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

AT THE

GLOBAL GAW STATION PALLAS, FINLAND, APRIL 2012

Submitted to the World Meteorological Organization by

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CONTENTS

Exectutive Summary and Recommendations 3
Station Location and Access 3
Station Facilities 3
Station Management and Operation 4
Air Inlet Systems 4
Surface Ozone Measurements 4
Carbon Monoxide Measurements 5
Methane Measurements 7
Carbon Dioxide Measurements 8
Nitrous Oxide Measurements 10
Parallel Measurements of Ambient Air 10
Data Acquisition and Management 13
Data Submission 13
Conclusions 13
Summary Ranking of the Pallas GAW Station 14
Appendix 15
Global GAW Station Pallas 15
Site description and measurement programme 15
Trace Gas Distributions at Pallas 15
Organisation and Contact Persons 15
Surface Ozone Measurements 16
Monitoring Set-up and Procedures 16
Comparison of the Ozone Analyser and Ozone Calibrator 17
Carbon Monoxide Measurements 19
Monitoring Set-up and Procedures 19
Comparison of the Carbon Monoxide Analyser 20
Methane Measurements 22
Monitoring Set-up and Procedures 22
Comparison with WCC-Empa travelling standards 23
Carbon Dioxide Measurements 24
Monitoring Set-up and Procedures 24
Comparison with WCC-Empa travelling standards 25
WCC-Empa Traveling Standards 27
Ozone 27

Greenhouse gases and carbon monoxide 29
GAW World Calibration Centre WCC-Empa 32
Ozone Audit Executive Summary (PAL) 32
Carbon Monoxide Audit Executive Summary (PAL) 33
Carbon Monoxide Audit Executive Summary (PAL) 34
Methane Audit Executive Summary (PAL) 35
Carbon Dioxide Audit Executive Summary (PAL) 36
Carbon Dioxide Audit Executive Summary (PAL) 37
References 38
List of abbreviations 39

EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The fourth system and performance audit at the Global GAW station Pallas was conducted by WCC-Empa[1] from 17 - 19 April 2012 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Pallas (PAL) GAW station is operated by the Finnish Meteorological Institute (FMI).

Previous audits at PAL were conducted in conducted in June 1997 [*Herzog et al.*, 1997], in April 2003 [*Zellweger et al.*, 2003] and in September 2007 [*Zellweger et al.*, 2007].

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr. Peter Graf	Empa Dübendorf, Technician
Mr. Juha Hatakka	FMI, Station manager
Mr. Timo Anttila	FMI, Technical support engineer

This report summarises the assessment of the Pallas GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide 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 Pallas 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 Pallas Station is located within the Pallas-Yllästunturi National Park, inside the northern boreal forest zone and consists of various research facilities. The main monitoring station, Sammaltunturi (67°58'N 24°07'E, 560 m a.s.l.) where all GAW related measurements are operated is on top of a sub-arctic hill. The station location is approx. 300 m above the surrounding area and ca. 100 m above the tree line. The surrounding vegetation consists mainly of shrub, moss, and lichen. The region is hilly with the highest elevations of 600-800 m within 3-6 km from the station. The sectors 180°-330° and 100-130° are very open. The Pallas area is free of significant local and regional pollution sources with the nearest town, Muonio with approx. 2500 inhabitants, being 19 km to the west. The second-nearest town, Kittilä, with 6000 inhabitants, is 46 km to the south-east. Further information is available from GAWSIS (http://gaw.empa.ch/gawsis) and the station web site (http://fmigaw.fmi.fi).

The location is adequate for the intended purpose. Year-round access to PAL is possible by snow mobile during winter and ATV (All-Terrain Vehicle) during the snow free period.

Station Facilities

The facilities at PAL have not significantly changed since the last WCC-Empa audit in 2007. The Sammaltunturi station is a 120 m^2 building consisting of a large room for the analytical equipment and separate rooms for pumps, storage and office. Two 7 m towers are attached to either end (east and west) of the building for air sampling. These towers are electrically heated to prevent clogging of the inlets by ice and snow. It is an ideal platform for continuous atmospheric monitoring as well as measurement campaigns.

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

Station Management and Operation

The station management and operation has not significantly changed since the last WCC-Empa audit in 2007. Measurements are carried out by the Finnish Meteorological Institute (FMI), while the station itself is managed by the Finnish Forest Research Institute (METLA). The station is routinely visited once a week by a station operator from METLA. In case of instrument calibrations or maintenance, staff from FMI visits the site.

Air Inlet Systems

Unchanged since the last WCC-Empa audit in 2007. The station has a state-of-the art inlet system; the main inlet manifold is made of acid-proof stainless steel with an outer diameter of 60 mm, and is continuously flushed with a nominal flow rate of 150 m^3h^{-1}. All instruments are connected to this manifold, except some of the aerosol and the radon instruments, which have their own dedicated inlet systems.

Surface Ozone Measurements

Surface ozone measurements at Pallas were established in 1994, and continuous time series are available since then.

Instrumentation. The station is currently equipped with a TEI 49i ozone analyser. The instrumentation is fully adequate for the measurement of surface ozone.

Standards. The station is not equipped with an ozone standard, but calibrations are made four times per year with a travelling standard from FMI (TEI 49C-PS) which is regularly calibrated against the ozone standard of FMI (SRP#37).

Intercomparison (Performance Audit). The PAL ozone analyser was compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The results of the comparison is 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, and no further corrections were applied. The following equations characterise the bias of the instrument:

TEI 49i #0619917500 (BKG -0.2 ppb, SPAN 1.010) – main analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.1 ppb) / 0.9825 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.78e-05 * X_{O3}^2) (1b)

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

The results of the comparison can be summarised as follows: The TEI 49i ozone analyser was measuring approx. 1.7 % lower compared to the WCC-Empa TS. Given the fact that the instrument is regularly calibrated with a NIST traceable travelling standard the deviation is relatively large. During the assessment by WCC-Empa, a relatively large bias of the OA pressure sensor (ambient pressure 701.1 hPa, OA 708.2 hPa) was found, which explains more than half of the observed bias. A re-assessment of the OA including pressure sensor calibration is recommended.

Otherwise the instrumentation at PAL is adequate for ozone measurements.

Recommendation 1 (, important, 2013)**
WCC-Empa recommends re-calibration of the TEI 49i instrument using the FMI travelling instrument. The pressure sensor must also be checked during calibrations. If the results are not consistent with the WCC-Empa results, further action has to be taken.

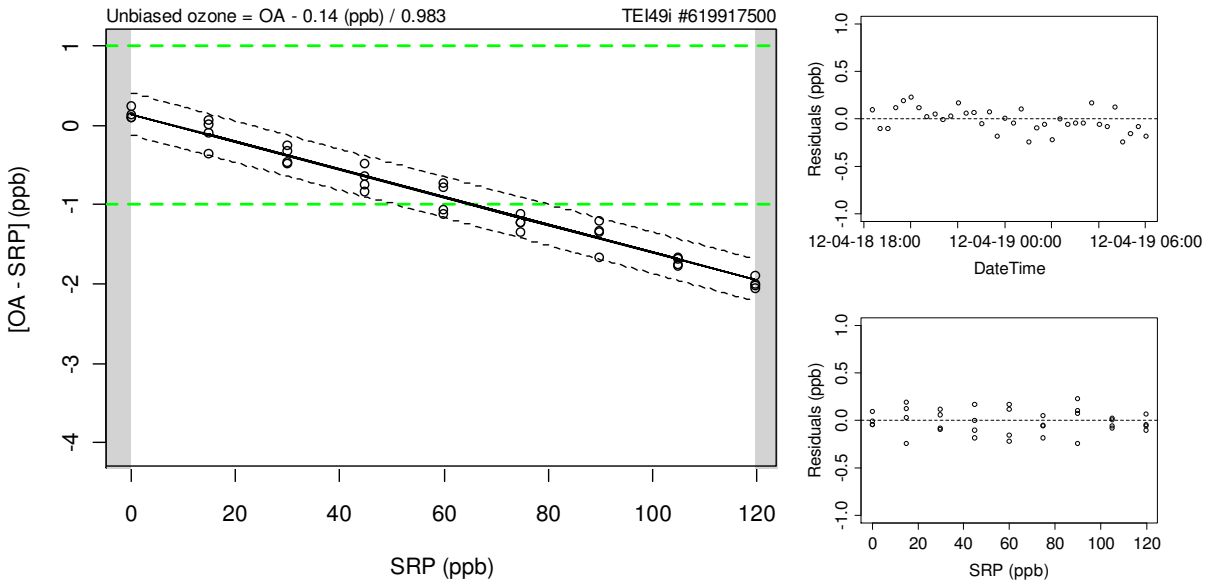

Figure 1. *Left: Bias of the PAL ozone analyser (TEI 49i #0619917500) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The white area represents the mole fraction range relevant for PAL, whereas the green lines 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).*

Carbon Monoxide Measurements

Continuous measurements of CO at PAL started in 2002. In the beginning, a GC system with a Mercuric oxide (HgO) detector (Trace Analytical) was used; however, this instrument was never running well. After that, since 2004, a GC with a flame ionisation detector (FID) and a new HgO detector system (PeakPerformer) was in use. More recently, a Cavity Ringdown Spectrometer (CRDS) was installed in November 2011.

Instrumentation. PeakPerformer PP1 GC/HgO system and Picarro G2401 CRDS analyser. The instrumentation is adequate for the measurement of CO.

Standards. The PAL station is equipped with 7 NOAA laboratory standards, which were purchased in 2005 and 2011. The standards are thoroughly compared against each other every time when a new set of NOAA standards is acquired to ensure consistency and stability of the calibration gases. In addition, working standards are available at PAL.

