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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 09/2

Submitted to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GAW GLOBAL STATION MT WALIGUAN AND THE CHINESE ACADEMY OF METEOROLOGICAL SCIENCES (CAMS) CHINA, JUNE 2009

Submitted by
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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The third system and performance audit at the GAW Global station Mt. Waliguan (WLG) was conducted by WCC-Empa[1] from 22 through 30 June 2009 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. WLG is coordinated by the Chinese Academy for Meteorological Sciences (CAMS) and the Qinghai Provincial Meteorological Bureau (QMB) under the China Meteorological Administration (CMA). The local infrastructure as well as the routine operation of WLG is maintained by QMB, Xining. The scientific and technical support, training, QA/QC and data management is provided by CAMS.

Previous audits at WLG were conducted in September 2000 [*Zellweger et al.*, 2000] and October 2004 [*Zellweger et al.*, 2004].

The following people contributed to the third audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Prof. Xiao-Ye Zhang	CAMS, China GAW Country Contact
Prof. Lingxi Zhou	CAMS, China GAW Station Contact & Coordinator
Prof. Xiao-bin Xu	CAMS
Dr. Shuangxi Fang	CAMS
Dr. Weili Lin	CAMS
Mrs. Fang Zhang	CAMS
WLG station staff	QMB

Our assessment of WLG in general, as well as the surface ozone, carbon monoxide, methane and nitrous oxide measurements in particular, is summarised below. The assessment criteria for the ozone comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer et al.*, 2000; *Klausen et al.*, 2003].

This report is distributed to the China GAW country contact (Prof. Xiao-Ye Zhang), the China GAW Station Contact & Coordinator (Prof. Ling-xi Zhou), QA/SAC Japan at JMA, CAMS, QMB, and the World Meteorological Organization (WMO) in Geneva. The audit 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

WLG (36.283°N, 100.900°E, 3810m a.s.l) is situated on the top of Mt. Waliguan, on the Tibetan plateau in Western China. WLG is a remote site, located away from major industrial sources. The closest major settlement is Gonghe (30000 inhabitants), located 30 km to the west. The surrounding area is covered with grass (no trees), and the overall region is sparsely covered with vegetation. The building was reconstructed in 1999, and renovated in 2005. The unique position of WLG in combination with the extensive and still growing measurement programme makes the station a valuable contribution for the GAW programme.

Access to the site is possible throughout the year on an unpaved road. 4WD vehicles are not required except for periods with snow.

Station Facilities

The facilities at the site consist of a large building complex. Spacious laboratories as well as rooms for station operators and visiting scientists, including basic kitchen and sanitary facilities, are available. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

[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 GAW Global stations every 2 – 4 years based on mutual agreement.

Calibration Facilities at CAMS

The central calibration facilities at CAMS are used to ensure traceability of the China GAW measurements to the WMO references. Furthermore, flask samples of the Chinese flask network are analysed at CAMS. The CAMS laboratories are equipped with modern instruments.

> **Recommendation 1 (*, ongoing)**
> *The central calibration facilities at CAMS are an important part of the China GAW programme. These facilities improve the quality of the measurements taken throughout China. CAMS activities should continue, and collaboration and scientific exchange with other central calibration facilities within GAW are made on a regular basis.*

Station Management and Operation

The WLG Facility is jointly managed and operated by CAMS and QMB under CMA. The station is permanently manned with a least two station operators, who are exchanged in shifts.

Air Inlet System

The air inlet systems were not changed since the last audit in October 2004. Each instrument has its own air inlet system or inlet line except for the Picarro G1301, which shares the inlet line with the methane gas chromatograph. The design of these systems is adequate for its intended purpose.

Surface Ozone Measurements

Instrumentation. Two TEI 49 ozone analysers are currently used at the station for continuous surface ozone measurements. One of the instruments did not pass the criteria for sufficient agreement due to a defective solenoid valve. Both instruments are becoming old, and replacement should be considered.

> **Recommendation 2 (***,2011)**
> *The ozone analysers should be replaced by new instruments; replacement should be made soon to allow for parallel measurements with the new and the existing instrumentation. Note: The backup analyser was already replaced by a TEI49i in May 2011.*

Standards. A TEI49-PS ozone calibrator is available at the site. The instruments are checked every three months using this standard. In addition, an ozone calibrator (TEI 49C-PS) is also available at the CAMS labs, which is being used as a travelling standard for on-site calibrations of the ozone instrument at all Chinese GAW stations.

> **Recommendation 3 (**,2011)**
> *The WLG ozone standard should also be replaced by a new model. The TEI49-PS is no longer suitable for accurate ozone calibrations by today's standards.*

Intercomparison (Performance Audit). Comparisons were made both at the WLG site and at CAMS. The results for the different instruments are summarised below and the following equations characterise the instrument bias:

WLG main analyser:

TEI 49 #47307-278 (OFFSET 51, SPAN 506): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.10 ppb) / 1.0073 (1a)

WLG backup analyser (decommissioned after the audit):

TEI 49 #47318-278 (OFFSET 50, SPAN 600): 0 – 90 ppb insufficient agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.05 ppb) / 0.9067 (1b)

WLG ozone standard:

TEI 49-PS #47651-279 (no settings possible): 0 – 90 ppb insufficient agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 1.97 ppb) / 0.9971 (1c)

CAMS ozone standard:

TEI 49C-PS #62349-335 (BKG 0.0, SPAN 1.010): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OC] + 0.33 ppb) / 1.0078 (1d)

The results of these comparisons are presented in Figure 1.

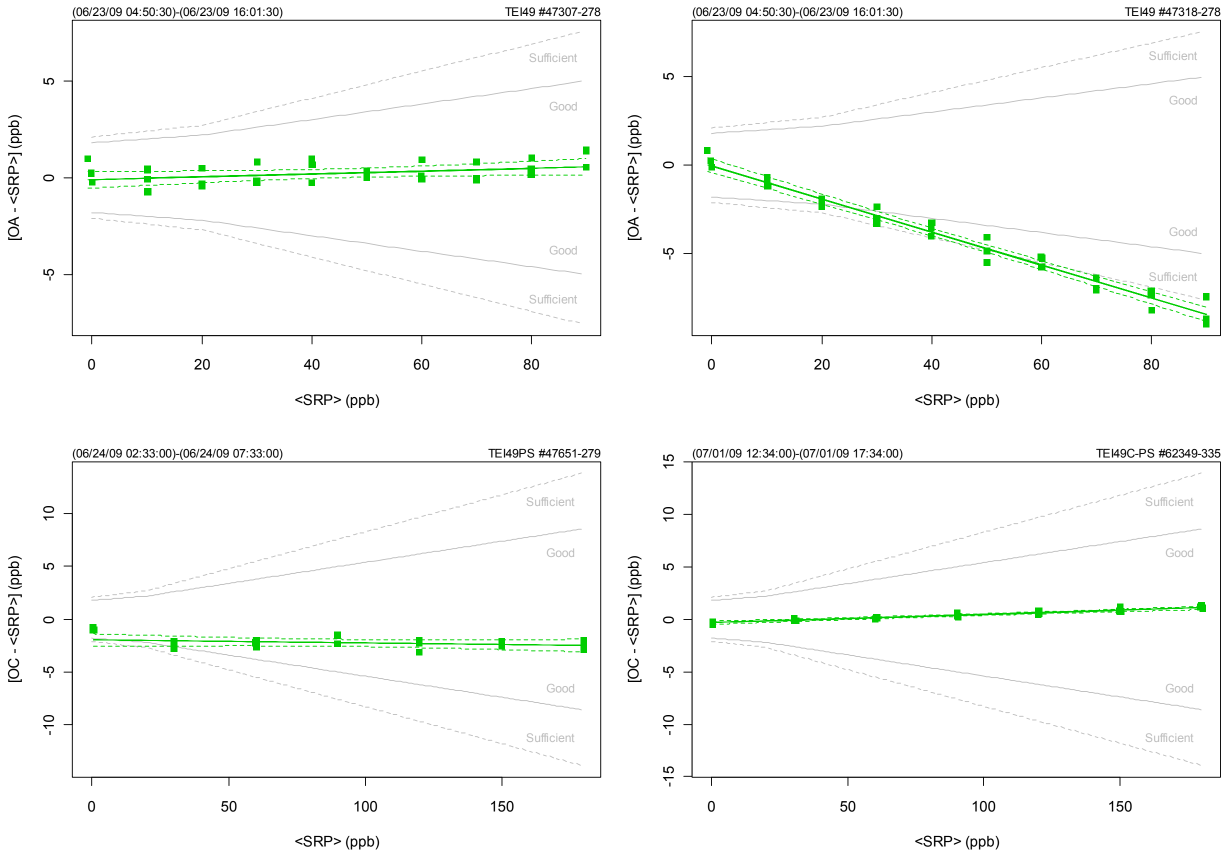

Figure 1. Upper panel: Bias of the WLG TEI 49 analyser with respect to the SRP as a function of mole fraction. Left: Main analyser, right backup instrument. Bottom panel: WLG TEI 49-PS ozone standard (left), CAMS TEI 49C-PS ozone standard (right). Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen et al.*, 2003] are delimited by grey lines. The dashed lines about the regression lines are the Working-Hoteling 95% confidence bands.

Carbon Monoxide Measurements

On-going measurement of carbon monoxide at WLG commenced in 1997, and continuous data series with some gaps (due to instrument malfunction) are available since then. The original instrument, a GC with HgO detector [*Zellweger et al.*, 2004], failed in 2007, and was replaced with a GC/FID system in 2008. An assessment of the previous instrument was not possible; however, data acquired with this system was reviewed during the audit. A manuscript describing the calibration history and data processing of this instrument was prepared by CAMS in collaboration with external partners [*Zhang et al.*, 2011].

Instrumentation. Mt. Waliguan is equipped with an Agilent 6890 GC-system for simultaneous measurements of CO, CH_4, N_2O and SF_6. Exactly the same instrumentation is also available at CAMS, which is mainly used for flask analysis and cylinder calibration. In addition, an Ametek GC system with HgO detector is available at CAMS mainly for the calibration of standards. The instrumentation is adequate for the intended purpose.

> **Recommendation 4 (**,2011)**
> *After the audit, additional CO instruments (Aerolaser AL5002, FTIR system of University of Wollongong, Picarro G1302) were purchased since it was recognized that calibrations using GC/HgO systems have shown to suffer from non-linearity issues in the past. However, some of these instruments are not yet operational, and resources need to be allocated to facilitate their use in the CAMS calibration laboratories.*

Standards. WLG used to have its own set of station standards [*Zellweger et al.*, 2004]; however, these standards are now empty, and the cylinders have been re-filled and are now used as working standards. The instrument was calibrated at CAMS before it was installed at WLG; only a working and a target standard are available at the site. A set of currently seven laboratory CO standards from WMO/CCL (NOAA/ESRL) is available at CAMS.

Intercomparison (Performance Audit). Comparisons were made both at the WLG site and at CAMS. The comparison involved repeated challenges of the instruments with randomised CO levels from travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 2:

Aglient 6890 #US 10719008 (WLG):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 7.8 ppb) / 0.9097 (2a)

Aglient 6890 #US 10681036 (CAMS):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 4.8 ppb) / 0.9271 (2b)

Ametek ta5000R #52PR181-06123 (CAMS):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 6.6 ppb) / 1.2200 (2c)

It can be seen that similar results were obtained for the two GC/FID instruments both at WLG and CAMS (2a and 2b). Both equations show a significant offset; in principle, the regression line should go through zero due to the linearity of the analytical method. An independent linearity check is therefore recommended for all instruments, including the Ametek system.

> **Recommendation 5 (**,2011)**
> *An independent system for linearity checks, e.g. by dilution of a CO standard with a high mole fraction, should be available for the CO measurement systems at CAMS. For this purpose, a set of 16 NOAA standards with a range from 50 to 1000 ppb became available after the audit for linearity checks, and the system has already been optimised. Continuation of these checks is highly recommended.*

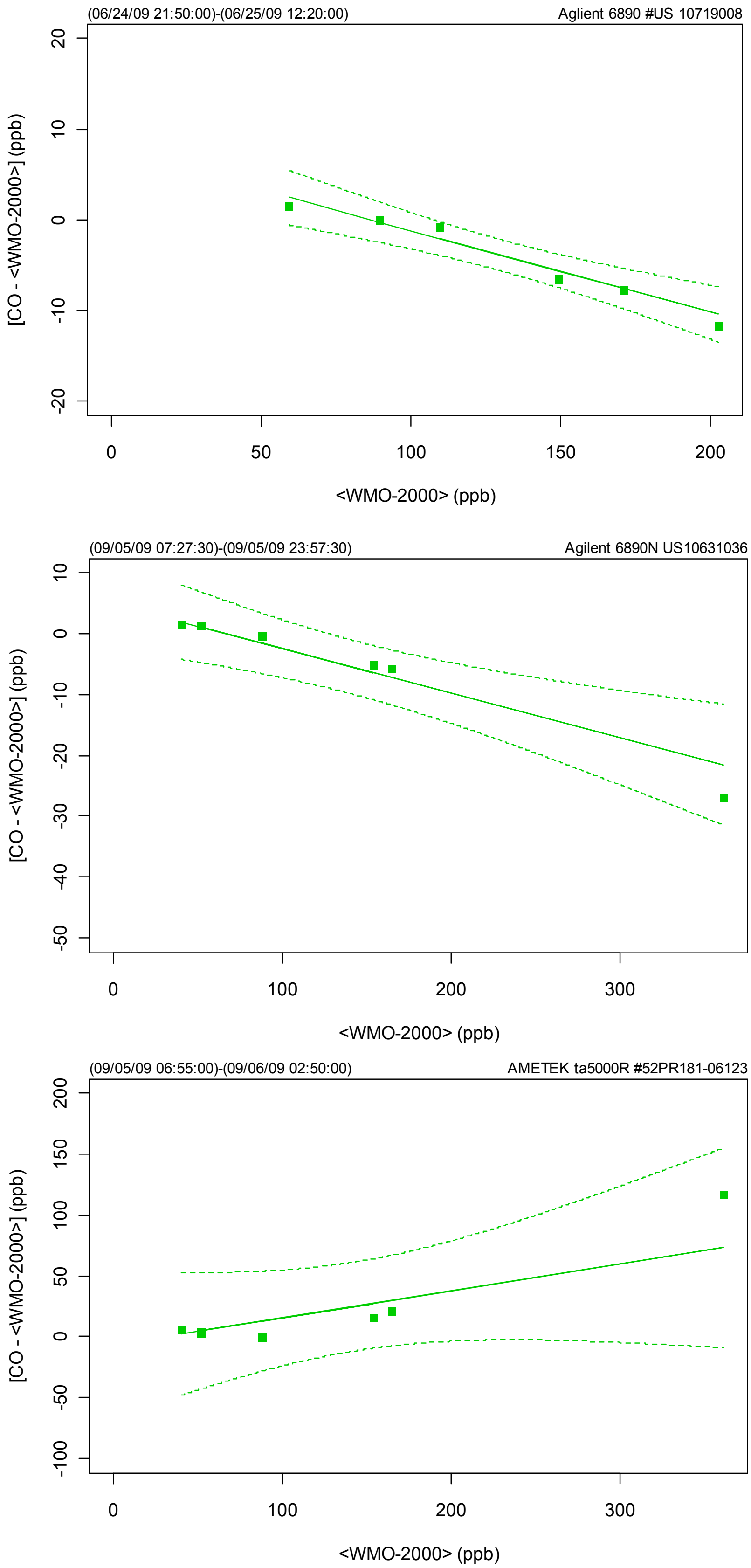

Figure 2. Top: Bias of the WLG carbon monoxide instrument (Agilent 6890) with respect to the WMO-2000 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hoteling 95% confidence bands. Middle and bottom: same figures for CAMS instruments.

Methane Measurements

On-going measurement of methane commenced in 1994 at WLG, and continuous data series are available since then.

Instrumentation. Currently, three different systems are used for methane measurements at WLG. The original GC/FID system (HP5890) is still operational and was complemented with a new GC system (Aglient 6890) in 2008 for multi-species analysis. In addition, a Picarro G1301 was installed in 2009. All instruments were assessed during the current audit.

Standards. Only working and target standards are available at WLG. These standards have been calibrated against the laboratory CH_4 standards from WMO/CCL (NOAA/ESRL) at CAMS. All measurements are referenced to the NOAA04 methane calibration scale [*Dlugokencky et al.*, 2005]. The new instruments were calibrated at CAMS before the installation at WLG.

Intercomparison (Performance Audit). The comparison involved repeated measurements of WCC-Empa travelling standards with both the WLG and CAMS instruments. The following equations characterise the instrument bias, and the results are illustrated in Figure 3 (WLG) and Figure 4 (CAMS):

Comparisons at WLG:

HP 5890 # C-128 183 (WLG):

$$X_{CH4}\ (ppb) = (CH_4) / 0.99921 \qquad (3a)$$

Agilent 6890 #US 10719008 (WLG):

$$X_{CH4}\ (ppb) = (CH_4) / 1.00010 \qquad (3b)$$

Picarro G1301 #CFADS023 (WLG):

$$X_{CH4}\ (ppb) = (CH_4) / 0.99973 \qquad (3c)$$

Comparisons at CAMS:

Agilent 6890 #US 10681036 (CAMS, integrated with the Ametek system):

$$X_{CH4}\ (ppb) = (CH_4) / 1.00090 \qquad (3d)$$

Agilent 6890 #US 10719007 (CAMS, Flask system):

$$X_{CH4}\ (ppb) = (CH_4) / 1.00150 \qquad (3e)$$

Picarro G1301 #CFADS021 (CAMS):

$$X_{CH4}\ (ppb) = (CH_4) / 1.00120 \qquad (3f)$$

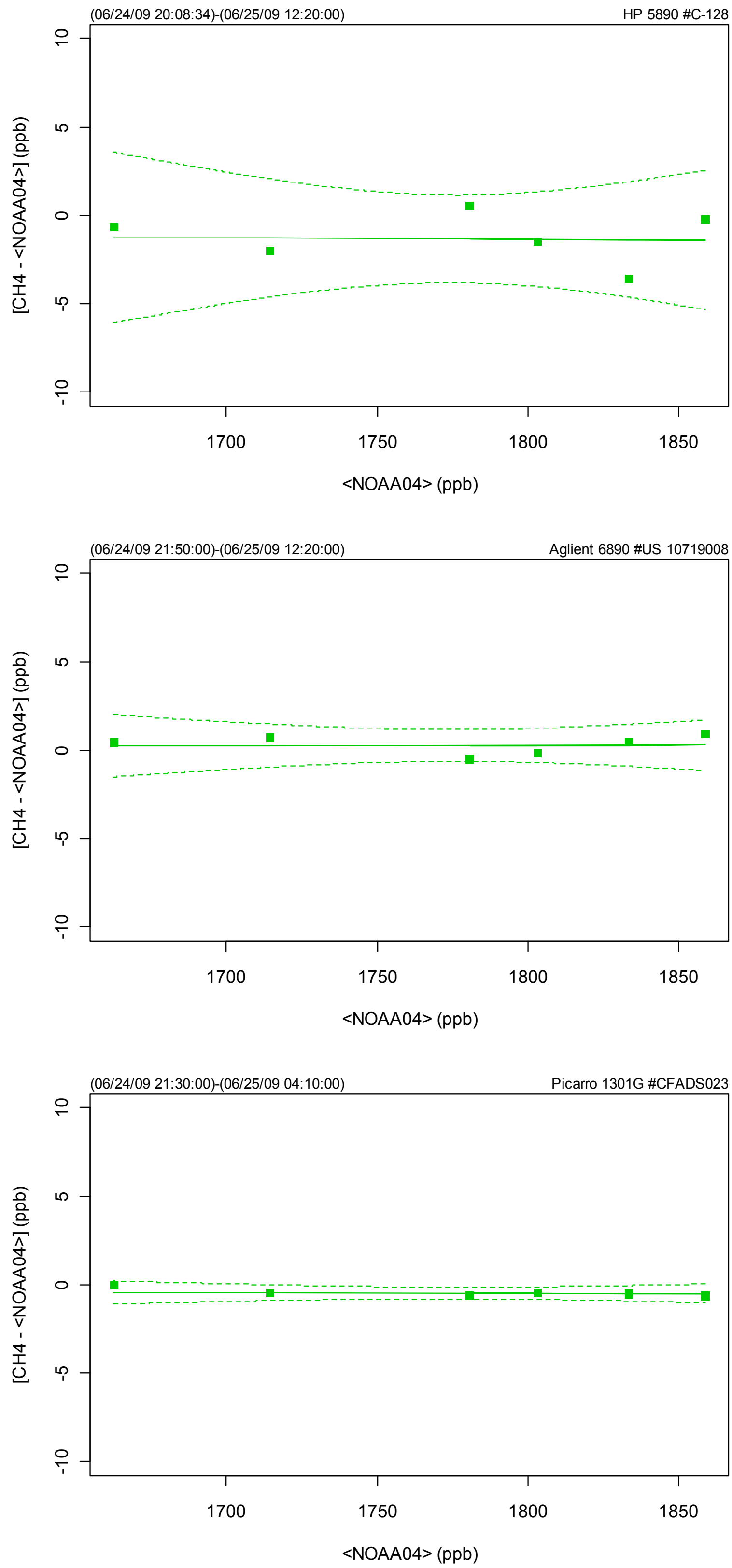

Figure 3. Bias of the WLG methane instruments with respect to the NOAA04 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hoteling 95% confidence bands. The regression line was forced through zero.

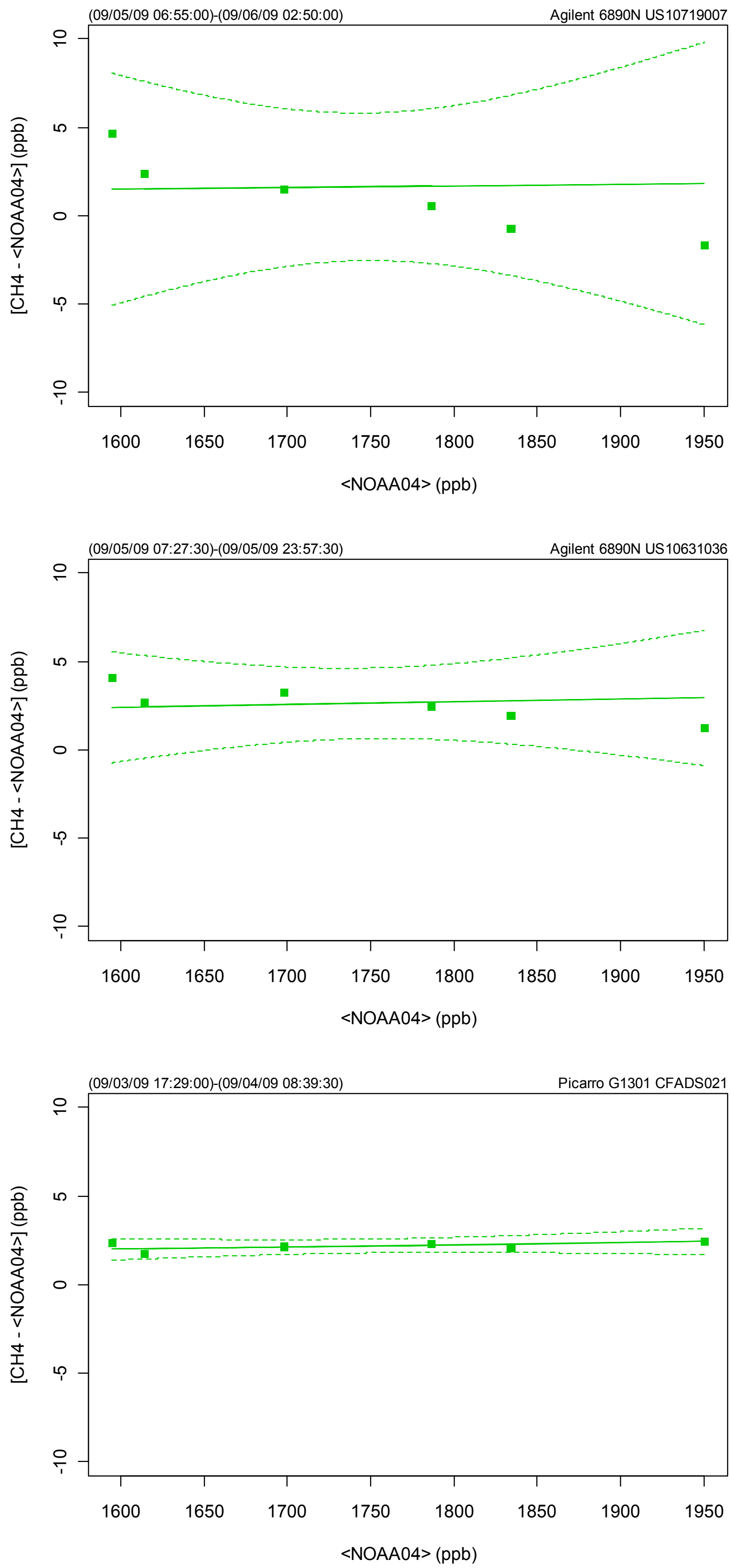

Figure 4. Bias of the CAMS methane instruments with respect to the NOAA04 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hoteling 95% confidence bands. The regression line was forced through zero.

It can be seen from Figure 3 that the WLG measurements meet the WMO/GAW recommendation of ±2 ppb [*WMO*, 2009] for all instruments; however, the associated uncertainty is higher for the GC instruments compared to the Picarro analyser. No significant deviations between the WLG instrument and WCC-Empa were found. A significantly larger bias was found for the calibrations made at CAMS (Figure 4), which is difficult to explain since the WLG instrument has been calibrate using CAMS laboratory standards. The repeatability of the WLG GC instrument reached values that are comparable to the best GC/FID instruments, but the Picarro analysers show a significantly better repeatability.

Recommendation 6 (,2011)**
Due to the fact that relatively high deviations were observed at CAMS, the methane calibration of the CAMS instruments should be regularly being re-assessed. The observed difference during the audit is difficult to understand, since the agreement at WLG was significantly better. It is well possible that the observed difference was due to temporary instrument problems. Results of the round robin carried out by JMA (WCC for CH_4 - Asia) in April 2009 did not show significant differences between WLG and CAMS measurements. Participation in these inter-comparisons provides valuable information, and continuation of these comparisons is encouraged.

Recommendation 7 (,2011)**
Since the version of the Picarro software used during the audit does not calculate dry methane mole fractions, a corresponding correction has to be applied to ambient air data. An upgrade to the latest software version should be considered. Note: This was done after the audit in 2010/11. A correction function has been determined, and corresponding corrections to the data were made. Corrected data was submitted to WDCGG and NOAA.

Nitrous Oxide Measurements

Continuous measurement of nitrous oxide commenced in June 2008 at WLG, and continuous data series are available since then. Calibration facilities at CAMS are also available since then and have been included in the scope of the current audit.

Instrumentation. An Agilent 6890 GC with an Electron Capture Detector (ECD) is used for nitrous oxide measurements at WLG. The same instrument types are also in use at CAMS for the calibration of standards and flask sample analysis.

Standards. At the WLG station, only a working and a target standard are available. A full calibration of the WLG instrument has been made at CAMS, where also a suite of laboratory N_2O standards from WMO/CCL (NOAA/ESRL) is available.

> **Recommendation 8 (***,2011)**
> *A set of three or more nitrous oxide standards should be available at WLG for the verification of the instrument response function. In the meantime, 13 N_2O standards are available at CAMS, and values are assigned to WS and target used at WLG.*

Intercomparison (Performance Audit). The comparison involved repeated measurements of WCC-Empa travelling standards with the WLG and the CAMS instruments. The N_2O mole fractions of the TS were assigned by the WCC-N_2O in 2007/2008, and have not been re-calibrated since then. The agreement was acceptable for the measurements made at CAMS, where the N_2O measurements did on average not significantly deviate from the GAW reference (NOAA-2006 mole fraction scale); however, large deviations were found for the comparison made at WLG. The following equations characterise the instrument bias, and the results are illustrated in Figure 5:

WLG (Aglient 6890N US10719008):

Unbiased N_2O mixing ratio (ppb): X_{N2O} (ppb) = (N_2O – 52.02 ppb) / 0.85331 (4a)

CAMS (Aglient 6890N US10719007):

Unbiased N_2O mixing ratio (ppb): X_{N2O} (ppb) = (N_2O) / 0.99964 (4b)

CAMS (Aglient 6890N US10631036):

Unbiased N_2O mixing ratio (ppb): X_{N2O} (ppb) = (N_2O) / 1.00100 (4c)

> **Recommendation 9 (***,2011)**
> *The reason for the large deviation between CAMS and WCC-Empa needs further attention. A full characterisation of the instrument response function is needed. The experiment must be made at the WLG site, since ambient pressure may have a significant impact on the signal. Furthermore, a full audit by the WCC-N_2O is strongly suggested.*
> ***Update November 2011:*** *The GC-ECD parameters were optimized, and two working and one target standards are regularly used and evaluated. In addition, a "Chinese round robin" programme will start very soon, which will include a full test for the WLG GC-EDC system.*
>
> **Recommendation 10 (***,2011)**
> *Multiple injections of WCC standards resulted in relatively high standard deviations (up to >1 ppb) especially for the instruments operated at CAMS. These GC systems need to be optimized for N_2O measurements since the GAW DQOs cannot be met with this repeatability.*
> ***Update November 2011:*** *The optimization of the GC/ECD system (better temperature control of sample loop and lab, tuning of instrument parameters) improved the standard deviation of multiple injections to approx. 0.1-0.2 ppb.*

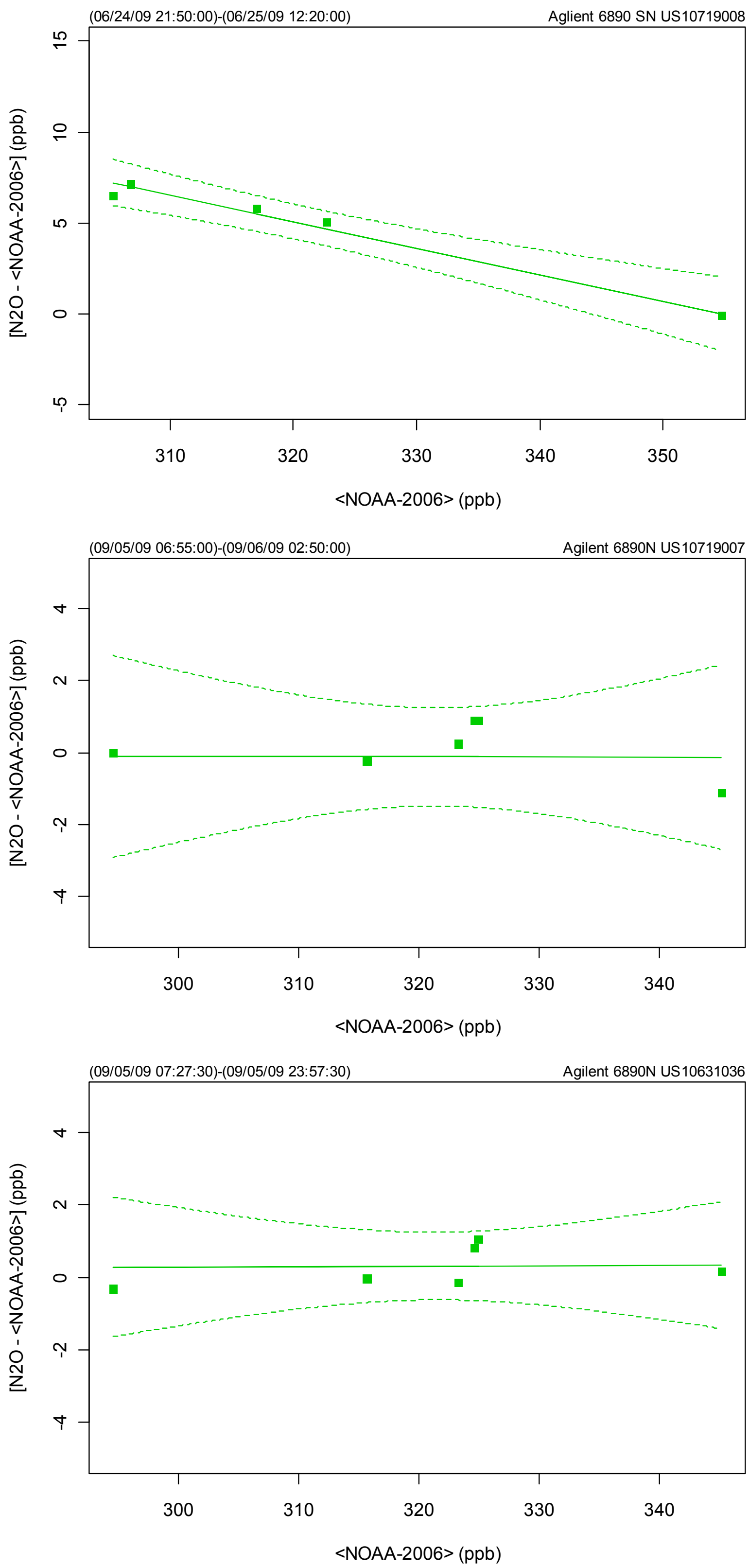

Figure 5. Bias of the WLG (upper panel) and CAMS (middle and lower panel) N_2O GC with respect to the NOAA-2006 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hoteling 95% confidence bands. The regression was forced through zero for the CAMS instruments.

Data Acquisition and Management

Ozone data at WLG are acquired using a Campell 21X data logger. The system has not been changed since the last audit in 2004. The Agilent GC systems are connected to an Agilent GC ChemStation; the Ametek GC (CAMS) is connected to the same data acquisition system with an Agilent interface model 35900E. The Picarro instruments use the internal data acquisition system. All data acquisition systems are appropriate for their purpose; however, the data acquisition system for surface ozone at WLG needs to be replaced when a new instrument is purchased (cf. recommendation 2).

Data Submission

To date, only few data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently, daily and monthly in-situ data for methane (1994 – 2010) and carbon dioxide (1994 – 2010) have been submitted by CMA to the WDCGG. The CMA and NOAA cooperative flask sampling data at WLG are available at WDCGG.

Recommendation 11 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year. Data should be submitted as hourly averages. Daily and monthly data are submitted, and high frequency data is available upon request.

Recommendation 12 (, ongoing)**
GAWSIS entries should be updated in regular intervals. In case of problems, the GAWSIS manager should be contacted.

Conclusions

The GAW Global station WLG carries out a comprehensive suite of measurements. The measurement programme as well as the quality of the measurements and the scientific know-how significantly evolved over the last ten years. Long time series in combination with the growing number of measured parameters makes the WLG station an important contribution to the GAW programme, especially because they cover a geographical area where only few data is available. Most of the assessed measurements were of high quality; however, an issue with the nitrous oxide calibration at WLG needs further attention.

Central calibration facilities at CAMS ensure traceability of the Chinese GAW stations to the WMO references. The CAMS facilities were initiated a few years ago, and provide now state-of-the-art QA/QC services. These facilities complement WLG and other Chinese GAW stations; most assessed measurements at CAMS were of high quality.

Summary Ranking of the WLG Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access possible
Facilities		
Laboratory and office space	(5)	Spacious facilities
Air Conditioning	(5)	
Power supply	(5)	
Internet access	(5)	
General Management and Operation		
Organisation	(5)	Well organised, clear responsibilities
Competence of staff	(4)	Good scientific skills at CAMS, further training of station operators needed
Air Inlet System	(4)	Each system uses own inlet
Instrumentation		
Ozone	(2)	TEI49 becoming old
Carbon monoxide	(4)	GC/FID with methanizer
Methane	(5)	3 instruments, best Performance: Picarro G1301
Nitrous Oxide	(5)	Agilent 6890 with ECD
Carbon Dioxide	(5)	Picarro G1301
Aerosol parameters*	(5)	Comprehensive programme
Flask sampling	(5)	CMA and NOAA/ESRL cooperative sampling programme
Meteo	(5)	
Standards		
Ozone	(2)	TEI 49-PS becoming old
Carbon monoxide	(4)	Only working standards at WLG
Methane	(4)	Only working standards at WLG
Nitrous Oxide	(2)	Insufficient number of standards
Data Management		
Data acquisition	(4)	Adequate DAQ systems
Data processing	(5)	In progress
Data submission	(2)	Only CO_2 and CH_4 data submitted, more data expected after completion of QA/QC

#0: inadequate thru 5: adequate; *refer to GAWSIS for a complete overview of measured parameters.

Dübendorf, December 2011

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Head of laboratory

APPENDIX

GAW Global Station WLG

Site description

The WLG observatory is located on the top of Mt. Waliguan at the Qinghai-Xizang Plateau (36°17'N, 100°54'E, 3810m asl). It is a remote site in an area with a very low population density. Major nearby cities are Gonghe (population 30,000), located 25 km to the west, and Xining (population 1.2 million), located 90 km north-east of the station. For more information, refer to the previous audit reports [*Zellweger et al.*, 2000; *Zellweger et al.*, 2004] and GAWSIS (http://gaw.empa.ch/gawsis).

Measurement Programme

An overview of the measurement programme and its status as of July 2009 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the WLG Station

Parameter*	Current Instrument
Ozone	
Surface ozone	UV absorption (TEI 49)
Total column ozone	Brewer
Greenhouse Gas	
CO_2	NDIR, GC-FID and CRDS
CH_4	GC-FID and CRDS
N_2O	GC-ECD
SF_6	GC-ECD
Reactive Gas	
CO	GC-FID
Flask Sampling	
CO_2, CH_4, N_2O, SF_6, CO, H_2, CO_2 isotopes	CMA and NOAA cooperative flask sampling programme
Aerosol	
Light absorption coefficient	Aethalometer
Light scattering coefficient	Nephelometry, integrating
Hemispheric backscattering coef.	Nephelometry, integrating
Multiwavelength optical depth	Pyrheliometer (direct, broadband)
Multiwavelength optical depth	Sunphotometry/Filter Radiometry
Number concentration	CPC
Precipitation Chemistry	
Conductivity, pH	
Solar radiation	
Diffuse, Direct, Global and long-wave radiation	Pyranometer and Pyrheliometer
Meteo	
PTU, wind speed + direction	

* Refer to GAWSIS for more details
\# Missing information about data coverage: information was not available, but general high data availabilities (>90%) are expected for most parameters.

Ozone, Carbon Monoxide, Methane and Nitrous Oxide Distributions at Mt. Waliguan

The monthly and yearly distributions for surface ozone, carbon monoxide and methane are shown in Figure 6.

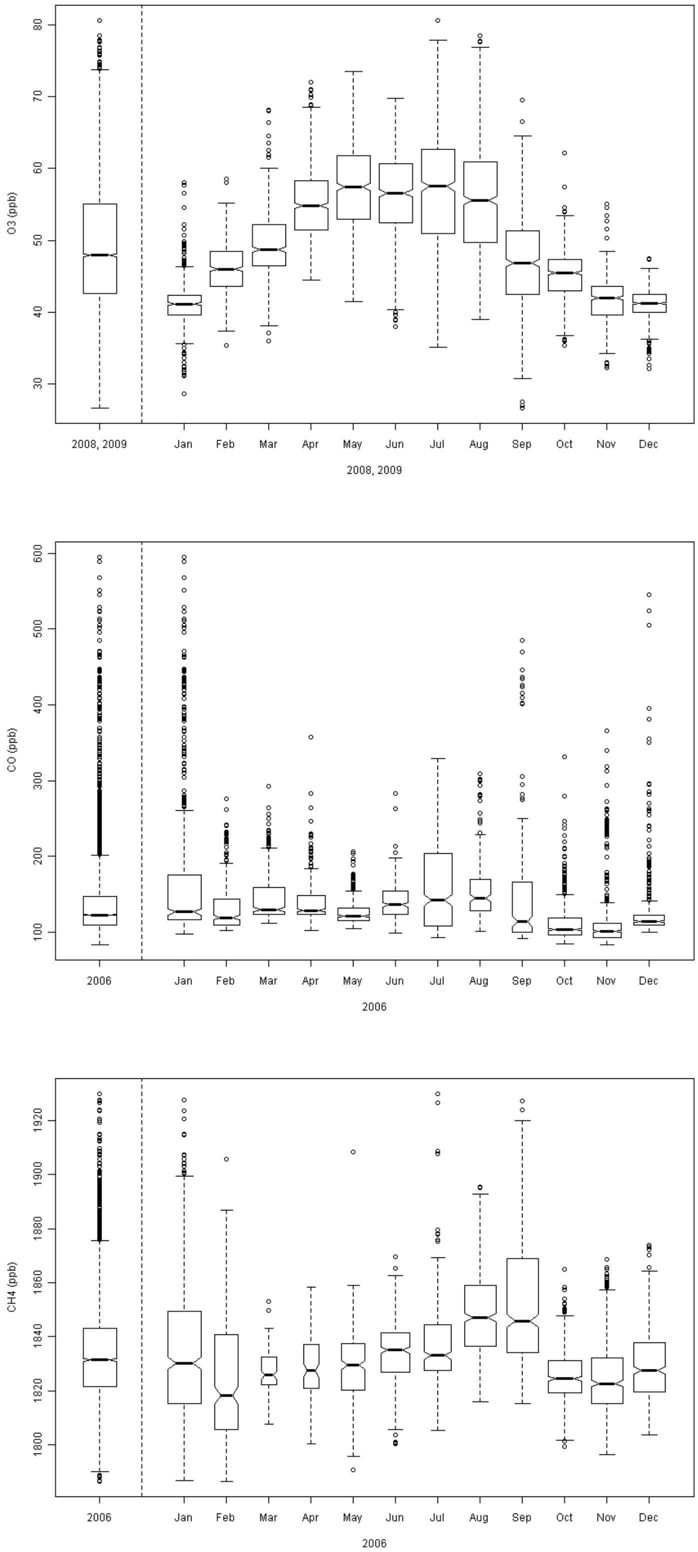


Figure 6. Yearly and monthly box plots for surface ozone (Nov 2008 – Oct 2009), carbon monoxide (2006) and methane (2006) (calculated from 1-hourly aggregates). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles 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 WLG observatory is coordinated by the Chinese Academy of Meteorological Sciences (CAMS) and the Qinghai Provincial Meteorological Bureau (QMB) under the China Meteorological Administration (CMA). An overview of the CAMS and WLG staff responsible for the station as of July 2009 for the parameters of the audit scope is given in Table 2 below.

Table 2. CAMS and WLG staff.

Name	**Position and duty**
CAMS	
Prof. Xiaoye Zhang	China GAW country contact
Prof. Lingxi Zhou	China GAW station contact & coordinator PI for greenhouse gases & relater tracers (including CO, H_2 and isotopes)
Dr. Shuangxi Fang	Key technician for greenhouse gases & relater tracers
Ms. Fang Zhang	PhD student for greenhouse gases & relater tracers
Dr. Xiaobin Xu	PI for reactive gases
Dr. Wie-li Lin	Key technician for reactive gases
QMB	
Mr. Deliger	Station director
Mr. Guoqing Zhang	Station deputy director
Mr. Hong Nie	Assistant station director, lead operator, senior engineer / solar radiation, CO_2, optical depth, Aerosol
Mr. Jianqing Huang	Operator, engineer/surface ozone, air compress
Mr. Jun Ji	Operator, engineer / BC;
Mr. Delin Li	Operator, assistant engineer/TSP, Climate, Aerosol
Mr. Donglin Qi	Operator, senior engineer /
Mr. Jianqiong Wang	Operator, engineer / Total ozone, precipitation chemistry
Mr. Ming Zheng	Operator, engineer / meteorology, flask sampling
Mr. Peng Liu	Operator, engineer / CH_4/CO_2,network management
Mr. Yucheng Zhao	Senior engineer / data processing, at Xining office
Ms.Yinlan Yang	Senior engineer / data analyzing, at Xining office
Mr. Yongxiang Cai	Engineer/data analyzing, at Xining office
Ms. Chunge Fu	Administration secretary
Mr. Faxiang He	Supporting staff, engineer
Mr. Qingchuan Wang	Driver

Surface Ozone Measurements

Surface ozone measurements started in July 1994 at the Mt. Waliguan site, and continuous one-hourly time series are available since then. The whole measurement set-up remained unchanged since the last audit by WCC-Empa [*Zellweger et al.*, 2004]. All comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning

All laboratories at WLG are air-conditioned to approx. 20°C.

Air Inlet System

Unchanged since the last WCC-Empa audit [*Zellweger et al.*, 2004].

Instrumentation

The station is equipped with two ozone analyzers (TEI 49). Instrumental details are summarised in Table 3 below. The instrumentation has not changed since the last WCC-Empa audit.

Standards

The station is equipped with one ozone calibrator (TEI 49PS), details see Table 3.

Operation and Maintenance

The system is checked daily for general operation by the station operators. A full instrument check (flow rates, intensities, noise, pressure and temperature sensors) is done weekly. An automatic zero check is performed every second day. Inlet filters are changed weekly. An inter-comparison with the station calibrator is performed approximately every three months. The inlet loss is determined once per year using a Teflon line leading to air intake. Loss of <0.5 – 2 % was usually observed; no correction is applied.

Data Acquisition and Data Transfer

Unchanged since the last WCC-Empa audit [*Zellweger et al.*, 2004]. One-minute averages including are stored on the Campbell 21X data loggers. No remote access is possible.

Data Treatment

The data is reprocessed at CAMS. All data is visually inspected before a validated data set is created.

Data Submission

At the time of the audit ozone data of has not been submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA.

Documentation

Electronic station and instrument logbooks are available. The information was sufficiently comprehensive and up-to-date. The instrument manuals are available at the site.

Comparison of Ozone Analyzers

Ozone comparisons were made at WLG and at the CAMS calibration facilities. Two different ozone travelling standards were used for the comparison. All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included comparisons of the travelling standards with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

Setup and Connections

Table 3 shows details of the experimental set-up.

Table 3. Experimental details of the ozone comparison.

WCC Transfer standard (TS1) at WLG	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
WCC Transfer standard (TS2) at CAMS	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.6; COEFF = 1.009
WLG main ozone analyser (OA1)	Model, S/N	TEI 49 #47307-278
	Principle	UV absorption
	Range	1 ppm
	Settings	OFFSET 51, SPAN 506
WLG backup ozone analyser (OA2)	Model, S/N	TEI 49 #47318-278
	Principle	UV absorption
	Range	1 ppm
	Settings	OFFSET 50, SPAN 600
WLG ozone calibrator (OC1)	Model, S/N	TEI 49-PS #47651-279
	Principle	UV absorption
	Range	1 ppm
	Settings	NA
CAMS ozone calibrator (OC2)	Model, S/N	TEI 49C-PS #62349-335
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.010
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 and OA/OC	C-series: 1-min aggregates from digital output (custom designed LabView programme of WCC-Empa); analogue signal was used for TEI 49 instruments.
Pressure readings at beginning of comparison (hPa)	TS1	646.1 (TS1), 646.7 (ref.), no adjustments were made
	TS2	998.2 (TS2), 1000.0 (ref.), no adjustments were made
	OA1	641.2 (OA1), 646.6 (ref.), no adjustments were made
	OA2	641.2 (OA2), 646.6 (ref.), no adjustments were made
	OC1	638.5 (OC1), 644.5 (ref.), no adjustments were made
	OC2	982.7 (OC2), 1000.0 (ref.), no adjustments were made
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90 (analyzers) 0, 30, 60, 90, 120, 150, 180 (calibrators)
Duration per level (min)		15 or 20
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		OA1 and OA2: 3 runs (2009-06-23) OC1: 3 runs (2009-06-24) OC2: 3 runs (2009-07-01)

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]. The results are shown in Table 4 (WLG main analyser), Table 5 (WLG backup analyser), Table 6 (WLG calibrator) and Table 7 (CAMS calibrator). All results refer to the calibration factors as given in Table 3 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 4. Ten-minute aggregates computed from the last 10 of a total of 20 one-minute values for the initial comparison of the main WLG ozone analyser (OA1) TEI 49C #47307-278 with the WCC-Empa transfer standard (TS1).

DateTime (UTC)	Run #	Level (ppb)	TS1 (ppb)	OA1 (ppb)	Flag#	sdTS1 (ppb)	sdOA1 (ppb)	OA1-TS1 (ppb)	OA1-TS1 (%)
2009-06-23 04:50	1	0	-0.81	0.17	0	0.51	0.08	0.97	NA
2009-06-23 05:10	1	30	30.02	30.81	0	0.17	0.13	0.79	2.63
2009-06-23 05:30	1	60	60.05	60.91	0	0.15	0.14	0.85	1.42
2009-06-23 05:50	1	40	40.01	40.91	0	0.14	0.15	0.90	2.25
2009-06-23 06:10	1	90	90.01	91.31	0	0.16	0.13	1.30	1.44
2009-06-23 06:30	1	50	50.04	50.30	0	0.16	0.13	0.26	0.52
2009-06-23 06:50	1	10	10.03	10.44	0	0.19	0.09	0.41	4.09
2009-06-23 07:10	1	20	19.99	20.44	0	0.25	0.07	0.45	2.25
2009-06-23 07:30	1	80	80.04	80.96	0	0.23	0.13	0.93	1.16
2009-06-23 07:50	1	70	70.02	70.76	0	0.16	0.17	0.74	1.05
2009-06-23 09:41	2	0	-0.23	0.00	0	0.28	0.07	0.23	NA
2009-06-23 10:01	2	30	29.98	29.76	0	0.22	0.14	-0.22	-0.75
2009-06-23 10:21	2	60	60.00	60.01	0	0.18	0.17	0.01	0.02
2009-06-23 10:41	2	40	40.04	40.67	0	0.22	0.29	0.63	1.57
2009-06-23 11:01	2	90	89.99	90.40	0	0.21	0.10	0.41	0.45
2009-06-23 11:21	2	50	50.01	49.98	0	0.08	0.17	-0.03	-0.06
2009-06-23 11:41	2	10	10.13	10.05	0	0.35	0.10	-0.07	-0.73
2009-06-23 12:01	2	20	20.02	19.66	0	0.16	0.07	-0.36	-1.79
2009-06-23 12:21	2	80	80.02	80.36	0	0.14	0.14	0.34	0.42
2009-06-23 12:41	2	70	70.00	69.79	0	0.22	0.16	-0.21	-0.30
2009-06-23 13:01	3	0	0.06	-0.16	0	0.24	0.04	-0.22	NA
2009-06-23 13:21	3	40	39.99	39.66	0	0.15	0.14	-0.33	-0.83
2009-06-23 13:41	3	70	69.99	69.88	0	0.14	0.15	-0.12	-0.16
2009-06-23 14:01	3	30	29.98	29.67	0	0.14	0.13	-0.31	-1.02
2009-06-23 14:21	3	90	89.98	90.41	0	0.17	0.18	0.42	0.47
2009-06-23 14:41	3	20	19.98	19.56	0	0.22	0.11	-0.42	-2.10
2009-06-23 15:01	3	10	10.15	9.42	0	0.53	0.47	-0.73	-7.20
2009-06-23 15:21	3	60	60.03	59.86	0	0.14	0.15	-0.17	-0.29
2009-06-23 15:41	3	50	50.00	49.95	0	0.15	0.13	-0.05	-0.09
2009-06-23 16:01	3	80	80.02	80.09	0	0.12	0.08	0.07	0.08

#0: valid data; 1: invalid data.

Table 5. Ten-minute aggregates computed from the last 10 of a total of 20 one-minute values for the final comparison of the backup WLG ozone analyser (OA2) TEI 49C #47318-278 with the WCC-Empa transfer standard (TS1).

DateTime (UTC)	Run #	Level (ppb)	TS1 (ppb)	OA2 (ppb)	Flag#	sdTS1 (ppb)	sdOA2 (ppb)	OA2-TS1 (ppb)	OA2-TS1 (%)
2009-06-23 04:50	1	0	-0.81	0.04	0	0.51	0.04	0.84	NA
2009-06-23 05:10	1	30	30.02	27.64	0	0.17	0.11	-2.38	-7.92
2009-06-23 05:30	1	60	60.05	54.74	0	0.15	0.11	-5.32	-8.85
2009-06-23 05:50	1	40	40.01	36.41	0	0.14	0.31	-3.60	-9.00
2009-06-23 06:10	1	90	90.01	80.96	0	0.16	0.14	-9.05	-10.05
2009-06-23 06:30	1	50	50.04	44.51	0	0.16	0.14	-5.53	-11.04
2009-06-23 06:50	1	10	10.03	9.32	0	0.19	0.11	-0.72	-7.13
2009-06-23 07:10	1	20	19.99	18.09	0	0.25	0.11	-1.90	-9.51
2009-06-23 07:30	1	80	80.04	71.77	0	0.23	0.10	-8.27	-10.33
2009-06-23 07:50	1	70	70.02	62.99	0	0.16	0.12	-7.03	-10.04
2009-06-23 09:41	2	0	-0.23	0.03	0	0.28	0.05	0.27	NA
2009-06-23 10:01	2	30	29.98	26.99	0	0.22	0.13	-3.00	-9.99
2009-06-23 10:21	2	60	60.00	54.77	0	0.18	0.16	-5.23	-8.71
2009-06-23 10:41	2	40	40.04	36.75	0	0.22	0.07	-3.29	-8.22
2009-06-23 11:01	2	90	89.99	82.44	0	0.21	0.14	-7.54	-8.38
2009-06-23 11:21	2	50	50.01	45.87	0	0.08	0.21	-4.14	-8.27
2009-06-23 11:41	2	10	10.13	9.04	0	0.35	0.08	-1.08	-10.68
2009-06-23 12:01	2	20	20.02	17.75	0	0.16	0.08	-2.26	-11.32
2009-06-23 12:21	2	80	80.02	72.84	0	0.14	0.14	-7.18	-8.97
2009-06-23 12:41	2	70	70.00	63.54	0	0.22	0.17	-6.46	-9.23
2009-06-23 13:01	3	0	0.06	-0.07	0	0.24	0.03	-0.13	NA
2009-06-23 13:21	3	40	39.99	35.92	0	0.15	0.09	-4.08	-10.19
2009-06-23 13:41	3	70	69.99	62.87	0	0.14	0.21	-7.13	-10.18
2009-06-23 14:01	3	30	29.98	26.64	0	0.14	0.21	-3.34	-11.14
2009-06-23 14:21	3	90	89.98	81.23	0	0.17	0.11	-8.76	-9.73
2009-06-23 14:41	3	20	19.98	17.59	0	0.22	0.15	-2.38	-11.92
2009-06-23 15:01	3	10	10.15	9.01	0	0.53	0.13	-1.15	-11.29
2009-06-23 15:21	3	60	60.03	54.21	0	0.14	0.13	-5.82	-9.69
2009-06-23 15:41	3	50	50.00	45.10	0	0.15	0.12	-4.89	-9.79
2009-06-23 16:01	3	80	80.02	72.57	0	0.12	0.09	-7.45	-9.32

#0: valid data; 1: invalid data.

Table 6. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the final comparison of the backup WLG ozone calibrator (OC1) TEI 49-PS #47651-279 with the WCC-Empa transfer standard (TS1).

DateTime (UTC)	Run #	Level (ppb)	TS1 (ppb)	OC1 (ppb)	Flag[#]	sdTS1 (ppb)	sdOC1 (ppb)	OC1-TS1 (ppb)	OC1-TS1 (%)
2009-06-24 02:33	1	0	0.45	-0.53	0	0.27	0.01	-0.97	NA
2009-06-24 02:48	1	30	29.94	27.12	0	0.34	0.25	-2.82	-9.41
2009-06-24 03:03	1	60	60.03	57.39	0	0.08	0.08	-2.65	-4.41
2009-06-24 03:18	1	120	119.97	116.66	0	0.04	0.16	-3.31	-2.76
2009-06-24 03:33	1	90	89.97	88.27	0	0.15	0.47	-1.70	-1.89
2009-06-24 03:48	1	150	150.03	147.34	0	0.10	0.10	-2.69	-1.79
2009-06-24 04:03	1	180	180.00	176.94	0	0.10	0.17	-3.06	-1.70
2009-06-24 04:18	2	0	0.61	-0.41	0	0.32	0.02	-1.02	NA
2009-06-24 04:33	2	90	89.97	87.49	0	0.06	0.18	-2.48	-2.76
2009-06-24 04:48	2	60	59.99	57.70	0	0.08	0.15	-2.29	-3.81
2009-06-24 05:03	2	180	180.01	177.36	0	0.14	0.24	-2.65	-1.47
2009-06-24 05:18	2	30	29.98	27.74	0	0.05	0.15	-2.24	-7.48
2009-06-24 05:33	2	150	150.03	147.39	0	0.16	0.30	-2.64	-1.76
2009-06-24 05:48	2	120	119.98	117.59	0	0.05	0.15	-2.39	-1.99
2009-06-24 06:03	3	0	0.40	-0.41	0	0.47	0.04	-0.81	NA
2009-06-24 06:18	3	180	179.98	177.71	0	0.13	0.10	-2.27	-1.26
2009-06-24 06:33	3	30	30.06	27.95	0	0.19	0.07	-2.10	-7.00
2009-06-24 06:48	3	150	149.99	147.73	0	0.16	0.18	-2.26	-1.51
2009-06-24 07:03	3	60	60.01	57.93	0	0.11	0.27	-2.08	-3.46
2009-06-24 07:18	3	90	89.98	88.38	0	0.20	0.24	-1.60	-1.78
2009-06-24 07:33	3	120	120.01	117.89	0	0.07	0.09	-2.11	-1.76

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

Table 7. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the final comparison of the CAMS ozone calibrator (OC2) TEI 49C-PS #62349-335 with the WCC-Empa transfer standard (TS2).

DateTime (UTC)	Run #	Level (ppb)	TS2 (ppb)	OC2 (ppb)	Flag[#]	sdTS2 (ppb)	sdOC2 (ppb)	OC2-TS2 (ppb)	OC2-TS2 (%)
2009-07-01 12:34	1	0	0.13	-0.18	0	0.06	0.04	-0.31	NA
2009-07-01 12:49	1	30	30.80	30.78	0	0.11	0.03	-0.02	-0.08
2009-07-01 13:04	1	90	90.51	90.91	0	0.03	0.05	0.40	0.44
2009-07-01 13:19	1	180	180.35	181.55	0	0.05	0.05	1.20	0.67
2009-07-01 13:34	1	60	60.40	60.71	0	0.07	0.06	0.31	0.51
2009-07-01 13:49	1	120	120.28	121.04	0	0.12	0.06	0.76	0.64
2009-07-01 14:04	1	150	150.27	151.15	0	0.10	0.06	0.88	0.59
2009-07-01 14:19	2	0	0.12	0.05	0	0.03	0.04	-0.08	NA
2009-07-01 14:34	2	30	30.17	30.44	0	0.07	0.07	0.27	0.88
2009-07-01 14:49	2	60	60.16	60.46	0	0.11	0.07	0.30	0.49
2009-07-01 15:04	2	150	150.02	151.31	0	0.07	0.06	1.29	0.86
2009-07-01 15:19	2	120	120.06	121.00	0	0.06	0.07	0.95	0.79
2009-07-01 15:34	2	180	179.88	181.36	0	0.07	0.10	1.48	0.82
2009-07-01 15:49	2	90	90.07	90.86	0	0.05	0.06	0.79	0.87
2009-07-01 16:04	3	0	0.13	0.08	0	0.10	0.02	-0.05	NA
2009-07-01 16:19	3	60	59.97	60.12	0	0.07	0.06	0.15	0.25
2009-07-01 16:34	3	180	179.77	181.09	0	0.06	0.05	1.32	0.73
2009-07-01 16:49	3	90	89.96	90.40	0	0.08	0.05	0.44	0.49
2009-07-01 17:04	3	30	29.95	30.00	0	0.03	0.03	0.05	0.15
2009-07-01 17:19	3	120	119.79	120.46	0	0.05	0.03	0.66	0.55
2009-07-01 17:34	3	150	149.83	150.78	0	0.12	0.06	0.96	0.64

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

Figure 7 show the regression residuals of the ozone analyzers and calibrators with respect to the SRP as a function of ozone mole fraction and time.

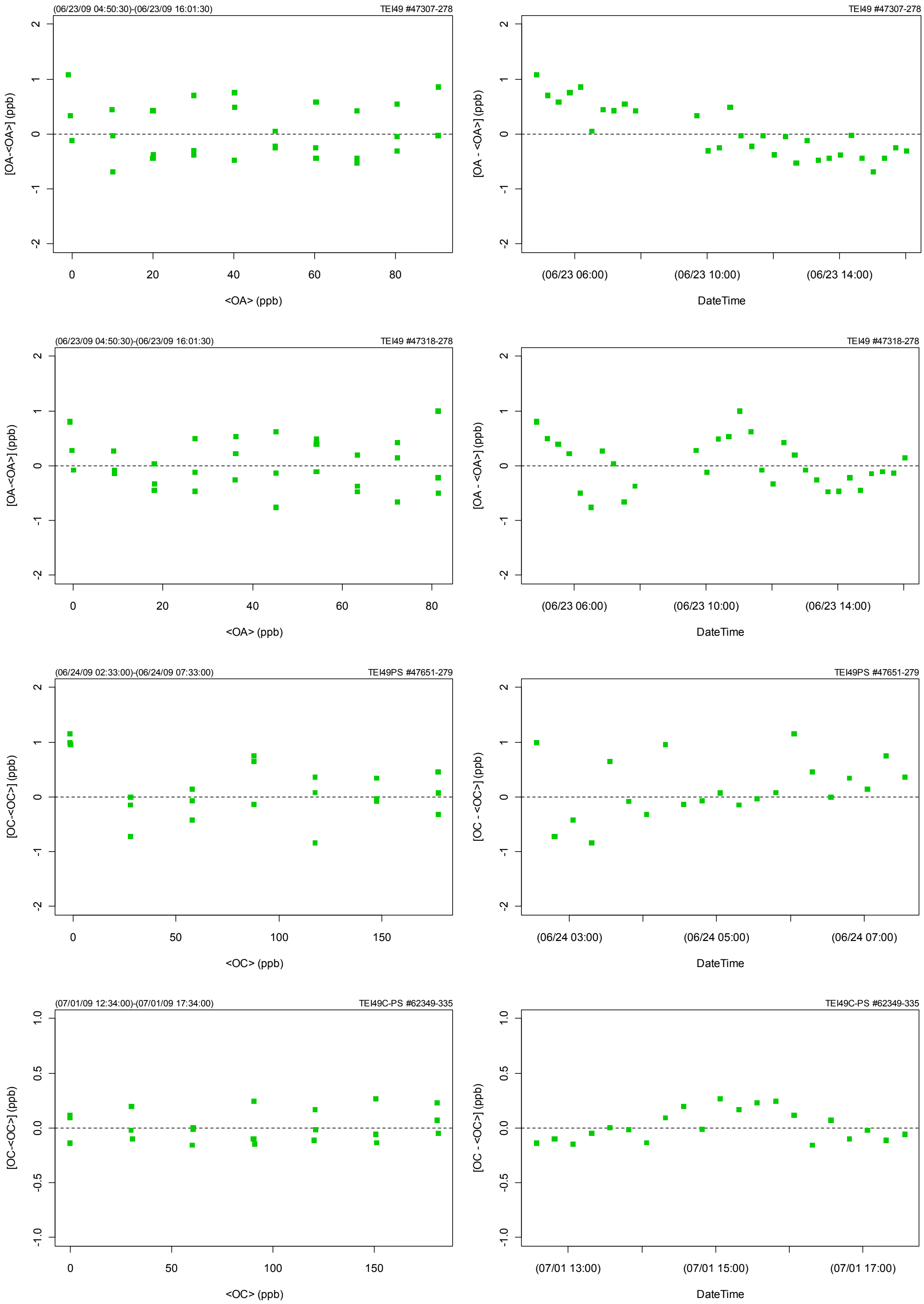


Figure 7. Regression residuals of the ozone comparisons as a function of concentration (left panel) and time (right panel). 1st row: WLG main analyser, 2nd row: WLG backup analyser, 3rd row: WLG calibrator, 4th row: CAMS calibrator.

Based on these 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 using equation (1) [*Klausen et al.*, 2003].

WLG main analyser [OA1]:

TEI 49 #47307-278 (OFFSET 51, SPAN 506):

X_{O3} (ppb) = ([OA] + 0.10 ppb) / 1.0073

u_{O3} (ppb) = sqrt (0.51 ppb^2 + 2.81e-05 * X_{O3}^2) (1a)

WLG backup analyzer [OA2]:

TEI 49 #47318-278 (OFFSET 50, SPAN 600):

X_{O3} (ppb) = ([OA] + 0.05 ppb) / 0.9067

u_{O3} (ppb) = sqrt (0.58 ppb^2 + 3.39e-05 * X_{O3}^2) (1b)

WLG calibrator [OC1]:

TEI 49-PS #47651-279 (no settings possible):

X_{O3} (ppb) = ([OA] + 1.97 ppb) / 0.9971

u_{O3} (ppb) = sqrt (0.57 ppb^2 + 2.71e-05 * X_{O3}^2) (1c)

CAMS calibrator [OC2]:

TEI 49C-PS #62349-335 (BKG 0.0, SPAN 1.010):

X_{O3} (ppb) = ([OC] + 0.33 ppb) / 1.0078

u_{O3} (ppb) = sqrt (0.28 ppb^2 + 2.56e-05 * X_{O3}^2) (1d)

Conclusions

The ozone measurements at WLG were within acceptable limits for the main ozone analyser, whereas the backup analyser was not functioning well due to an internal leak in the solenoid valves. Both WLG analyzers as well as the station calibrator are at the station since 1994 and reach the end of their useful lifetime. All instruments should be replaced. The ozone calibrator at CAMS was in good condition and agreed well compared to the WCC-Empa travelling standard.

Carbon Monoxide Measurements

In-situ carbon monoxide measurements started in 1997 at WLG using a gas chromatograph with a mercuric oxide detector. In June 2008, this system was replaced by an Agilent 6890 GC/FID. Time series of carbon monoxide are available from the beginning of the measurements until August 2007 when the old system failed. The audit comprised comparison of six travelling standards covering the mole fraction range from approx. 60 to 200 ppb (WLG) and 40 to 360 ppb (CAMS) carbon monoxide in air. All comparisons were done according to Standard Operating Procedures [*WMO*, 2007b].

Monitoring Set-up and Procedures

Air Conditioning

All laboratories at WLG are air-conditioned to approx. 20°C.

Air Inlet System

Unchanged since the last WCC-Empa audit [*Zellweger et al.*, 2004].

Sampling-location: Located at the top of the 80 m tower.

Sample inlet / manifold: The inlet consists of a 93 m long ⅜" Dekoron tube followed by a metal bellow pump. The flow rate through the sample line is ~1 L/min. After the pump, a valve bleed reduces the flow to approx., 230 mL/min. The air is then filtered with a 7 micron inline filter and dried using a glass trap / cryo cooler (-65°C). The air is then distributed to the two separate GC systems (Agilent 6890 for CO, CH_4, N_2O and SF_6 and Agilent 5890 for CH_4 only). Individual needle valves located on each system are used to control their respective flow rates.

Residence time in the sampling line: ca. 120 s

Instrumentation

AT WLG an Agilent 6890N GC/FID with a methanizer is used for the measurements of CO since June 2008. This equipment replaced the RGA-3 [*Zellweger et al.*, 2004] which failed in August 2007. The instrumentation at CAMS comprises also of an Agilent 6890N GC/FID with a methanizer; in addition, an Ametek ta500R with a HgO detector is available. Instrumental details are summarized in Table 9.

Standards and Calibration

WLG used to have its own set of station standards [*Zellweger et al.*, 2004]; however, these standards are now empty, and the cylinders are used as working standards. The history of the WLG CO standards and calibrations is summarized in Zhang et al. [2011]. The current instrument was calibrated at CAMS before it was installed at WLG; only a working and a target standard are available at the site. A set of seven laboratory standards from WMO/CCL (NOAA/ESRL) is available at CAMS. Table 8 gives details of the laboratory standards (LS) at CAMS and the WLG working standards (WS). The WS contain dry natural air from WLG calibrated against the LS.

Table 8. Laboratory standards at CAMS and working standards at WLG as of July 2009

Standard	Type	CO (ppb)	CH_4 (ppb)	N_2O (ppb)	start of use	end of use
CA07490	LS	63.6	NA	NA	2007	ongoing
CA07487	LS	91.7	NA	NA	2007	ongoing
CA07470	LS	139.5	NA	NA	2007	ongoing
CA07481	LS	155.5	NA	NA	2007	ongoing
CA07403	LS	160.2	NA	NA	2007	ongoing
CA07411	LS	205.2	NA	NA	2007	ongoing
CA07493	LS	276.1	NA	NA	2007	ongoing
CA07372	LS	NA	1795.5	NA	2007	ongoing
CA05682	LS	NA	1859.9	NA	2007	ongoing
CA08328	LS	53.3	1609.0	322.17	2009	ongoing
CA08304	LS	107.7	1703.5	336.07	2009	ongoing
CA08338	LS	151.0	1789.2	340.42	2009	ongoing
CA08312	LS	309.7	2000.3	349.34	2009	ongoing
CA08314	LS	498.1	2297.0	368.19	2009	ongoing
CA08301	LS	977.1	2495.6	391.69	2009	ongoing
CA01212	WS	127.0	1743.3	306.73	2008	ongoing
CA01222	WS	129.2	1761.9	315.33	2008	ongoing

Operation and Maintenance

A daily check list containing all important instrument information and pressures of the working standards is filled in and sent via e-mail to CAMS. The cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

Data Acquisition and Data Transfer

GC ChemStation Rev. B.03.01[317].

Data Treatment

The data treatment is done at CAMS in Beijing. One hourly averages are calculated for the final data set.

Data Submission

At the time of the 3rd audit in 2009 the data needed further processing and QA/QC and thus have not been submitted to the GAW Data Centre for Greenhouse Gases (WDCGG).

Documentation

In addition to the check lists, all relevant information is entered in electronic log books. The log book entries were comprehensive and up-to-date. Instrument manuals are 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 9.

Setup and Connections

All CO instruments were inter-compared by direct measurements of travelling standards. Details of the experiments are shown in Table 9. The data used for the evaluation was recorded by the WLG and CAMS data acquisition system.

Table 9. Experimental details of the carbon monoxide comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 071122_FF31496 / 40.24 / 0.42 2 / 070808_FA02786 / 51.64 / 1.17 3 / 070808_FA02783 / 59.26 / 0.55 4 / 070807_FA02773 / 88.08 / 2.94 5 / 070808_FA02769 / 89.30 / 0.46 6 / 071122_FA30491 / 109.63 / 0.55 7 / 070807_FA02770 / 149.56 / 0.91 8 / 070807_FA02782 / 153.88 / 0.82 9 / 071122_FA01477 / 165.23 / 0.93 10 / 050701_FA02464 / 171.26 / 1.05 11 / 070927_FA02493 / 202.80 / 1.25 12 / 050701-2 FA02505 / 361.73 / 2.17
Field instruments	Model, S/N	Agilent 6890 #US 10719008 (WLG)
	Principle	GC with FID Detector, Methanizer Pre-column: Molsieve 5 Å 60/80 1/8", 3 ft Analytical column: Unibeads 1S 60/80 1/8", 4 ft Carrier: Nitrogen 99.999%, 70 ml/min Column temp. 75°C, Detector temp. 175°C Sample loop 10 ml
	Model, S/N	Agilent 6890 #US 10681036 (CAMS)
	Principle	GC with FID Detector, Methanizer Pre-column: Molsieve 5 Å 60/80 1/8", 3 ft Analytical column: Unibeads 1S 60/80 1/8", 4 ft Carrier: Parker Balston nitrogen generator, 70 ml/min Column temp. 75°C, Detector temp. 175°C Sample loop 10 ml
	Model, S/N	Ametek ta5000R #52PR181-06123 (CAMS)
	Principle	GC with HgO Reduction Detector Pre-column: Unibeads 1S 60/80 Analytical column: Mole sieve 5Å 60/80 Carrier: Nitrogen 99.999% Column temp. 65°C, Detector temp. 265°C Sample loop 1 ml
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Sequence of levels		Randomised sequence, total 6-12 injections per level
Runs		WLG: 1 run (2009-06-24 to 2009-06-24) CAMS: 1 run (2009-09-05 to 2009-09-06)

Results

All GC systems were compared using WCC-Empa travelling standards. Each level was injected between 6 and 12 times. This resulted in a maximum of 12 useable single injections per level. These were further aggregated by level before use in the assessment. The results are summarized in the following Tables: Agilent GC WLG (Table 10), Agilent GC CAMS (Table 11), Ametek GC CAMS (Table 12).

Table 10. CO aggregates computed from single injections for each level and repetition during the comparison of the WLG Agilent 6890 analyser (AL) with WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(06/24/09 21:50:00)	071122_FA30491	109.63	0.55	108.75	0.45	6	-0.88	-0.81
(06/24/09 22:50:00)	070927_FA02493	202.80	1.25	191.02	1.58	6	-11.79	-5.81
(06/24/09 23:50:00)	050701_FA02464	171.26	1.05	163.43	1.46	6	-7.83	-4.57
(06/25/09 00:50:00)	070807_FA02770	149.56	0.91	142.93	0.85	6	-6.62	-4.43
(06/25/09 01:50:00)	070808_FA02769	89.30	0.46	89.22	1.19	6	-0.08	-0.09
(06/25/09 12:20:00)	070808_FA02783	59.26	0.55	60.74	0.86	6	1.48	2.49

Table 11. CO aggregates computed from single injections for each level and repetition during the comparison of the CAMS Agilent 6890 analyser (AL) with WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/05/09 23:57:30)	070807_FA02773	88.08	2.94	87.68	0.73	12	-0.40	-0.46
(09/05/09 14:50:00)	070807_FA02770	153.88	0.82	148.66	0.99	12	-5.22	-3.39
(09/05/09 07:27:30)	070808_FA02786	51.64	1.17	52.91	0.72	12	1.27	2.45
(09/05/09 13:46:30)	050701_FA02505	361.73	2.17	334.83	1.13	12	-26.91	-7.44
(09/05/09 13:46:30)	071122_FA01477	165.23	0.93	159.48	1.06	12	-5.76	-3.48
(09/05/09 16:35:00)	071122_FF31496	40.24	0.42	41.71	0.66	12	1.47	3.66

Table 12. CO aggregates computed from single injections for each level and repetition during the comparison of the CAMS Ametek ta5000R analyser (AL) with WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/05/09 18:45:00)	070807_FA02773	88.08	2.94	87.59	0.59	12	-0.49	-0.55
(09/05/09 06:55:00)	070807_FA02770	153.88	0.82	169.28	1.02	12	15.41	10.01
(09/05/09 15:00:00)	070808_FA02786	51.64	1.17	54.98	0.64	12	3.34	6.47
(09/05/09 11:15:00)	050701_FA02505	361.73	2.17	478.26	5.36	12	116.53	32.21
(09/05/09 11:15:00)	071122_FA01477	165.23	0.93	185.71	3.79	12	20.48	12.39
(09/06/09 02:50:00)	071122_FF31496	40.24	0.42	45.70	0.30	12	5.46	13.58

Figure 8 shows the regression residuals of the above instruments plotted against time and mole fraction. Significant mole fraction dependence was observed for the Ametek GC, indicating that the non-linearity of the system has not sufficiently been determined.

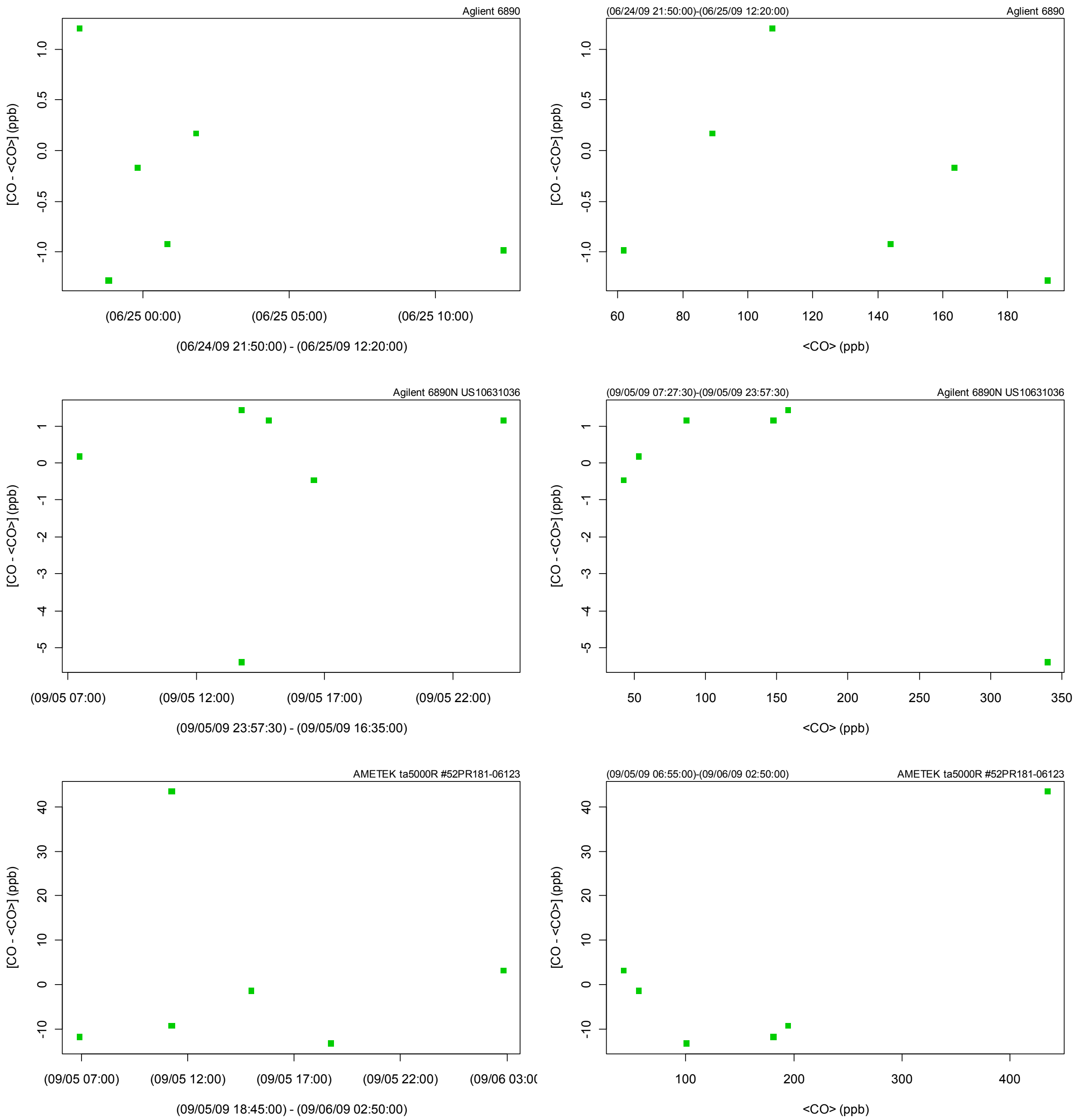


Figure 8. Regression residuals of the WLG Agilent GC (top), the CAMS Agilent GC (middle) and the CAMS Ametek GC (bottom) based on the comparison with travelling standards. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

Based on these comparison results, unbiased carbon monoxide volume mole fractions X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed using the following equations:

Aglient 6890 #US 10719008 (WLG):

X_{CO} (ppb) = ([CO] – 7.8 ppb) / 0.9097

u_{CO} (ppb) = sqrt (2.1 ppb^2 + 9.84e-05 * X_{CO}^2) (2a)

Aglient 6890 #US 10681036 (CAMS):

X_{CO} (ppb) = ([CO] – 4.8 ppb) / 0.9271

u_{CO} (ppb) = sqrt (8.1 ppb^2 + 5.25e-05 * X_{CO}^2) (2b)

Ametek ta500R #52PR181-06123 (CAMS):

X_{CO} (ppb) = ([CO] + 6.6 ppb) / 1.2200

u_{CO} (ppb) = sqrt (308.0 ppb^2 + 4.40e-05 * X_{CO}^2) (2c)

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

Changes made to the instruments

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

Conclusions

Relatively good agreement was found between WCC-Empa travelling standards and the WLG CO GC-FID system (Agilent 6890) at mole fractions lower than 110 ppb. Similar results were found for the CAMS GC-FID system; for both systems, the differences were larger at higher CO levels. The results also suggested that the non-linearity of the Ametek GC needs to be re-assessed; however, part of these results may be influenced by high H2 content of the WCC-Empa travelling standards (Ametek GC only).

Methane Measurements

Methane measurements started at WLG in 1994, and a complete time series is available since then. The original system has not changed since the last audit by WCC-Empa in 2004 [*Zellweger et al.*, 2004]; in addition, the Agilent 6890 GC installed for CO measures also CH_4, and a Picarro G1301 methane analyser was installed in January 2009. At the central calibration facilities at CAMS, two Agilent 6890 GCs and a Picarro G1301 are available for CH_4 calibrations and flask analysis. The audit comprised comparison of travelling standards covering the mole fraction range from approx. 1600 to 2000 ppb methane in air. All comparisons were done according to Standard Operating Procedures [*WMO*, 2007b].

Monitoring Set-up and Procedures

Air Conditioning

All laboratories at WLG are air-conditioned to approx. 20°C.

Air Inlet System

GC instruments: Unchanged since the last WCC-Empa audit [*Zellweger et al.*, 2004]. The new analytical systems were connected to the existing inlet line. The inlet design is adequate for methane measurements concerning materials and residence time.

Picarro: 3 direct sampling lines to the 10, 40 and 80 m level of the tower (10 mm Dekabon tubing). The 3 lines are equipped with individual pumps; the sample air is dried to -65°C using a cryo cooler. A Valco valve is used for the selection of the sample lines and working standards. The flow rate is controlled by a mass flow controller.

Instrumentation

WLG: Agilent 5890 [*Zhou et al.*, 2004] and 6890, Picarro G1301. CAMS: 2 Agilent 6890, Picarro G1301. Instrument details are summarised in Table 13.

Standards and Calibration

Several laboratory standards (LS) from WMO/CCL (NOAA/ESRL) are available at CAMS, and working standards (WS) calibrated against LS are used at WLG. Refer to Table 8 for an overview of the current standards.

Operation and Maintenance

A daily check list containing all important instrument information and pressures of the working standards is filled in and sent via e-mail to CAMS. The cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

Data Acquisition and Data Transfer

GC: ChemStation Rev. B.03.01[317], Picarro: Picarro data acquisition software incl. valve sequencer.

Data Treatment

GC: Peak integration is performed automatically, and two working tank signals are used to calculate the ambient air mixing ratios. Peak height is used for data evaluation, and a linear fit through zero is used as a calibration function. Picarro: The working tank signals are used to calculate the ambient air mixing ratios. One hourly averages are calculated for the final data set.

Data Submission

Currently, daily and monthly data for in-situ methane (1994 – 2010) have been submitted by CMA to the WDCGG. The CMA and NOAA cooperative flask sampling data are available at WDCGG (submitted by NOAA).

Documentation

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

Comparison of Methane 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 standard to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 13 below.

Setup and Connections

Table 13 shows details of the experimental setup during the comparison of the transfer standard and the WLG and CAMS instruments. The data used for the evaluation was recorded by the individual data acquisition systems, and no further corrections were applied.

Table 13. Experimental details of the methane comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (aluminium cylinder containing natural dry air)
Levels (ppb)		Level Cylinder Reference St. Uncert. 1 070808_FA02786 1594.89 0.63 2 071122_FF31496 1614.27 0.20 3 070808_FA02783 1662.68 0.30 4 070807_FA02773 1698.23 0.19 5 070808_FA02769 1714.41 0.21 6 070927_FA02493 1780.68 0.62 7 070807_FA02782 1786.63 0.20 8 071122_FA30491 1803.11 0.75 9 050701_FA02464 1833.41 0.21 10 050701_FA02505 1834.44 0.39 11 070807_FA02770 1858.86 0.22 12 071122_FA01477 1950.44 0.27
Field instruments	Model, S/N	HP5890 Series II # C-128 183 (WLG)
	Principle	GC with FID Detector, Methanizer Pre-column: None Analytical column: Porapak QS 100/120 Carrier: Nitrogen 99.999% Column temp. 40°C, Detector temp. 150°C Sample loop 3 ml
	Model, S/N	Agilent 6890 #US 10719008 (WLG)
	Principle	GC with FID Detector Pre-column: Molsieve 5 Å 60/80 1/8", 3 ft Analytical column: Unibeads 1S 60/80 1/8", 4 ft Carrier: Nitrogen 99.999%, 70 ml/min Column temp. 75°C, Detector temp. 175°C Sample loop 10 ml
	Model, S/N	Picarro G1301 #CFADS023 (WLG)
	Principle	Cavity Ring Down Spectroscopy (CDRS)
	Model, S/N	Agilent 6890 #US 10681036 (CAMS)
	Principle	GC with FID Detector Pre-column: Molsieve 5 Å 60/80 1/8", 3 ft Analytical column: Unibeads 1S 60/80 1/8", 4 ft Carrier: Parker Balston nitrogen generator, 70 ml/min Column temp. 75°C, Detector temp. 175°C Sample loop 10 ml
	Model, S/N	Agilent 6890 #US 10719007 (CAMS)
	Principle	Identical to Agilent 6890 #US 10681036
	Model, S/N	Picarro G1301 #CFADS021 (CAMS)
	Principle	Cavity Ring Down Spectroscopy (CDRS)
Connection of TS to field instrument		TS were connected to the sample selection valve of the GC and Picarro analyzers
Data Acquisition		WLG and CAMS data acquisition systems
Number of analysis		Total 6-12 injections per level (GC systems) or 8 1-min averages (Picarro instruments)
Sequence of levels		Randomised sequence

Results

All GC systems and the CRDS system were compared using WCC-Empa travelling standards. Each standard was measured between 6 and 12 times (GC systems). On the Picarro instruments the standards were measured for 20 minutes, but only the last 4 1-min averages were used in the assessment. The results were further aggregated by level before use in the assessment. The results are summarized in the following Tables: HP 5890 GC WLG (Table 14), Agilent 6890 GC WLG (Table 15), Picarro G1301 WLG (Table 16), Agilent 6890#US 10719007 GC CAMS (Table 17), Agilent 6890#US 10681036 GC CAMS (Table 18), Picarro G1301 CAMS (Table 19).

Table 14. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the WLG HP 5890 methane GC with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(06/24/09 20:08:34)	071122_FA30491	1803.11	0.75	1801.61	1.15	7	-1.50	-0.08
(06/24/09 23:00:00)	070927_FA02493	1780.68	0.62	1781.22	2.10	6	0.54	0.03
(06/25/09 00:10:00)	050701_FA02464	1833.41	0.21	1829.83	5.28	8	-3.59	-0.20
(06/24/09 23:40:00)	070807_FA02770	1858.86	0.22	1858.64	5.46	7	-0.22	-0.01
(06/24/09 22:30:00)	070808_FA02769	1714.41	0.21	1712.40	1.00	6	-2.01	-0.12
(06/25/09 12:20:00)	070808_FA02783	1662.68	0.30	1662.00	1.96	6	-0.67	-0.04

Table 15. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the WLG Agilent 6890 methane GC with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(06/24/09 21:50:00)	071122_FA30491	1803.11	0.75	1802.95	0.89	6	-0.16	-0.01
(06/24/09 22:50:00)	070927_FA02493	1780.68	0.62	1780.15	1.07	6	-0.52	-0.03
(06/24/09 23:50:00)	050701_FA02464	1833.41	0.21	1833.88	0.66	6	0.47	0.03
(06/25/09 00:50:00)	070807_FA02770	1858.86	0.22	1859.73	0.85	6	0.87	0.05
(06/25/09 01:50:00)	070808_FA02769	1714.41	0.21	1715.08	0.64	6	0.67	0.04
(06/25/09 12:20:00)	070808_FA02783	1662.68	0.30	1663.10	1.64	6	0.42	0.03

Table 16. CH_4 aggregates computed from 1-min average values (mean and standard uncertainty of mean) for each level during the comparison of the WLG Picarro G1301 analyser with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(06/24/09 21:30:00)	071122_FA30491	1803.11	0.75	1802.60	0.16	8	-0.51	-0.03
(06/24/09 22:50:00)	070927_FA02493	1780.68	0.62	1780.07	0.13	8	-0.61	-0.03
(06/25/09 00:10:00)	050701_FA02464	1833.41	0.21	1832.89	0.19	8	-0.52	-0.03
(06/25/09 01:30:00)	070807_FA02770	1858.86	0.22	1858.21	0.20	8	-0.65	-0.04
(06/25/09 02:50:00)	070808_FA02769	1714.41	0.21	1713.91	0.22	8	-0.51	-0.03
(06/25/09 04:10:00)	070808_FA02783	1662.68	0.30	1662.62	0.17	8	-0.06	0.00

Table 17. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the CAMS Agilent 6890 #US 10719007 methane GC with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/05/09 23:57:30)	070807_FA02773	1698.23	0.19	1701.48	1.15	12	3.25	0.19
(09/05/09 14:50:00)	070807_FA02782	1786.63	0.20	1789.03	1.74	12	2.40	0.13
(09/05/09 07:27:30)	070808_FA02786	1594.89	0.63	1598.93	1.10	12	4.05	0.25
(09/05/09 13:46:30)	050701_FA02505	1834.44	0.39	1836.38	0.86	12	1.93	0.11
(09/05/09 13:46:30)	071122_FA01477	1950.44	0.27	1951.67	0.80	12	1.23	0.06
(09/05/09 16:35:00)	071122_FF31496	1614.27	0.20	1616.92	1.51	12	2.65	0.16

Table 18. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the CAMS Agilent 6890 #US 10681036 methane GC with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/05/09 18:45:00)	070807_FA02773	1698.23	0.19	1699.70	0.89	12	1.47	0.09
(09/05/09 06:55:00)	070807_FA02782	1786.63	0.20	1787.14	0.69	12	0.51	0.03
(09/05/09 15:00:00)	070808_FA02786	1594.89	0.63	1599.51	2.69	12	4.62	0.29
(09/05/09 11:15:00)	050701_FA02505	1834.44	0.39	1833.70	1.08	12	-0.74	-0.04
(09/05/09 11:15:00)	071122_FA01477	1950.44	0.27	1948.74	1.20	12	-1.70	-0.09
(09/06/09 02:50:00)	071122_FF31496	1614.27	0.20	1616.62	0.86	12	2.35	0.15

Table 19. CH_4 aggregates computed from 1-min average values (mean and standard uncertainty of mean) for each level during the comparison of the CAMS Picarro G1301 analyser with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/04/09 08:39:30)	070807_FA02773	1698.23	0.19	1700.36	0.29	8	2.13	0.13
(09/04/09 08:39:30)	070807_FA02782	1786.63	0.20	1788.91	0.32	8	2.28	0.13
(09/03/09 17:29:00)	070808_FA02786	1594.89	0.63	1597.25	0.21	8	2.36	0.15
(09/03/09 18:15:00)	050701_FA02505	1834.44	0.39	1836.51	0.21	8	2.07	0.11
(09/03/09 18:15:00)	071122_FA01477	1950.44	0.27	1952.84	0.20	8	2.40	0.12
(09/03/09 17:29:00)	071122_FF31496	1614.27	0.20	1616.01	0.17	8	1.74	0.11

Based on these comparison results, unbiased mixing ratios of the methane analysers and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed using the following equations.

HP 5890 # C-128 183 (WLG):

X_{CH4} (ppb) = (CH_4) / 0.99921

u_{CH4} (ppb) = sqrt (8.0 ppb^2 + 1.89e-07 * X_{CH4}^2) (3a)

Agilent 6890 #US 10719008 (WLG):

X_{CH4} (ppb) = (CH_4) / 1.00014

u_{CH4} (ppb) = sqrt (0.9 ppb^2 + 2.94e-08 * X_{CH4}^2) (3b)

Picarro G1301 #CFADS023 (WLG):

X_{CH4} (ppb) = (CH_4) / 0.99973

u_{CH4} (ppb) = sqrt (0.04 ppb^2 + 1.44e-08 * X_{CH4}^2) (3c)

Agilent 6890 (#US 10719007, CAMS):

X_{CH4} (ppb) = (CH_4) / 1.00090

u_{CH4} (ppb) = sqrt (5.7 ppb^2 + 5.31e-07 * X_{CH4}^2) (3d)

Agilent 6890 (#US 10681036, CAMS):

X_{CH4} (ppb) = (CH_4) / 1.00150

u_{CH4} (ppb) = sqrt (1.4 ppb^2 + 8.38e-08 * X_{CH4}^2) (3e)

Picarro G1301 #CFADS021 (CAMS):

X_{CH4} (ppb) = (CH_4) / 1.00120

u_{CH4} (ppb) = sqrt (0.06 ppb^2 + 1.49e-08 * X_{CH4}^2) (3f)

Conclusions

In general, no significant deviations between WLG and CAMS measurements and WCC-Empa were found. The results show that the CRDS instruments have a significantly better reproducibility compared to the GC systems. Furthermore, the repeatability of the WLG HP 5890 GC was not as good (average standard deviation of 0.16%) as of the Agilent 6890 GC (average standard deviation of 0.05%, which is state-of-the-art for GC/FID systems); therefore, the data of the newer GC and the CRDS should be considered for data submission. The good results of the comparison measurements show that the whole measurement system is appropriate for the measurement of methane, and no further technical recommendations are made by WCC-Empa.

Nitrous Oxide Measurements

In-situ continuous measurement of nitrous oxide commenced in June 2008 at WLG, and continuous data series are available since then. Calibration facilities at CAMS are also available since then and have been included in the scope of the current audit.

Monitoring Set-up and Procedures

Air Conditioning

All laboratories at WLG are air-conditioned to approx. 20°C.

Air Inlet System

The same air inlet as for the methane GC system is used for N_2O measurements. This system is adequate for analysing N_2O concerning materials and residence time.

Instrumentation

Three identical GC/ECD systems are operated by CAMS; one of these instruments is at WLG, the other two systems are used at the Beijing lab for flask analysis and standard calibrations. Instrument details are summarised in Table 20

Standards and Calibration

Several laboratory standards (LS) from WMO/CCL (NOAA/ESRL) are available at CAMS, and working standards (WS) calibrated against the LS are used at WLG. Refer to Table 8 for an overview of the current standards. The WLG GC system was only calibrated at CAMS in Beijing, and only a working standard and a target gas are used at WLG for the calibration of the instrument.

Operation and Maintenance

A daily check list containing all important instrument information and pressures of the working standards is filled in and sent via e-mail to CAMS. The cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

Data Acquisition and Data Transfer

GC: ChemStation Rev. B.03.01[317].

Data Treatment

Peak integration is performed automatically, and the working and target tank signals are used to calculate the ambient air mixing ratios. Peak area is used for data evaluation. One hourly averages are calculated for the final data set.

Data Submission

N_2O data have not yet been fully processed and submitted to the GAW Data Centre for Greenhouse Gases (WDCGG).

Documentation

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

Comparison of Nitrous Oxide Measurements

The travelling standards used for the comparison were calibrated by WCC-N_2O in April 2008. Since then, no re-calibrations have been made. Details of the traceability of the travelling standard to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 13 below.

Setup and Connections

Table 20 shows details of the experimental setup during the comparison of the WCC transfer standards with the WLG station GC and the CAMS GCs. The data used for the evaluation was recorded by the WLG and CAMS data acquisition systems, and no further corrections were applied.

Table 20. Experimental details of the N_2O comparison.

Travelling standard (TS)		WCC-Empa* Travelling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level / TS for WLG / Reference* / std dev 1 / 071122_FA30491 / 317.03 / 0.22 2 / 070927_FA02493 / 354.71 / 0.31 3 / 070807_FA02770 / 322.68 / 0.19 4 / 070808_FA02769 / 306.79 / 0.28 5 / 070808_FA02783 / 305.42 / 0.21 Level / TS for CAMS / Reference* / std dev 1 / 070807_FA02773 / 324.97 / 0.23 2 / 070807_FA02782 / 324.68 / 0.19 3 / 070808_FA02786 / 294.61 / 0.23 4 / 050701_FA02505 / 315.73 / 0.30 5 / 071122_FA01477 / 323.34 / 0.19 6 / 071122_FF31496 / 345.21 / 0.23
Field-instruments	Model, S/N	Agilent 6890 #US 10719008 (WLG) Agilent 6890N #US10719007 (CAMS) Agilent 6890N #US 10681036 (CAMS)
	Principle	GC with ECD Detector Pre-column: HayeSep Q 3/16" 80/100, 2m Analytical column: HayeSep Q 3/16" 80/100, 2m Carrier: CH_4(5%)/Ar 90-100 ml/min Column temp. 75°C, Detector temp. 395°C Sample loop 15 ml
Connection of TS to field instrument		TS were connected to the sample selection valve of the WLG and CAMS systems
Data Acquisition		Station data acquisition
Sequence of levels		Randomised sequence
Runs		1 run at WLG (2009-06-24 to 2009-06-25) 1 run at CAMS (2009-09-09)

* Mixing ratios were assigned by the WCC-N_2O

Results

Each TS was injected 6 times (WLG) or 12 times (CAMS), which resulted in a maximum of 6 to 12 useable injections per level. These were further aggregated by level before use in the assessment. The results are summarised in following Tables.

Table 21. N_2O aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the WLG N_2O GC (Aglient 6890N US10719008) with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(06/24/09 21:50:00)	071122_FA30491	317.03	0.22	322.79	0.16	6	5.76	1.82
(06/24/09 22:50:00)	070927_FA02493	354.71	0.31	354.59	0.23	6	-0.13	-0.04
(06/25/09 00:50:00)	070807_FA02770	322.68	0.19	327.67	0.55	6	4.99	1.55
(06/25/09 01:50:00)	070808_FA02769	306.79	0.28	313.92	0.05	6	7.13	2.32
(06/25/09 12:20:00)	070808_FA02783	305.42	0.21	311.91	0.29	6	6.48	2.12

Table 22. N_2O aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the CAMS N_2O GC (Aglient 6890N US10719007) with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/05/09 18:45:00)	070807_FA02773	324.97	0.23	325.86	0.65	12	0.89	0.27
(09/05/09 06:55:00)	070807_FA02782	324.68	0.19	325.58	0.27	12	0.90	0.28
(09/05/09 15:00:00)	070808_FA02786	294.61	0.23	294.58	0.43	12	-0.04	-0.01
(09/05/09 11:15:00)	050701_FA02505	315.73	0.30	315.50	0.61	12	-0.23	-0.07
(09/05/09 11:15:00)	071122_FA01477	323.34	0.19	323.58	0.91	12	0.24	0.07
(09/06/09 02:50:00)	071122_FF31496	345.21	0.23	344.07	1.13	12	-1.14	-0.33

Table 23. N_2O aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the comparison of the CAMS N_2O GC (Aglient 6890N US10631036) with the WCC-Empa travelling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(09/05/09 23:57:30)	070807_FA02773	324.97	0.23	326.01	0.92	12	1.04	0.32
(09/05/09 14:50:00)	070807_FA02782	324.68	0.19	325.49	0.27	12	0.81	0.25
(09/05/09 07:27:30)	070808_FA02786	294.61	0.23	294.29	0.72	12	-0.32	-0.11
(09/05/09 13:46:30)	050701_FA02505	315.73	0.30	315.69	0.38	12	-0.04	-0.01
(09/05/09 13:46:30)	071122_FA01477	323.34	0.19	323.19	0.35	12	-0.16	-0.05
(09/05/09 16:35:00)	071122_FF31496	345.21	0.23	345.38	0.56	12	0.16	0.05

The deviations between WCC-Empa TS calibrated by WCC-N_2O and WLG were found to be large except for a very high N_2O standard. This issue was later confirmed during personal communication with CAMS staff, and further calibrations have been made in 2010 by CAMS. Results of the systems operated in the Beijing calibration laboratory were significantly better and in most cases not significantly different from the values assigned by WCC-N_2O; however, the analytical reproducibility of the GC systems was relatively poor with standard deviations ranging from 0.27 to 1.13 ppb for multiple injections of the same standard. This is clearly nor sufficient to comply with the GAW DQO of 0.1 ppb, and the GC systems need to be optimized.

Based on the comparison results, unbiased N_2O mixing ratios of the Agilent 6890N GC X_{N2O} and an estimate for the remaining combined standard uncertainty u_{N2O} can be computed from the single injection comparison data using equation (4).

WLG (Aglient 6890N US10719008):

X_{N2O} (ppb) = (N_2O – 52.02 ppb) / 0.85331

U_{N2O} (ppb) = sqrt (1.74 ppb^2 + 1.21e-05 * X_{N2O}^2) (4a)

CAMS (Aglient 6890N US10719007):

X_{N2O} (ppb) = (N_2O) / 0.99964

U_{N2O} (ppb) = sqrt (0.59 ppb^2 + 2.22e-06 * X_{N2O}^2) (4b)

CAMS (Aglient 6890N US10631036):

X_{N2O} (ppb) = (N_2O) / 1.00100

U_{N2O} (ppb) = sqrt (0.30 ppb^2 + 1.67e-06 * X_{N2O}^2) (4c)

Conclusions

Significant deviations were found for N_2O especially for the comparisons made at WLG. A re-calibration of some travelling standards at WCC-N2O as well as measurements made by WCC-Empa in 2001 indicated that the large bias cannot be explained by instability or drift of the TS. Therefore, another independent assessment, preferably by WCC-N_2O, of the WLG and CAMS N_2O measurements is strongly suggested after the systems have been re-calibrated and further optimized by WLG and CAMS staff.

WCC-Empa Travelling Standards

Ozone

The WCC-Empa travelling standards (TS) were compared with the Standard Reference Photometer before and after use during the field audit. Details of these comparisons at the Empa calibration laboratory are summarised in Table 24, the comparison data is given in Table 25 and Table 26.

Table 24. Experimental details of the comparison of the travelling standards (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Travelling standard (TS1) used at WLG	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
Travelling standard (TS2) used at CAMS	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.6; COEFF = 1.009
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 (2009-04-03 and 2009-05-12), 3 runs after return of TS (31 2009-10-23)

Table 25. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard TEI 49i-PS (TS1).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2009-05-12	1	0	-0.26	0.31	0.12	0.11
2009-05-12	1	140	138.12	0.23	138.69	0.20
2009-05-12	1	30	31.38	0.22	31.63	0.19
2009-05-12	1	90	90.06	0.38	90.28	0.29
2009-05-12	1	60	60.89	0.33	60.77	0.26
2009-05-12	1	190	185.95	0.26	186.39	0.36
2009-05-12	1	0	-0.24	0.25	-0.23	0.17
2009-05-12	2	0	-0.03	0.27	0.03	0.19
2009-05-12	2	30	31.56	0.34	31.63	0.24
2009-05-12	2	90	90.40	0.31	90.38	0.18
2009-05-12	2	190	186.61	0.20	186.92	0.18
2009-05-12	2	60	60.69	0.28	60.77	0.22
2009-05-12	2	140	137.85	0.27	137.93	0.24
2009-05-12	2	0	-0.13	0.21	-0.02	0.32
2009-05-12	3	0	-0.22	0.32	0.10	0.22
2009-05-12	3	30	31.27	0.35	31.45	0.13
2009-05-12	3	60	60.90	0.27	60.81	0.25
2009-05-12	3	140	138.25	0.43	138.26	0.14
2009-05-12	3	190	186.24	0.20	186.53	0.25
2009-05-12	3	90	89.75	0.29	90.03	0.48
2009-05-12	3	0	-0.06	0.24	0.00	0.11
2009-10-23	4	0	-0.02	0.22	-0.20	0.29
2009-10-23	4	60	61.65	0.23	61.41	0.14
2009-10-23	4	140	143.64	0.26	143.75	0.10
2009-10-23	4	90	93.33	0.18	93.46	0.16
2009-10-23	4	190	194.63	0.29	194.91	0.29
2009-10-23	4	30	31.38	0.21	31.39	0.27
2009-10-23	4	0	0.10	0.34	0.14	0.28
2009-10-23	5	0	0.13	0.26	-0.13	0.17
2009-10-23	5	30	31.62	0.25	31.83	0.14
2009-10-23	5	140	144.10	0.37	143.96	0.15
2009-10-23	5	190	195.34	0.25	195.71	0.33
2009-10-23	5	90	93.24	0.49	93.43	0.09
2009-10-23	5	60	61.63	0.45	61.51	0.27
2009-10-23	5	0	0.22	0.26	0.05	0.09
2009-10-23	6	0	0.06	0.30	-0.18	0.20
2009-10-23	6	60	61.87	0.35	61.81	0.22
2009-10-23	6	30	31.66	0.19	31.66	0.15
2009-10-23	6	140	143.95	0.28	144.35	0.17
2009-10-23	6	190	194.95	0.26	195.37	0.38
2009-10-23	6	90	93.47	0.16	93.31	0.21
2009-10-23	6	0	0.15	0.24	0.11	0.22

[#]the level is only indicative.

Table 26. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard TEI 49C-PS (TS2).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2009-04-06	1	0	0.09	0.41	0.00	0.09
2009-04-06	1	140	139.78	0.27	139.85	0.08
2009-04-06	1	30	32.39	0.36	32.25	0.11
2009-04-06	1	90	90.90	0.30	91.04	0.07
2009-04-06	1	190	187.78	0.22	187.92	0.23
2009-04-06	1	60	61.06	0.17	61.09	0.13
2009-04-06	1	0	-0.18	0.24	0.04	0.17
2009-04-06	2	0	-0.01	0.28	-0.09	0.10
2009-04-06	2	60	61.26	0.15	61.24	0.08
2009-04-06	2	140	139.98	0.22	139.89	0.06
2009-04-06	2	90	91.09	0.33	91.05	0.08
2009-04-06	2	190	188.00	0.55	187.87	0.17
2009-04-06	2	30	32.22	0.26	32.17	0.11
2009-04-06	2	0	0.11	0.20	0.02	0.10
2009-04-06	3	0	-0.01	0.16	0.04	0.09
2009-04-06	3	30	32.32	0.34	32.29	0.12
2009-04-06	3	140	140.09	0.28	139.94	0.15
2009-04-06	3	190	188.15	0.39	188.24	0.15
2009-04-06	3	90	90.75	0.24	90.88	0.15
2009-04-06	3	60	61.38	0.27	61.12	0.13
2009-04-06	3	0	0.08	0.13	0.06	0.25
2009-10-23	4	0	-0.02	0.22	-0.20	0.06
2009-10-23	4	60	61.65	0.23	61.32	0.11
2009-10-23	4	140	143.64	0.26	143.32	0.12
2009-10-23	4	90	93.33	0.18	93.00	0.08
2009-10-23	4	190	194.63	0.29	194.29	0.13
2009-10-23	4	30	31.38	0.21	31.29	0.09
2009-10-23	4	0	0.10	0.34	-0.05	0.08
2009-10-23	5	0	0.13	0.26	-0.17	0.07
2009-10-23	5	30	31.62	0.25	31.35	0.10
2009-10-23	5	140	144.10	0.37	143.58	0.10
2009-10-23	5	190	195.34	0.25	194.96	0.17
2009-10-23	5	90	93.24	0.49	93.11	0.10
2009-10-23	5	60	61.63	0.45	61.14	0.10
2009-10-23	5	0	0.22	0.26	-0.21	0.07
2009-10-23	6	0	0.06	0.30	-0.20	0.09
2009-10-23	6	60	61.87	0.35	61.38	0.06
2009-10-23	6	30	31.66	0.19	31.43	0.07
2009-10-23	6	140	143.95	0.28	143.74	0.13
2009-10-23	6	190	194.95	0.26	194.80	0.16
2009-10-23	6	90	93.47	0.16	92.99	0.08
2009-10-23	6	0	0.15	0.24	-0.21	0.09

[#]the level is only indicative.

The travelling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 9). 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]).

TEI 49i-PS:

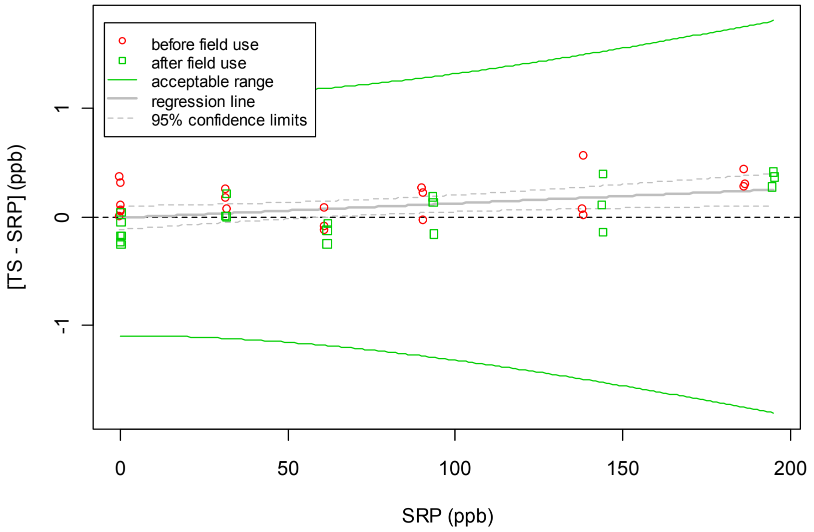
$$X_{TS}\text{ (ppb)} = ([TS] + 0.01\text{ ppb}) / 1.0013$$

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

TEI 49C-PS:

$$X_{TS}\text{ (ppb)} = ([TS] + 0.16\text{ ppb}) / 0.9999$$

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



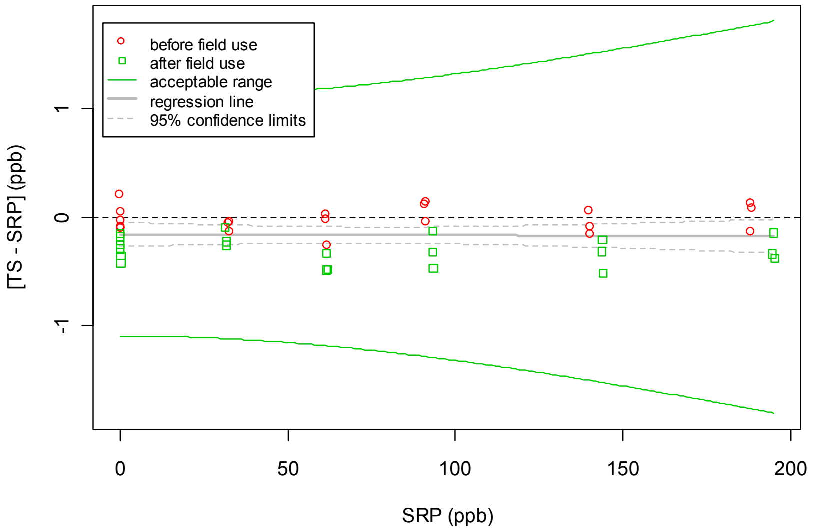


Figure 9. Deviations between the WCC travelling standards (TS) and the Standard Reference Photometer (SRP) before and after use of the TS at the field site. Upper panel: TEI49i-PS (TS1), Lower panel: TEI49C-PS (TS2).

Carbon Monoxide

WCC-Empa refers to the 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 (NOAA/ESRL) 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 27 and Table 28.

Table 27. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the travelling standard (TS) used during the field comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale is based on one specific cylinders, CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Travelling standard - cylinders		Carbon monoxide cylinders for direct comparisons. (cf. Table 28)
Connection between instruments		Ca. 2 meter 1/16” stainless steel tubing.
Range (ppb)		40 – 380 ppb cf. Table 28
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 28. Calibration of the carbon monoxide travelling standards with the WCC-Empa reference before and after the audit.

dte	050701-2 FA02505	050701-2 FA02505_sd	050701_FA02464	050701_FA02464_sd	070808_FA02786	070808_FA02786_sd	071122_FA01477	071122_FA01477_sd	071122_FF31496	071122_FF31496_sd	070807_FA02773	070807_FA02773_sd	070807_FA02770	070807_FA02770_sd	070807_FA02782	070807_FA02782_sd	070808_FA02769	070808_FA02769_sd	070808_FA02783	070808_FA02783_sd	070927_FA02493	070927_FA02493_sd	071122_FA30491	071122_FA30491_sd
2009-05-11							164.9	0.6					149.2	0.7			89.4	0.6			203.3	0.8	109.6	0.6
2009-05-12									40.0	0.5	86.0	0.6			154.1	0.8								
2009-05-13	360.9	0.7	170.8	0.6	50.8	0.5													58.9	0.6				
2009-11-20	362.6	1.0	171.7	0.8	52.4	0.8	165.5	0.7	40.5	0.5														
2009-11-25											90.1	1.0	149.9	0.7	153.7	0.9	89.2	0.6	59.6	0.6	202.3	0.8	109.6	0.5

The average of the two measurements was used for the evaluation of the audit results.

Methane

WCC-Empa refers to the 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 (NOAA/ESRL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 29). The scale was transferred to the travelling standards using a Picarro G1301 analyser. Details of the travelling standards are given in Table 30.

Table *29*. NOAA/ESRL CH_4 laboratory standards at WCC-Empa. The uncertainty represents the measured standard deviation.

Cylinder#	Methane [ppb]* (NOAA04)
CA05373	1608.57 ± 0.08 ppb
CA05316	1712.54 ± 0.16 ppb
CA04462	1817.39 ± 0.19 ppb
CA04580	1905.36 ± 0.25 ppb

*Certificates (CMDL83) from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316 and CA05373). Values were converted to NOAA04 scale by applying a factor of 1.0124.

Table 30. Calibration of the methane travelling standards with the WCC-Empa reference (Average mole fraction in ppb ± ds (n = 10)).

dte	**050701_FA02464**	050701_FA02464_sd	**050701_FA02505**	050701_FA02505_sd	**071122_FF31496**	071122_FF31496_sd	**071122_FA01477**	071122_FA01477_sd	**070808_FA02786**	070808_FA02786_sd	**070807_FA02773**	070807_FA02773_sd
May 2009	**1833.44**	1.04	**1834.68**	1.04	**1614.33**	1.66	**1950.55**	1.02	**1594.46**	1.29	**1698.23**	1.52
Nov 2009	**1833.39**	0.05	**1834.20**	0.05	**1614.20**	0.11	**1950.32**	0.07	**1595.31**	0.06	**1698.22**	0.07

dte	**070807_FA02770**	070807_FA02770_sd	**070807_FA02782**	070807_FA02782_sd	**070808_FA02769**	070808_FA02769_sd	**070808_FA02783**	070808_FA02783_sd	**070927_FA02493**	070927_FA02493_sd	**071122_FA30491**	071122_FA30491_sd
May 2009	**1858.91**	0.99	**1786.62**	0.58	**1714.34**	2.45	**1662.51**	1.07	**1781.09**	0.79	**1803.62**	1.32
Nov 2009	**1858.81**	0.06	**1786.64**	0.08	**1714.48**	0.10	**1662.84**	0.08	**1780.26**	0.09	**1802.59**	0.08

Nitrous Oxide

WCC-Empa refers to the WMO/GAW nitrous oxide scale (hereafter: NOAA-2006 scale) [*Hall et al.*, 2007]. The TS used during this audit have been calibrated by the WCC-N_2O in April 2008. In June 2011 a few of the standards were re-calibrated at WCC-N2O, and the standards were also measured on an Aerodyne QCL system at WCC-Empa. The results are shown in Table 31. Some TS showed a drift over the period between 2008 and 2011, and therefore the results of the comparisons made at CAMS should be interpreted with care. However, the large deviations found at WLG are clearly exceeding any possible uncertainty of the TS.

Table 31. N_2O TS calibrated at WCC-N_2O in 2008, and re-calibrations in 2011 at WCC-N_2O and WCC-Empa.

Cylinder	WCC-N2O (2008)	so	WCC-N2O (2011)	WCC-Empa (2011)
071122_FA30491	317.03	0.22	317.22	317.52
070927_FA02493	354.71	0.31	354.6	354.43
070807_FA02770	322.68	0.19	322.86	322.94
070808_FA02769	306.79	0.28	NA	307.95
070808_FA02783	305.42	0.21	NA	306.05
070807_FA02773	324.97	0.23	NA	NA
070807_FA02782	324.68	0.19	NA	NA
070808_FA02786	294.61	0.23	NA	NA
050701_FA02505	315.73	0.3	NA	NA
071122_FA01477	323.34	0.19	NA	NA
071122_FF31496	345.21	0.23	NA	NA

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-06-22 to 2009-06-30
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Dr. Lin Wei-li
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49i PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0013±0.0010) × [SRP] - (0.01±0.14)
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49 #47307-278
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	OFFSET = 51; SPAN = 506
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.0073±0.0015) × [SRP] - (0.10±0.11)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] + 0.10) / 1.0073
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.51\ \text{ppb}^2 + 2.81\text{e-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	NA
1.5.8	Calibration after audit (ppb):	NA
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.6	Comments:	WLG main ozone analyzer
1.7	Reference:	WCC-Empa Report 09/2

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

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Ozone Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-06-22 to 2009-06-30
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Dr. Lin Wei-li
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49i PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0013±0.0010) × [SRP] - (0.01±0.14)
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49 #47318-278
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	OFFSET = 50; SPAN = 600
1.5.4	Calibration at start of audit (ppb):	[OA] = (0.9067±0.0014) × [SRP] - (0.05±0.10)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] + 0.05 ppb) / 0.9067
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.58\ \text{ppb}^2 + 3.39\text{e-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	NA
1.5.8	Calibration after audit (ppb):	NA
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.6	Comments:	WLG backup ozone analyzer; Data are not considered as valid due to instrumental problems.
1.7	Reference:	WCC-Empa Report 09/2

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

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Ozone Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-06-22 to 2009-06-30
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Dr. Lin Wei-li
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49i PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0013±0.0010) × [SRP] - (0.01±0.14)
1.5	Ozone Calibrator [OC]	
1.5.1	Model:	TEI 49-PS #47651-279
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	OFFSET = 50; SPAN = 600
1.5.4	Calibration at start of audit (ppb):	[OC] = (0.9971±0.0010) × [SRP] - (1.97±0.11)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OC] + 1.97 ppb) / 0. 9971
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.57\ \text{ppb}^2 + 2.71\text{e-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	NA
1.5.8	Calibration after audit (ppb):	NA
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.6	Comments:	WLG ozone calibrator.
1.7	Reference:	WCC-Empa Report 09/2

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

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Ozone Audit Executive Summary (CAMS)

0.1	Facility Name:	CAMS Calibration Laboratory
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-06-22 to 2009-06-30
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Staff involved in audit:	Dr. Lin Wei-li
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):	(0.9999±0.0010) × [SRP] - (0.16±0.09)
1.5	Ozone Calibrator [OC]	
1.5.1	Model:	TEI 49C-PS # 62349-335
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG = 0.0; SPAN = 1.010
1.5.4	Calibration at start of audit (ppb):	[OC] = (1.0078±0.0010) × [SRP] - (0.33±0.08)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OC] + 0.33 ppb) / 1.0078
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.55e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	NA
1.5.8	Calibration after audit (ppb):	NA
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.6	Comments:	CAMS ozone calibrator.
1.7	Reference:	WCC-Empa Report 09/2

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

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Carbon Monoxide Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Station staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	070808_FA02783	59.26±0.55 ppb
		070808_FA02769	89.30±0.46 ppb
		071122_FA30491	109.63±0.55 ppb
		070707_FA02770	149.56±0.91 ppb
		050701_FA02464	171.26±1.05 ppb
		070927_FA02493	202.80±1.25 ppb
1.5	CO Instrument:		
1.5.1	Model:	Aglient 6890 #US 10719008	
1.5.2	Range of calibration:	59 – 203 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	CO = (0.9097±0.0075) $\times$ X + (7.8±0.8)	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO – 7.8) / 0.9097	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (2.2\ \text{ppb}^2 + 9.84\text{e-}05 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	NA	
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:	GC, main instrument	
1.7	Reference:	WCC-Empa Report 09/2	

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

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Carbon Monoxide Audit Executive Summary (CAMS)

0.1	Facility Name:	CAMS Calibration Laboratory
	Parameter:	Carbon Monoxide

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	071122_FF31496	40.24±0.42 ppb
		070808_FA02786	51.64±1.17 ppb
		070807_FA02773	88.08±2.94 ppb
		070807_FA02770	153.88±0.82 ppb
		071122_FA01477	165.23±0.93 ppb
		050701_FA02505	361.73±2.17 ppb
1.5	CO Instrument:		
1.5.1	Model:	Agilent 6890 #US 10681036	
1.5.2	Range of calibration:	40 – 362 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	CO = (0.9271±0.0045) $\times$ X + (4.8±0.5)	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO – 4.8) / 0.9271	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (8.1 \text{ ppb}^2 + 5.25\text{e-}05 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	NA	
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:	GC FID system	
1.7	Reference:	WCC-Empa Report 09/2	

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

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Carbon Monoxide Audit Executive Summary (CAMS)

0.1	Facility Name:	CAMS Calibration Laboratory	
Parameter:		Carbon Monoxide	

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	071122_FF31496	40.24±0.42 ppb
		070808_FA02786	51.64±1.17 ppb
		070807_FA02773	88.08±2.94 ppb
		070807_FA02770	153.88±0.82 ppb
		071122_FA01477	165.23±0.93 ppb
		050701_FA02505	361.73±2.17 ppb
1.5	CO Instrument:		
1.5.1	Model:	Ametek ta500R #52PR181-06123	
1.5.2	Range of calibration:	40 – 362 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	$CO = (1.2200 \pm 0.0064) \times X - (6.6 \pm 0.6)$	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO + 6.6) / 1.2200$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (307.98\ ppb^2 + 4.40e\text{-}05 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	NA	
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:	GC HgO system	
1.7	Reference:	WCC-Empa Report 09/2	

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

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Methane Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02783	1662.68±0.30 ppb
		070808_FA02769	1714.41±0.21 ppb
		070927_FA02493	1780.68±0.62 ppb
		071122_FA30491	1803.11±0.75 ppb
		050701_FA02464	1833.41±0.21 ppb
		070807_FA02770	1858.86±0.22 ppb
1.5	CH_4 analyzer:		
1.5.1	Model:	HP5890 Series II # C-128 183	
1.5.2	Range of calibration:	1663 – 1859 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (0.99921 \pm 0.00042) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 0.99921$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (8.0\ ppb^2 + 1.89e\text{-}07 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/2	

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

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Methane Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02783	1662.68±0.30 ppb
		070808_FA02769	1714.41±0.21 ppb
		070927_FA02493	1780.68±0.62 ppb
		071122_FA30491	1803.11±0.75 ppb
		050701_FA02464	1833.41±0.21 ppb
		070807_FA02770	1858.86±0.22 ppb
1.5	CH_4 analyzer:		
1.5.1	Model:	Agilent 6890 #US 10719008	
1.5.2	Range of calibration:	1663 – 1859 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00014 \pm 0.00013) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00014$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (0.9\ ppb^2 + 2.94e\text{-}08 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/2	

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

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Methane Audit Executive Summary (WLG)

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	WLG
0.3	Coordinates/Elevation:	36.28750°N 100.89630°E (3810 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02783	1662.68±0.30 ppb
		070808_FA02769	1714.41±0.21 ppb
		070927_FA02493	1780.68±0.62 ppb
		071122_FA30491	1803.11±0.75 ppb
		050701_FA02464	1833.41±0.21 ppb
		070807_FA02770	1858.86±0.22 ppb
1.5	CH_4 analyzer:		
1.5.1	Model:	Picarro G1301 #CFADS023	
1.5.2	Range of calibration:	1663 – 1859 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (0.99973 \pm 0.00004) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 0.99973$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (0.04\ ppb^2 + 1.44e\text{-}08 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/2	

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

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Methane Audit Executive Summary (CAMS)

0.4	Facility Name:	CAMS Calibration Laboratory	
	Parameter:	Methane	
1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02786	1594.89±0.63 ppb
		071122_FF31496	1614.27±0.20 ppb
		070807_FA02773	1698.23±0.19 ppb
		070807_FA02786	1786.63±0.20 ppb
		050701_FA02505	1834.44±0.39 ppb
		071122_FA01477	1950.44±0.27 ppb
1.5	CH_4 analyzer:		
1.5.1	Model:	Agilent 6890 #US 10719007	
1.5.2	Range of calibration:	1595 – 1950 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00093 \pm 0.00072) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00093$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (5.7\ ppb^2 + 5.31e\text{-}07 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/2	

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

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Methane Audit Executive Summary (CAMS)

0.1	Facility Name:	CAMS Calibration Laboratory
	Parameter:	Methane

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02786	1594.89±0.63 ppb
		071122_FF31496	1614.27±0.20 ppb
		070807_FA02773	1698.23±0.19 ppb
		070807_FA02786	1786.63±0.20 ppb
		050701_FA02505	1834.44±0.39 ppb
		071122_FA01477	1950.44±0.27 ppb
1.5	CH_4 analyzer:		
1.5.1	Model:	Agilent 6890 #US 10681036	
1.5.2	Range of calibration:	1595 – 1950 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00150 \pm 0.00027) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00150$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (1.4\ ppb^2 + 8.38e\text{-}08 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/2	

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

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Methane Audit Executive Summary (CAMS)

0.1	Facility Name:	CAMS Calibration Laboratory
	Parameter:	Methane

1.1	Date of Audit:	2009-06-22 to 2009-06-30	
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen	
1.2.1	Staff involved in audit:	Dr. Shuangxi Fang, Mrs. Fang Zhang	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02786	1594.89±0.63 ppb
		071122_FF31496	1614.27±0.20 ppb
		070807_FA02773	1698.23±0.19 ppb
		070807_FA02786	1786.63±0.20 ppb
		050701_FA02505	1834.44±0.39 ppb
		071122_FA01477	1950.44±0.27 ppb
1.5	CH_4 analyzer:		
1.5.1	Model:	Picarro G1301 CFADS021	
1.5.2	Range of calibration:	1595 – 1950 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00124 \pm 0.00027) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00124$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (0.06\ ppb^2 + 1.49e\text{-}08 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/2	

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

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LIST OF ABBREVIATIONS

a.s.l.	above sea level
CCL	Central Calibration Laboratory
CAMS	Chinese Academy of Meteorological Sciences
CMA	China Meteorological Administration
CRDS	Cavity Ring Down Spectroscopy
DAQ	Data Acquisition System
ECD	Electron Capture Detector
FID	Flame Ionization Detector
GAW	Global Atmosphere Watch
GC	Gas Chromatograph
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyser
OC	Ozone Calibrator
WLG	Mt. Waliguan GAW Global Station
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Travelling Standard
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation