SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, METHANE, CARBON DIOXIDE, NITROUS OXIDE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION ZUGSPITZE-SCHNEEFERNERHAUS GERMANY, JUNE 2011

Submitted to the World Meteorological Organization by

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EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The fifth system and performance audit at the Global GAW station Zugspitze-Schneefernerhaus was conducted by WCC-Empa[1] from 28 thru 30 June 2011 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Zugspitze-Schneefernerhaus (ZSF) GAW station is jointly operated by the Federal Environment Agency (Umweltbundesamt, UBA) and the German Weather Service (Deutscher Wetterdienst, DWD).

Previous audits at ZSF were conducted in conducted in April 1996 [*Herzog et al.*, 1996], November 1997 [*Herzog et al.*, 1997], February 2001 [*Zellweger et al.*, 2001], and in June 2006 [*Zellweger et al.*, 2006].

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Ludwig Ries	Zugspitze-Schneefernerhaus, UBA, Station Manager
Mr. Ralph Sohmer	UBA, Station Operator
Mr. Steffen Knabe	UBA, Station Operator

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

The report is distributed to the Zugspitze-Schneefernerhaus GAW station and the World Meteorological Organization in Geneva. The report will be posted on the internet.

The recommendations found in this report are graded as minor, important and critical and are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

The Zugspitze-Schneefernerhaus Station (2656 m a.s.l.) is located on the southern slope of Zugspitze, the highest mountain of the German Alps (2964 m a.s.l.). The station was moved from the summit to Schneefernerhaus during 2001/2002. Measurements on the summit are partly ongoing but are no longer considered as part of the GAW programme. Further information is available from GAWSIS (http://gaw.empa.ch/gawsis) and the station web site (www.schneefernerhaus.de).

The location is adequate for the intended purpose. Year-round access to ZSF is possible by cable car and cog railway.

Station Facilities

The Environmental Research Station Schneefernerhaus is managed by the Bavarian State Ministry of the Environment as a Virtual Institute for altitude and climate research. The Schneefernerhaus offers extensive laboratory and office facilities. It is an ideal platform for continuous atmospheric research as well as measurement campaigns.

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

Station Management and Operation

The station is permanently staffed during working days (Mon-Fri) with a scientist and two operators. The current team has long-term technical and scientific expertise; however, one position (engineer) was vacant during the audit.

> **Recommendation 1 (**, important, 2013)**
> *The workload of the current station staff is high, and vacant positions should be filled by qualified staff as soon as possible.*

Air Inlet Systems

The design of the air inlet system is state of the art (for all parameters) and adequate for its intended purpose.

Surface Ozone Measurements

Surface ozone measurements at Zugspitze-Schneefernerhaus were established in 2001, and continuous time series are available since then. Before this time, measurements were made at the Zugspitze-Gipfel (ZUG) station, next to the summit at about 300 m higher altitude. In order to assess the influence of the different locations, parallel surface ozone measurements have been made at the ZUG and the ZSF sites.

Figure 1 shows monthly surface ozone data acquired on both stations as well as the difference between the two sites. The measurements at ZSF were on average 0.82 ppb lower compared to ZUG. Data of the ZUG station were provided by Eckhart Scheel.

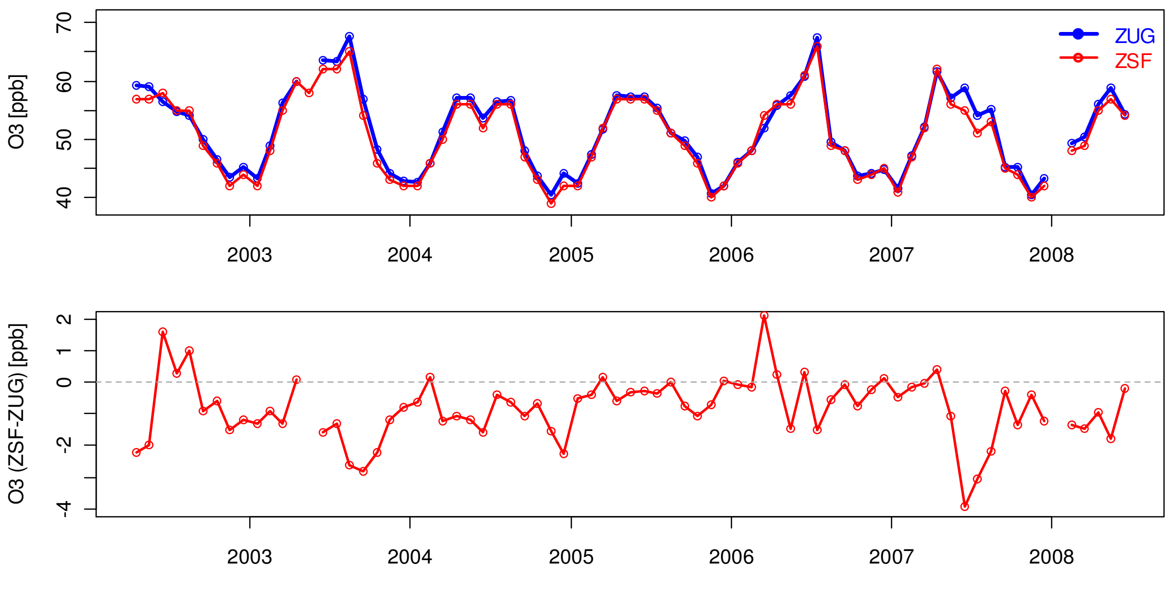

Figure 1. *Comparison of monthly surface ozone data at ZUG and ZSF for the period April 2002-June 2008 (upper panel) and the difference ZSF-ZUG (lower panel).*

Instrumentation. The station is currently equipped with two ozone analysers (TEI 49i and Horiba APOA-370). The instrumentation is fully adequate for its intended purpose.

Standards. The station is equipped with an ozone standard (TEI 49C-PS) which is calibrated against the ozone standard of UBA (SRP#29) on a yearly basis.

Intercomparison (Performance Audit). The ozone analysers as well as the ozone calibrator of Zugspitze-Schneefernerhaus were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The results of the comparisons are summarised below. The data acquired by the WCC-Empa data acquisition system (TS and TEI 49i) and the ZSF data acquisition (APOA-370) was used for data evaluation, and no further corrections were applied. The following equations characterise the bias of the instruments:

TEI 49i #CM08490061 (BKG 0.0 ppb, SPAN 1.004) – main analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.1 ppb) / 0.9977 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.77e-05 * $X_{O3}{}^2$) (1b)

APOA-370 #J006B37 (BKG 0.0 ppb, SPAN 0.99884) – backup analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.7 ppb) / 1.0162 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.66e-05 * $X_{O3}{}^2$) (1d)

TEI 49C-PS #58686-319 (BKG 0.0 ppb, SPAN 1.000) – station calibrator:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] - 0.0 ppb) / 0.9941 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.67e-05 * $X_{O3}{}^2$) (1f)

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

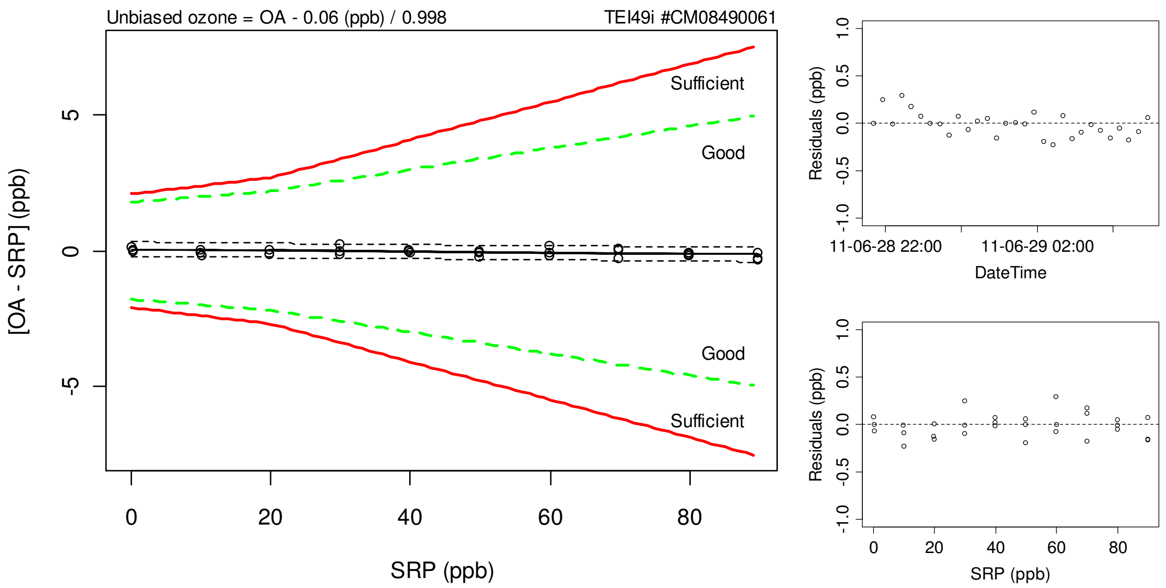

Figure 2. *Left: Bias of the ZSF ozone analyser (TEI 49i #CM08490061) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria are delimited by green and red lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

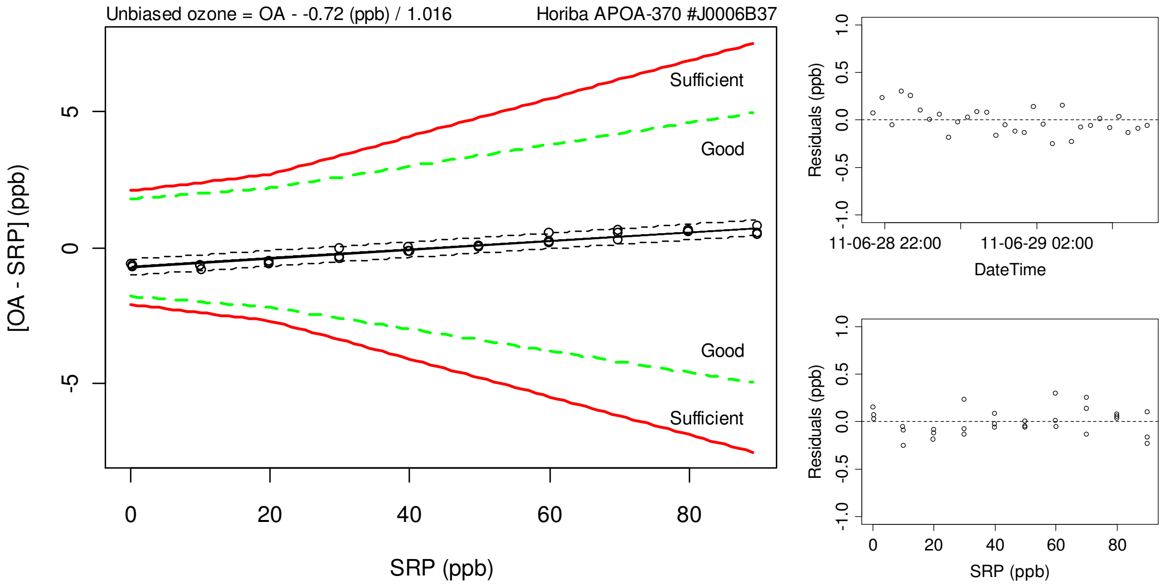

Figure 3. *Same as Figure 1, for the APOA-370 #J006B37 backup analyser.*

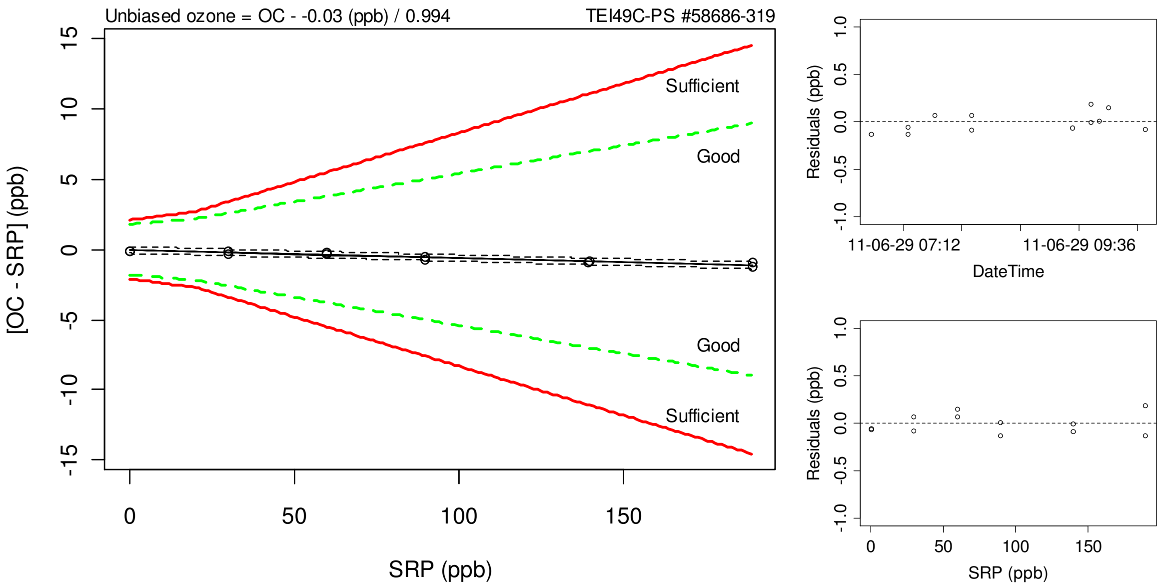

Figure 4. *Same as Figure 1, for TEI 49C-PS #58686-319 station calibrator.*

The results of the ozone comparisons can be summarised as follows: The new TEI 49i analyser as well as the TEI 49C-PS calibrator have been confirmed to be in very good calibration and are adequate for ozone measurements. A slightly larger deviation was found for the Horiba APOA-370 instrument.

The results of parallel ozone measurements between the measurement site at the Zugspitze summit and ZSF showed also good agreement for monthly averages. The values at ZSF were slightly lower which can be explained by the altitude difference between the two sites.

Carbon Monoxide Measurements

Continuous measurements of CO at ZSF started in 2002, and data is available since then. Before this time, measurements were made at the Zugspitze-Gipfel (ZUG) station.

Instrumentation. Two Aerolaser Vacuum UV Fluorescence analysers (AL5001 and AL5002) are available at ZSF. The instrument set-up has not been changed since the last WCC-Empa audit in 2006. In addition, a gas chromatograph (GC) with a mercuric oxide detector (Peak Performer 1) was installed. The latter also allows simultaneous detection of molecular hydrogen (H_2) next to CO; however, due to lack of manpower this instrument has not been calibrated, and CO data of the instrument will not be used. It is therefore not considered in the current audit. All instrumentation is adequate for the measurement of CO.

Standards. The ZSF station is equipped with 6 NOAA laboratory standards. For the calibration of the Aerolaser instruments, two 1 ppm CO standards from Deuste-Steininger are used; one of the tanks is used to calibrate the instrument (working standard), whereas the other tank is measured as a target cylinder. The working standard is lasting for approx. 1 year, and the target approx. 3 years.

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the ZSF instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 5 and Figure 6 with respect to the WMO GAW Data Quality Objectives (DQOs) [WMO, 2010; 2011]:

Aerolaser AL5002#148 (main CO analyser):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 1.4) / 0.9870 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (2.6 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

Aerolaser AL5001#145 (backup CO analyser):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 1.7) / 0.9767 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (2.4 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

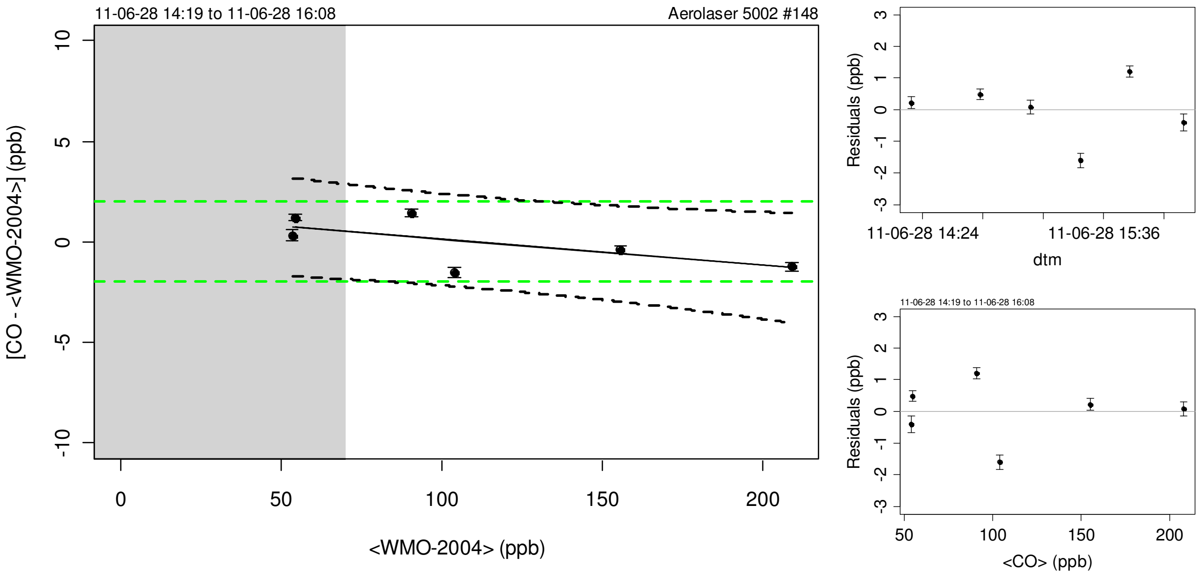

Figure 5. *Left: Bias of the ZSF Aerolaser AL5002 carbon monoxide instrument with respect to the WMO2000 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZSF, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

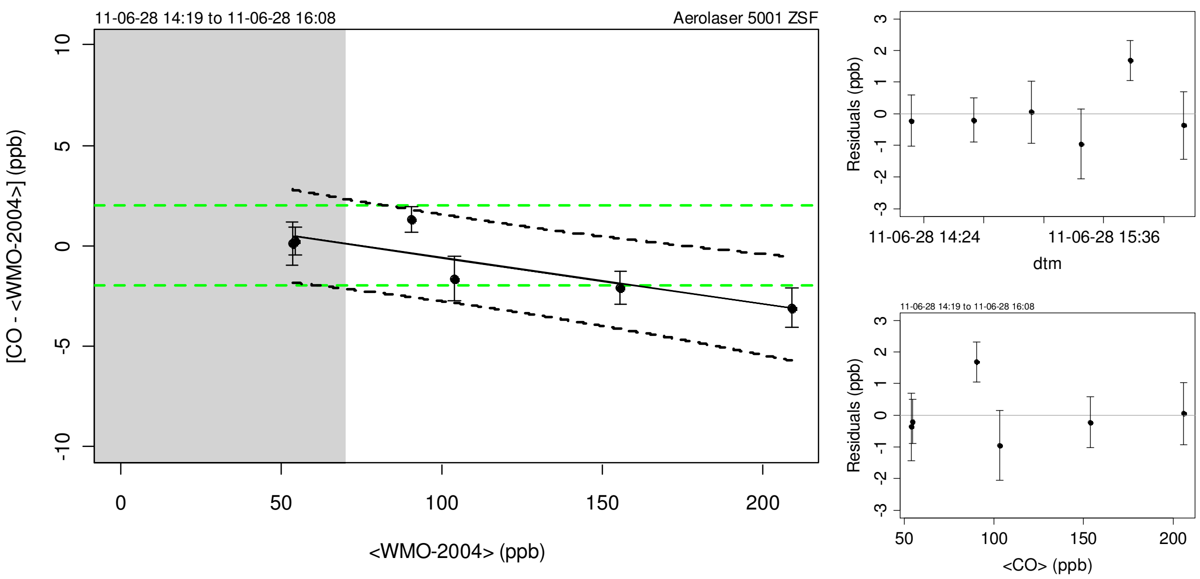

Figure 6. *Same as above for the Aerolaser AL5001 instrument.*

The results of the carbon monoxide comparisons can be summarised as follows: The comparisons showed good agreement between the ZSF and WCC-Empa measurements for the two Aerolaser instruments. The PeakPerformer instrument was not calibrated and was consequently not considered for the current audit. Only CO data of the Aerolaser instruments will be considered for data submission to the WDCGG. Due to the good results, no further technical recommendations are made by WCC-Empa.

Greenhouse Gas Measurements (CO_2, CH_4 and N_2O)

Continuous measurements of CH_4, CO_2 and N_2O at ZSF started in 2000 using a GC/FID/ECD system. The instrumental setup was complemented by the Peak Performer instrument in 2009 for additional CO and H_2 measurements. The system was optimised within the framework of a Diploma Thesis (Luisa Müller, Group of Ingeborg Levin, University of Heidelberg). In addition, a Picarro ESP-1000 CH_4, CO_2 and H_2O analyser was installed in 2009; however, the calibration unit that was ordered with the instrument from Metcon GmbH was not delivered until the date of the audit. At the time of the audit the instrument has not been calibrated due to the lack of the calibration unit. In the meantime, the calibration unit was delivered and regular calibrations are performed.

Instrumentation. A GC/FID/ECD system for CH_4, CO_2 and N_2O measurements and a Picarro ESP-1000 CO_2, CH_4 and H_2O analyser are available at ZSF.