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the PAL 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 2 - Figure 3 with respect to the WMO GAW Data Quality Objectives (DQOs) [WMO, 2010; 2011]:

Picarro G2401 #CFKADS-2018 (main CO analyser):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 1.1) / 1.0009 (2a)

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

PeakPerformer PP1#084 (backup CO analyser):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 2.8) / 1.0422 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (27.3 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

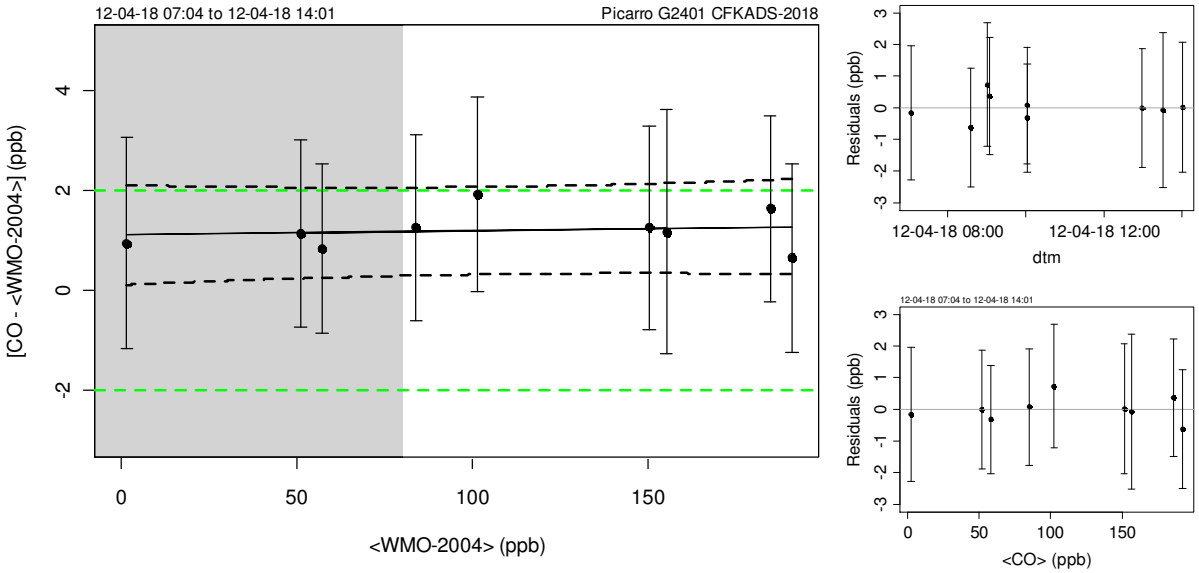

Figure 2. Left: Bias of the PAL Picarro G2401 carbon monoxide instrument with respect to the WMO-2004 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for PAL, whereas the green lines correspond to the DQOs. Each point represents the average of 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).

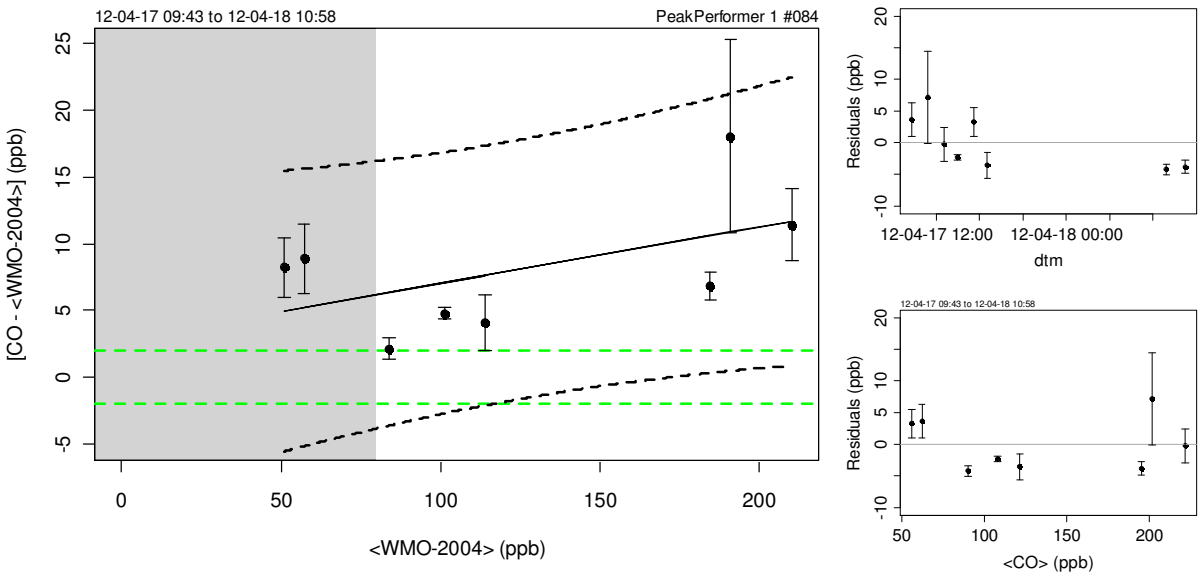

Figure 3. Same as above for the Peak Performer PP1 GC instrument.

The results of the comparisons show good agreement between the PAL and WCC-Empa measurements for the Picarro G2401 instrument; an offset of approx. 1.4 ppb was observed, most likely due to calibration issues of the PAL instrument. In contrast, a much larger bias was observed for the Peak Performer PP1 GC/HgO system. The PAL measurements were significantly higher compared to WCC-Empa; with higher associated uncertainties.

Recommendation 2 (*, important, ongoing)**
Due to the significantly better performance of the Picarro instrument compared to the PeakPerformer, the Picarro data should be considered as the main CO data for future data submission and use.

Methane Measurements

Continuous measurements of CH_4 at PAL started in 2004 using GC / flame ionization (FID) detection. Since 2009 CH_4 measurements are made using CRDS technique.

Instrumentation. Picarro G2401 and Picarro G1301 CRDS analysers (the latter is not regularly used, but kept at PAL as backup system). The instrumentation is adequate for the measurement of CH_4.

Standards. The PAL station is equipped with 7 NOAA laboratory standards, which were purchased in 2005 and 2012. In addition, working standards are available at PAL.

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

The following equation characterises the instrument bias. The result is further illustrated in Figure 4 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Picarro G2401 #CFKADS-2018:

Unbiased CH_4 mixing ratio: $X_{CH4}\ (ppb) = (CH_4 - 12.4) / 0.99292$ (3a)

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

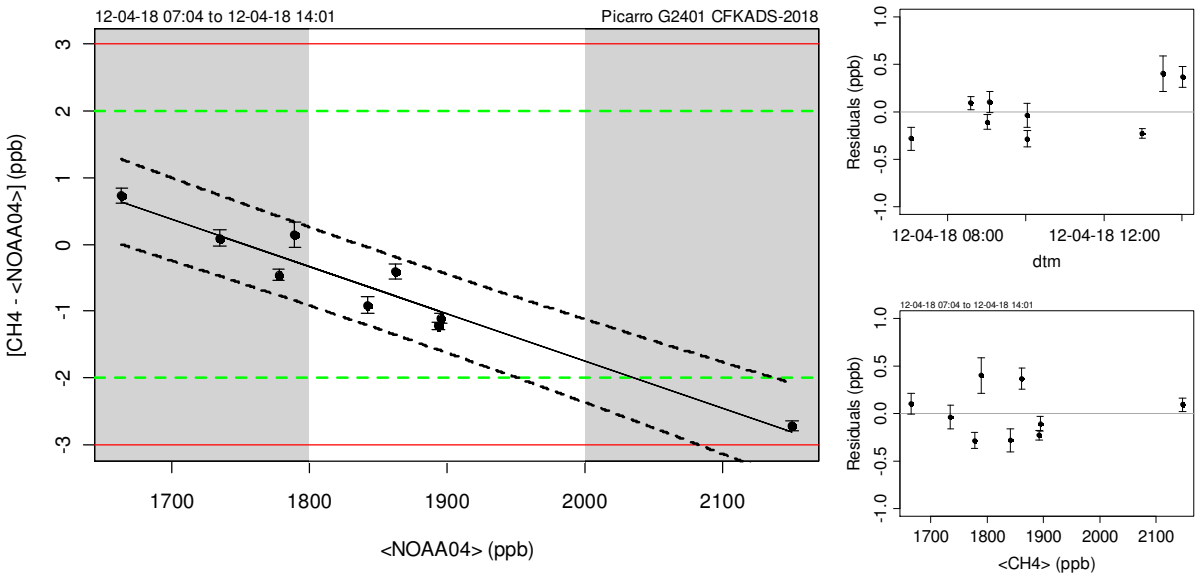

Figure 4. *Left: Bias of the Picarro G2401 #CFKADS-2018 methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for PAL, whereas the red and green lines correspond to the DQOs. Each point represents the average 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 over the relevant mole fraction range. Due to the excellent results, no further actions are required and the measurement set-up is fully adequate for the measurements of methane.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at PAL commenced in 1999 using NDIR technique and continuous data is available since then. Since 2009 CO_2 measurements are made using CRDS technique.

Instrumentation. LI-COR LI-7000 (NDIR) , Picarro G2401 (since 2012) and Picarro G1301 CRDS analysers (the latter is not regularly used, but kept at PAL as backup system). The instrumentation is adequate for the measurement of CO_2.

Standards. The PAL station is equipped with 11 NOAA laboratory standards, which were purchased in 2000 and 2012. In addition, working standards are available at PAL.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the PAL 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 #CFKADS-2018. The results is further illustrated in Figure 5 and Figure 6 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Picarro G2401 #CFKADS-2018:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 - 0.85) / 0.99781 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.003 ppm^2 + 3.28e-08 * X_{CO2}^2) (4b)

LI-COR LI-7000:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.62) / 0.99863 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.01 ppm^2 + 3.28e-08 * X_{CO2}^2) (4d)

The results of the comparison can be summarised as follows:

The overall agreement between FMI CO_2 measurements at PAL and WCC-Empa was reasonable good for both CO_2 instruments in the relevant mole fraction range; however, both analysers showed larger deviations at low mole fractions, which potentially can be improved with calibration of the instruments over a wider mole fraction range.

Recommendation 3 (, important, 2013)**
It is recommended to calibrate the Picarro G2401 and the LI-COR LI-7000 CO_2 instruments with a set of standards that covers a wider mole fraction range (e.g. 350 – 500 ppm).

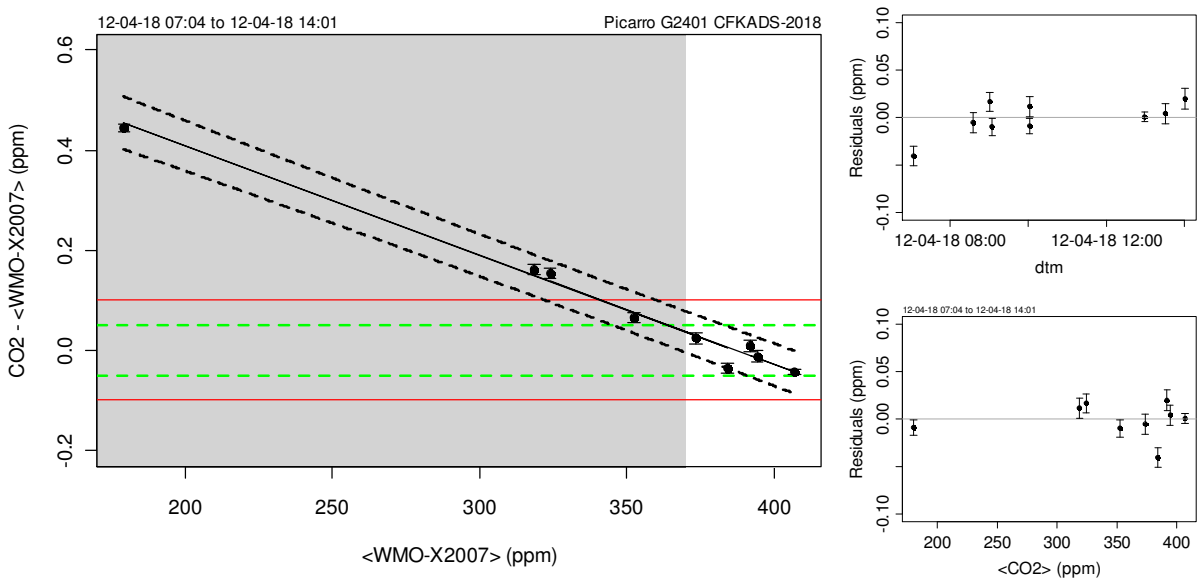

Figure 5. *Left: Bias of Pallas Picarro G2401 #CFKADS-2018 analyser with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for PAL, whereas the red and green lines correspond to the DQOs. Each point represents the average 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).*

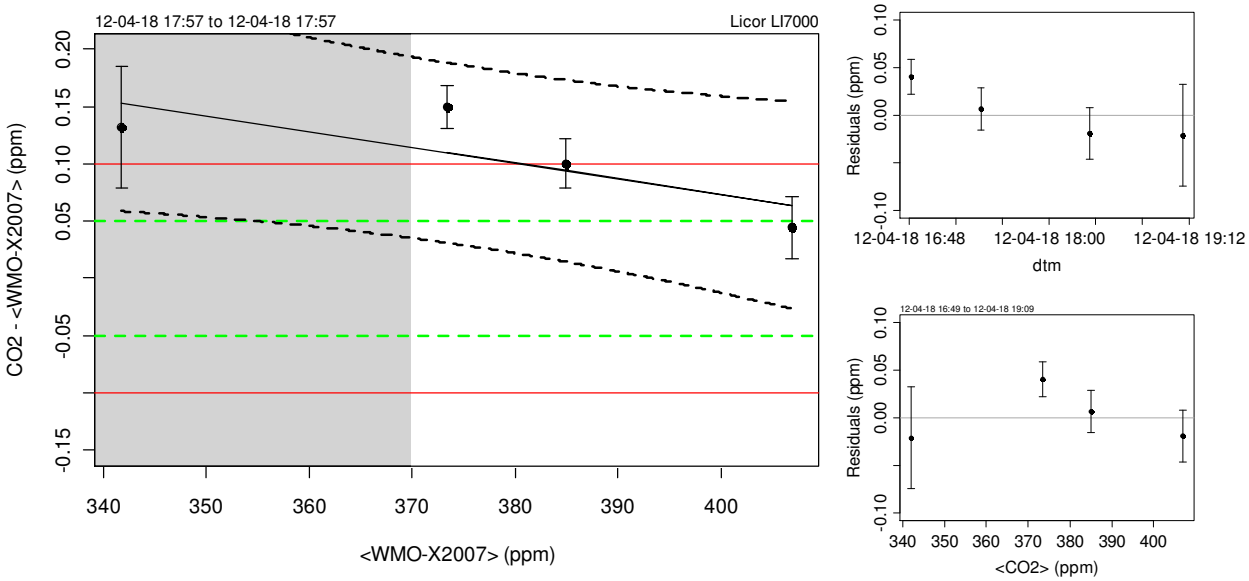

Figure 6. *Same as above for the LI-COR LI-7000 analyser.*

Nitrous Oxide Measurements

An N_2O audit was conducted by the WCC-N_2O in 2007; the measurement set-up did not significantly change since then. During the current audit the WCC-Empa TS were also measured on the PAL instrument. The deviation ranged from 0.4 to 0.9 ppb, with the PAL instrument measuring lower compared to WCC-Empa. Furthermore, the repeatability of the PAL GC/ECD system was relatively poor, with standard deviations ranging from 0.3 to 0.7 ppb for multiple injections. In addition calibration issues were identified by the PAL station manager which needs further attention. It was therefore decided not to include the present comparison results in the current report, and an audit of the WCC-N_2O should be foreseen as soon as the current issues have been solved.

Recommendation 4 (critical, as soon as N_2O calibration issues are solved)
Re-assessment of the PAL N_2O measurements by the WCC-N_2O is highly recommended as soon as the current technical issues with the measurement system are solved.

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). The TI was running from 21 April 2012 through 9 June 2012. Most of the comparison results were already published [*Rella et al.*, 2013]. Excellent results within the WMO/GAW DQOs were found even on the level of one-minute data between FMI and WCC-Empa for the Picarro G2401 instrument for CO_2 and CH_4 after correction of the PAL data based on the performance audit results. Rella et al. [2013] shows only data until 30 May 2012 due to the fact that after this time the manifold of the PAL station sampled partly laboratory air due to an uncapped inlet port at the manifold. This resulted in higher methane mole fractions of the PAL measurements, because indoor CH_4 is significantly elevated due to the use of CH_4 in Ar as a carrier gas of the GC/ECD N_2O measurement system.

Figure 7 shows the CH_4 comparison as also presented by Rella et al. [2013] but for the complete period of parallel measurements. It can be seen that the CH_4 measurements of PAL are significantly elevated after 30 Mai 2012 for the periods when the WCC-Empa travelling instrument was measuring on its own dedicated inlet system. The reason for this was an open cap in the PAL manifold, which was closed again on 5 June. It is therefore extremely important that the inlet system is completely

tight. Furthermore, it should be considered to actively exhaust the carrier gas emissions of the GC/ECD system to a location downwind of the laboratory building.

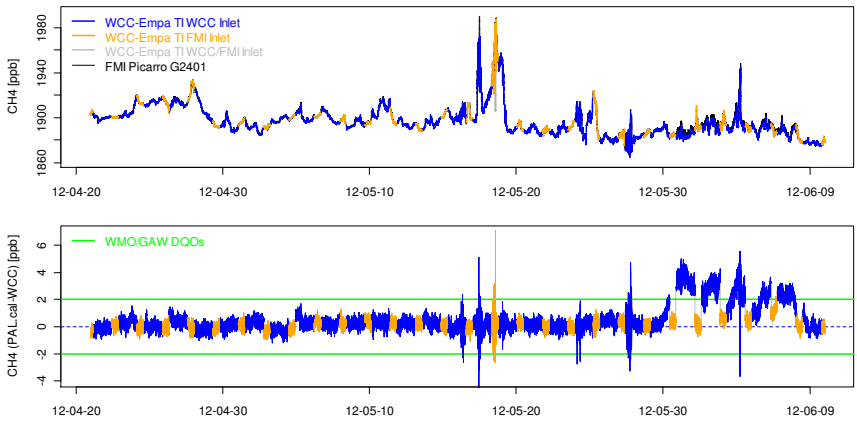

Figure 7. *Upper panel: CH_4 time series (1-min averages) measured at PAL with the Picarro G2401 travelling instrument and the PAL Picarro G2401 of FMI. Lower panel: Deviation of the FMI system compared to the travelling instrument. The green lines refer to the WMO/GAW DQOs.*

Recommendation 5 (, important, 2013)**
CH_4 emissions of the GC/ECD system can be problematic for the methane measurements at PAL. It must be made sure that the exhaust of the GC system is not compromising the CH_4 measurements.

Figure 8 shows the CO_2 comparison between the LI-COR LI-7000 instrument and the WCC-Empa TI. As it could already be shown for the Picarro G2401 analyser of PAL [*Rella et al.*, 2013], most of the individual 1-min values were within the WMO/GAW DQOs. No difference between the WCC-Empa and the PAL inlet was observed, which indicates that the whole measurement set-up of PAL is fully appropriate. For CO_2, no bias was present during the period with the open manifold cap, which indicates that indoor CO_2 mole fractions were not significantly elevated during this period.

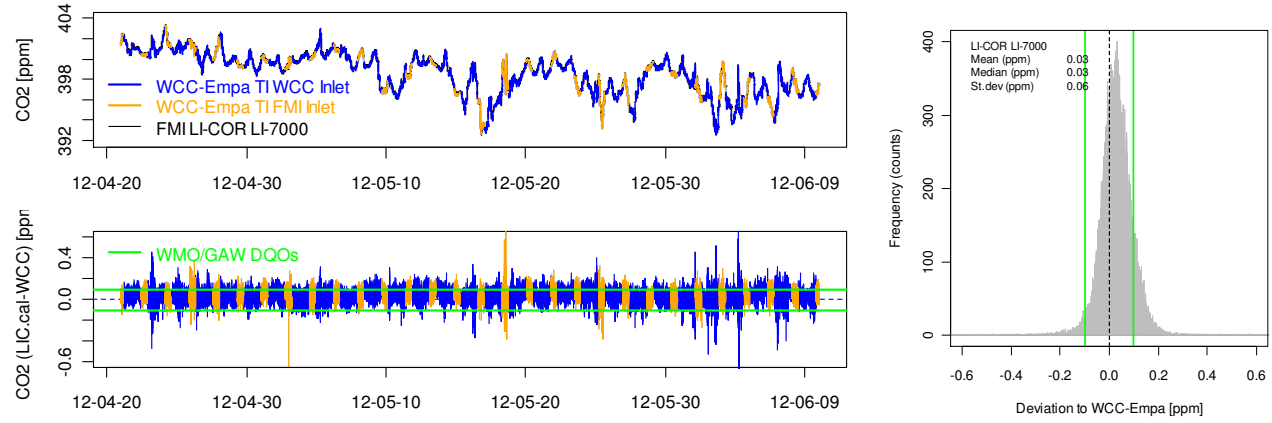

Figure 8. *Upper left panel: CO_2 time series (1-min averages) measured at PAL with the Picarro G2401 travelling instrument and the LI-COR LI-7000 system of FMI. Lower left panel: Deviation of the PAL system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

In contrast to the CO_2 and CH_4 comparison, the results for the ambient CO comparison were significantly worse. Figure 9 shows the CO comparison between the PAL Picarro G2401 and the WCC-Empa TI.

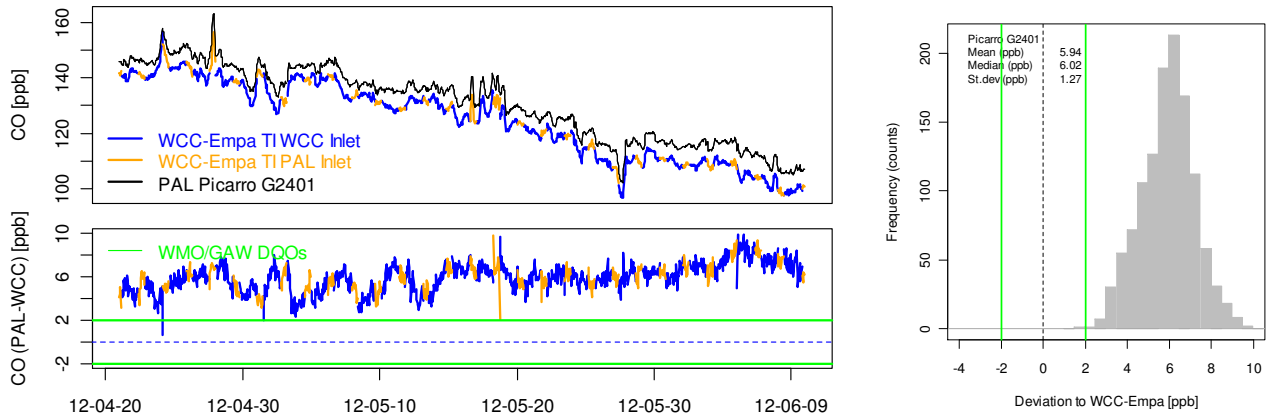

Figure 9. *Upper left panel: CO time series (1-h averages) measured at PAL with the Picarro G2401 travelling instrument and the Picarro G2401 #CFKADS-2018 system of FMI. Lower left panel: Deviation of the PAL system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

The temporal variation of CO was well captured by both instruments; however, a negative bias in the range of 2 – 10 ppb CO was observed for the WCC-Empa measurements. Most likely the bias is due to imperfect correction of the water vapour interference of the WCC-Empa TI. A clear indication is the fact that a dependency of the bias and the H_2O levels at PAL was observed, which is further illustrated in Figure 10.

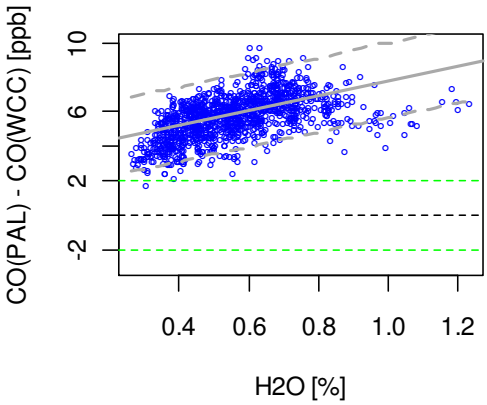

Figure 10. *Dependency of the difference between PAL and WCC-Empa CO measurements and the H_2O mixing ratio. The green lines refer to the WMO/GAW DQOs. The grey lines correspond to a linear fit with 95% confidence intervals.*

These findings indicate that special care is needed when CO measurements are made with CRDS technique without sample drying. PAL plans to remove the Nafion driers due to the fact that they can cause problems, e.g. humidification of standard gases, for CO_2 and CH_4 measurements. Therefore a full assessment of the CO water vapour correction is needed in case of the operation of the Picarro system without a Nafion drier.

Recommendation 6 (, important, 2013)**
The water vapour correction of the PAL Picarro G2401 needs to be fully evaluated if the instrument is operated without a sample drying system. This is highly important for CO but also recommended for CH_4 and CO_2.

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

CO_2 and CH_4, Picarro G2401 #CFKADS-2018 instrument: The results of the ambient air comparison confirmed the results of the performance audit. The whole measurement set-up is fully adequate. No differences were found between the two inlet systems, which indicate that the FMI air inlet is fully appropriate.

CO, Picarro G2401 #CFKADS-2018 instrument: During the audit the system was operated using a Nafion dryer. In case of humid measurements, further characterisation of the Picarro implemented H_2O correction is needed.

CO_2, LI-COR LI-7000 instrument: Same as above, with slightly larger variability due to higher instrumental noise of the LI-COR instrument compared to the Picarro G2401.

Data Acquisition and Management

Data of all instruments is acquired using a custom made data acquisition system (DAQ) programmed in Python. One minute averaged data is stored for further analysis. Remote access to all instruments is possible, and the data is backed up in regular intervals.

Recommendation 7 (, important, 2013)**
The DAQ software of PAL is a very powerful and sophisticated system, which is fully adequate for its intended purpose. However, all technical knowledge of the DAQ system resides with the programmer (Juha Hatakka). It must be assured that all technical details (documented programming code) is documented and shared with others.

Data Submission

For the parameters of the audit scope, in-situ data for surface ozone (1995 – 2006), methane (2004-2010) and carbon dioxide (1999-2010) was available at the World Data Centre for Greenhouse Gases (WDCGG) at the time of the audit. Carbon monoxide and nitrous oxide data have not yet been submitted.

Recommendation 8 (, 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. Missing data need to be submitted, and GAWSIS entries need also to be regularly updated by the PAL station manager.

Conclusions

The Global GAW station Pallas carries out a comprehensive suite of measurements. The combination of long-term time series with the large number of measured parameters makes the PAL station an important contribution to the GAW programme. All assessed parameters were of high quality. Continuation of the measurements at PAL on a long-term basis is highly recommended.

Summary Ranking of the Pallas GAW Station

System Audit Aspect	Adequacy[#]	Comment
Access	(5)	Year-round access
Facilities		
Laboratory and office space	(5)	Appropriate facilities
Internet access	(5)	FMI intranet and GSM connection possible
Air Conditioning	(5)	Fully operational
Power supply	(5)	Few power outages
General Management and Operation		
Organisation	(4)	Well organised, knowledge concentrated on too few people
Competence of staff	(5)	Highly experienced staff
Air Inlet System	(4)	State-of-the-art, must be leak tight
Instrumentation		
Ozone	(5)	Up-to-date instrumentation
CO (Picarro G2401)	(4)	Up-to-date instrumentation
CO (Peak Performer PP1)	(3)	Calibration / stability issues
CO_2 and CH_4 (Picarro)	(4)	Up-to-date instrumentation
N_2O (GC/ECD)	(3)	Calibration issues
Standards		
Ozone	(5)	FMI TS with SRP traceability
CO, CH_4, CO_2	(5)	NOAA and working standards
Data Management		
Data acquisition	(5)	Python based central DAQ
Data processing	(5)	Highly experienced staff
Data submission	(2)	Partly long submissions delays (>3yrs), CO and N_2O not submitted

[#]0: inadequate thru 5: adequate.

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Dübendorf, July 2013

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

APPENDIX

Global GAW Station Pallas

Site description and measurement programme

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

Links: http://fmigaw.fmi.fi/
http://gaw.empa.ch/gawsis/reports.asp?StationID=6

Trace Gas Distributions at Pallas

The monthly and yearly distribution for surface ozone, carbon monoxide, methane and carbon dioxide at Pallas is shown in Figure 11.

Organisation and Contact Persons

The GAW activities of Finland are coordinated by the Finnish Meteorological institute under the Research and Development department (Director Yrjö Viisanen). Further information about the organisation can be found on the station (http://fmigaw.fmi.fi) and FMI (www.fmi.fi) web sites. The PAL station is also part of the European ICOS (Integrated Carbon Observing System) programme (http://en.ilmatieteenlaitos.fi/GHG-measurement-sites#Pallas_Sammaltunturi).

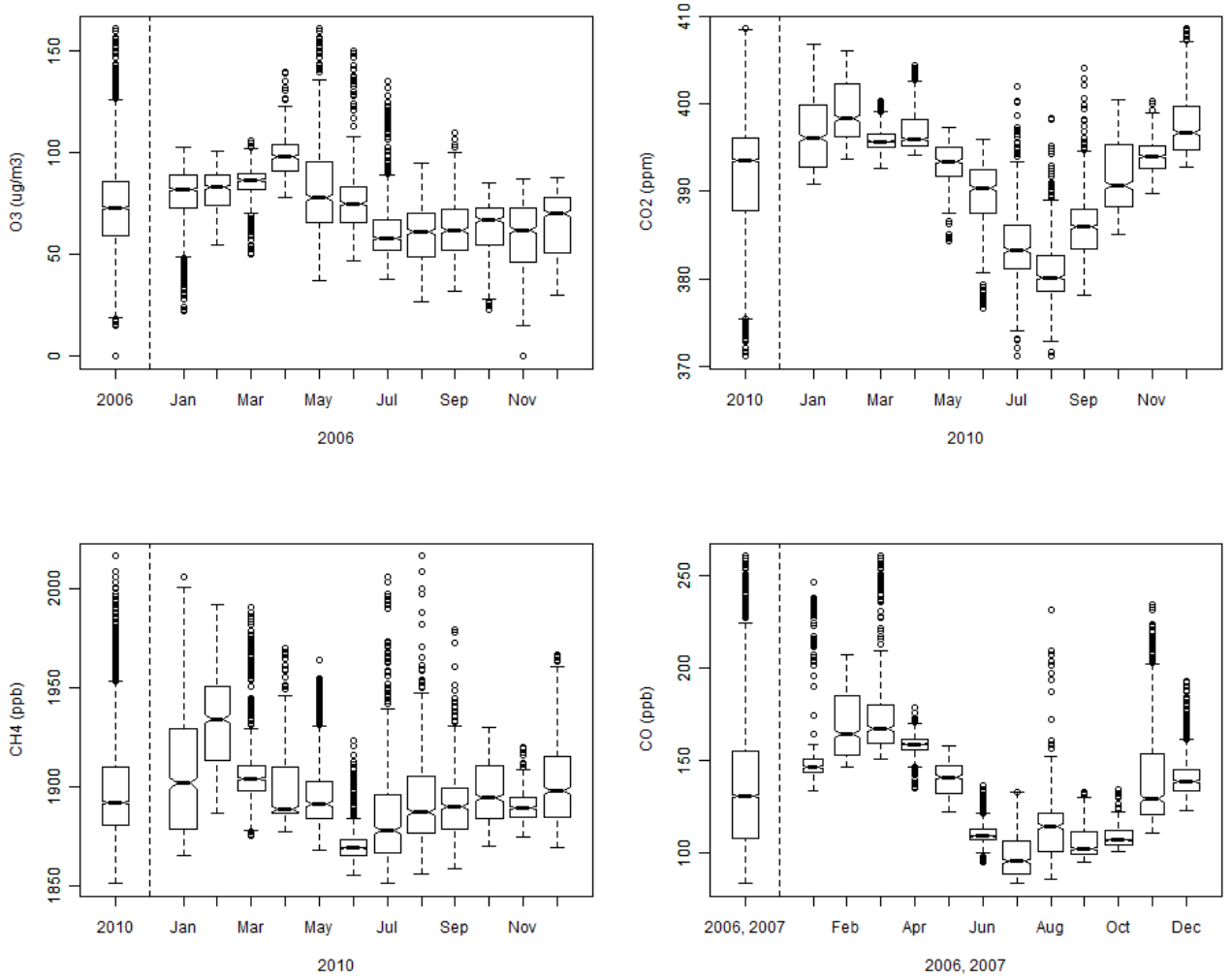

Figure 11. Yearly and monthly box plots for surface ozone (2006), carbon monoxide (2006/07), carbon dioxide and methane (both 2010). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this 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

The air inlet system has not been changed since the last audit by WCC-Empa in 2007.

Location of air intake:	7 m above ground on top of the laboratory building.
Inlet protection:	Protection against rain water / snow / insects.
Tubing / Material:	3 m heated sample inlet on the roof, leading to the laboratory where all instruments are connected to the common sampling line. Outer/inner diameter 60/54 mm, acid resistant stainless steel. Total length ca. 12 m. Ozone instruments are connected after a total length of ca. 8 m. Flow rate 150 m^3 per hour.
Inlet filter:	Teflon inlet filter before analyser exchanged 3-monthly or when dirty.
Residence time:	approx. 2 s

Instrumentation

The station is currently equipped with one TEI 49i ozone analyser. Instrumental details are summarised in Table 1.

Standards

No ozone standard is available at the site, but 3 monthly calibrations are made with a travelling standard calibrated at FMI against SRP#37.

Operation and Maintenance

Check for general operation:	Once a week by station operator.
Zero / Span check:	No automatic checks are made.
Calibration/checks with standard:	Four times per year with SRP traceable TS.
Inlet filter exchange:	Usually every 3 months.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

Unchanged since the last audit in 2007. A commercial system (Envidas, Envitech Ltd.) is used for data acquisition. Data is automatically transferred to FMI.

Data Treatment

Unchanged since the last audit in 2007. Data processing is done at FMI and consists of a daily visual inspection of time series. Invalid values, i.e. data from manual calibrations, are flagged as invalid data but are not removed from the database. Furthermore, concentrations lower 0 and higher 200 ppb are automatically flagged as invalid. Based on the results of the quarterly calibrations a recalculation of the acquired data is made.

Documentation

Electronic station and instrument logbooks were available. 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 120 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).

Table 1. Experimental details of the PAL ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
Settings	BKG = -0.2; COEFF = 1.009
Pressure readings (hPa)	Ambient 701.1, TS 701.1, no adjustments were made
Station Analyser (OA)	
Model, S/N	TEI 49i #0619917500
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = -0.2; COEFF = 1.010
Pressure readings (hPa)	Ambient 701.1, OA 708.2, 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 and pressure sensor readings 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 Table (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 PAL ozone analyser (OA) TEI 49i #0619917500 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 (%)
2012-04-18 18:21	1	0	0.21	0.29	0.17	0.05	0.08	NA
2012-04-18 18:41	1	45	45.04	44.07	0.12	0.07	-0.97	-2.2
2012-04-18 19:01	1	120	119.96	117.58	0.08	0.08	-2.38	-2.0
2012-04-18 19:21	1	30	29.99	29.53	0.14	0.07	-0.46	-1.5
2012-04-18 19:41	1	15	14.99	14.88	0.16	0.05	-0.11	-0.7
2012-04-18 20:01	1	90	90.00	88.51	0.07	0.05	-1.49	-1.7
2012-04-18 20:21	1	60	60.02	58.98	0.10	0.07	-1.04	-1.7
2012-04-18 20:41	1	105	104.99	103.01	0.05	0.08	-1.98	-1.9
2012-04-18 21:01	1	75	74.99	73.61	0.07	0.06	-1.38	-1.8
2012-04-18 21:21	2	0	0.31	0.28	0.08	0.03	-0.03	NA
2012-04-18 21:41	2	15	15.02	14.75	0.13	0.05	-0.27	-1.8
2012-04-18 22:01	2	60	60.02	59.04	0.11	0.09	-0.98	-1.6

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-04-18 22:21	2	30	30.03	29.51	0.15	0.08	-0.52	-1.7
2012-04-18 22:41	2	120	119.99	117.77	0.11	0.07	-2.22	-1.9
2012-04-18 23:01	2	75	75.01	73.52	0.08	0.06	-1.49	-2.0
2012-04-18 23:21	2	90	89.99	88.34	0.10	0.09	-1.65	-1.8
2012-04-18 23:41	2	45	44.99	43.94	0.10	0.07	-1.05	-2.3
2012-04-19 00:01	2	105	105.01	103.01	0.13	0.10	-2.00	-1.9
2012-04-19 00:21	3	0	0.31	0.24	0.17	0.03	-0.07	NA
2012-04-19 00:41	3	90	89.99	88.37	0.09	0.07	-1.62	-1.8
2012-04-19 01:01	3	15	15.01	14.47	0.26	0.08	-0.54	-3.6
2012-04-19 01:21	3	30	30.03	29.35	0.13	0.07	-0.68	-2.3
2012-04-19 01:41	3	75	74.98	73.48	0.05	0.07	-1.50	-2.0
2012-04-19 02:01	3	60	59.98	58.61	0.10	0.10	-1.37	-2.3
2012-04-19 02:21	3	45	45.00	44.13	0.09	0.06	-0.87	-1.9
2012-04-19 02:41	3	105	104.99	102.94	0.09	0.09	-2.05	-2.0
2012-04-19 03:01	3	120	120.01	117.68	0.11	0.07	-2.33	-1.9
2012-04-19 03:21	4	0	0.28	0.21	0.21	0.03	-0.07	NA
2012-04-19 03:41	4	45	45.00	44.30	0.12	0.10	-0.70	-1.6
2012-04-19 04:01	4	120	120.00	117.65	0.13	0.09	-2.35	-2.0
2012-04-19 04:21	4	30	30.01	29.35	0.21	0.11	-0.66	-2.2
2012-04-19 04:41	4	15	14.98	14.81	0.20	0.11	-0.17	-1.1
2012-04-19 05:01	4	90	89.96	88.00	0.14	0.13	-1.96	-2.2
2012-04-19 05:21	4	60	60.01	58.71	0.09	0.12	-1.30	-2.2
2012-04-19 05:41	4	105	105.01	102.92	0.15	0.12	-2.09	-2.0
2012-04-19 06:01	4	75	74.97	73.35	0.11	0.09	-1.62	-2.2

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 PeakPerformer instrument shares a Nafion drier with the GC/ECD system. The Picarro CRDS analyser takes its sample air from the manifold through a 1/8" SS-tube. This tube goes from the manifold to a 3-way magnetic valve, from valve to a Nafion dryer (PermaPure MD-070-96S-2), and from dryer to the analyser. Purge air for the Nafion is taken from the analyser's vacuum line (re-flux method).

Inlet filter: Picarro built-in internal filter is used. PeakPerformer has its own inlet filter.

Residence time: < 2 s

Instrumentation

PeakPerformer PP1 GC/HgO system and Picarro G2401 CRDS analyser. Instrumental details are listed in Table 4.

Standards

The PAL station is equipped with 7 NOAA laboratory standards. Table 3 shows an overview of the standards available at PAL. The data refers to the WMO-2004 calibration scale. The CRDS instrument

is calibrated using a target cylinder of dried compressed air which is measured every 9.5 hours for 15 minutes. The target tank was calibrated against the NOAA tanks available at PAL.

Table 3. CO Standards at PAL.

Cylinder ID	Type	At PAL since	CO (ppb)	sd (ppb)	FMI assigned (ppb)	sd (ppb)
CA06177	NOAA	2005	72.35	1.45	71.90	0.80
CA06249	NOAA	2005	151.92	0.62	151.5	0.2
CA06206	NOAA	2005	233.77	1.62	236.9	0.5
CC339465	NOAA	2011	89.03	0.08	NA	NA
CC2551	NOAA	2011	157.32	0.10	NA	NA
CC2590	NOAA	2011	224.30	0.18	NA	NA
CC2588	NOAA	2011	293.21	0.36	NA	NA

Operation and Maintenance

Check for general operation: week by station operator, more often by remote access.

Other maintenance: As required.

Data Acquisition and Data Transfer

Custom made (Python) as well as Picarro software.

Data Treatment

Before further processing the analyser raw data is calculated as one minute averages with standard deviations. Results are calculated taking into consideration the calibrations, i.e. possible changes in analyser's response for each component. The target cylinder results are (currently) not used to adjust the results between calibrations. Entries in the station log book are also considered for data validation.

Documentation

All information is entered in electronic log books. 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 16 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 PAL data acquisition system.

Table 4. Experimental details of PAL 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 16.	
Station Analyser (AL)	
Model, S/N	Picarro G2401 #CFKADS-2018 (main CO analyser)
Principle	CRDS
Drying system	PERMAPURE Nafion drier in sample line (PermaPure MD-070-96S-2)
Calibration settings	Target tank measurement every 9.5 hours
Model, S/N	PeakPerformer PP1 #084
Principle	GC/HgO Reduction Gas Detector
Calibration settings	Frequent calibrations using a working standard (every third sample is WS, in addition a target cylinder is measured every 2h for 15 minutes)
Comparison procedures	
Connection	Picarro G2401: 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 5 and Table 6.

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 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 (%)
(12-04-18 09:01:30)	110511_FB03384	101.3	1.3	103.2	1.9	18	1.9	1.9
(12-04-18 07:04:00)	100122_FA02469	1.4	0.1	2.4	2.1	9	1.0	NA
(12-04-18 10:02:30)	110511_FB03358	57.2	1.1	58.0	1.7	18	0.8	1.5
(12-04-18 10:02:00)	080814_FA02466	83.9	0.2	85.1	1.9	18	1.3	1.5
(12-04-18 08:36:00)	110808_FA02505	191.0	0.6	191.7	1.9	9	0.7	0.3
(12-04-18 09:05:00)	070927_FF21167	184.7	0.1	186.3	1.9	9	1.6	0.9
(12-04-18 12:59:00)	100122_FA02479	51.0	0.7	52.2	1.9	9	1.2	2.3
(12-04-18 13:31:00)	070807_FA02782	155.2	0.2	156.4	2.4	9	1.2	0.8
(12-04-18 14:01:00)	070807_FA02770	150.3	0.5	151.5	2.1	9	1.3	0.8

Table 6. Same as Table 5 for the PeakPerformer PP1.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	GC (ppb)	sdGC (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-04-17 09:43:30)	110511_FB03358	57.2	1.1	66.1	2.6	10	8.9	15.6
(12-04-17 11:13:30)	110808_FA02505	191.0	0.6	209.1	7.2	14	18.1	9.5
(12-04-17 12:43:30)	110512_FB03350	210.4	0.7	221.8	2.7	10	11.4	5.4
(12-04-17 13:58:30)	110511_FB03384	101.3	1.3	106.1	0.5	10	4.8	4.7
(12-04-17 15:28:30)	100122_FA02479	51.0	0.7	59.3	2.2	10	8.3	16.2
(12-04-17 16:43:30)	110512_FB03346	114.1	0.6	118.1	2.1	10	4.1	3.6
(12-04-18 09:13:30)	080814_FA02466	83.9	0.2	86.0	0.8	14	2.2	2.6
(12-04-18 10:58:30)	070927_FF21167	184.7	0.1	191.5	1.0	14	6.8	3.7

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

Same as for carbon monoxide.

Instrumentation

Picarro G2401 and Picarro G1301 (not used, at PAL as backup system). Instrumental details are listed in Table 8.

Standards

Currently, 7 NOAA CH_4 standards (NOAA04 scale) are available at PAL. Table 7 shows an overview of the currently available standards at PAL. The CRDS instrument is calibrated using a target cylinder of dried compressed air which is measured every 9.5 hours for 15 minutes. The target tank was calibrated against the NOAA tanks available at PAL.

Table 7. CH_4 NOAA standards at PAL.

Cylinder ID	Type	At PAL since	CH_4 (ppb)	sd (ppb)	FMI assigned (ppb)	sd (ppb)
CA06177	NOAA	2005	1813.34	0.12	1812.76	0.12
CA06249	NOAA	2005	1946.48	0.48	1945.05	0.07
CA06206	NOAA	2005	1996.65	0.55	1995.09	0.18
CC339477	NOAA	2012	1732.32	0.14	NA	NA
CB08943	NOAA	2012	1846.18	0.25	NA	NA
CB09049	NOAA	2012	1899.89	0.03	NA	NA
CB09035	NOAA	2012	1996.76	0.19	NA	NA

Operation and Maintenance

Same as for carbon monoxide.

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 16 below.

Setup and Connections

Table 8 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 8. Experimental details of the PAL CH_4 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 16.	
Station Analyser (OA)	
Model, S/N	Picarro G2401 #CFKADS-2018
Principle	CRDS
Drying system	Nafion PermaPure MD-070-96S-2
Comparison procedures	
Connection	The TS were connected to a 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 the following Table.

Table 9. CH_4 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Picarro G2401 #CFKADS-2018 (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 (%)
(12-04-18 09:01:30)	110511_FB03384	1895.34	0.14	1894.23	0.08	18	-1.11	-0.06
(12-04-18 07:04:00)	100122_FA02469	1842.37	0.03	1841.46	0.12	9	-0.91	-0.05
(12-04-18 10:02:30)	110511_FB03358	1777.80	0.06	1777.35	0.08	18	-0.45	-0.03
(12-04-18 10:02:00)	080814_FA02466	1734.92	0.06	1735.01	0.12	18	0.09	0.01
(12-04-18 08:36:00)	110808_FA02505	2150.34	0.14	2147.62	0.07	9	-2.72	-0.13
(12-04-18 09:05:00)	070927_FF21167	1664.08	0.09	1664.82	0.11	9	0.74	0.04
(12-04-18 12:59:00)	100122_FA02479	1893.42	0.09	1892.20	0.05	9	-1.22	-0.06
(12-04-18 13:31:00)	070807_FA02782	1789.53	0.18	1789.68	0.19	9	0.15	0.01
(12-04-18 14:01:00)	070807_FA02770	1862.54	0.31	1862.13	0.11	9	-0.41	-0.02

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

Picarro: Same as for carbon monoxide.

LI-COR: Sample air is taken from the manifold through a 1/8" SS-tube by a Metal Bellows MB-158E pump. After the pump the sample air is dried with two Nafion dryers in series (PermaPure MD-070-96S-2), which uses dried (dew point ca. -40 C) compressed air as purge gas. Total sample air flow rate is ca. 2 l/min. After the dryer the flow is divided between the N_2O GC, H_2/CO GC and the Licor systems. The flow going to the Licor system is further dried with a chemical desiccant (ca. 80 ml of magnesium perchlorate), through which a continuous sample flow is maintained. After the dryer the sample is connected to a 12-port Valco rotary valve, to which also a reference gas, a target gas and three station standards are connected. In addition a secondary 10-port Valco rotary valve, to which seven WMO/CCL standards are connected, is connected to this valve. Sample flow rate through the analyser is set to 100 ml/min and the reference flow rate to 10 ml/min. All flows are controlled by MFCs. Total sample air residence time is ca. 3 seconds.

Instrumentation

LI-COR LI-7000, Picarro G2401 (since 2012) and Picarro G1301 (not used, at PAL as backup system).

Standards

The following Table gives an overview of the available CO_2 standards at PAL. The data refers to the WMO X2007 calibration scale.

Table 10. CO_2 Standards at PAL.

Cylinder ID	Type	At PAL since	CO_2 (ppm)	sd (ppm)	FMI assigned (ppm)	sd (ppm)
CA04160	NOAA	2000	337.54	0.05	337.48	0.02
CA04187	NOAA	2000	358.14	0.02	358.13	0.02
CA04185	NOAA	2000	366.05	0.02	366.05	0.02
CA04191	NOAA	2000	380.69	0.00	380.69	0.01
CA04182	NOAA	2000	390.62	0.01	390.62	0.01
CA04163	NOAA	2000	410.58	0.01	410.55	0.01
CA04151	NOAA	2000	446.84	0.02	446.70	0.01
CC339477	NOAA	2012	352.142	0.01	NA	NA
CB08943	NOAA	2012	396.162	0.00	NA	NA
CB09049	NOAA	2012	451.266	0.02	NA	NA
CB09035	NOAA	2012	497.264	0.02	NA	NA

Operation and Maintenance

Same as for methane.

Data Acquisition and Data Transfer

Same as for methane.

Data Treatment

Same as for methane.

Documentation

Same as for methane.

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 16 below.

Setup and Connections

Table 11 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 systems.

Table 11. Experimental details of the PAL CO_2 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 16.	
Station Analysers (OA)	
Model	Picarro G2401 #CFKADS-2018
Principle	CRDS
Drying system	(Permapure MD-070-96S-2)
Model	LI-COR LI-7000
Principle	NDIR
Drying system	Two Nafion dryers in series (Permapure MD-070-96S-2), followed by $Mg(ClO_4)_2$ trap
Comparison procedures	
Connection	The TS were connected to a spare calibration gas ports (LI-COR) and to the sample port with excess flow (Picarro).

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 12. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Picarro G2401 #CFKADS-2018 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 (%)
(12-04-18 09:01:30)	110511_FB03384	323.92	0.05	324.07	0.01	18	0.15	0.05
(12-04-18 07:04:00)	100122_FA02469	384.14	0.04	384.11	0.01	9	-0.03	-0.01
(12-04-18 10:02:30)	110511_FB03358	318.53	0.02	318.69	0.01	18	0.16	0.05
(12-04-18 10:02:00)	080814_FA02466	179.25	0.01	179.70	0.01	18	0.45	0.25
(12-04-18 08:36:00)	110808_FA02505	373.41	0.02	373.43	0.01	9	0.02	0.01
(12-04-18 09:05:00)	070927_FF21167	352.37	0.01	352.44	0.01	9	0.07	0.02
(12-04-18 12:59:00)	100122_FA02479	406.94	0.02	406.90	0.01	9	-0.04	-0.01
(12-04-18 13:31:00)	070807_FA02782	394.24	0.04	394.23	0.01	9	-0.01	0.00
(12-04-18 14:01:00)	070807_FA02770	391.76	0.04	391.77	0.01	9	0.01	0.00

Table 13. 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 (%)
(12-04-18 17:57:00)	110808_FA02505	373.41	0.02	373.56	0.02	8	0.15	0.04
(12-04-18 17:57:00)	110512_FB03350	384.92	0.02	385.02	0.02	8	0.10	0.03
(12-04-18 17:57:00)	100122_FA02479	406.94	0.02	406.98	0.03	8	0.04	0.01
(12-04-18 17:57:00)	110512_FB03346	341.83	0.04	341.96	0.05	8	0.13	0.04

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 –zero air generator (Breitfuss) – 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 14. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 12). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in [*Klausen et al.*, 2003]).

$$X_{TS}\ (\text{ppb}) = ([TS] - 0.16\ \text{ppb}) / 1.0015 \qquad (6a)$$

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

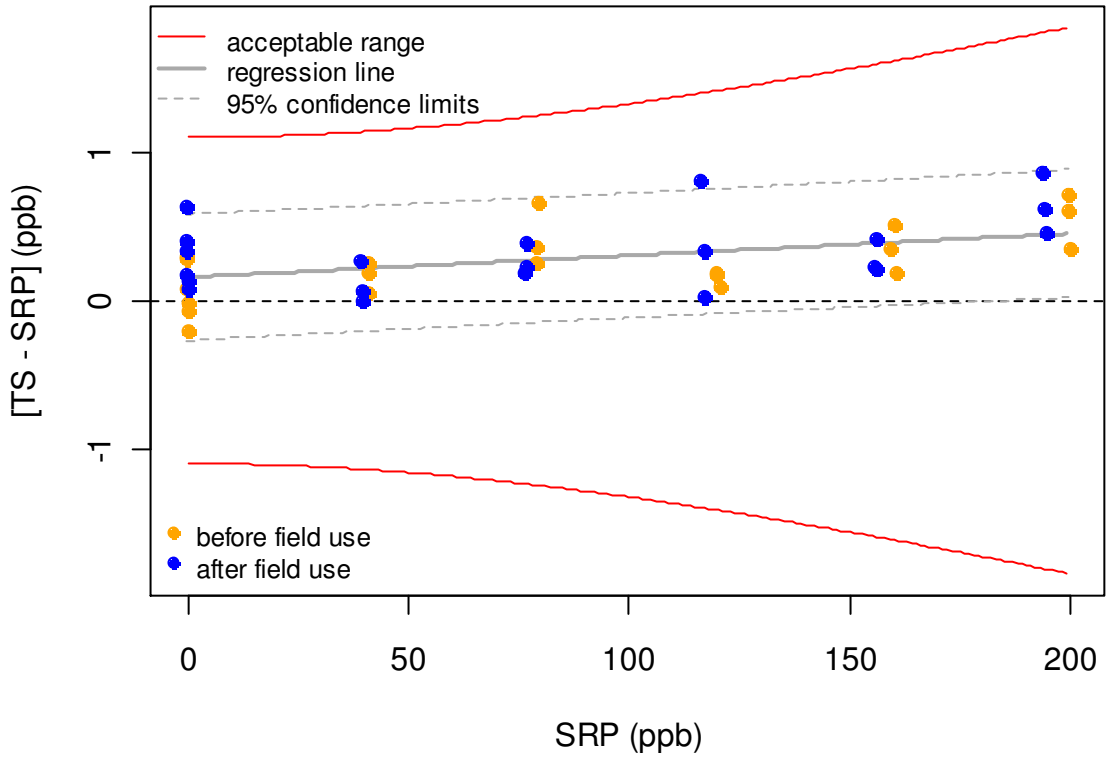

Figure 12. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 14. 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)
2011-12-20	1	0	0.27	0.23	0.06	0.13
2011-12-20	1	80	41.05	0.20	41.22	0.18
2011-12-20	1	160	160.53	0.27	160.72	0.26
2011-12-20	1	120	199.80	0.32	200.15	0.30
2011-12-20	1	200	78.98	0.24	79.35	0.20
2011-12-20	1	40	119.91	0.27	120.09	0.17
2011-12-20	1	0	-0.14	0.33	0.14	0.11
2011-12-20	2	0	-0.07	0.54	0.01	0.22
2011-12-20	2	40	79.27	0.48	79.93	0.18
2011-12-20	2	160	160.12	0.40	160.64	0.34
2011-12-20	2	200	40.78	0.62	41.04	0.20
2011-12-20	2	120	199.40	0.26	200.11	0.15
2011-12-20	2	80	119.85	0.30	120.02	0.12
2011-12-20	2	0	0.02	0.35	0.01	0.14
2011-12-20	3	0	-0.13	0.28	0.16	0.22
2011-12-20	3	80	120.76	0.15	120.86	0.18
2011-12-20	3	40	79.16	0.20	79.42	0.15
2011-12-20	3	160	159.32	0.22	159.67	0.35
2011-12-20	3	200	199.31	0.26	199.91	0.23
2011-12-20	3	120	41.03	0.27	41.08	0.20
2011-12-20	3	0	0.15	0.25	0.08	0.23
2012-07-03	4	0	-0.21	0.32	0.12	0.17
2012-07-03	4	80	76.82	0.12	77.21	0.36
2012-07-03	4	160	155.81	0.31	156.02	0.28
2012-07-03	4	120	39.40	0.23	39.40	0.24
2012-07-03	4	200	194.46	0.22	194.92	0.26
2012-07-03	4	40	116.12	0.37	116.93	0.29
2012-07-03	4	0	0.22	0.20	0.30	0.25
2012-07-03	5	0	-0.09	0.34	0.32	0.41
2012-07-03	5	40	117.25	0.40	117.59	0.33
2012-07-03	5	160	76.53	0.25	76.75	0.12
2012-07-03	5	200	155.54	0.27	155.77	0.17
2012-07-03	5	120	194.03	0.29	194.65	0.27
2012-07-03	5	80	39.30	0.41	39.57	0.34
2012-07-03	5	0	-0.04	0.19	0.13	0.20
2012-07-03	6	0	-0.32	0.18	0.32	0.10
2012-07-03	6	80	155.95	0.37	156.36	0.28
2012-07-03	6	40	39.43	0.16	39.50	0.25
2012-07-03	6	160	116.95	0.41	116.98	0.21
2012-07-03	6	200	193.68	0.37	194.54	0.24
2012-07-03	6	120	76.26	0.17	76.45	0.21
2012-07-03	6	0	-0.01	0.35	0.12	0.10

[#]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:

CO: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).

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

Table 15 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 16, and Figure 13 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 15. 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	322.52	0.12	396.88	0.06	348.4	0.3	1855.31	0.03	322.52	0.02	396.94	0.02
CC339524	390.7	0.2	1980.28	0.30	355.42	0.16	795.42	0.06	391.0	0.4	1981.77	0.04	355.42	0.02	796.36	0.04
CC311846	166.4	0.1	1805.24	0.12	338.27	0.11	377.86	0.04	167.3	0.3	1805.31	0.11	338.27	0.01	377.84	0.02

Table 16. Calibration summary of the WCC-Empa travelling standards.

TS	CO (ppb)	sdCO (ppb)	CH_4 (ppb)	sdCH_4 (ppb)	CO_2 (ppm)	sdCO_2 (ppm)	N_2O (ppb)	sdN_2O (ppb)
070807_FA02770	150.25	0.54	1862.54	0.31	391.76	0.04	322.94	0.07
070807_FA02782	155.21	0.21	1789.53	0.18	394.24	0.04	326.1	0.02
070927_FF17309	216.18	0.5	1821.57	0.1	387.6	0.01	340.22	0.21
070927_FF21167	184.68	0.1	1664.08	0.09	352.37	0.01	401.97	0.05
080814_FA02466	83.88	0.17	1734.92	0.06	179.25	0.01	137.29	0.66
100122_FA02469	1.4	0.12	1842.37	0.03	384.14	0.04	304.45	0.07
100122_FA02479	51.04	0.69	1893.42	0.09	406.94	0.02	305.53	0.07
110511_FB03358	57.16	1.13	1777.8	0.06	318.53	0.02	314.04	0.04
110511_FB03384	101.25	1.32	1895.34	0.14	323.92	0.05	307.38	0.07
110512_FB03346	114.05	0.63	2772.65	0.1	341.83	0.04	321.46	0.04
110512_FB03350	210.36	0.72	2761.41	0.07	384.92	0.02	312.72	0.04
110808_FA02505	191.03	0.62	2150.34	0.14	373.41	0.02	322.5	0.05

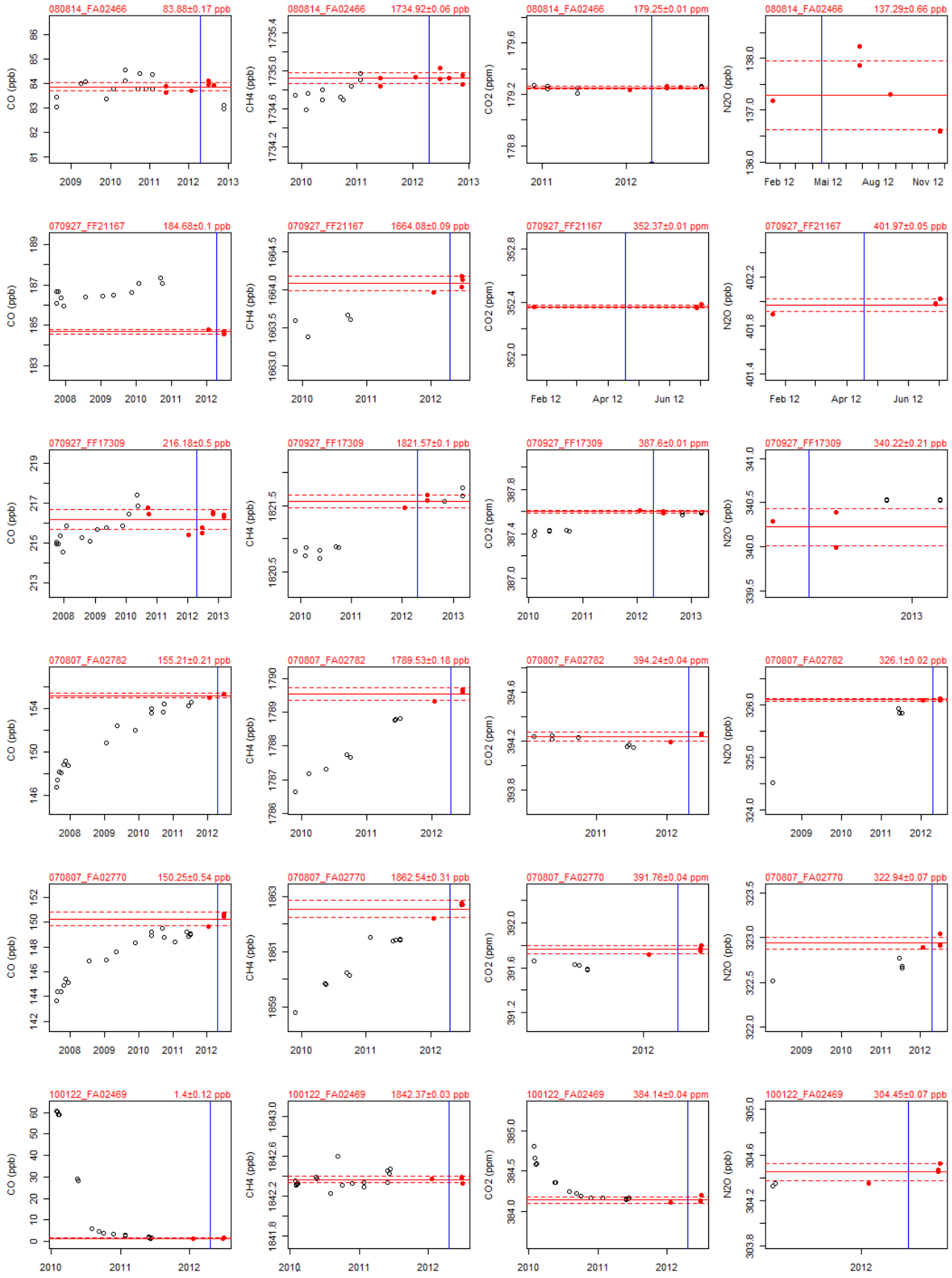

Figure 13. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue horizontal line refers to the date of the audit.*

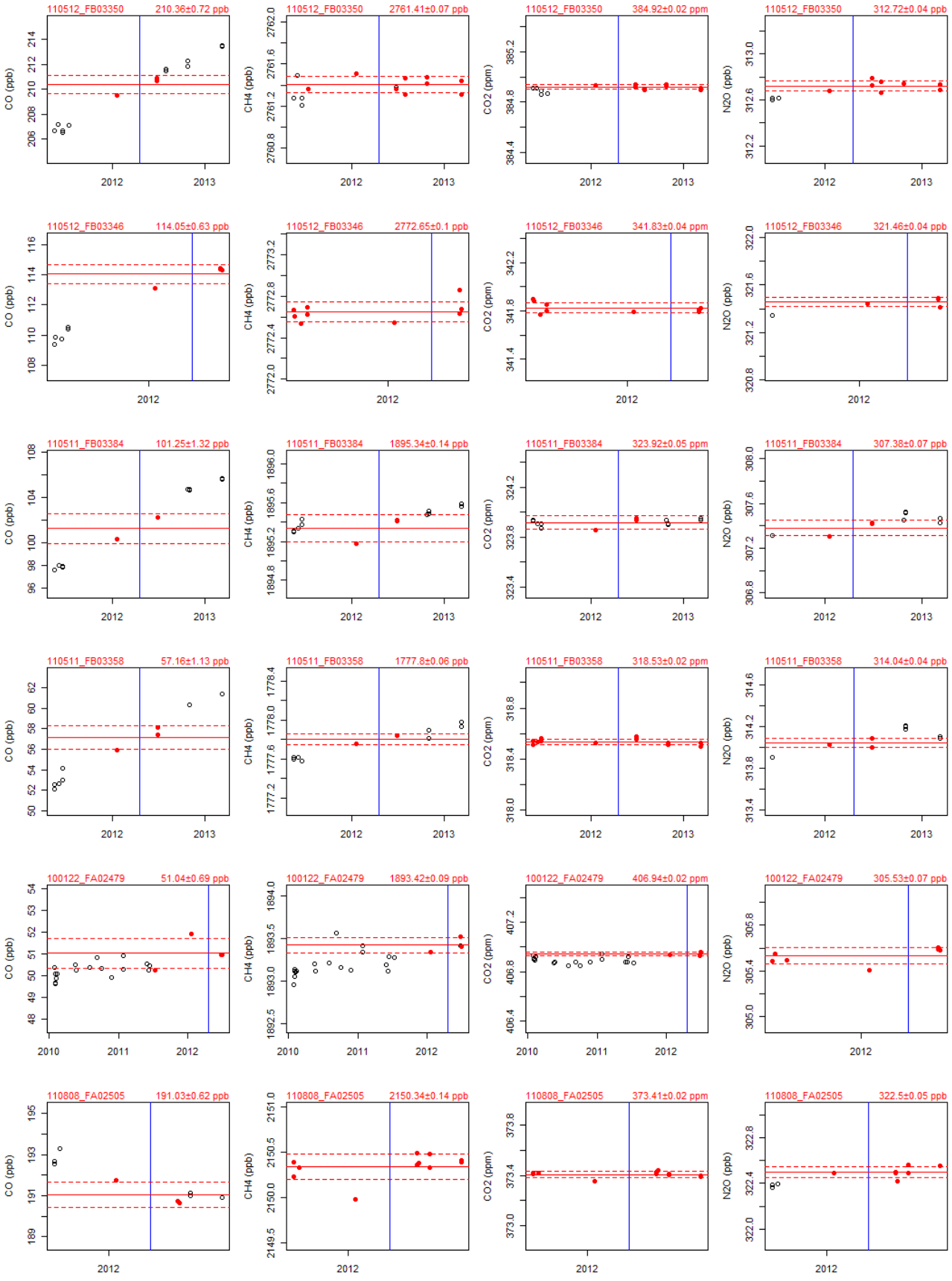

Figure 14. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.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

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Ozone Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.97361°N, 24.11583°E (560 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-04-18 through 2012-04-18
1.2	Auditor:	Dr. C. Zellweger, Mr. P. Graf
1.3	Station staff involved in audit:	Mr. Juha Hatakka, Mr. Timo Anttila
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):	(1.0015±0.0012) · [SRP] + (0.16±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #0619917500
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = -0.2; COEFF = 1.010
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9825±0.0006) · [SRP] + (0.1±0.0)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.1 ppb) / 0.9825
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.3 ppb^2 + 2.78e-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:	OA pressure sensor 1 % higher than ambient
1.8	Reference:	WCC-Empa Report 12/1

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

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Carbon Monoxide Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.97361°N, 24.11583°E (560 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-04-18
1.2	Auditor:	Dr. C. Zellweger, Mr. P. Graf
1.3	Station staff involved in audit:	Mr. Juha Hatakka
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 #CFKADS-2018
1.6.2	Range of calibration:	0 – 191 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CO = (1.0009 \pm 0.0022) \cdot X_{CO} + (1.1 \pm 0.3)$
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 1.1) / 1.0009
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:	Main CO analyser
1.8	Reference:	WCC-Empa Report 12/1

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

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Carbon Monoxide Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.97361°N, 24.11583°E (560 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-04-18
1.2	Auditor:	Dr. C. Zellweger, Mr. P. Graf
1.3	Station staff involved in audit:	Mr. Juha Hatakka
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:	PeakPerformer PP1 #084
1.6.2	Range of calibration:	50 – 210 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CO = (1.0422 \pm 0.0276) \cdot X_{CO} + (2.8 \pm 3.8)$
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 2.8) / 1.0422
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (27.3 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 12/1

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

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Methane Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.97361°N, 24.11583°E (560 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2012-04-18
1.2	Auditor:	Dr. C. Zellweger, Mr. P. Graf
1.3	Station staff involved in audit:	Mr. Juha Hatakka
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 #CFKADS-2018
1.6.2	Range of calibration:	1664 – 2150 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99292 \pm 0.00071) \cdot X_{CH4} + (12.4 \pm 1.3)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 12.4) / 0.99292
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 12/1

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

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Carbon Dioxide Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.97361°N, 24.11583°E (560 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-04-18
1.2	Auditor:	Dr. C. Zellweger, P. Graf
1.3	Station staff involved in audit:	Mr. Juha Hatakka
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 #CFKADS-2018
1.6.2	Range of calibration:	179 – 407 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.99781 \pm 0.0001) \cdot X_{CO2} + (0.85 \pm 0.03)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 - 0.85) / 0.99781
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:	Main CO_2 analyser
1.8	Reference:	WCC-Empa Report 12/1

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

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Carbon Dioxide Audit Executive Summary (PAL)

0.1	Station Name:	Pallas
0.2	GAW ID:	PAL
0.3	Coordinates/Elevation:	67.97361°N, 24.11583°E (560 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-04-18
1.2	Auditor:	Dr. C. Zellweger, P. Graf
1.3	Station staff involved in audit:	Mr. Juha Hatakka
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:	342 – 407 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.99863 \pm 0.0008) \cdot X_{CO2} + (0.62 \pm 0.30)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 – 0.62) / 0.99863
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.01 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:	Backup CO_2 analyser
1.8	Reference:	WCC-Empa Report 12/1

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

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LIST OF ABBREVIATIONS

AD	Analogue/Digital
AL	Analyser
BKG	Background
COEF	Coefficient
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
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
ICOS	Integrated Carbon Observing System
LS	Laboratory Standard
MFC	Mass Flow Controller
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PAL	Pallas
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
TI	Travelling Instrument
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