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

AT THE

GLOBAL GAW STATION ZEPPELIN MOUNTAIN, NORWAY, SEPTEMBER 2012

World Meteorological Organization

GLOBAL ATMOSPHERE WATCH

EMPA Materials Science & Technology

WCC-Empa Report 12/2

Submitted to the World Meteorological Organization by

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WCC-Empa Report 12/2

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EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The fourth system and performance audit by WCC-Empa[1] at the Global GAW station Zeppelin Mountain was conducted from 30 August - 2 September 2012 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Zeppelin Mountain (ZEP) GAW station is part of the research facilities at Ny Ålesund. Research in Ny Ålesund is coordinated by the Ny-Ålesund Science Managers Committee (NySMAC) and the Svalbard Science Forum (SSF). The measurements at the ZEP site are mainly carried out by the Norwegian Institute for Air Research (NILU) and the Stockholm University (SU).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
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Mr. Chris Lunder	NILU, Station scientist

This report summarises the assessment of the Zeppelin Mountain GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide measurements in particular. The ozone assessment was made according to the method developed by WCC-Empa and QA/SAC Switzerland [*Klausen et al.*, 2003].

This report is distributed to the station manager of the Zeppelin Mountain GAW station and to the World Meteorological Organization in Geneva. It 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 Zeppelin Mountain GAW Station (78.91 N, 11.88 E, 474 m a.s.l.) is located in the European Arctic in the King's fjord on north-western Spitsbergen, which is the largest of the Svalbard islands. The monitoring station was built in 1988/89 on a small plateau east of the top of Zeppelin Mountain. The station is easily accessed by cable car. A new and larger station was built in 1999/2000 at the same location. Several identical air inlets and some meteorological equipment are mounted on the top of the roof and the nearby tower. Before the first station at Zeppelin Mountain was built NILU had operated a measuring site for many years in Ny-Ålesund. However, this site was influenced by local pollution of Ny-Ålesund, particularly during low wind and inversion conditions. Ny-Ålesund is permanently maintained by about 30 people and additional approx. 150 scientists during summer peak season. Further information is available from the following web sites:

[1] WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide. 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.

GAWSIS:
http://gaw.empa.ch/gawsis

NILU station web site:
http://www.nilu.no/Miljøovervåkning/Zeppelinobservatoriet/tabid/214/language/en-GB/Default.aspx

SU station web site:
http://www.itm.su.se/zeppelin/index.html

The location is adequate for the intended purpose. Year-round access to ZEP is possible by the cable car.

Station Facilities

Zeppelin Mountain offers appropriate laboratory and office facilities with internet access. No sanitary facilities are available at the site. The laboratories are air-conditioned. ZEP provides an ideal platform for continuous atmospheric research as well as smaller measurement campaigns.

Station Management and Operation

The station is visited during working days by the station operators for routine work. NILU and SU scientists and technicians visit the station whenever needed. Usually, several visits per year are made. All facilities at Ny Ålesund are managed by Kings Bay AS (www.kingsbay.no). Kings Bay AS manages all necessary services in the community such as the provision of food, electricity and water. Kings Bay is also responsible for the infrastructure in Ny-Ålesund and runs the settlement throughout the year. The measurements made at the ZEP site are mainly coordinated by NILU and SU.

Air Inlet Systems

All instruments are connected to different air inlets. The inlet systems as well as the materials used are adequate. Refer to the Appendix for details of the air inlets.

Surface Ozone Measurements

The surface ozone measurements at Zeppelin Mountain were established in 1989 and continuous time series are available since then.

Instrumentation. The station is currently equipped a Teledyne API 400E ozone analyser. The instrumentation is fully adequate for its intended purpose.

Standards. No ozone standard is available at ZEP, but NILU uses a travelling standard (TEI 49C-PS) for calibrations at the site once per year. The NILU standard is traceable to the standard reference photometer maintained at SU. Usually, yearly calibrations are made.

Intercomparison (Performance Audit). The ZEP ozone analyser was compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The results of the comparisons are summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) [*WMO*, 2013]. The data was acquired by the WCC-Empa data acquisition system (TS) and the ZEP data acquisition, and no further corrections were applied. The following equations characterise the bias of the instruments:

API 400E #1136 (Offset -1.0 ppb, Slope 1.017):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.28 ppb) / 1.0102 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.10 ppb^2 + 2.66e-05 * $X_{O3}{}^2$) (1b)

The results of the comparison are further presented in Figure 1.

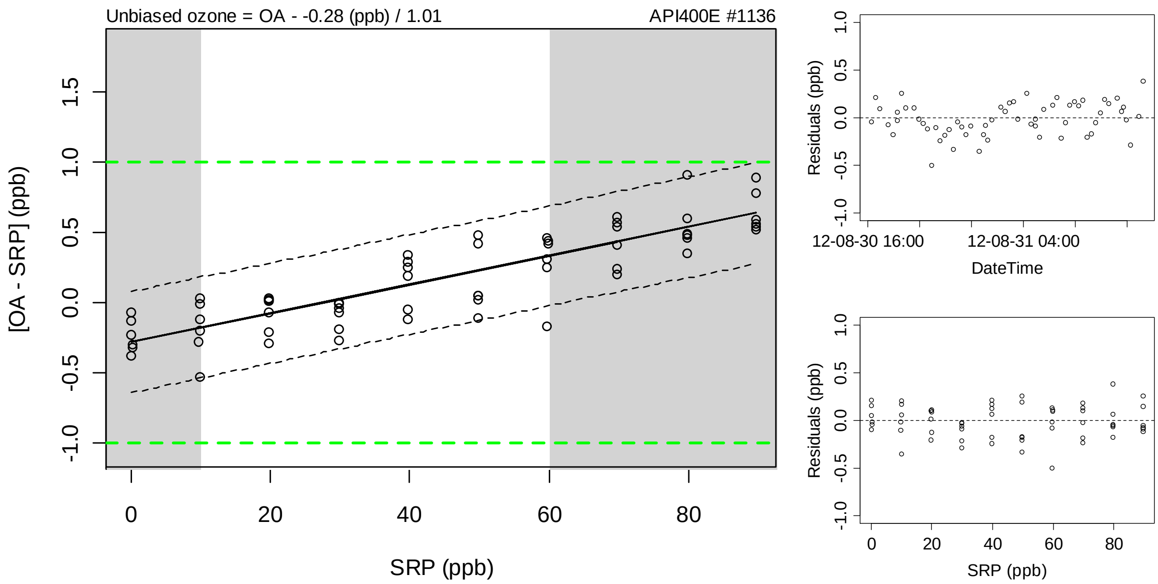

Figure 1. *Left: Bias of the ZEP ozone analyser (API 400E #1136) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The white area represents the mole fraction range relevant for ZEP, whereas the green lines correspond to the DQOs. 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).*

The results of the comparison can be summarised as follows: The API 400E ozone analyser is in good calibration and adequate for ozone measurements. No further actions are required.

Carbon Monoxide Measurements

Continuous measurements of CO at ZEP started in 1994 using gas chromatography (GC) / Mercuric Oxide Reduction (RGD) detection. Continuous time series of this instrument are available since then with a few gaps. Two Cavity Ring Down Spectroscopy (CRDS) instruments were additionally installed in 2012 by NILU.

Instrumentation. RGA-3 GC/RGD (Trace Analytical Inc.), Picarro G2401, Picarro G2302. The Picarro G2302 instrument was not running at the time of the audit due to a broken pump. The instrumentation is adequate for the measurement of CO.

Standards. Currently, two NOAA CO standards (WMO-2004 scale) are available at ZEP. A set of four additional NOAA CO standards was ordered in 2011 but these standards have not yet been delivered to ZEP by NOAA. The standards are used for both the RGA-3 and Picarro instruments.

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the ZEP instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. For the RGA-3 instrument, two data sets are presented: The first analysis was made using a one point calibration using the working standards, whereas the second analysis was done with a two point calibration with NOAA standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 2 - Figure 4 with respect to the WMO GAW DQOs [WMO, 2010; 2011]:

Picarro G2401 #948-CFKADS2019 (CRDS CO analyser):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 2.5 / 1.0147 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.9 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

RGA-3, #020190-005 (GC/RGD), one point calibration:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 11.4) / 1.0964 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (4.7 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

RGA-3, #020190-005 (GC/RGD), two point calibration with two ZEP NOAA standards:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 3.7) / 1.0358 (2e)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (4.7 ppb^2 + 1.01e-04 * X_{CO}^2) (2f)

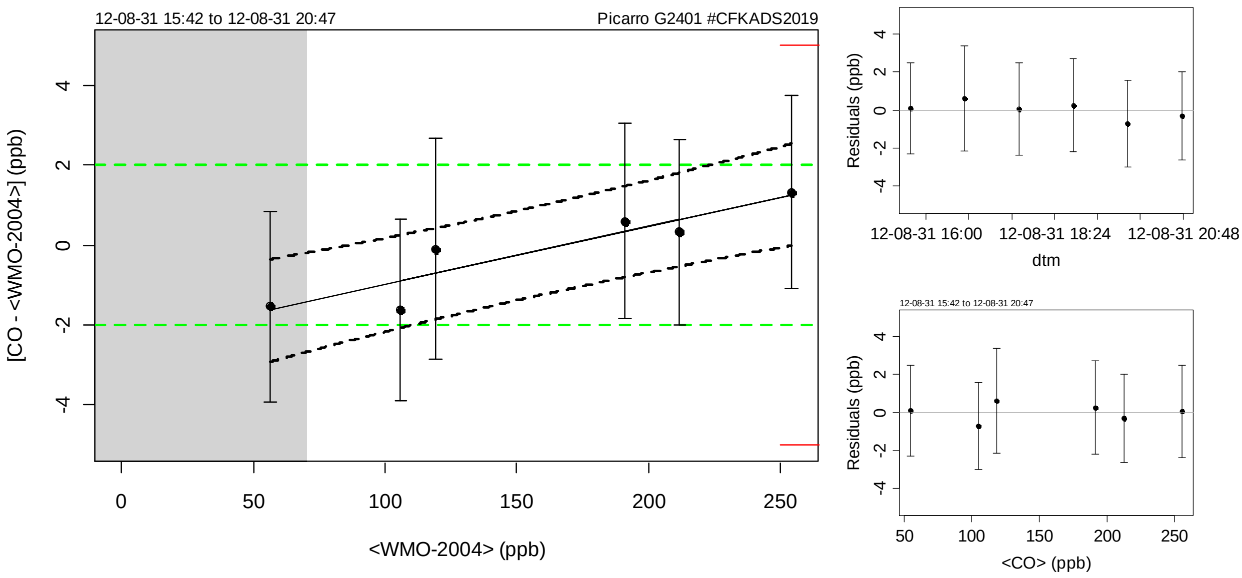

Figure 2. *Left: Bias of the ZEP Picarro G2401 carbon monoxide instrument with respect to the WMO2004 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZEP, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

