 meter 1/8” stainless steel tubing (cylinders).
Data acquisition		1-min averages
Levels (ppb)		Dilution unit: 0, 75, 100, 150, 200, 250, 300, 400, 500 Cylinders: cf. Table 5
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 15. Calibration of the carbon monoxide travelling standards with the WCC-Empa reference before and after the audit.

Date	2006-05-03			2006-06-27			2006-11-24		
Cylinder identification	CO (ppb)#			CO (ppb)#			CO (ppb)#		
040719_ 0653B	84.29	±	0.80				84.81	±	0.42
041109_FA01467				135.02	±	0.25	135.40	±	0.30
FF30491				160.91	±	0.27	160.93	±	0.51
030703_FA01477				199.29	±	0.27	199.59	±	0.57
060602_0664B				211.24	±	0.44	211.67	±	0.97
050701_FA02505				359.02	±	0.44	359.71	±	0.87

#Average±sd (n = approx. 100)

Methane

WCC-Empa refers to the latest WMO/GAW methane scale (hereafter: NOAA04 scale) [*Dlugokencky, et al.*, 2005] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 16). The scale was transferred to the travelling standards using a Varian 3400 gas chromatograph with an FID detector. Details of the travelling standards are given in Table 17.

Table 16. NOAA/GMD CH_4 laboratory standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

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

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

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

Date	2006-06-26			2006-08-07		
Cylinder identification	CH_4 (ppb)#			CH_4 (ppb)#		
030703_FA01477	1800.02	±	1.59	1799.51	±	1.44
050701_FA02505	1833.32	±	1.19	1831.08	±	1.49
FF30491	1844.25	±	1.67	1842.45	±	1.37
040719_0653B	1847.11	±	1.63	1848.32	±	1.05
060602_0664B	1874.92	±	0.85	1873.47	±	2.38
041109_FA01467	1906.51	±	1.39	1907.51	±	1.66

#Average±sd (n = 10)

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Ozone Audit Executive Summary (JFJ)

0.1	Station Name:	Jungfraujoch
0.2	GAW ID:	JFJ
0.3	Coordinates/Elevation:	46.584°N, 7.987°E (3580 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	25 – 26 July, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. M. Steinbacher
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):	(1.0008±0.0010) × [SRP] + (0.17±0.09)
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49C #0532213860
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG: 0.0 COEF: 1.024
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.005±0.001) × [SRP] + (0.17±0.05)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] - 0.17) / 1.005
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.67e\text{-}5 \times X^2)^{1/2}$
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 06/4

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

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Carbon Monoxide Audit Executive Summary (JFJ)

0.1	Station Name:	Jungfraujoch
0.2	GAW ID:	JFJ
0.3	Coordinates/Elevation:	46.584°N, 7.987°E (3580 m a.s.l)
Parameter:		Carbon Monoxide (NDIR)

1.1	Date of Audit:	26 – 27 July, 2006
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Dr. M. Steinbacher
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	051010_FA02474, 10000±50 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	Reference instrument	Aerolaser AL5001 S/N 117
1.4.5	Range of calibration:	0 – 500 ppb
1.5	CO analyser [CA]	
1.5.1	Model:	HORIBA APMA-360 CE #510007
1.5.2	Range of calibration:	0 – 500 ppb
1.5.3	Coefficients at start of audit	Zero = -5; SPAN = 1.075
1.5.4	Calibration at start of audit (ppb):	CO = (1.008±0.004) $\times$ X + (1.8±1.0)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO – 1.8) / 1.008
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (14.6\ ppb^2 + 4.21e\text{-}05 \times X^2)^{1/2}$
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:	Results shown for NDIR instrument
1.7	Reference:	WCC-Empa Report 06/4

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

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Carbon Monoxide Audit Executive Summary (JFJ)

0.1	Station Name:	Jungfraujoch	
0.2	GAW ID:	JFJ	
0.3	Coordinates/Elevation:	46.584°N, 7.987°E (3580 m a.s.l)	
Parameter:		Carbon Monoxide (GC-FID)	
1.1	Date of Audit:	26 – 27 July, 2006	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Dr. M. Steinbacher	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	040719_ 0653B	84.55±0.56 ppb
		041109_FA01467	135.21±0.73 ppb
		FF30491	160.92±0.80 ppb
		030703_FA01477	199.44±1.02 ppb
		060602_0664B	211.45±1.10 ppb
		050701_FA02505	359.36±1.86 ppb
1.5	CO analyser [CA]		
1.5.1	Model:	AGILENT 6890 Series	
1.5.2	Range of calibration:	85 –360 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	CO = (0.983±0.009) × X + (2.5±1.5)	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO – 2.5) / 0.983	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (4.2\ ppb^2 + 1.04e\text{-}04 \times X^2)^{1/2}$	
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 06/4	

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

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Methane Audit Executive Summary (JFJ)

0.1	Station Name:	Jungfraujoch
0.2	GAW ID:	JFJ
0.3	Coordinates/Elevation:	46.584°N, 7.987°E (3580 m a.s.l)
Parameter:		Methane

1.8	Date of Audit:	26 – 27 July, 2006	
1.9	Auditor:	Dr. C. Zellweger	
1.9.1	Station staff involved in audit:	Dr. M. Steinbacher	
1.10	CH_4 Reference:	NOAA04	
1.11	CH_4 Transfer Standard [TS]		
1.11.1	CH_4 Cylinders:	030703_FA01477	1799.77±0.46 ppb
		050701_FA02505	1832.20±1.61 ppb
		FF30491	1843.35±1.30 ppb
		040719_0653B	1847.71±0.91 ppb
		060602_0664B	1874.19±1.07 ppb
		041109_FA01467	1907.01±0.77 ppb
1.12	CH_4 analyser [CA]		
1.12.1	Model:	AGILENT 6890 Series	
1.12.2	Range of calibration:	1800 –1910 ppb	
1.12.3	Coefficients at start of audit	not applicable	
1.12.4	Calibration at start of audit (ppb):	CO = (1.00115±0.00026) × X	
1.12.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X = CH_4 / 1.00115	
1.12.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (2.0\ ppb^2 + 1.24e\text{-}07 \times X^2)^{1/2}$	
1.12.7	Coefficients after audit	unchanged	
1.12.8	Calibration after audit (ppb):	unchanged	
1.12.9	Unbiased CH_4 mixing ratio (ppb) after audit:	unchanged	
1.12.10	of calibration bias after audit (ppb):	Standard uncertainty after compensation unchanged	
1.13	Comments:		
1.14	Reference:	WCC-Empa Report 06/4	

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

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