Standards. The ZSF station is equipped with 6 NOAA laboratory standards. The GC system is calibrated using two working standards, which contain natural air. The Picarro instrument has not been calibrated due to a lack of peripherals that were ordered together with the instrument from the German Picarro distributor.

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

The following equations characterise the instrument bias for the GC/FID/ECD system. The results are further illustrated in Figure 7 to Figure 9 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

HP 6890 GC/FID/ECD:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 9.15) / 0.99470 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (2.60 ppb^2 + 1.30e-07 * $X_{CH4}{}^2$) (3b)

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 2.83) / 0.99286 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.07 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4b)

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 38.77) / 0.87233 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (9.75 ppb^2 + 1.01e-07 * $X_{N2O}{}^2$) (5b)

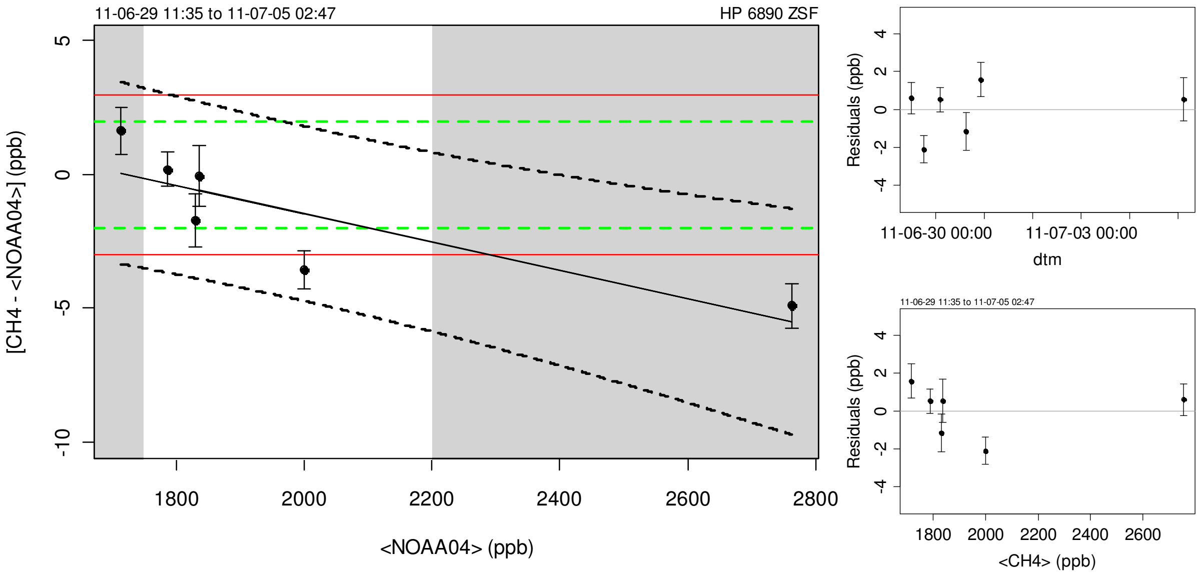

Figure 7. *Left: Bias of Zugspitze-Schneefernerhaus GC/FID methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZSF, whereas the red and green lines correspond to the DQOs. Each point represents the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

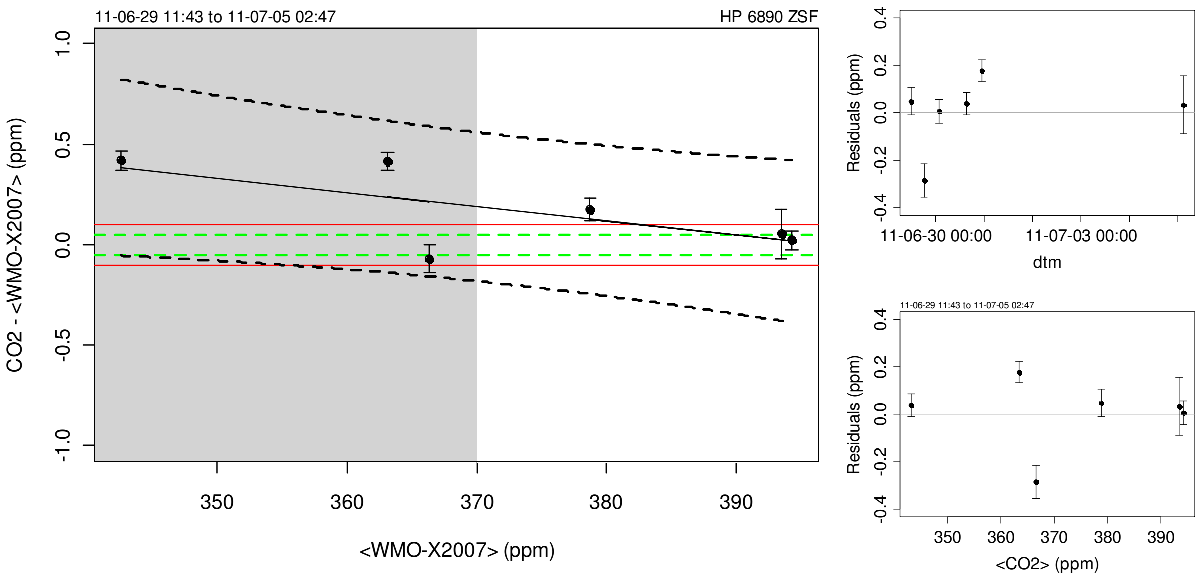

Figure 8. *Left: Bias of Zugspitze-Schneefernerhaus GC/FID carbon dioxide instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZSF, whereas the red and green lines correspond to the DQOs. Each point represents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

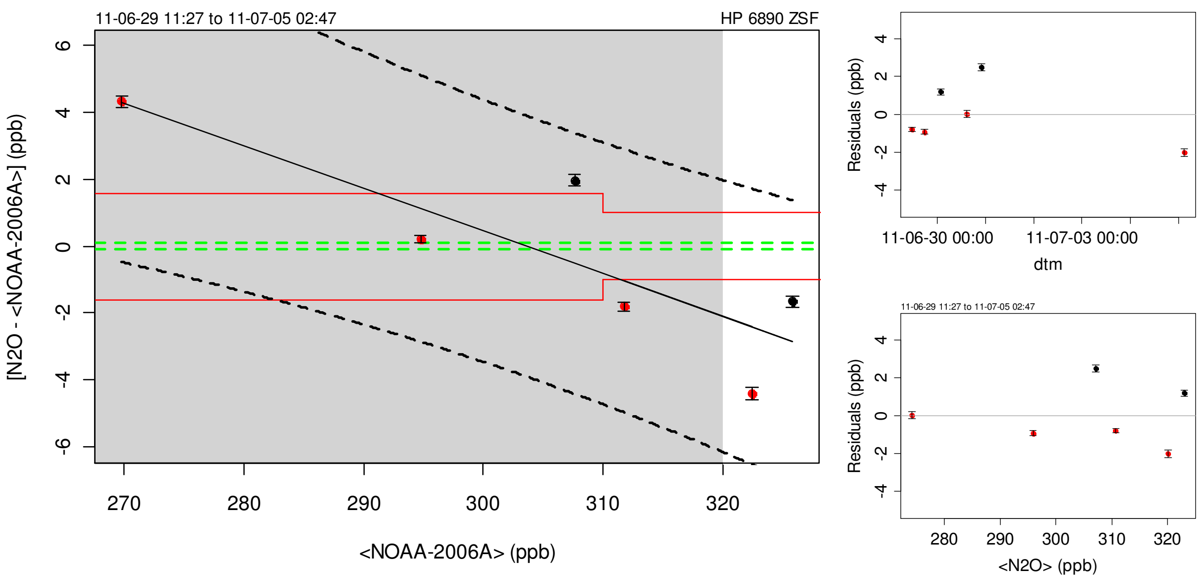

Figure 9. *Left: Bias of Zugspitze-Schneefernerhaus GC/ECD nitrous oxide instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZSF, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Red points denote to WCC-Empa TS with high SF_6 content, which potentially interferes with the N_2O measurement.*

The agreement of the GC system with the WCC-Empa TS was good for the relevant mole fraction range of CO_2 and CH_4. However, both species showed a slight mole fraction dependence of the results, and the corresponding uncertainties were relatively large especially for CO_2 in comparison to the WMO DQOs. It is therefore recommended that the Picarro instrument is equipped with calibration peripherals as soon as possible to have additional CO_2 and CH_4 measurements at ZSF.

Large deviations were found between the ZSF N_2O measurements and the WCC-Empa TS. Most likely the non-linearity of the ECD detector is insufficiently characterised. However, some of the WCC-Empa TS had a high SF_6 content, which potentially biased the results of the ZSF GC due to chromatographic interferences (red points in above Figure). Nevertheless the two WCC-Empa TS with only slightly elevated SF_6 levels also resulted in a bias which is significantly larger than the WMO DQOs. Therefore, an independent verification of performance of the system by the WCC-N_2O is highly recommended.

Recommendation 2 (*, important, 2014)**
The calibration and the performance of the N_2O GC system need to be assessed. An independent audit by the WCC-N_2O is recommended.
Update October 2013: The performance of the system is still unsatisfactory; A Los Gatos N_2O system has been ordered and is due for delivery. It is recommended that an audit by the WCC-N_2O is made after the new system has been installed.

Picarro ESP-1000 #063-CFADS18:

Unbiased CH_4 mixing ratio:	X_{CH4} (ppb) = (CH_4 – 1.80) / 0.99542	(6a)
Remaining standard uncertainty:	u_{CH4} (ppb) = sqrt (0.36 ppb^2 + 1.30e-07 * X_{CH4}^2)	(6b)
Unbiased CO_2 mixing ratio:	X_{CO2} (ppm) = (CO_2 – 0.06) / 0.99595	(7a)
Remaining standard uncertainty:	u_{CO2} (ppm) = sqrt (0.003 ppm^2 + 3.28e-08 * X_{CO2}^2)	(7b)

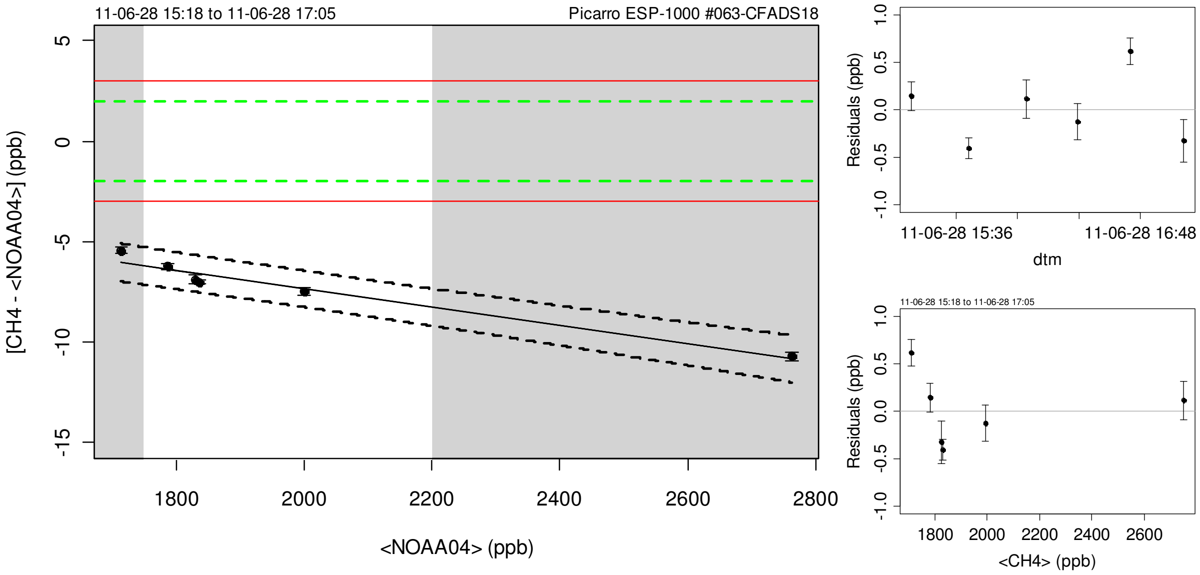

Figure 10. *Left: Bias of Zugspitze-Schneefernerhaus Picarro ESP-1000 methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZSF, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

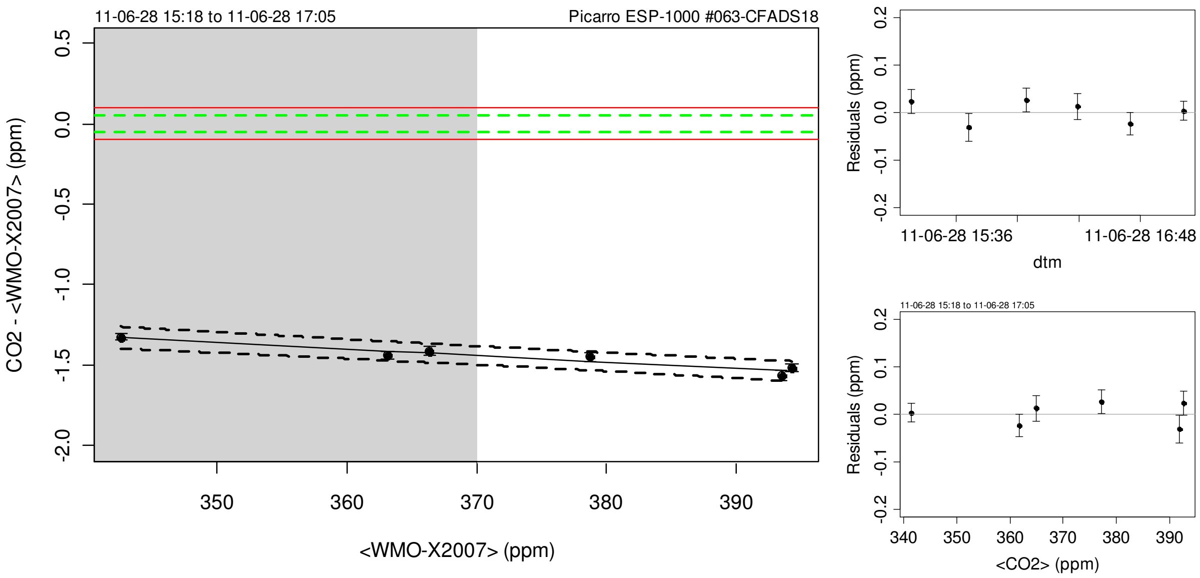

Figure 11. *Left: Bias of Zugspitze-Schneefernerhaus Picarro ESP-1000 carbon dioxide instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZSF, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The above results show that the Picarro system is working well but not calibrated; compared to the GC system, better repeatability can be achieved with this instrument. It is therefore of utmost importance that the measurement set-up is completed with peripherals for automatic calibrations as soon as possible.

Currently, no drying system is used for the Picarro instrument. A characterisation of the water vapour interference is needed to re-evaluate existing data.

Since the calibration of the CRDS instruments are usually stable over long periods, post processing of the existing data might be possible, and data could be compared with results of the GC system. T

Based on the above results, the following recommendations are made:

Recommendation 3 (*, done, 2013)**
The Picarro instrument needs immediate calibration. All peripherals should immediately be delivered and installed by Meteorologie consult GmbH (completed in 2013). Update Oct 2013: The unit is now installed. After the audit (since summer 2011), weekly manual calibrations with a standard gas were performed.

Recommendation 4 (*, important, 2013)**
Water vapour correction functions need to be determined for the Picarro instrument for data processing and validation.

Recommendation 5 (, important, 2013)**
It should be explored if the existing data can be re- processed. Comparison with the GC data is encouraged. Update Oct 2013: This is foreseen for the near future (2014).

Data Acquisition and Management

Data of the gas chromatograph system (greenhouse gases and CO) is acquired using custom made software programmed by the University of Heidelberg. The software uses the reports that are generated by the HPChemStation software.

Data of all other instruments is acquired on a self-developed data acquisition system (DAQAS). DAQAS was developed in an R+D project of the UBA in collaboration with external partners (Fell&Kernbach, Berlin, QuoData, Dresden). One minute data is stored for further analysis. Remote access to all instruments is possible, and the data is backed up in regular intervals.

Further data processing is done on a self-programmed data evaluation tool which is part of the DAQAS system. The tool provides very powerful data visualization, verification and correction options, and is also linked with the electronic logbooks. It further logs all data processing steps, and the processed data is saved in the data base system.

Data Submission

For the parameters of the audit scope, in-situ data for surface ozone (2002 – 2007), methane (2002-2007), carbon dioxide (2002-2009) and nitrous oxide (2003-2007) was available at the World Data Centre for Greenhouse Gases (WDCGG) at the time of the audit. After the audit, the data series for the above parameters until December 2011 were submitted, as well as carbon monoxide data (2006, 2007, 2010). The data is now directly submitted by the ZSF station manager and not by the UBA data manager as it used to be. This will shorten the delay of future data submissions. Furthermore, a software tool (DAFIT) has been written which should allow faster data validation and submission in the future.

> **Recommendation 6 (**, minor, ongoing)**
> *Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year. The change of responsibilities from UBA to the ZSF station manager is expected to improve the data submission frequency and should therefore continue. GAWSIS entries need also to be regularly updated by the ZSF station manager.*

Conclusions

The Global GAW station Zugspitze-Schneefernerhaus carries out a comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the ZSF station an important contribution to the GAW programme. However, some of the instrumentation was not yet fully calibrated due to a lack of station personnel and delivery delay of important peripherals. In addition, several technical issues were identified which need further attention.

Long-term parallel measurements of surface ozone at the Zugspitze Gipfel site and ZSF showed that the two sites are comparable in terms of the air masses that are measured. Nevertheless, small differences were found, and the data of the two sites are potentially difficult to homogenise. The evaluation of other parameters that are measured in parallel (e.g. CO) is strongly encouraged.

Summary Ranking of the Zugspitze-Schneefernerhaus GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access
Facilities		
Laboratory and office space	(5)	Large research facilities
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully operational
Power supply	(5)	Few power outages
General Management and Operation		
Organisation	(4)	Well organised, but limited human resources
Competence of staff	(5)	Highly experienced staff
Air Inlet System	(5)	State-of-the-art
Instrumentation		
Ozone	(5)	Up-to-date instrumentation
CO (Aerolaser)	(5)	Up-to-date instrumentation
Greenhouse gases (GC)	(4)	Calibration issues (N_2O)
CO_2 and CH_4 (Picarro)	(5)	Calibration unit available since 2013
Standards		
Ozone	(5)	TEI 49C-PS, traceability to SRP
CO, CH_4, CO_2 and N_2O	(5)	NOAA and working standards
Data Management		
Data acquisition	(5)	DAQAS system
Data processing	(5)	Adequate data evaluation tools, experienced staff
Data submission	(3)	Relatively long submissions delays (>3yrs)

#0: inadequate thru 5: adequate.

Dübendorf, October 2013

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QA/SAC Switzerland

Dr. B. Buchmann
Head of Department

APPENDIX

Global GAW Station Zugspitze-Schneefernerhaus

Site description and measurement programme

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

Links: http://www.umweltbundesamt.de/luft/luftmessnetze/stationen/zug/index.htm
www.schneefernerhaus.de
http://gaw.empa.ch/gawsis/reports.asp?StationID=-739518684

Trace Gas Distribution at Zugspitze-Schneefernerhaus

The monthly and yearly distribution for surface ozone, carbon monoxide, methane, carbon dioxide, nitrous oxide and ambient temperature at Zugspitze-Schneefernerhaus is shown in Figure 12.

Organisation and Contact Persons

The Zugspitze-Schneefernerhaus GAW station is run by the Environmental Research Station Schneefernerhaus, which is managed by the Bavarian State Ministry of the Environment. It coordinates the activities of ten German research institutes for altitude, environment and climate research. The parameters of the scope of WCC-Empa are run by UBA. Refer to GAWSIS for more detailed contact information.

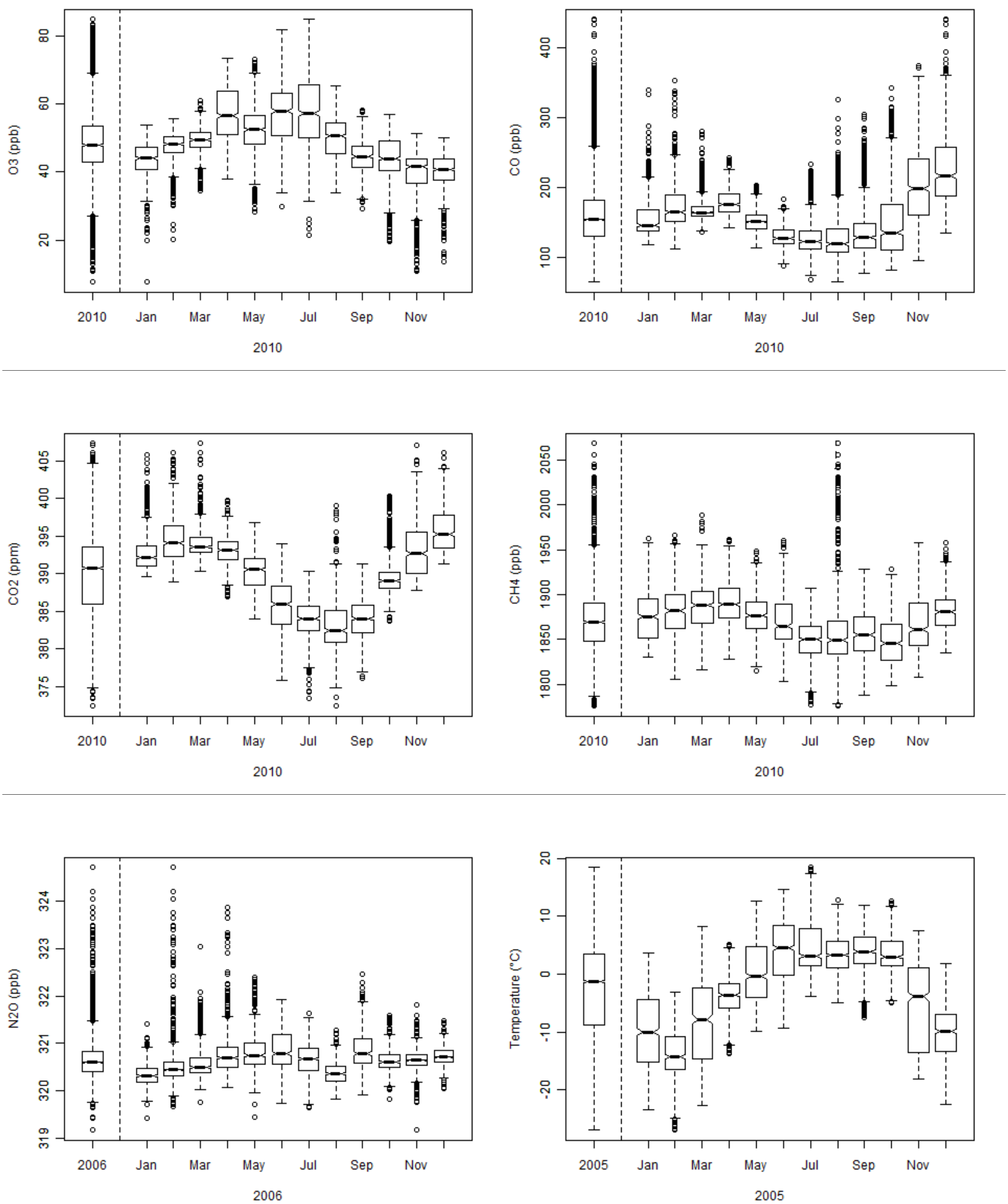

Figure 12. *Yearly and monthly box plots for surface ozone, carbon monoxide, carbon dioxide and methane (all 2010), nitrous oxide (2009) and ambient temperature (2005). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.*

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The laboratory where the instruments are installed is air-conditioned, and the instruments are protected from direct sunlight. No modifications are necessary.

Air Inlet System

Location of air intake:	Schneefernerhaus, on a terrace above the laboratory, 2.5 m above the roof. The common manifold is used for the measurements of all gaseous species.
Inlet protection:	Protection against rain water / snow / insects.
Tubing / Material:	Manifold: length = 4.2 m, inner diameter = 8 cm, glass, flow 500 l/min Connection of O3 instruments by ca. 1 m ¼ inch PFA lines, flow approx. 1 l/min.
Inlet filter:	PTA filter holder, Whatman TE38 PTFE inlet filter, 5µm pore size.
Residence time:	approx. 5 s

Instrumentation

The station is currently equipped with two ozone analysers (TEI 49i and Horiba APOA-370). Instrumental details are summarised in Table 1.

Standards

A TEI 49C-PS ozone standard is available, for details refer to Table 1.

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri).
Zero / Span check:	Weekly, with TEI49C-PS, levels 0, 20, 40, 60, 80 ppb.
Calibration/checks with standard:	Weekly checks but no adjustments of calibration factors.
Inlet filter exchange:	Usually every 6-8 weeks, more frequent in case of pollution episodes.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

The DAQAS system is used to acquire the ozone data.

Data Treatment

Data is evaluated by the station staff using the DAQAS system. DAQAS provides comprehensive tools for data evaluation and quality control.

Documentation

Electronic field logbooks are available. The field logbook contains more general information about the station, and additional log books are available for all instrument. SOPs as well as check list are available for all instruments. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison of the Ozone Analyser and Ozone Calibrator

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

Setup and Connections

The internal ozone generator of the WCC-Empa travelling standard was used for the generation of a randomised sequence of ozone levels ranging from 0 to 90 ppb. Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser including its inlet filter using approx. 1.5 m of PFA tubing. Table 1 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa DAQ (TS) and the station data acquisition system (station analysers).

Table 1. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
Settings	BKG = -0.2; COEFF = 1.009
Station Analyser (OA) – main instrument	
Model, S/N	TEI 49i #CM08490061
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = 0.0; COEFF = 1.004
Pressure readings (hPa)	744, no adjustments were made
Station Analyser (OA) – backup instrument	
Model, S/N	APOA-370 #J006B37
Principle	UV absorption
Range	0-1 ppm
Settings	Span = 0.99884
Pressure readings (hPa)	744, no adjustments were made
Station Calibrator (OC)	
Model, S/N	TEI 49C-PS #58686-319
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = 0.0; COEFF = 1.000
Pressure readings (hPa)	Ambient 740.7, OC 737.7, no adjustments were made

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison as described elsewhere *[Klausen et al., 2003]*. All results are valid for the calibration factors as given in Table 1 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

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

Table 2. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main ZSF ozone analyser (OA) TEI 49i #CM08490061 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-06-28 21:40	1	0	0.41	0.33	0.22	0.03	-0.08	NA
2011-06-28 21:55	1	30	30.06	30.12	0.20	0.08	0.06	0.20
2011-06-28 22:10	1	10	9.96	9.83	0.29	0.10	-0.13	-1.30
2011-06-28 22:25	1	60	59.99	59.99	0.09	0.14	0.00	0.00
2011-06-28 22:40	1	70	70.02	69.87	0.13	0.09	-0.15	-0.20
2011-06-28 22:55	1	90	89.99	89.67	0.10	0.11	-0.32	-0.40
2011-06-28 23:10	1	50	49.97	49.71	0.13	0.08	-0.26	-0.50
2011-06-28 23:25	1	80	80.02	79.65	0.09	0.11	-0.37	-0.50
2011-06-28 23:40	1	20	19.94	19.67	0.18	0.10	-0.27	-1.40
2011-06-28 23:55	1	40	40.00	39.85	0.09	0.11	-0.15	-0.40
2011-06-29 00:10	2	0	0.39	0.24	0.30	0.03	-0.15	NA
2011-06-29 00:25	2	40	39.97	39.77	0.17	0.10	-0.20	-0.50
2011-06-29 00:40	2	80	80.03	79.72	0.12	0.06	-0.31	-0.40
2011-06-29 00:55	2	90	90.00	89.45	0.13	0.08	-0.55	-0.60
2011-06-29 01:10	2	60	60.02	59.73	0.12	0.09	-0.29	-0.50
2011-06-29 01:25	2	20	20.01	19.86	0.23	0.08	-0.15	-0.70
2011-06-29 01:40	2	30	29.98	29.79	0.12	0.11	-0.19	-0.60
2011-06-29 01:55	2	70	69.99	69.78	0.08	0.09	-0.21	-0.30
2011-06-29 02:10	2	50	50.00	49.55	0.12	0.10	-0.45	-0.90
2011-06-29 02:25	2	10	10.17	9.82	0.44	0.11	-0.35	-3.40
2011-06-29 02:40	3	0	0.18	0.18	0.24	0.03	0.00	NA
2011-06-29 02:55	3	90	89.99	89.44	0.07	0.12	-0.55	-0.60
2011-06-29 03:10	3	30	30.01	29.73	0.15	0.07	-0.28	-0.90
2011-06-29 03:25	3	40	40.05	39.81	0.15	0.09	-0.24	-0.60
2011-06-29 03:40	3	60	59.99	59.62	0.12	0.11	-0.37	-0.60
2011-06-29 03:55	3	20	20.01	19.70	0.24	0.10	-0.31	-1.50
2011-06-29 04:10	3	80	80.00	79.59	0.12	0.14	-0.41	-0.50
2011-06-29 04:25	3	70	70.02	69.52	0.18	0.10	-0.50	-0.70
2011-06-29 04:40	3	10	10.12	9.92	0.31	0.10	-0.20	-2.00
2011-06-29 04:55	3	50	50.02	49.82	0.15	0.08	-0.20	-0.40

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the backup ZSF ozone analyser (OA) APOA-370 #J006B37 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2011-06-28 21:40	1	0	0.41	-0.38	0.22	0.05	-0.79	NA
2011-06-28 21:55	1	30	30.06	29.88	0.20	0.08	-0.18	-0.60
2011-06-28 22:10	1	10	9.96	9.19	0.29	0.08	-0.77	-7.70
2011-06-28 22:25	1	60	59.99	60.32	0.09	0.12	0.33	0.60
2011-06-28 22:40	1	70	70.02	70.46	0.13	0.08	0.44	0.60
2011-06-28 22:55	1	90	89.99	90.57	0.10	0.08	0.58	0.60
2011-06-28 23:10	1	50	49.97	49.86	0.13	0.06	-0.11	-0.20
2011-06-28 23:25	1	80	80.02	80.41	0.09	0.08	0.39	0.50
2011-06-28 23:40	1	20	19.94	19.19	0.18	0.10	-0.75	-3.80
2011-06-28 23:55	1	40	40.00	39.71	0.09	0.05	-0.29	-0.70
2011-06-29 00:10	2	0	0.39	-0.44	0.30	0.03	-0.83	NA
2011-06-29 00:25	2	40	39.97	39.79	0.17	0.11	-0.18	-0.50
2011-06-29 00:40	2	80	80.03	80.44	0.12	0.08	0.41	0.50
2011-06-29 00:55	2	90	90.00	90.32	0.13	0.07	0.32	0.40
2011-06-29 01:10	2	60	60.02	60.00	0.12	0.06	-0.02	0.00
2011-06-29 01:25	2	20	20.01	19.33	0.23	0.06	-0.68	-3.40
2011-06-29 01:40	2	30	29.98	29.43	0.12	0.11	-0.55	-1.80
2011-06-29 01:55	2	70	69.99	70.31	0.08	0.08	0.32	0.50
2011-06-29 02:10	2	50	50.00	49.84	0.12	0.09	-0.16	-0.30
2011-06-29 02:25	2	10	10.17	9.21	0.44	0.14	-0.96	-9.40
2011-06-29 02:40	3	0	0.18	-0.53	0.24	0.04	-0.71	NA
2011-06-29 02:55	3	90	89.99	90.25	0.07	0.07	0.26	0.30
2011-06-29 03:10	3	30	30.01	29.52	0.15	0.05	-0.49	-1.60
2011-06-29 03:25	3	40	40.05	39.73	0.15	0.09	-0.32	-0.80
2011-06-29 03:40	3	60	59.99	60.04	0.12	0.10	0.05	0.10
2011-06-29 03:55	3	20	20.01	19.36	0.24	0.09	-0.65	-3.20
2011-06-29 04:10	3	80	80.00	80.37	0.12	0.12	0.37	0.50
2011-06-29 04:25	3	70	70.02	70.08	0.18	0.10	0.06	0.10
2011-06-29 04:40	3	10	10.12	9.32	0.31	0.16	-0.80	-7.90
2011-06-29 04:55	3	50	50.02	49.85	0.15	0.06	-0.17	-0.30

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

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2011-06-29 06:30	1	0	0.46	0.18	0.23	0.03	-0.28	NA
2011-06-29 06:45	1	190	190.05	188.41	0.12	0.07	-1.64	-0.90
2011-06-29 07:00	1	60	59.97	59.40	0.12	0.05	-0.57	-1.00
2011-06-29 07:15	1	90	89.98	89.03	0.12	0.10	-0.95	-1.10
2011-06-29 07:30	1	30	30.00	29.76	0.12	0.06	-0.24	-0.80
2011-06-29 07:45	1	140	140.02	138.61	0.10	0.08	-1.41	-1.00
2011-06-29 08:00	2	0	0.34	0.15	0.21	0.05	-0.19	NA
2011-06-29 08:15	2	60	60.01	59.52	0.10	0.08	-0.49	-0.80
2011-06-29 08:30	2	140	139.99	138.90	0.19	0.10	-1.09	-0.80
2011-06-29 08:45	2	30	29.98	29.57	0.18	0.06	-0.41	-1.40
2011-06-29 09:00	2	90	89.97	89.12	0.14	0.10	-0.85	-0.90
2011-06-29 09:15	2	190	190.02	188.61	0.13	0.10	-1.41	-0.70
2011-06-29 09:30	3	0	0.38	0.14	0.28	0.05	-0.24	NA
2011-06-29 09:45	3	140	140.04	138.87	0.16	0.07	-1.17	-0.80
2011-06-29 10:00	3	60	59.99	59.54	0.16	0.08	-0.45	-0.80
2011-06-29 10:15	3	190	190.03	188.77	0.11	0.09	-1.26	-0.70
2011-06-29 10:30	3	30	29.97	29.49	0.15	0.08	-0.48	-1.60
2011-06-29 10:45	3	90	90.02	89.26	0.11	0.07	-0.76	-0.80

Conclusions

The ozone measurements made with the main ozone analyser (TEI 49i) at Zugspitze-Schneefernerhaus agreed perfectly with the WCC-Empa travelling standard. Slightly larger deviations were found between the back-up analyser and WCC-Empa. A station ozone standard with traceability to a SRP was also available at the station. Due to the good results, no recommendations were necessary. The measurements should be continued using the current set-up and QA/QC system.

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

The inlet system is identical as for surface ozone, and the CO instruments are also connected to the manifold. The Aerolaser instruments are connected with a common ¼" PTFE tubing (length 1 m) and share an inlet filter. After the filter each instrument is connected with 0.3 m ¼" PTFE tubing to the external Nafion drier. The PeakPerformer 1 is connected to the manifold with 2 m ¼" stainless steel tubing. A metal below pump is used to flush the inlet line with 2 l/min. An inlet filter is mounted after the pump, and the air is dried with a cold trap (-40°C). The residence time is estimated to be approximately 10 s.

Inlet filter(Aerolaser): Midisart 2000 PTFE filter 0.45 µm.

Residence time: < 10 s

Instrumentation

Zugspitze-Schneefernerhaus is equipped with two Aerolaser Vacuum UV Fluorescence analysers (AL5001 and AL5002). The instrument set-up has not been changed since the last WCC-Empa audit in 2006. In addition, a gas chromatograph (GC) with a mercuric oxide detector (Peak Performer 1) was installed, but has not yet been calibrated due to lack of manpower. Consequently, this instrument was not considered for the audit, since CO data will also not be used according to the station manager. Instrumental details are listed in Table 6.

Standards

The ZSF station is equipped with 6 NOAA laboratory standards. For the calibration of the Aerolaser instruments, two 1 ppm CO standards from Deuste-Steininger are used. Table 5 shows an overview of the standards available at ZSF. The data refers to the following calibration scales: CO: WMO-2004, CH_4: NOAA-04, CO_2: WMO X2007, N_2O: NOAA-2006.

Table 5. CO, CO_2, CH_4 and N_2O Standards at ZSF.

Cylinder ID	Type	CO (ppb)	U_{CO} (ppb)	CH_4 (ppb)	U_{CH4} (ppb)	CO_2 (ppm)	U_{CO2} (ppb)	N_2O (ppb)	U_{N2O} (ppb)
CA04543	NOAA	103.8	0.7	1700.10	0.07	365.75	0.01	310.21	0.13
CA04555	NOAA	155.1	1.1	1791.20	0.14	378.80	0.04	313.34	0.13
CA04552	NOAA	301.9	2.1	1903.72	0.30	395.86	0.04	326.33	0.12
CA05606	NOAA	206.2	2.1	1847.72	0.34	374.30	0.00	328.91	0.15
CA05769	NOAA	389.0	7.2	1946.81	0.20	393.80	0.00	340.39	0.15
CA05775	NOAA	115.6	1.2	1813.77	0.23	362.40	0.02	298.83	0.15

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri).
Instrument check list:	Daily check list.
Inlet filter exchange:	Every 2 weeks, more often in case of pollution episodes.
Instrument service:	Once per year an overhaul of the optical system is done by qualified service personnel of Aerolaser GmbH.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

The Aerolaser instruments were integrated into the DAQAS system. The PeakPerformer 1 was integrated into the data acquisition system of the 'Klima-GC', which is based on the ChemStation software (Agilent ChemStation Rev. B.03.01, 2001-2007). Peak area, peak height and retention times are written into a report file which can be used for further evaluation. Custom made software (GC organizer) is used to calculate the mixing ratio corresponding to the peak area or peak height. For the final data evaluation, CH_4, CO_2, N_2O and SF_6 are analysed based on peak area, and H_2 and CO based on peak height. A description of the system is given in the Master thesis of Luisa Müller [2009].

Data Treatment

Data-processing is done by self-programmed software which allows data review, flagging and archiving. The quality of the data is assessed using data visualization, calculation of statistical parameters and trajectories. Entries in the station log book are also considered for data validation.

Documentation

All information is entered in electronic log books and checklists. The information was comprehensive and up-to-date. The instrument manuals were 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 the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 17 below.

Setup and Connections

Table 9 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the ZSF data acquisition system.

Table 6. Experimental details of ZSF CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 17.	
Station Analyser (AL)	
Model, S/N	Aerolaser AL5002#148 (main CO analyser) and AL5001#145 (backup CO analyser)
Principle	Vacuum UV Fluorescence (VURF)
Drying system	PERMAPURE Nafion drier in sample line
Calibration settings	Frequent calibrations using a working standard
Model, S/N	PeakPerformer 1 (GC System, University of Heidelberg) Remark: Not considered for the audit, reason see above.
Principle	GC/HgO Reduction Gas Detector
Calibration settings	Frequent calibrations using a working standard (every 15 minutes). In addition the instrument requires the run of a dilution series every 4 weeks or after every change of the UV lamp.
Comparison procedures	
Connection	Aerolaser: WCC-Empa TS were measured using the sample inlet, including the Nafion drier with excess flow GC: WCC-Empa TS were connected to spare calibration gas port.

Results

The results of the assessment are shown in the Executive Summary (figures and equations), and the individual measurements of the TS are presented in Table 7 and Table 8.

Table 7. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Aerolaser AL5002 instrument with the WCC-Empa TS (WMO-2000 CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(11-06-28 14:19:30)	070807_FA02782	155.64	0.40	155.26	0.18	12	-0.38	-0.24
(11-06-28 14:47:00)	100122_FA01469	54.20	0.24	55.39	0.17	17	1.19	2.20
(11-06-28 15:07:00)	110512_FB03374	209.13	0.27	207.90	0.22	17	-1.23	-0.59
(11-06-28 15:27:00)	100204_FA02505	103.90	0.44	102.37	0.23	17	-1.53	-1.47
(11-06-28 15:46:30)	070708_FA02769	90.56	1.92	92.01	0.17	16	1.45	1.60
(11-06-28 16:08:00)	100204_FA02470	53.26	1.24	53.58	0.27	19	0.32	0.60

Table 8. Same as Table 7 for the backup analyser AL 5001.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(11-06-28 14:19:00)	070807_FA02782	155.64	0.40	153.52	0.81	13	-2.12	-1.36
(11-06-28 14:44:00)	100122_FA01469	54.20	0.24	54.46	0.69	23	0.26	0.48
(11-06-28 15:07:00)	110512_FB03374	209.13	0.27	206.04	0.98	17	-3.09	-1.48
(11-06-28 15:27:00)	100204_FA02505	103.90	0.44	102.25	1.11	17	-1.65	-1.59
(11-06-28 15:46:30)	070708_FA02769	90.56	1.92	91.86	0.63	16	1.30	1.44
(11-06-28 16:08:00)	100204_FA02470	53.26	1.24	53.38	1.07	19	0.12	0.23

Conclusions

The current audit showed that the agreement between the main ZSF CO analyser and WCC-Empa was within the GAW DQOS over the relevant mole fraction range. Slightly larger deviations were found for the backup analyser.

Greenhouse Gas Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Same as for CO (PeakPerformer)

Instrumentation

A GC/FID/ECD system built by the University of Heidelberg and a Picarro ESP-1000 CO_2, CH_4 and H_2O analyser is available at ZSF. A detailed description of the instrumental set-up is given in Müller [2009].

Standards

Table 5 (section carbon monoxide) shows an overview of the standards available at ZSF.

Operation and Maintenance

Check for general operation: Daily (Mon – Sun).

No other regular maintenance has been carried until now for the Picarro instrument due to a lack of resources. The GC system is checked for general operation whenever the station is visited. Instrument parameters such as baseline value and noise, cylinder pressures and cold trap are checked and noted in a check list. Data of the previous day(s) is inspected. The calibration of the system is checked every two weeks using the data of the automatic injections of the working standard and the target gas. The stability of the measured target gas values throughout the time within the GAW DQO is used as quality criterion.

Data Acquisition and Data Transfer

The data of the Picarro system has not been actively acquired due to a lack of resources; however, the data was stored on the internal computer of the instrument. Monthly back-up of the data to the central data server were made. GC system: see CO (analogue to PeakPerformer). GC data are mirrored on a second disk. Annual data are transferred to the central data server.

Data Treatment

Until now the Picarro data has not been systematically evaluated by the station staff. GC system: see CO (analogue to PeakPerformer).

Documentation

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

Comparison with WCC-Empa travelling standards

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

Setup and Connections

Table 9 shows details of the experimental setup during the comparison of the transfer standards and the station analysers. The data used for the evaluation was recorded by the station data acquisition system.

Table 9. Experimental details of the comparison.

Travelling standard (TS)	
WCC-Empa Traveling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 17.	
Station Analysers (OA)	
Model, S/N	Picarro ESP-1000
Technique	Cavity Ring Down Spectroscopy (CRDS)
Model, S/N	Klima-GC instrument (GC System, University of Heidelberg)
Principle	GC/HgO Reduction Gas Detector
Calibration settings	Frequent calibrations using a working standard (every 15 minutes)
Comparison procedures	
Connection	GC system: The TS were connected to a spare calibration gas port. Picarro: The TS were sampled through the sample inlet of the analyser.

Results

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

Table 10. CH_4 aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Picarro ESP-1000 instrument (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(11-06-28 15:18:30)	070807_FA02782	1787.47	0.28	1781.23	0.15	18	-6.24	-0.35
(11-06-28 15:41:00)	100122_FA01469	1836.34	0.08	1829.32	0.11	23	-7.02	-0.38
(11-06-28 16:03:30)	110512_FB03374	2762.84	0.09	2752.10	0.20	18	-10.74	-0.39
(11-06-28 16:23:30)	100204_FA02505	2000.37	0.19	1992.88	0.19	18	-7.49	-0.37
(11-06-28 16:44:00)	070708_FA02769	1714.92	0.62	1709.48	0.14	17	-5.44	-0.32
(11-06-28 17:05:00)	100204_FA02470	1830.76	0.04	1823.85	0.22	21	-6.91	-0.38

Table 11. CO_2 aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Picarro ESP-1000 instrument (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(11-06-28 15:18:30)	070807_FA02782	394.24	0.01	392.72	0.02	18	-1.52	-0.39
(11-06-28 15:41:00)	100122_FA01469	393.40	0.02	391.83	0.03	23	-1.57	-0.40
(11-06-28 16:03:30)	110512_FB03374	378.72	0.03	377.27	0.03	18	-1.45	-0.38
(11-06-28 16:23:30)	100204_FA02505	366.39	0.02	364.98	0.03	18	-1.41	-0.38
(11-06-28 16:44:00)	070708_FA02769	363.18	0.02	361.74	0.02	17	-1.44	-0.40
(11-06-28 17:05:00)	100204_FA02470	342.71	0.02	341.38	0.02	21	-1.33	-0.39

Table 12. CH_4 aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Klima-GC instrument (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(11-06-30 14:58:16)	100204_FA02470	1830.76	0.04	1829.05	0.99	27	-1.71	-0.09
(11-06-29 17:59:29)	100204_FA02505	2000.37	0.19	1996.82	0.72	25	-3.55	-0.18
(11-06-30 22:11:20)	070808_FA02769	1714.92	0.62	1716.56	0.89	24	1.64	0.10
(11-06-30 02:01:30)	070807_FA02782	1787.47	0.28	1787.67	0.64	26	0.20	0.01
(11-06-29 11:35:24)	110512_FB03374	2762.84	0.09	2757.94	0.84	20	-4.90	-0.18
(11-07-05 02:47:57)	100122_FA01469	1836.34	0.08	1836.29	1.14	22	-0.05	0.00

Table 13. CO_2 aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Klima-GC instrument (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(11-06-30 15:22:42)	100204_FA02470	342.71	0.02	343.13	0.05	24	0.42	0.12
(11-06-29 18:15:47)	100204_FA02505	366.39	0.02	366.32	0.07	23	-0.07	-0.02
(11-06-30 23:00:13)	070808_FA02769	363.18	0.02	363.59	0.04	18	0.41	0.11
(11-06-30 01:45:09)	070807_FA02782	394.24	0.01	394.26	0.05	28	0.02	0.01
(11-06-29 11:43:32)	110512_FB03374	378.72	0.03	378.89	0.06	19	0.17	0.04
(11-07-05 02:47:57)	100122_FA01469	393.40	0.02	393.45	0.12	22	0.05	0.01

Table 14. N_2O aggregates computed from single analysis (mean and standard deviation of mean using 1-min data) for each level during the comparison of the Klima-GC instrument (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(11-06-30 14:50:06)	100204_FA02470	269.80	0.15	274.14	0.18	28	4.34	1.61
(11-06-29 17:51:21)	100204_FA02505	294.75	0.04	294.97	0.12	26	0.22	0.07
(11-06-30 22:03:10)	070808_FA02769	307.65	0.03	309.62	0.18	25	1.97	0.64
(11-06-30 01:45:09)	070807_FA02782	325.87	0.11	324.23	0.17	28	-1.64	-0.50
(11-06-29 11:27:14)	110512_FB03374	311.76	0.03	309.95	0.12	21	-1.81	-0.58
(11-07-05 02:47:57)	100122_FA01469	322.50	0.10	318.09	0.20	22	-4.41	-1.37

Conclusions

The results of the GC system were within the WMO GAW DQOs for most cylinders in the relevant mole fraction range for CH_4 and CO_2. However, a significantly larger bias was found for N_2O. This instrument needs better linearization of the ECD detector, and an audit by the WCC-N_2O is recommended.

The Picarro ESP-1000 instrument installed at Zugspitze-Schneefernerhaus is a very valuable addition to the existing measurement programme, but the instrument was running without calibration at the time of the audit. The station manager was aware that this needs to be urgently solved, but lack of manpower and a very long delivery delay of the calibration unit ordered from Metcon were the main reasons for this unfortunate situation. Once this has been solved, the Picarro data is expected to better meet the WMO GAW DOQs for CH_4 and CO_2.

As an immediate action, weekly manual calibrations of the instrument were started after the audit, and the calibration unit became finally operation in 2013.

WCC-Empa Traveling Standards

Ozone

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

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

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

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

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 15. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 13). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in [*Klausen et al.*, 2003]).

X_{TS} (ppb) = ([TS] - 0.14 ppb) / 1.0012 (6a)

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

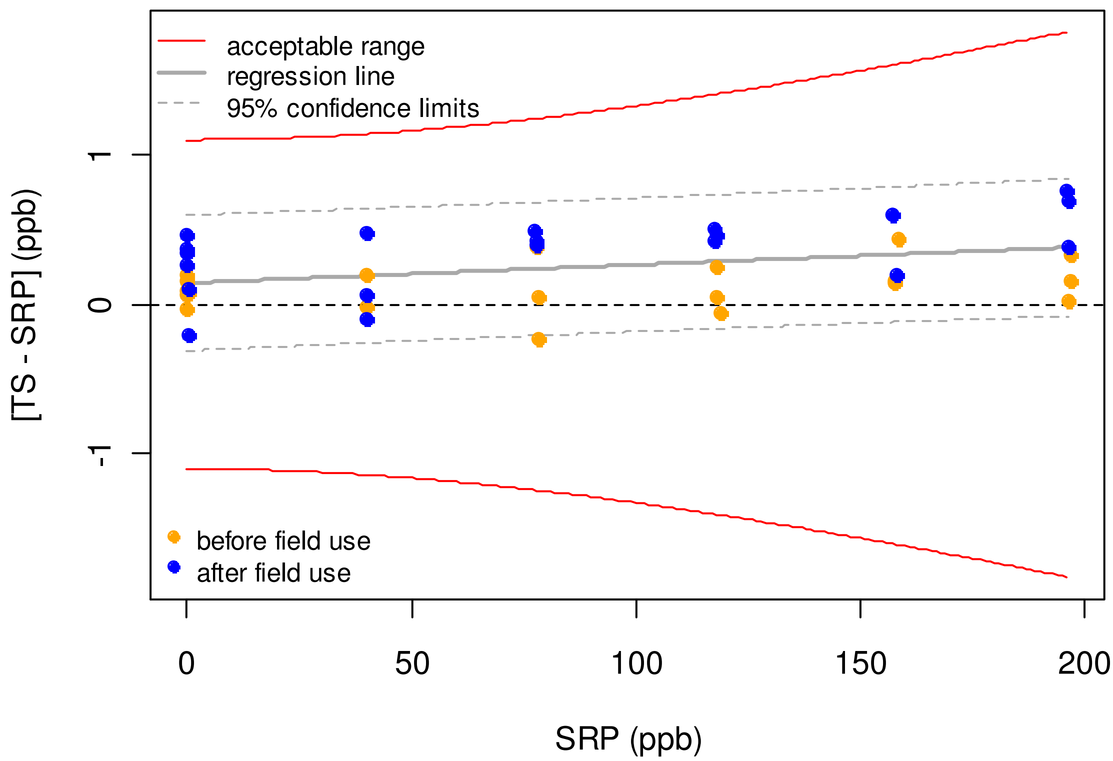

Figure 13. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

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

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

#the level is only indicative.

Greenhouse gases and carbon monoxide

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

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

CO_2: WMO-X2007 scale [*Zhao and Tans*, 2006]

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

N_2O: WMO-2006A

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

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

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

Table 16 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. For internal consistency among the available LS at WCC-Empa, new values have been assigned to the NOAA standards for some tanks. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 17, and Figure 14 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS.

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

Cylinder	CO	sd	CH_4	sd	N_2O	sd	CO_2	sd	CO	sd	CH_4	sd	N_2O	sd	CO_2	sd
	NOAA assigned values								WCC-Empa assigned values							
	(ppb)		(ppb)		(ppb)		(ppm)		(ppb)		(ppb)		(ppb)		(ppm)	
CA05373	130.0*	0.4	1608.57	0.08	NA	NA	326.96	0.00	131.7	0.2	1607.82	0.04	294.11	0.03	326.70	0.01
CC339523	347.9*	0.3	1854.60	0.13	322.49	0.12	396.88	0.06	352.2	0.3	1855.31	0.03	322.49	0.02	396.88	0.02
CC339524	390.7*	0.2	1980.28	0.30	355.40	0.16	795.42	0.06	395.4	0.4	1981.77	0.04	355.24	0.02	796.42	0.04
CC311846	166.4*	0.1	1805.24	0.12	317.27	0.11	377.86	0.04	168.9	0.3	1805.61	0.11	317.27	0.01	377.78	0.02
CA02854	295.5#	3.0	NA	NA	NA	NA	NA	NA	295.3	0.6	1677.14	0.08	NA	NA	347.29	0.03

*WMO-2004, #WMO-2000

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

TS	CO	sdCO	CH_4	$sdCH_4$	CO_2	$sdCO_2$	N_2O	sdN_2O
	(ppb)	(ppb)	(ppb)	(ppb)	(ppm)	(ppm)	(ppb)	(ppb)
100204_FA02470	53.26	1.24	1830.76	0.04	342.71	0.02	269.80	0.15
100204_FA02505	103.90	0.44	2000.37	0.19	366.39	0.02	294.75	0.04
070808_FA02769	90.56	1.92	1714.92	0.62	363.18	0.02	307.65	0.03
070807_FA02782	155.64	0.40	1787.47	0.28	394.24	0.01	325.87	0.11
110512_FB03374	209.13	0.27	2762.84	0.09	378.72	0.03	311.76	0.03
100122_FA01469	54.20	0.24	1836.34	0.08	393.40	0.02	322.50	0.10

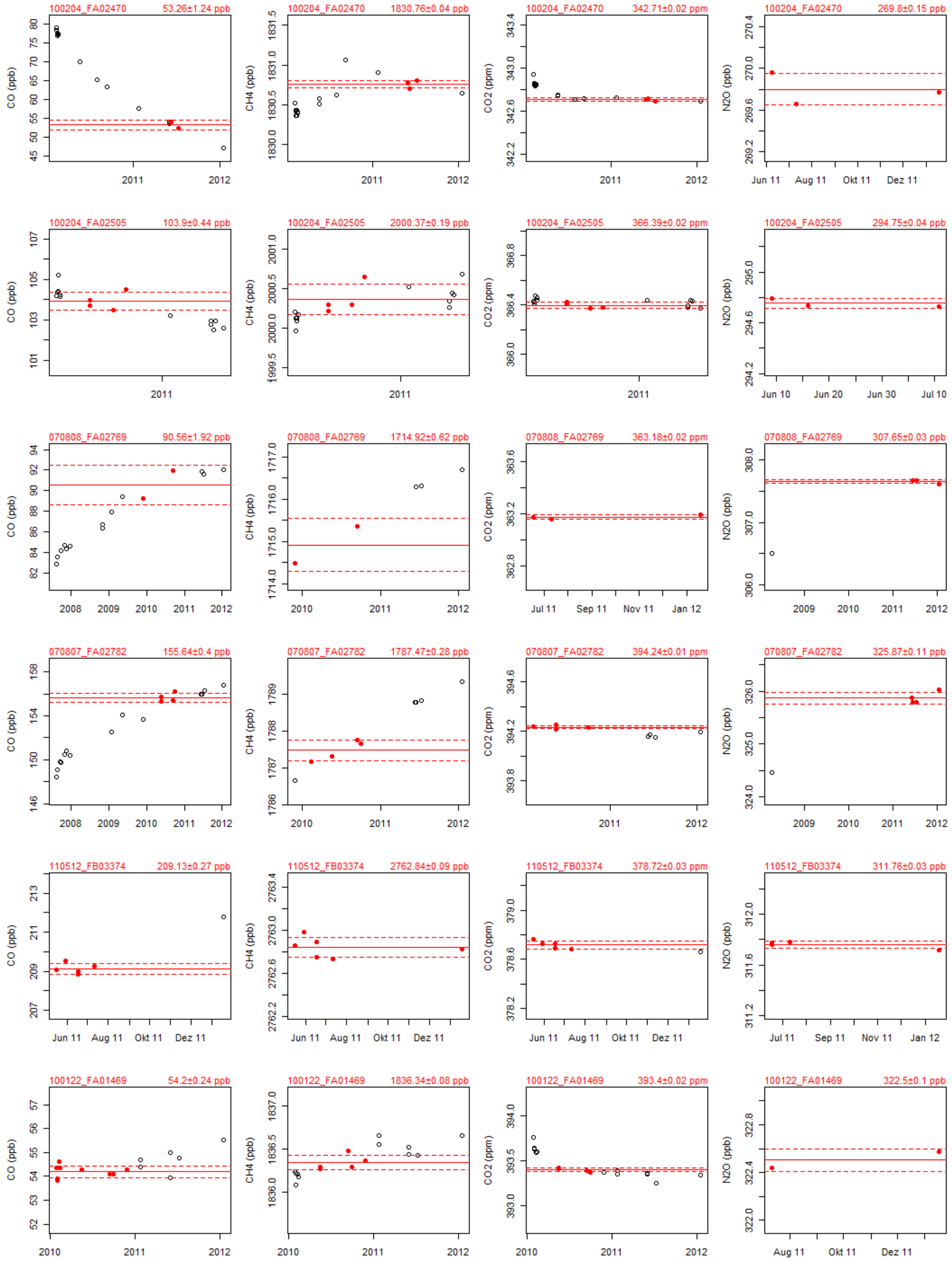

Figure 14. *Results of the WCC-Empa TS calibrations. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.*

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Ozone Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2011-06-28 through 2011-06-29
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0012±0.0010) · [SRP] + (0.14±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #CM08490061
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.0; COEFF = 1.004
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9977±0.0007) · [SRP] + (0.1±0.1)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.1 ppb) / 0.9977
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.77e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	Main ozone analyser
1.8	Reference:	WCC-Empa Report 11/2

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

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Parameter:		Surface Ozone

1.1	Date of Audit:	2011-06-28 through 2011-06-29
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0012±0.0010) • [SRP] + (0.14±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	Horiba APOA-370 #J0006B37
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.0; SPAN = 0.99884
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0162±0.0012) • [SRP] - (0.7±0.1)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.7 ppb) / 1.0162
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.66e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	Backup ozone analyser
1.8	Reference:	WCC-Empa Report 11/2

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

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Ozone Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2011-06-28 through 2011-06-29
1.1	Auditor:	Dr. C. Zellweger
1.2	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i PS #0810-153, BKG -0.2, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0012±0.0010) • [SRP] + (0.14±0.10)
1.6	Ozone Calibrator [OC]	
1.6.1	Model:	TEI 49C-PS #58686-319
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = 0.0; COEF = 1.000
1.6.4	Calibration at start of audit (ppb):	[OC] = (0.9941±0.0006) • [SRP] + (0.0±0.1)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OC] - 0.0 ppb) / 0.9941
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.67e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments: Station calibrator	
1.8	Reference:	WCC-Empa Report 11/2

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

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Carbon Monoxide Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2011-06-28
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2000 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2000 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Aerolaser AL5002#148
1.6.2	Range of calibration:	53 – 209 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9870±0.0077) · X_{CO} + (1.4±1.0)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 1.4) / 0.9870
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (2.6 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	Main CO analyser
1.8	Reference:	WCC-Empa Report 11/2

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

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Carbon Monoxide Audit Executive Summary (ZSF)

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0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2011-06-28
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2000 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2000 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Aerolaser AL5001#145
1.6.2	Range of calibration:	53 – 209 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9767±0.0073) · X_{CO} + (1.7±0.9)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 1.7) / 0.9767
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (2.4 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	Backup CO analyser
1.8	Reference:	WCC-Empa Report 11/2

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

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Methane Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2011-06-29 to 2011-07-05
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	HP6890
1.6.2	Range of calibration:	1715 – 2763 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CH_4 = (0.99470±0.00173) · X_{CH4} + (9.15±3.50)
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 9.15) / 0.99470
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (2.60 ppb^2 + 1.30e-07 * $X_{CH4}{}^2$)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	GC system University of Heidelberg
1.8	Reference:	WCC-Empa Report 11/2

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

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Methane Audit Executive Summary (ZSF)

0.4	Station Name:	Zugspitze-Schneefernerhaus
0.5	GAW ID:	ZSF
0.6	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Methane

1.9	Date of Audit:	2011-06-28
1.10	Auditor:	Dr. C. Zellweger
1.11	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.12	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.13	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.14	Station Analyser:	
1.14.1	Analyser Model:	Picarro ESP-1000 #063-CFADS18
1.14.2	Range of calibration:	1715 – 2763 ppb
1.14.3	Coefficients at start of audit	NA
1.14.4	Calibration at start of audit (ppb):	$CH_4 = (0.99542 \pm 0.00048) \cdot X_{CH4} + (1.80 \pm 0.97)$
1.14.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 – 1.80) / 0.99542$
1.14.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.36 ppb^2 + 1.30e-07 * X_{CH4}^2)
1.14.7	Coefficients after audit	NA
1.14.8	Calibration after audit (ppb):	NA
1.14.9	Unbiased CH_4 mixing ratio (ppb) after audit:	NA
1.14.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.15	Comments:	Uncalibrated instrument
1.16	Reference:	WCC-Empa Report 11/2

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

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Carbon Dioxide Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2011-06-29 to 2011-07-05
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	HP6890
1.6.2	Range of calibration:	342 – 394 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.99286 \pm 0.00383) \cdot X_{CO2} + (2.83 \pm 1.43)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 – 2.83) / 0.99286$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.07 ppm^2 + 3.28e-08 * X_{CO2}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	GC system University of Heidelberg
1.8	Reference:	WCC-Empa Report 11/2

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

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Carbon Dioxide Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2011-06-28
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro ESP-1000 #063-CFADS18
1.6.2	Range of calibration:	342 – 394 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.99595 \pm 0.00064) \cdot X_{CO2} + (0.06 \pm 0.24)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 - 0.06) / 0.99595$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.003 ppm^2 + 3.28e-08 * X_{CO2}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	Uncalibrated instrument
1.8	Reference:	WCC-Empa Report 11/2

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

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Nitrous Oxide Audit Executive Summary (ZSF)

0.1	Station Name:	Zugspitze-Schneefernerhaus
0.2	GAW ID:	ZSF
0.3	Coordinates/Elevation:	47.416516°N, 10.979651°E (2650 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2011-06-29 to 2011-07-05
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. L. Ries, Mr. R. Sohmer, Mr. S. Knabe
1.4	WCC-Empa N_2O Reference:	NOAA laboratory standards (WMO-2006A scale)
1.5	N_2O Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	HP6890
1.6.2	Range of calibration:	270 – 326 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$N_2O = (0.87233 \pm 0.03905) \cdot X_{N2O} + (38.77 \pm 11.94)$
1.6.5	Unbiased N_2O mixing ratio (ppb) at start of audit:	X_{N2O} (ppb) = (N_2O – 38.77) / 0.87233
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{N2O} (ppb) = sqrt (9.75 ppb^2 + 1.01e-07 * X_{N2O}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased N_2O mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	GC system University of Heidelberg
1.8	Reference:	WCC-Empa Report 11/2

[N_2O]: Instrument readings; X: mixing ratios on the WMO-2006A N_2O scale.

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LIST OF ABBREVIATIONS

BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DAQ	Data Acquisition System
DQO	Data Quality Objective
dtm	Date/Time
ECD	Electron Capture Detector
FID	Flame Ionisation Detector
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
LS	Laboratory Standard
MFC	Mass Flow Controller
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
TS	Traveling Standard
UPS	Uninterruptible Power Supply
UV	Ultra Violet
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard
ZSF	Zugspitze-Schneefernerhaus
ZUG	Zugspitze summit