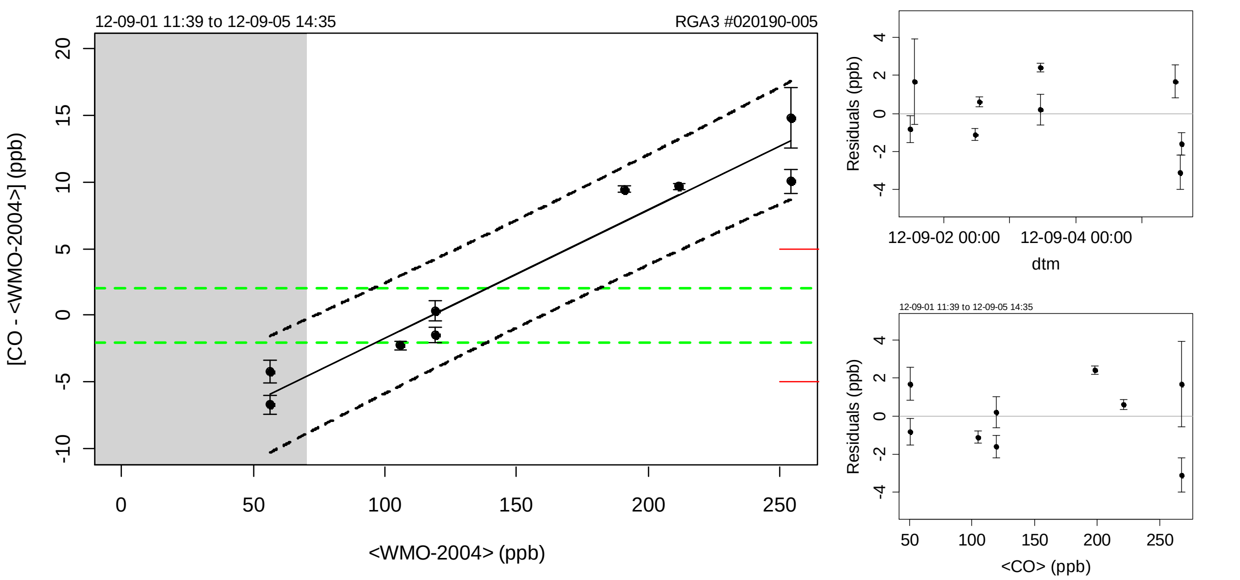

Figure 3. *Same as above for the RGA-3 instrument. RGA-3 results based on a one point calibration of the instrument.*

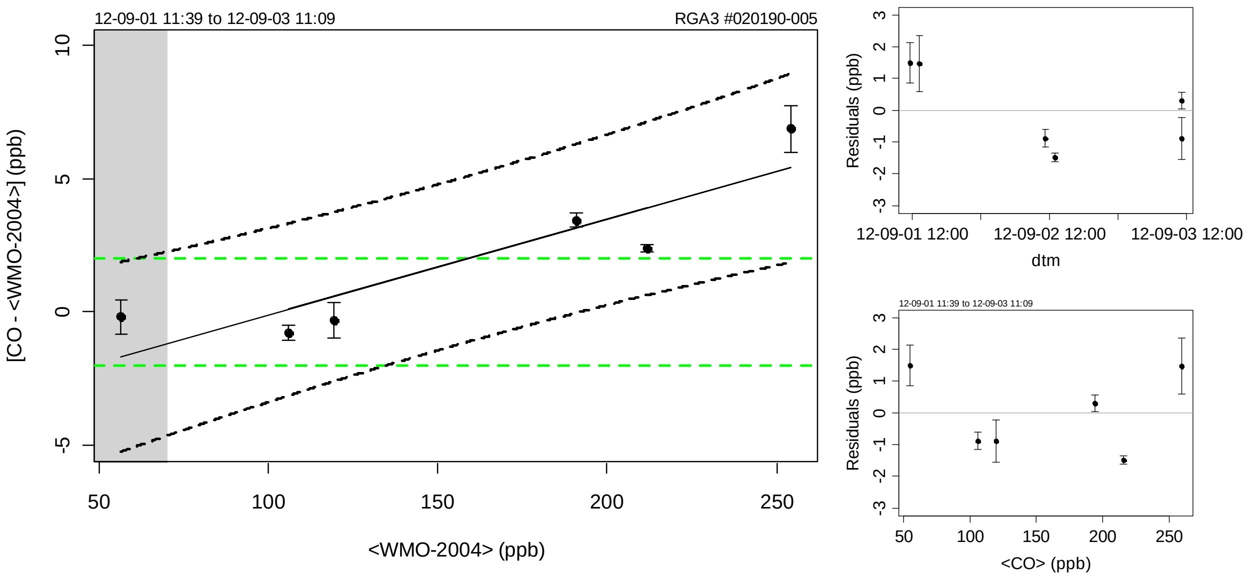

Figure 4. *Same as above, but RGA-3 results based on a two point calibration of the instrument.*

The results of the comparisons can be summarised as follows:

Good agreement within the WMO/GAW DQOs of ±2 ppb was found between the Picarro G2401 analyser and the WCC-Empa TS. These CO measurements should be continued without modification of the current set-up.

The first analysis of the RGA-3 data using a one point calibration instrument showed only good agreement at mole fractions between 100 and 140 ppb CO; after this a two point calibration was applied which significantly improved the agreement over the entire range. However, the response function of the instrument is still not sufficiently well characterised for the measurement of CO mole fractions above 150 ppb.

Recommendation 1 (3, important, 2013)**
The linearity of the RGA-3 instrument needs to be re-assessed for mole fractions up to 300 ppb CO.

Methane Measurements

Continuous measurements of CH_4 at ZEP started in 1997 using GC / flame ionization detection (FID). Two Cavity Ring Down Spectrometers (CRDS) were additionally installed in 2012 by NILU.

Instrumentation. Hewlett Packard 5890 Series II with FID, Picarro G2401, Picarro G2302. The instrumentation is adequate for the measurement of CH_4. At the time of the audit, the GC/FID instrument was not running properly; the problem started in July 2012 and could not be fixed during the audit. The WCC-Empa TS were measured on this system but the deviations were large.

> **Recommendation 2 (***, important, 2013)**
> *The methane GC/FID system was not working during the audit. A decision has to be made if these measurements should be continued since the performance of the CRDS instrument is much better compared to a GC/FID system. Update April 2013: The system was repaired in March 2013 and will be run for another few weeks. After that, the GC/FID measurements will be stopped.*

Standards. A set of three NOAA standards (NOAA-04 scale) spanning the mole fraction range from 1845 to 1947 ppb methane is available at ZEP. A control tank is run every third day and a second control tank every thirty days to check for standard drift.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the ZEP instruments with randomised methane levels from traveling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below. The HP 5890 Series II could not be properly assessed due to the above reasons.

The following equation characterises the instrument bias. The result is further illustrated in Figure 5 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Picarro G2401 #948-CFKADS2019 (CRDS CH_4 analyser):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 11.3) / 0.99392 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.2 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

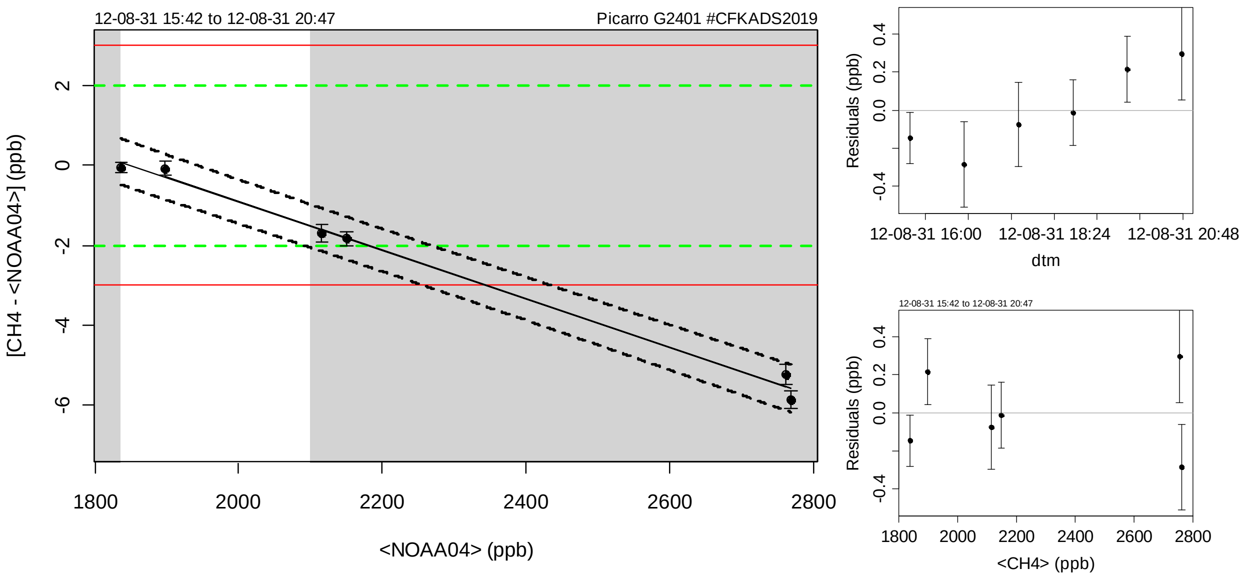

Figure 5. *Left: Bias of Zeppelin Mountain Picarro G2401 methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZEP, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The results of the comparisons can be summarised as follows:

Good agreement within the WMO/GAW DQOs of ±2 ppb was found between the Picarro G2401 analyser and the WCC-Empa TS in the relevant mole fraction range. A slightly larger bias was found for TS with high mole fractions, indicating that the instrument calibration could be improved using multipoint calibration spanning a wider mole fraction. The GC/FID instrument could not be assessed due to instrument problems at the time of the audit. However, comparisons that were made by NILU between the GC/FID and the CRDS instruments before July 2012 indicated good agreement between the two system while the CRDS analyser showed significantly less analytical noise.

Recommendation 3 (, important, 2013)**
It is recommended to calibrate the Picarro G2401 instrument with at least two standards spanning a wide mole fraction range. The standards currently available at ZEP span only the mole fraction range from 1845 – 1947 ppb CH_4.

Carbon Dioxide Measurements

Continuous measurements of CO_2 operated by the Stockholm University / Department of Applied Environmental Science) commenced in 1988 at ZEP, and continuous data is available since then. Additional CO_2 measurements are made by NILU since 2012.

Instrumentation. Stockholm University: LI-COR LI-7000 NDIR analyser. NILU: Picarro G2401, Picarro G2302 (this instrument was not working during the audit). The instrumentation is adequate for the measurement of CO_2.

Standards. Stockholm University: 3 working standard (WS) as well as a NOAA primary laboratory standard are available at ZEP. The WS were calibrated at SU against a set of 5 NOAA standards in 2007 (WMO-X2007 scale). The WS are run every 2 hours to calibrate the measurements of the LI-COR system. NILU: No standards for CO_2 are currently available at ZEP for the NILU instruments. The SU NOAA standard was used to calibrate the NILU Picarro systems.

> **Recommendation 4 (***, critical, 2013)**
> *CO_2 NOAA standards must be purchased for the NILU Picarro instruments. It is recommended to span a relatively wide mole fraction range, e.g. 360 – 450 ppm. In addition, at least one working and one target tank should be available for regular checks of the instruments.*

Intercomparison (Performance Audit). The comparison involved repeated challenges of the ZEP instruments with randomised CO_2 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 LI-COR LI-7000 and the Picarro G2401. The results is further illustrated in Figure 6 and Figure 7 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Picarro G2401 #948-CFKADS2019 (NILU CRDS CO_2 analyser):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 + 0.25) / 1.0012 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.00 ppm^2 + 3.28e-08 * X_{CO2}^2) (4b)

LI-COR LI-7000 (SU NDIR analyser):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 3.59) / 0.9900 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.16 ppm^2 + 3.28e-08 * X_{CO2}^2) (4d)

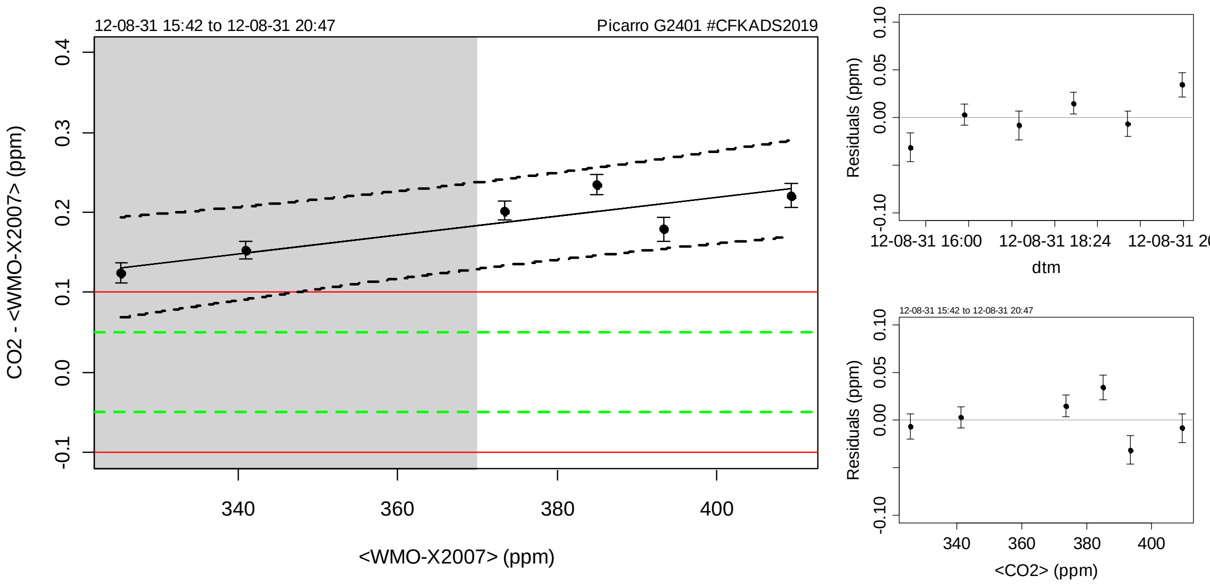

Figure 6. *Left: Bias of Zeppelin Mountain Picarro G2401analyser (NILU) with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for ZEP, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

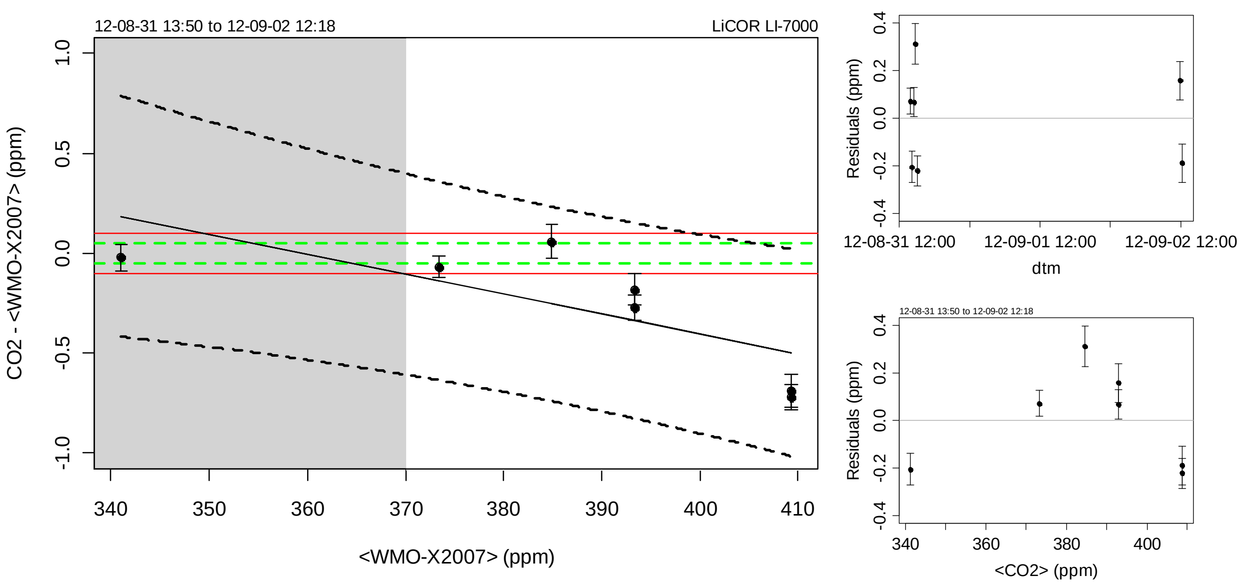

Figure 7. *Same as above for the LI-COR LI-7000.*

The results of the comparison can be summarised as follows:

Slightly higher CO_2 measurements compared to the WCC-Empa TS were observed with the NILU Picarro G2401 instrument. About half of the bias might be explained with differences in the calibration standards (difference between the SU standard and WCC-Empa measurements), whereas the remaining bias of approx. 0.1 ppm needs further investigation.

The LI-COR LI-7000 NDIR instrument agreed well for the comparisons with the travelling standards with lower CO2 mole fractions up to 385 ppm, and slightly larger deviations were observed for higher mole fractions. Part of the difference (approx. 0.1 ppm might be explained by the uncertainty of the NOAA reference and the working standards. It is recommended to recalibrate the WS and the NOAA standard at SU.

Recommendation 5 (, important, 2013)**
The CO_2 calibration of the NILU Picarro should be checked with additional standard gases over the relevant mole fraction range (370 – 420 ppm).

Recommendation 6 (, important, 2013)**
It is recommended to re- check the linearity of the CO_2 NDIR system over the mole fraction range of 370 – 420 ppm CO_2. For this purpose, the calibration of the existing standards (WS and NOAA) should be confirmed at SU. Alternatively, additional standards might be brought to the ZEP station.

Recommendation 7 (, important, ongoing)**
Continuation of the ZEP CO_2 measurements is highly recommended, since it is one of the longest time series in Europe. Since NILU also started with CO_2 measurement recently, strong collaboration between SU and NILU is regarded as important (e.g. data comparison, exchange of standards etc.).

Nitrous Oxide Measurements

Continuous measurements of N_2O at ZEP were made in the 1990s and were re-started recently. At the time of the audit, the N_2O system was not running due to problems with the pressure control of the GC system (same GC as for CH_4 which could also not be assessed). The WCC-Empa TS were run on the instrument but the deviations were large, and no clear pattern could be recognised. The system was repaired in March 2013 and should be running now.

Recommendation 8 (, important, 2014/15)**
Since the performance of the instrument could not be assessed by WCC-Empa, a follow-up audit by WCC-N_2O is recommended.

Parallel Measurements of Ambient Air

The audit included parallel measurements of CO, CH_4 and CO_2 with a WCC-Empa travelling instrument (TI) (Picarro G2401) that was run over the period from 5 September through 1 October 2012. The travelling instrument was connected to an identical but unused separate inlet (WCC Inlet). In addition, the same inlet as the ZEP system was used. The Picarro G2401 was calibrated every 30 h using one working standard, and two additional tanks were used as target cylinders (CH_4 and CO_2). Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data. The maximum drift between two WS measurements was approx. 0.5 ppb for CH_4 and <0.02 ppm for CO_2. For CO, three working tanks were used to calibrate the instrument. No significant drift was observed for CO, and no further corrections were applied. The sample air of the WCC-Empa Picarro G2401 was not dried, and a water vapour correction as described by Rella et al. [2013] was applied. The following Figures show the results of the ambient air comparisons.

Carbon monoxide:

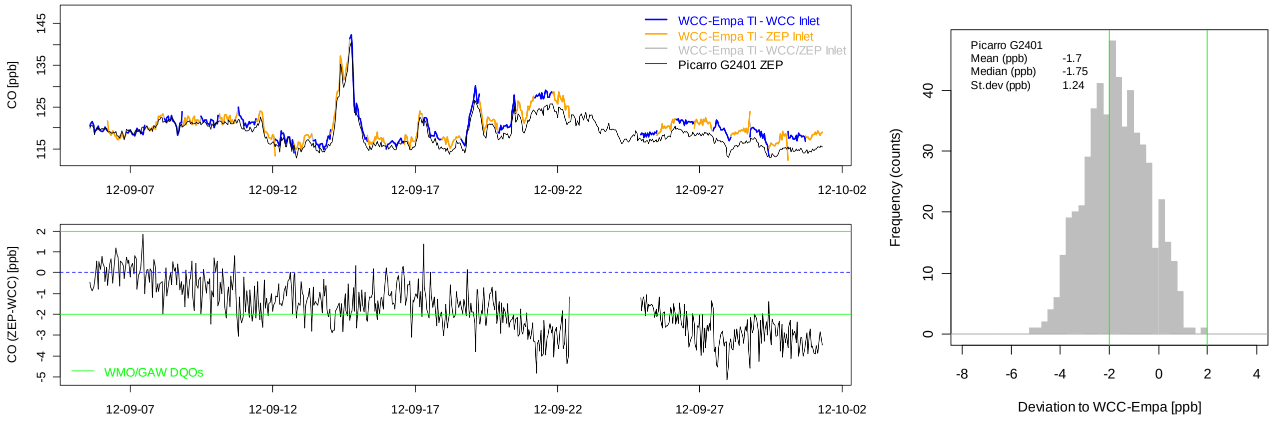

Figure 8. *Upper left panel: CO time series (hourly averages) measured at ZEP with the Picarro G2401 travelling instrument and the Picarro G2401 system of NILU. Lower left panel: Deviation of the ZEP system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

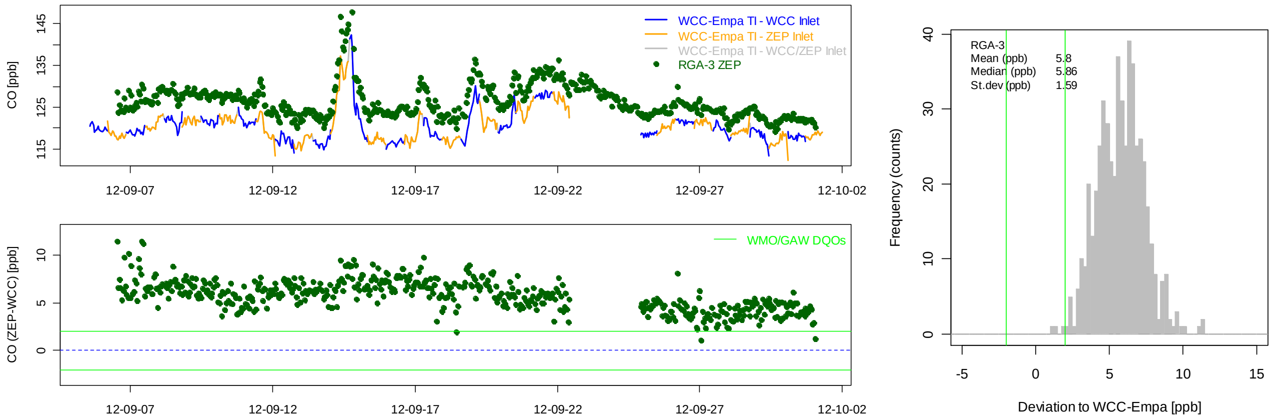

Figure 9. *Same as above for the RGA-3 CO instrument.*

It can be seen that the agreement between the two Picarro systems was very good during the first few days of the comparison. Most likely, the WCC-Empa travelling instrument was slightly drifting, and the bias between the two instruments became larger towards the end of the comparison campaign. A more significant bias was observed between the two Picarro instruments (WCC and ZEP) and the RGA-3. This was not expected because the agreement for the performance audit of the RGA-3 instrument was relatively good for the CO mole fraction range measured during the comparison campaign. The reason for the bias needs to be assessed.

Methane:

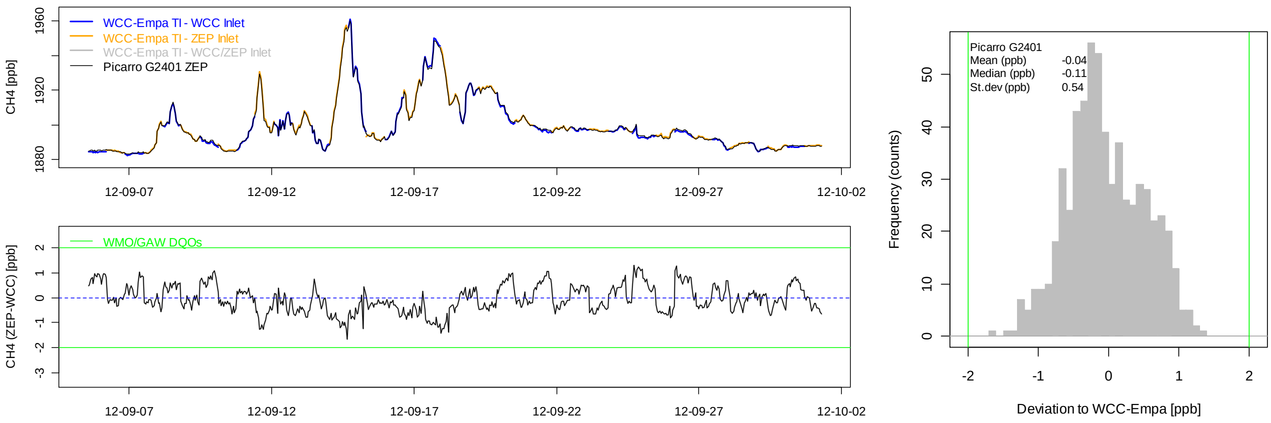

Figure 10. *Upper left panel: CH_4 time series (hourly averages) measured at ZEP with the Picarro G2401 travelling instrument and the Picarro G2401 system of NILU. Lower left panel: Deviation of the ZEP system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

Very good agreement was found between the two Picarro G2401 CH_4 measurements, with an average deviation of -0.04±0.12 ppb of the ZEP instrument compared to WCC-Empa (all data). However, a small difference was observed between the two inlets, which is further illustrated in Figure 11.

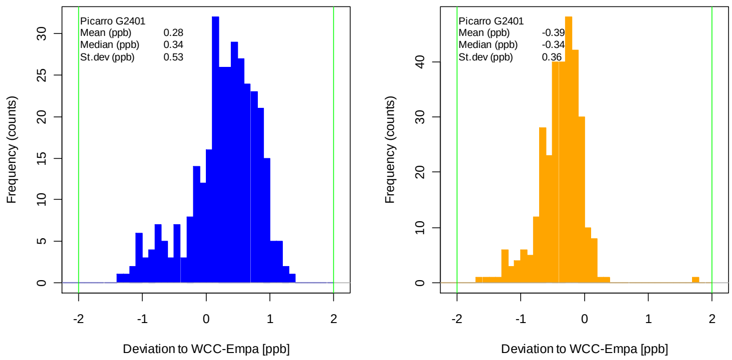

Figure 11. *Right panel: Frequency distribution of the CH_4 deviation ZEP-WCC for the periods when the WCC instrument was connected to the independent inlet. Same as left panel, both instruments connected to ZEP inlet.*

The deviation that was found for the periods when both instruments were connected to the ZEP inlet corresponds well with the results of the TS comparisons. The fact that the ZEP inlet values were higher indicates a potential leak in one of the inlet system or more likely in the connections between the manifold and the instrument. Since methane mole fractions are usually higher inside the laboratory, a very small leak in the ZEP inlet or in the connections of the Picarro analyser cannot be excluded. A further indication for a leak is the fact that no differences were observed for the CO_2 measurements between the two inlets. The methane mole fraction inside the laboratory is expected to be significantly elevated due the exhaust of the GC/ECD carrier gas.

Recommendation 9 (, important, 2013)**
The fittings / connections between the Picarro analyser and the inlet line should be checked for tightness.

Carbon dioxide:

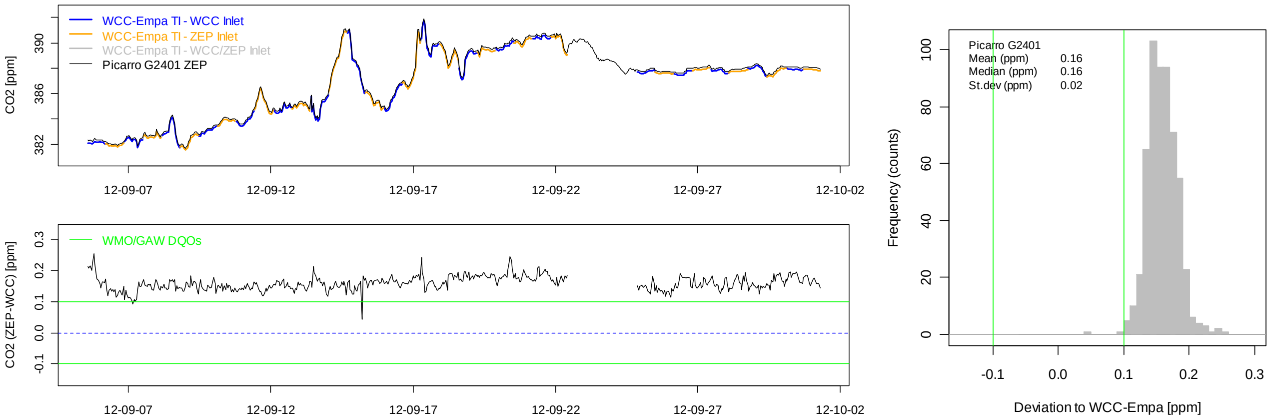

Figure 12. *Upper left panel: CO_2 time series (hourly averages) measured at ZEP with the Picarro G2401 travelling instrument and the Picarro G2401 system of NILU. Lower left panel: Deviation of the NILU system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

The NILU CO_2 measurements were by 0.16 ppm higher compared to the WCC-Empa travelling standards. This is in very good agreement with the results of the TS comparison, which indicate a bias of approx. 0.2 ppm at CO_2 mole fractions of 385 ppm. In contrast to CH_4, no difference was observed between the two inlets.

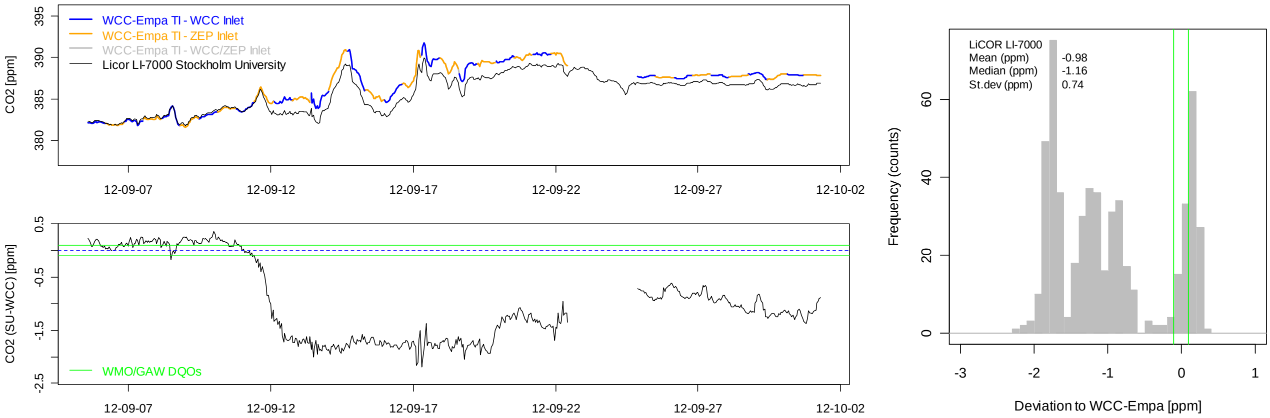

Figure 13. *Same as above for the LI-COR LI-7000 CO_2 analyser.*

The following conclusions can be drawn from the ambient air comparison results:

CO_2, NILU instrument (Picarro G2401): The small positive bias that was observed during the comparison of the TS was confirmed by the parallel measurements. Half of the bias can be explained by differences/uncertainty of the NOAA standards, whereas the reason for the remaining approx. 0.1 ppm CO_2 bias could not be identified. Most likely, the reason is related to the Nafion dryer. During calibration of the NILU instrument, the standard gas is slightly humidified (diluted) by the Nafion dryer, which potentially explains the observed bias.

Recommendation 10 (, important, 2013)**

The influence of the Nafion drier on the CO_2 measurements needs to be re-assessed. It must be made sure that the drying has no influence on the calibration of the instrument.

CO_2, SU instrument (LI-COR LI-7000): The parallel measurement showed that the instrument is very sensitive to humidity changes. For this reason, a magnesium perchlorate dryer is used. During the comparison campaign, water break through occurred, which resulted in significantly low CO_2 values of the SU instrument. In addition, the performance of the NDIR instrument is not as good as of the CDRS system. The following recommendations are made:

Recommendation 11 (*, critical, ongoing)**
It must be made sure that the water traps are well maintained and timely exchanged. If water break through occurs, all data must be flagged as invalid.

Recommendation 12 (*, minor, 2014)
The parallel measurements between SU and NILU are currently valuable to assess the quality of both instruments / time series. After a sufficiently long overlap of the two analysers is available (e.g. one year), it could be considered to discontinue the NDIR system and use the resources for other measurements.

Data Acquisition and Management

Data of the gas chromatograph system (greenhouse gases and CO) is acquired using GCWerks (GC Soft, Inc.), a GC control software package originally developed at the Scripps Institution for Oceanography (SIO) within the AGAGE programme. Remote access is possible through the internet. Custom made instrument specific software is used for the other instruments (O_3, Picarro, LI-COR). Remote access to the data is possible. All data acquisition systems are appropriate, and no further action is required.

Data Submission

For the parameters of the audit scope, in-situ data for surface ozone (1990 – 2000, NILU), nitrous oxide (1990-1995, NILU) and carbon dioxide (1988-2006, SU) was available at the World Data Centre for Greenhouse Gases (WDCGG) at the time of the audit. The N_2O data from the early 90s is obviously of very poor quality and should be removed from WDCGG. Complete time series were submitted to the EBAS data base (http://ebas.nilu.no/). However, all data found in this data base are in units of $\mu g/m^3$ (or analogue) and therefore is not easily useable for WMO/GAW purposes.

Recommendation 13 (, important, 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. GAWSIS entries need also to be regularly updated by the ZEP station manager. The data at EBAS cannot easily be used for GAW purposes due to units of $\mu g/m^3$ *(or analogue).*

Conclusions

The Global GAW station Zeppelin Mountain has a very comprehensive set of measurements and participates in many international programmes. The combination of long-term measurements and the large number of measured parameters make the ZEP station a very important contribution to the GAW programme. The recent renewal of instruments with up-to-date techniques will help to maintain the high quality of the data provided by ZEP. The assessed parameters were mostly of high quality; however, the GC system for CH_4 and N_2O was not functioning at the time of the audit. Continuation of the ZEP measurement series and the scientific collaboration with external partners is highly recommended.

Summary Ranking of the Zeppelin Mountain GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Remote but all year access
Facilities		
Laboratory and office space	(5)	Adequate research facilities
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully functional
Power supply	(5)	Few power outages
General Management and Operation		
Organisation	(5)	Well organised
Competence of staff	(5)	Highly experienced staff
Air Inlet System (except O_3)	(5)	New tower, fully adequate
Air Inlet System (O_3)	(3)	Location above roof would be preferable
Instrumentation		
Ozone	(5)	Adequate instrumentation
CO (RGA-3)	(3)	Linearity issues
CO (Picarro)	(4)	Adequate instrumentation
CO_2/CH_4 (Picarro)	(5)	State-of-the-art instrument
CO_2 (LI-COR)	(3)	Calibration/stability issues
Standards		
Ozone	(4)	TEI 49i-PS,traceability to SRP
CO	(4)	More NOAA tanks needed
CH_4	(4)	NOAA, larger range needed
CO_2	(3)	More NOAA tanks needed, recalibration of SU tanks
Data Management		
Data acquisition	(5)	Adequate systems
Data processing	(5)	Experienced staff
Data submission	(2)	Only partly submitted

#0: inadequate thru 5: adequate.

Dübendorf, October 2013

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

APPENDIX

Global GAW Station Zeppelin Mountain

Site description and measurement programme

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

http://www.nilu.no/Miljøovervåkning/Zeppelinobservatoriet/tabid/214/language/en-GB/Default.aspx
http://www.itm.su.se/zeppelin/index.html
http://gaw.empa.ch/gawsis/reports.asp?StationID=18
www.kingsbay.no

Trace Gas Distributions at Zeppelin Mountain

The monthly and yearly distribution for surface ozone, carbon monoxide, methane and carbon dioxide at Zeppelin Mountain is shown in Figure 14.

Organisation and Contact Persons

The facilities at the Zeppelin Mountain GAW station are owned and run by Kings Bay AS. Different institutes are using the observatory for research, and measurements at ZEP are mainly carried out by NILU and SU. Technicians and scientist from these institutes visit the station whenever needed.

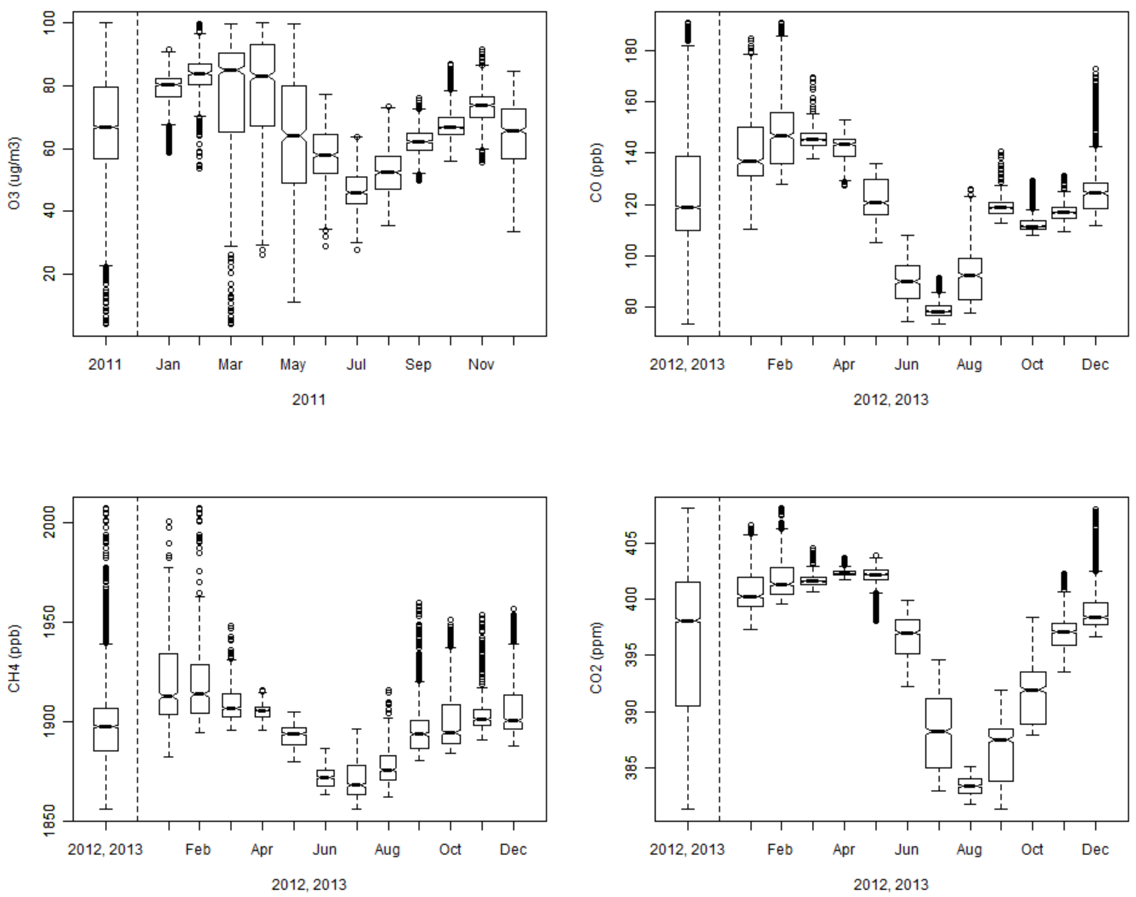

Figure 14. *Yearly and monthly box plots for surface ozone (2011), carbon monoxide, carbon dioxide and methane (May 2012- May 2013). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this 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 laboratories at ZEP are air conditioned.

Air Inlet System

Unchanged since the last WCC-Empa audit in 2005.

Location of air intake:	Outside the building on the west side approx. 1 m from the building wall.
Inlet protection:	Protection against rain water / snow / insects.
Tubing:	Ca. 3.5 m 6 mm PFA line, flow approx. 0.8 l/min.
Inlet filter:	PTFE (Millipore LSWP 5 µm) inlet filter inside API 400E
Residence time:	approx. 4 s

Instrumentation

The station is currently equipped with a Teledyne API 400E analyser. Instrumental details are summarised in Table 1.

Standards

No ozone calibrator is available at the site. Calibrations with a NIST traceable transfer standard (TEI 49C-PS) are made once per year. The NILU transfer standard is calibrated against NIST SRP#11 (SU, Sweden) once per year.

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri) by the station operator.
Zero / Span check:	Weekly, manually by remote access from NILU, level 200 ppb.
Calibration/checks with standard:	Yearly with TEI 49C-PS, no change of calibration settings.
Inlet filter exchange:	Usually every 3 months followed by ozone conditioning.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

No change since last audit. An NDL2 data logger collects data from the ozone monitor every 10 seconds via the RS232 serial interface. The data is automatically transferred to NILU once per hour using the ISDN telephone line. The current system will soon be replaced. Ozone data is acquired in UTC+1.

Data Treatment

Data is evaluated by the station technicians at NILU using custom made data evaluation software (visual inspection, consistency checks using additional parameter such as zero/span checks, meteorological data, and statistical checks). No changes were made since the last WCC-Empa audit.

Documentation

Electronic station and instrument logbooks were available at the site. 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 transfer standard was used for 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 (TS) and the station data acquisition system (OA).

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)	
Model, S/N	API 400E #1136
Principle	UV absorption
Range	0-1 ppm
Settings	Offset = -1.0; Span = 1.017
Pressure readings (hPa)	Ambient 960.0, OA 877.1 under operating conditions, no adjustments were made

Results

Each ozone level was applied for 20 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. 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) value.

The results of the assessment is shown in the following Table (individual measurement points) and further presented in the Executive Summary (Figure 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 ZEP ozone analyser (OA) API 400E #1136 with the WCC-Empa travelling standard (TS) before adjustment of the calibration factors.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-08-30 16:15	1	0	0.47	-0.05	0.30	0.07	-0.52	NA
2012-08-30 16:35	1	40	40.03	40.13	0.10	0.03	0.10	0.2
2012-08-30 16:55	1	60	60.04	60.21	0.11	0.10	0.17	0.3
2012-08-30 17:35	1	90	89.96	90.23	0.10	0.07	0.27	0.3
2012-08-30 17:55	1	80	80.02	80.10	0.07	0.08	0.08	0.1
2012-08-30 18:15	1	10	10.17	9.84	0.33	0.09	-0.33	-3.2
2012-08-30 18:15	1	30	29.99	29.75	0.14	0.05	-0.24	-0.8
2012-08-30 18:35	1	50	49.99	50.23	0.11	0.06	0.24	0.5
2012-08-30 18:55	1	20	19.99	19.79	0.05	0.03	-0.20	-1.0
2012-08-30 19:35	1	70	70.00	70.27	0.09	0.07	0.27	0.4
2012-08-30 19:55	2	0	0.39	-0.11	0.13	0.05	-0.50	NA
2012-08-30 20:15	2	30	30.00	29.73	0.13	0.10	-0.27	-0.9

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-08-30 20:35	2	90	89.99	90.23	0.11	0.04	0.24	0.3
2012-08-30 20:55	2	60	60.00	59.57	0.57	0.26	-0.43	-0.7
2012-08-30 21:15	2	10	9.99	9.50	0.19	0.07	-0.49	-4.9
2012-08-30 21:35	2	40	39.97	39.61	0.08	0.06	-0.36	-0.9
2012-08-30 21:55	2	70	70.03	70.01	0.08	0.08	-0.02	0.0
2012-08-30 22:15	2	20	20.01	19.58	0.17	0.08	-0.43	-2.1
2012-08-30 22:35	2	50	49.99	49.64	0.10	0.07	-0.35	-0.7
2012-08-30 22:55	2	80	80.03	80.24	0.08	0.06	0.21	0.3
2012-08-30 23:15	3	0	0.28	-0.30	0.24	0.04	-0.58	NA
2012-08-30 23:35	3	50	49.98	49.78	0.11	0.04	-0.20	-0.4
2012-08-30 23:55	3	90	90.02	90.28	0.06	0.07	0.26	0.3
2012-08-31 00:35	3	10	10.15	9.41	0.27	0.06	-0.74	-7.3
2012-08-31 00:55	3	40	39.97	39.68	0.10	0.13	-0.29	-0.7
2012-08-31 01:05	3	60	60.00	59.98	0.09	0.06	-0.02	0.0
2012-08-31 01:15	3	70	70.02	69.95	0.14	0.06	-0.07	-0.1
2012-08-31 01:35	3	30	30.01	29.78	0.10	0.08	-0.23	-0.8
2012-08-31 02:15	3	20	20.01	19.82	0.11	0.09	-0.19	-0.9
2012-08-31 02:35	3	80	80.02	80.34	0.10	0.09	0.32	0.4
2012-08-31 02:55	4	0	0.23	-0.10	0.24	0.05	-0.33	NA
2012-08-31 03:15	4	40	40.00	40.06	0.10	0.06	0.06	0.2
2012-08-31 03:35	4	60	59.99	60.05	0.05	0.08	0.06	0.1
2012-08-31 04:15	4	90	90.00	90.61	0.07	0.07	0.61	0.7
2012-08-31 04:35	4	80	80.00	80.19	0.11	0.05	0.19	0.2
2012-08-31 04:55	4	10	10.03	9.62	0.19	0.09	-0.41	-4.1
2012-08-31 04:55	4	30	29.99	29.70	0.13	0.04	-0.29	-1.0
2012-08-31 05:15	4	50	49.99	49.76	0.09	0.07	-0.23	-0.5
2012-08-31 05:35	4	20	20.00	19.79	0.18	0.09	-0.21	-1.0
2012-08-31 06:15	4	70	69.99	70.29	0.10	0.09	0.30	0.4
2012-08-31 06:35	5	0	0.16	-0.11	0.25	0.08	-0.27	NA
2012-08-31 06:55	5	30	29.98	29.56	0.18	0.07	-0.42	-1.4
2012-08-31 07:15	5	90	90.00	90.30	0.09	0.06	0.30	0.3
2012-08-31 07:35	5	60	59.98	60.19	0.06	0.06	0.21	0.4
2012-08-31 07:55	5	10	10.07	9.85	0.20	0.04	-0.22	-2.2
2012-08-31 08:15	5	40	40.02	40.03	0.11	0.06	0.01	0.0
2012-08-31 08:35	5	70	69.99	70.33	0.07	0.08	0.34	0.5
2012-08-31 08:55	5	20	19.98	19.48	0.17	0.10	-0.50	-2.5
2012-08-31 09:15	5	50	50.00	49.81	0.08	0.08	-0.19	-0.4
2012-08-31 09:35	5	80	79.98	80.19	0.06	0.07	0.21	0.3
2012-08-31 09:55	6	0	0.30	-0.13	0.18	0.12	-0.43	NA
2012-08-31 10:15	6	50	50.05	50.22	0.12	0.09	0.17	0.3
2012-08-31 10:35	6	90	90.01	90.51	0.11	0.11	0.50	0.6
2012-08-31 11:15	6	10	10.12	9.94	0.34	0.07	-0.18	-1.8
2012-08-31 11:35	6	40	40.03	39.98	0.16	0.07	-0.05	-0.1
2012-08-31 11:45	6	60	60.01	60.20	0.07	0.04	0.19	0.3
2012-08-31 11:55	6	70	70.02	70.17	0.09	0.10	0.15	0.2
2012-08-31 12:15	6	30	29.99	29.49	0.18	0.04	-0.50	-1.7
2012-08-31 12:55	6	20	19.96	19.68	0.16	0.12	-0.28	-1.4
2012-08-31 13:15	6	80	80.01	80.65	0.08	0.10	0.64	0.8

Conclusions

The ozone measurements made at Zeppelin Mountain agreed well with the WCC-Empa travelling standard. The current set-up of ozone measurements at ZEP is adequate and no modifications are necessary. However, the inlet location close to the wall of the building is still not optimal, and relocation to the roof of the building should be considered.

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Both the Picarro instruments and the RGA-3 are connected to the new inlet system on the 15 m tower. Two absolutely identical inlet lines are available.

Location of air intake:	Top of 15 m tower, 8 m SE of the station building. Inlet tube is 1 inch heated (35°C) stainless steel. Total length approx. 20 m, flow speed held constant at approx. 5.3 m/s.
Inlet protection:	Protection against rain water / snow / insects.
Instrument connection:	Instruments are directly connected to the 1 inch SS tube, see picture on the right.
Inlet filter:	Swagelok SS-6F-60 particle filter.
Residence time:	Approx. 5 s

ZEP inlet tower and connection port

Instrumentation

Currently two independent CO measurements are carried out at Zeppelin Mountain with a GC/RGD instrument (RGA-3) and a Picarro G2410 analyser. The Picarro G2302 instrument was not running at the time of the audit due to a broken pump. Instrumental details are listed in Table 4.

Standards

Currently, two NOAA CO standards (WMO-2004 scale) are available at ZEP. A set of four additional NOAA CO standards was ordered in 2011 but these standards have not yet been delivered to ZEP by NOAA. The standards are used for both the RGA-3 and Picarro instruments. Table 3 shows an overview of the currently available standards at ZEP.

Table 3. Carbon monoxide CO standards at ZEP.

Cylinder ID	Type	CO (ppb)	sd_{CO} (ppb)
CC309305	NOAA	121.11	0.08
CC311859	NOAA	194.98	0.15

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri) by the station operator.
Other (cleaning, leak check etc.):	As required. The instruments are remotely monitored from NILU and usually several visits are made per year for maintenance and corrective actions.

Data Acquisition and Data Transfer

RGA-3 as well as CH_4/N_2O GC: Data of the gas chromatograph system (greenhouse gases and CO) is acquired using GCWerks (GC Soft, Inc.), a GC control software package originally developed at the Scripps Institution for Oceanography (SIO) within the AGAGE programme. Remote access is possible through the internet. Picarro: Custom made data acquisition system in addition to the instrument data acquisition system.

Data Treatment

Data-processing is done at NILU. The quality of the data is assessed using data visualization and the calculation of statistical parameters. Entries in the station and instrument log books are also considered for data validation.

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently 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 analysers. 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 4 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 ZEP data acquisition system.

Table 4. Experimental details of ZEP 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	Picarro G2401 #948-CFKADS2019
Principle	CRDS
Drying system	PERMAPURE Nafion drier
Model, S/N	RGA-3, #020190-005
Principle	GC/HgO Reduction Detector (RGD)
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port (GC/FID) and the sample port with overflow (Picarro G2401).

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 5 to Table 7.

Table 5. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 instrument (AL) with the WCC-Empa TS (WMO-2004 CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-08-31 15:42:30)	100122_FA01469	56.35	0.64	54.81	2.40	50	-1.54	-2.73
(12-08-31 16:43:00)	110512_FB03348	119.15	0.33	119.06	2.75	51	-0.09	-0.08
(12-08-31 17:44:00)	120723_FA02789	254.34	0.12	255.67	2.42	51	1.33	0.52
(12-08-31 18:45:00)	110808_FA02505	190.88	0.20	191.47	2.45	51	0.59	0.31
(12-08-31 19:46:00)	110511_FB03383	105.85	0.73	104.23	2.27	51	-1.62	-1.53
(12-08-31 20:47:00)	110512_FB03350	211.78	0.34	212.10	2.32	51	0.32	0.15

Table 6. Same as Table 5 for the RGA-3 (one point calibration).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	GC (ppb)	sdGC (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-09-01 11:39:00)	100122_FA01469	56.35	0.64	49.62	0.70	5	-6.73	-11.94
(12-09-01 13:19:00)	120723_FA02789	254.34	0.54	269.17	2.24	5	14.83	5.83
(12-09-02 11:19:00)	110511_FB03383	105.85	0.73	103.58	0.31	5	-2.27	-2.14
(12-09-02 12:59:00)	110512_FB03350	211.78	0.34	221.46	0.26	5	9.68	4.57
(12-09-03 11:09:00)	110512_FB03348	119.15	0.33	119.48	0.80	5	0.33	0.28
(12-09-03 11:09:00)	110808_FA02505	190.88	0.20	200.33	0.24	6	9.45	4.95
(12-09-05 14:35:40)	110512_FB03348	119.15	0.33	117.67	0.58	6	-1.48	-1.24
(12-09-05 12:19:00)	100122_FA01469	56.35	0.64	52.11	0.86	5	-4.24	-7.52
(12-09-05 13:59:00)	120723_FA02789	254.34	0.12	264.41	0.90	5	10.07	3.96

Table 7. Same as above (RGA-3, two point calibration).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	GC (ppb)	sdGC (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-09-01 11:39:00)	100122_FA01469	56.35	0.64	56.17	0.64	5	-0.18	-0.32
(12-09-01 13:19:00)	120723_FA02789	254.34	0.54	261.22	0.88	5	6.88	2.71
(12-09-02 11:19:00)	110511_FB03383	105.85	0.73	105.06	0.28	5	-0.79	-0.75
(12-09-02 12:59:00)	110512_FB03350	211.78	0.34	214.17	0.13	5	2.39	1.13
(12-09-03 11:09:00)	110512_FB03348	119.15	0.33	118.83	0.66	5	-0.32	-0.27
(12-09-03 11:09:00)	110808_FA02505	190.88	0.20	194.32	0.26	6	3.44	1.80

Conclusions

The Picarro G2401 CO measurements of ZEP agreed very well with the WCC-Empa TS. The bias was not larger than ± 2 ppb (WMO/GAW DQOs) for 1-h values. The Picarro system is fully adequate for the measurements of CO. The RGA-3 GC agreed well in the mole fraction range from 100 to 140 ppb CO; measurements outside this range were biased most likely due to an insufficient characterisation of the non-linearity of the RGD detector.

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Same as for carbon monoxide.

Instrumentation

Currently two independent CH_4 measurements are carried out at Zeppelin Mountain with Picarro G2401 analyser and a HP 5890 Series II GC/FID system. Instrumental details are listed in Table 9. The GC/FID instrument could not be assessed due to instrumental problems at the time of the audit.

Standards

Currently, three NOAA CH_4 standards (NOAA04 scale) are available at ZEP. The standards are used for both the GC/FID and Picarro instruments. Table 8 shows an overview of the currently available standards at ZEP.

Table 8. CH_4 NOAA standards at ZEP.

Cylinder ID	Type	CH_4 (ppb)	sd_{CH4} (ppb)
CC324508	NOAA	1845.48	0.12
CC324505	NOAA	1890.73	0.18
LL73784J	NOAA	1947.40	0.18

Operation and Maintenance

Check for general operation: Daily (Mon – Fri) by the station operator.

Other (cleaning, leak check etc.): As required. The instruments are remotely monitored from NILU and usually several visits are made per year for maintenance and corrective actions.

Data Acquisition and Data Transfer

Same as for carbon monoxide.

Data Treatment

Same as for carbon monoxide.

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were 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 G2401 #948-CFKADS2019
Principle	CRDS
Drying system	PERMAPURE Nafion drier
Model, S/N	HP 5890 Series II
Technique	GC/FID
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port (GC/FID) and the sample port with overflow (Picarro G2401).

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 injections) for each level during the comparison of the Picarro G2401 (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 (%)
(12-08-31 15:42:30)	100122_FA01469	1836.71	0.04	1836.66	0.13	50	-0.05	0.00
(12-08-31 16:43:00)	110512_FB03348	2769.15	0.10	2763.29	0.22	51	-5.86	-0.21
(12-08-31 17:44:00)	120723_FA02789	2116.13	0.06	2114.45	0.22	51	-1.68	-0.08
(12-08-31 18:45:00)	110808_FA02505	2150.40	0.06	2148.57	0.17	51	-1.83	-0.09
(12-08-31 19:46:00)	110511_FB03383	1898.17	0.04	1898.10	0.17	51	-0.07	0.00
(12-08-31 20:47:00)	110512_FB03350	2761.41	0.07	2756.17	0.24	51	-5.24	-0.19

Conclusions

The Picarro G2401 CH_4 measurements of ZEP agreed very well with the WCC-Empa TS. The bias was not larger than ± 2 ppb (WMO/GAW DQOs) for 1-h values. The Picarro system is fully adequate for the measurements of CH_4. However, the calibration of the system can potentially be improved using standard gases covering a wider mole fraction range or include zero air in the calibration procedure.

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Stockholm University:

Location of air intake:	Main laboratory building, approx. 4 m above the roof. 4 m ¼ inch stainless steel (SS) tubing inside a 7 cm SS tube. Flow rate 2 l/min.
Inlet protection:	Protection against rain / snow / insects.
Tubing:	From air intake: ca. 5 m ¼ inch Synflex 1300 tubing to the dryer, which are two 30 cm long 1 cm SS tubes filled with magnesium perchlorate. The dryers are switched after approx. 3 months. After the dryer ca. 1 m 1/8 inch SS tubing to the instrument manifold. Sample flow rate of instrument approx. 100 ml/min.
Inlet filter:	Nupro, 7 µm pore size SS filter.
Residence time:	Approx. 14 s.

The PTFE line is not optimal for CO_2 measurements and should be replaced by Synflex 1300 (Dekabon).

NILU:

Same as for carbon monoxide.

Instrumentation

LI-COR LI-7000 NDIR analyser. The current instrument was installed in 2005 at ZEP. From 1995 (or 1997, time not clear) a LI-COR-6251 analyser was used, and before that, a Maihak UNOR 4N. Measurements prior to March 1990 were made at the foot of Zeppelin Mountain.

Standards

The following Table gives an overview of the available CO_2 standards at ZEP (SU). The data refers to the WMO X2007 calibration scale. The standards were also measured on the WCC-Empa travelling instrument (Picarro G2401). The values measured by WCC-Empa agreed on average well with the standards at ZEP; the deviation was within ± 0.1 ppm.

Table 11. SU CO_2 Standards at ZEP.

Cylinder	Type	CO_2 (SU) (ppm)	sd_{CO2} (ppm)	CO_2 (WCC) (ppm)	sd_{CO2} (ppm)	Deviation (ppm)
Low	WS	353.04	NA	353.00	0.01	0.04
Middle	WS	374.63	NA	374.66	0.01	-0.03
High	WS	398.32	NA	398.42	0.01	-0.10
CA06748	NOAA	382.78	0.01	382.69	0.01	0.09

Operation and Maintenance

NILU Picarro: Same as for CH_4.

Check for general operation:	Daily (Mon – Fri) by the station operator.
Other (cleaning, leak check etc.):	As required. Remote access to the data is possible, but otherwise no remote control of the system is possible.
Change of cold trap:	Humidity trap changes are made every three months.
Calibration:	Every 2 h using three working standards and manually using the NOAA primary laboratory standard.

Data Acquisition and Data Transfer

NILU: see carbon monoxide. SU: A self-programmed data LabView based acquisition system is in use. All data is acquired in UTC+1, and 1-min averages are available.

Data Treatment

NILU: Same as for carbon monoxide. SU: Data validation is done at SU. 1-min data is visually inspected and hourly data files are prepared from validated raw data.

Documentation

NILU: Same as for carbon monoxide. SU: All information is entered in electronic log book. 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 12 shows details of the experimental setup during the comparison of the transfer standards and the station analyser. The data used for the evaluation was recorded by the station data acquisition system.

Table 12. 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	LI-COR LI-7000
Principle	NDIR
Model	Picarro G2401
Principle	CRDS
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port (LI-COR).

Results

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

Table 13. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Picarro G2401 analyser (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 (%)
(12-08-31 15:42:30)	100122_FA01469	393.34	0.02	393.52	0.02	50	0.18	0.05
(12-08-31 16:43:00)	110512_FB03348	341.03	0.02	341.18	0.01	51	0.15	0.04
(12-08-31 17:44:00)	120723_FA02789	409.33	0.01	409.55	0.01	51	0.22	0.05
(12-08-31 18:45:00)	110808_FA02505	373.41	0.02	373.61	0.01	51	0.20	0.05
(12-08-31 19:46:00)	110511_FB03383	325.44	0.01	325.56	0.01	51	0.12	0.04

Table 14. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the LI-COR LI-7000 analyser (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 (%)
(12-08-31 13:50:00)	110808_FA02505	373.41	0.02	373.34	0.06	9	-0.07	-0.02
(12-08-31 14:09:00)	110512_FB03348	341.03	0.02	341.01	0.07	11	-0.02	-0.01
(12-08-31 14:29:00)	100122_FA01469	393.34	0.02	393.07	0.06	9	-0.27	-0.07
(12-08-31 14:42:30)	110512_FB03350	384.92	0.02	384.98	0.08	14	0.06	0.02
(12-08-31 15:03:30)	120723_FA02789	409.33	0.01	408.61	0.06	12	-0.72	-0.18

Conclusions

A bias of approx. 0.2 ppm was observed for the NILU Picarro system compared to WCC-Empa. This bias was also verified during the comparison of ambient air, which means that the complete measurement setup is fully working. Half of the bias can be explained by differences in the calibration standards, and the remaining 0.1 ppm potentially can be attributed to effects of the Nafion dryer. The agreement between the SU LI-COR LI-7000 station analyser and WCC-Empa was also good up to mole fractions of 390 ppm CO_2, and slightly larger deviations were observed for higher mole fractions. Therefore, recalibration and characterisation of the instrument non-linearity is recommended. In addition, the humidity trap needs to be changed before breakthrough of water occurs.

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 15). 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] - 0.19 ppb) / 1.0010 (6a)

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

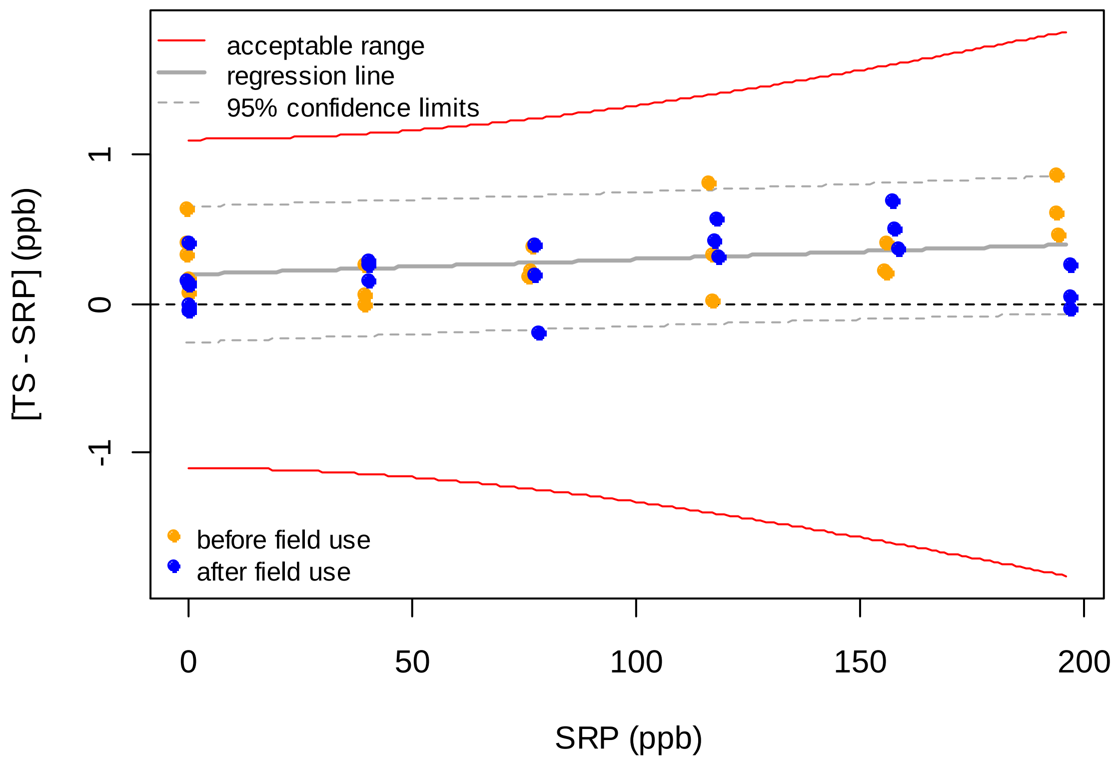

Figure 15. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

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)**
2012-07-03	1	0	-0.21	0.32	0.12	0.17
2012-07-03	1	80	76.82	0.12	77.21	0.36
2012-07-03	1	160	155.81	0.31	156.02	0.28
2012-07-03	1	40	39.40	0.23	39.40	0.24
2012-07-03	1	200	194.46	0.22	194.92	0.26
2012-07-03	1	120	116.12	0.37	116.93	0.29
2012-07-03	1	0	0.22	0.20	0.30	0.25
2012-07-03	2	0	-0.09	0.34	0.32	0.41
2012-07-03	2	120	117.25	0.40	117.59	0.33
2012-07-03	2	80	76.53	0.25	76.75	0.12
2012-07-03	2	160	155.54	0.27	155.77	0.17
2012-07-03	2	200	194.03	0.29	194.65	0.27
2012-07-03	2	40	39.30	0.41	39.57	0.34
2012-07-03	2	0	-0.04	0.19	0.13	0.20
2012-07-03	3	0	-0.32	0.18	0.32	0.10
2012-07-03	3	160	155.95	0.37	156.36	0.28
2012-07-03	3	40	39.43	0.16	39.50	0.25
2012-07-03	3	120	116.95	0.41	116.98	0.21
2012-07-03	3	200	193.68	0.37	194.54	0.24
2012-07-03	3	80	76.26	0.17	76.45	0.21
2012-07-03	3	0	-0.01	0.35	0.12	0.10
2012-10-24	4	0	-0.19	0.16	-0.03	0.27
2012-10-24	4	160	158.41	0.31	158.78	0.25
2012-10-24	4	40	40.15	0.13	40.42	0.17
2012-10-24	4	120	118.45	0.26	118.78	0.23
2012-10-24	4	200	196.88	0.24	197.14	0.15
2012-10-24	4	80	77.57	0.19	77.77	0.26
2012-10-24	4	0	-0.02	0.28	0.38	0.17
2012-10-24	5	0	-0.02	0.29	-0.03	0.19
2012-10-24	5	80	78.38	0.31	78.19	0.20
2012-10-24	5	160	157.50	0.29	158.19	0.24
2012-10-24	5	120	118.11	0.28	118.68	0.14
2012-10-24	5	200	196.84	0.41	196.81	0.17
2012-10-24	5	40	40.13	0.30	40.28	0.19
2012-10-24	5	0	0.15	0.37	0.28	0.19
2012-10-24	6	0	-0.02	0.19	0.12	0.25
2012-10-24	6	40	40.20	0.30	40.49	0.31
2012-10-24	6	160	157.63	0.41	158.14	0.30
2012-10-24	6	200	196.82	0.21	196.87	0.20
2012-10-24	6	120	117.77	0.37	118.19	0.22
2012-10-24	6	80	77.43	0.18	77.83	0.24
2012-10-24	6	0	0.22	0.30	0.18	0.38

[#]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-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: 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 16 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	130.2	0.2	1607.82	0.04	NA	NA	326.69	0.01
CC339523	347.9	0.3	1854.60	0.13	322.49	0.12	396.88	0.06	348.4	0.3	1855.31	0.03	322.49	0.02	396.94	0.02
CC339524	390.7	0.2	1980.28	0.30	355.40	0.16	795.42	0.06	391.0	0.4	1981.77	0.04	355.40	0.02	796.36	0.04
CC311846	166.4	0.1	1805.24	0.12	317.27	0.11	377.86	0.04	167.3	0.3	1805.31	0.11	317.27	0.01	377.84	0.02

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)
110511_FB03383	105.85	0.73	1898.17	0.04	325.44	0.01	306.76	0.02
100122_FA01469	56.35	0.64	1836.71	0.04	393.34	0.02	322.74	0.07
110512_FB03350	211.78	0.34	2761.41	0.07	384.92	0.02	312.65	0.05
110512_FB03348	119.15	0.33	2769.15	0.1	341.03	0.02	323.99	0.01
120723_FA02789	254.34	0.12	2116.13	0.06	409.33	0.01	322.78	0.07
110808_FA02505	190.88	0.2	2150.4	0.06	373.41	0.02	322.43	0.05

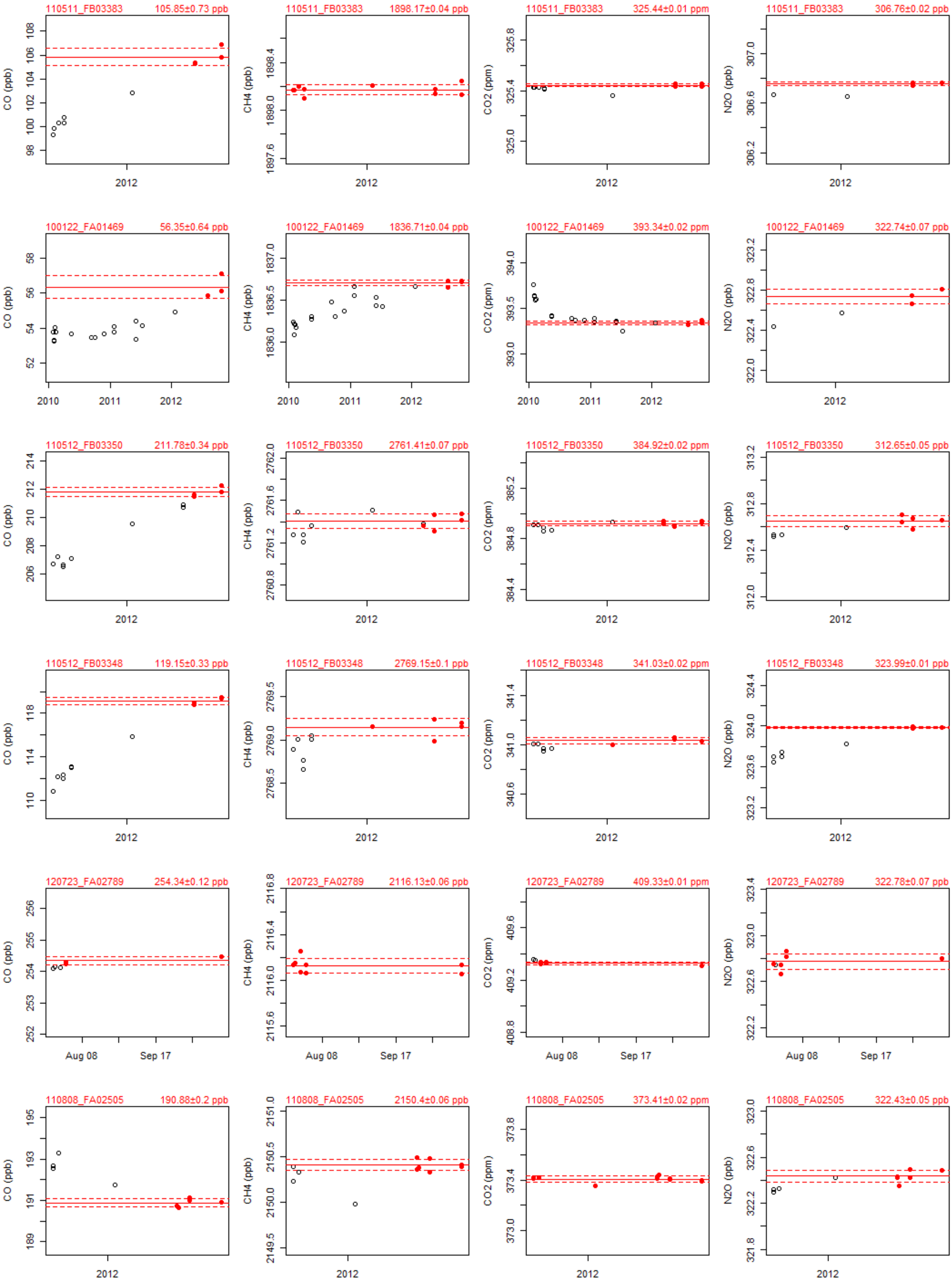

Figure 16. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.*

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Ozone Audit Executive Summary (ZEP)

0.1	Station Name:	Zeppelin Mountain
0.2	GAW ID:	ZEP
0.3	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-08-30 through 2012-08-31
1.2	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.3	Station staff involved in audit:	Mr. O. Hermansen, Mr. A. Backlund
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):	(1.0010±0.0010) • [SRP] + (0.19±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	API 400E #1136
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset = -1.0; Span = 1.017
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0103±0.0007) • [SRP] - (0.28±0.04)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.28 ppb) / 1.0103
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.10 ppb^2 + 2.66e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 12/2

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

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Carbon Monoxide Audit Executive Summary (ZEP)

0.1	Station Name:	Zeppelin Mountain
0.2	GAW ID:	ZEP
0.3	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-08-31
1.2	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.3	Station staff involved in audit:	Mr. O. Hermansen, Dr. N. Schmidbauer
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro G2401 #948-CFKADS2019
1.6.2	Range of calibration:	56 – 255 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.0147±0.0031) • X_{CO} - (2.5±0.5)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 2.5) / 1.0147
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (0.9 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:	NDIR CO analyser
1.8	Reference:	WCC-Empa Report 12/2

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

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Carbon Monoxide Audit Executive Summary (ZEP)

0.1	Station Name:	Zeppelin Mountain
0.2	GAW ID:	ZEP
0.3	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-09-01 through 2012-09-05
1.2	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.3	Station staff involved in audit:	Mr. O. Hermansen, Dr. N. Schmidbauer, Dr. C. Lunder
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	RGA3, #020190-005
1.6.2	Range of calibration:	56 – 255 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.0964±0.0087) · X_{CO} - (11.4±1.5)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 11.4) / 1.0964
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (4.7 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:	One point calibration.
1.8	Reference:	WCC-Empa Report 12/2

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

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Carbon Monoxide Audit Executive Summary (ZEP)

0.4	Station Name:	Zeppelin Mountain
0.5	GAW ID:	ZEP
0.6	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Carbon Monoxide

1.9	Date of Audit:	2012-09-01 through 2012-09-05
1.10	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.11	Station staff involved in audit:	Mr. O. Hermansen, Dr. N. Schmidbauer, Dr. C. Lunder
1.12	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.13	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.14	Station Analyser:	
1.14.1	Analyser Model:	RGA3, #020190-005
1.14.2	Range of calibration:	56 – 255 ppb
1.14.3	Coefficients at start of audit	NA
1.14.4	Calibration at start of audit (ppb):	CO = (1.0358±0.0086) · X_{CO} - (3.7±1.5)
1.14.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 3.7) / 1.0358
1.14.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (4.7 ppb^2 + 1.01e-04 * X_{CO}^2)
1.14.7	Coefficients after audit	NA
1.14.8	Calibration after audit (ppb):	NA
1.14.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.14.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.15	Comments:	Two point calibration.
1.16	Reference:	WCC-Empa Report 12/2

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

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Methane Audit Executive Summary (ZEP)

0.1	Station Name:	Zeppelin Mountain
0.2	GAW ID:	ZEP
0.3	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2012-08-31
1.2	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.3	Station staff involved in audit:	Mr. O. Hermansen, Dr. N. Schmidbauer
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:	Picarro G2401 #948-CFKADS2019
1.6.2	Range of calibration:	1836 – 2770 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99392\pm0.00026) \cdot X_{CH4} + (11.3\pm0.6)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 - 11.3) / 0.99392$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.2 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:	NA
1.8	Reference:	WCC-Empa Report 12/2

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

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Carbon Dioxide Audit Executive Summary (ZEP)

0.1	Station Name:	Zeppelin Mountain
0.2	GAW ID:	ZEP
0.3	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-08-31
1.2	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.3	Station staff involved in audit:	Mr. O. Hermansen, Dr. N. Schmidbauer
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 G2401 #948-CFKADS2019
1.6.2	Range of calibration:	325 – 409 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (1.0012 \pm 0.0004) \cdot X_{CO2} - (0.25 \pm 0.14)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 + 0.25) / 1.0012$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.00 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:	NA
1.8	Reference:	WCC-Empa Report 12/2

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

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Carbon Dioxide Audit Executive Summary (ZEP)

0.1	Station Name:	Zeppelin Mountain
0.2	GAW ID:	ZEP
0.3	Coordinates/Elevation:	78.90669°N, 11.889342°E (474 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-08-31 through 2012-09-02
1.2	Auditor:	Dr. C. Zellweger, Dr. M. K. Vollmer
1.3	Station staff involved in audit:	Mrs. Birgitta Noone
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:	LI-COR LI-7000
1.6.2	Range of calibration:	325 – 409 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.9900 \pm 0.0039) \cdot X_{CO2} + (3.59 \pm 1.52)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 - 3.59) / 0.9900$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.16 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:	NA
1.8	Reference:	WCC-Empa Report 12/2

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

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LIST OF ABBREVIATIONS

AGAGE	Advanced Global Atmospheric Gases Experiment
AL	Analyser
BKG	Background
COEF	Coefficient
ZEP	Zeppelin Mountain GAW station
CRDS	Cavity Ring-Down Spectroscopy
DAQ	Data Acquisition System
DQO	Data Quality Objective
dtm	Date/Time
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
FID	Flame Ionisation Detector
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
LS	Laboratory Standard
MFC	Mass Flow Controller
NILU	Norwegian Institute for Air Research
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
NySMAC	Ny-Ålesund Science Managers Committee
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
SSF	Svalbard Science Forum
SU	Stockholm University
TI	Travelling Instrument
TS	Traveling Standard
UPS	Uninterruptible Power Supply
UV	Ultra Violet
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard