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

AT THE

GLOBAL GAW STATION MACE HEAD JULY 2013

Submitted to the World Meteorological Organization by

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CONTENTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The seventh system and performance audit by WCC-Empa[1] at the Global GAW station Mace Head was conducted from 22 - 26 July 2013 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). The Mace Head (MHD) atmospheric research station has the dual status of a WMO GAW research and monitoring 'global' station and an EMEP supersite and is operated by the National University of Ireland (NUI) Galway's School of Physics and the University's Ryan Institute Centre for Climate and Air Pollution studies. The MHD research station hosts additional measurement programmes. It is part of the National Oceanic and Atmospheric Administration (NOAA) flask sampling programme, and greenhouse gas measurements are carried out by the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) and the Irish Environmental Protection Agency (EPA). Furthermore, it participates in the Advanced Global Atmospheric Gases Experiment (AGAGE) programme.

Previous audits at MHD were conducted in October 1996 (Herzog et al., 1996), May 1998 (Herzog et al., 1998), August 2002 (Zellweger et al., 2002), May 2005 (Zellweger et al., 2005), and December 2009 (Zellweger et al., 2009).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr Gerry Spain	NUI, Galway, station manager
Prof. Dr Simon O'Doherty	University of Bristol
Dr. Michel Ramonet	LSCE, Measurement Leader Greenhouse Gases
Mr. Benoit Wastine	LSCE, Measurement Leader Greenhouse Gases

This report summarises the assessment of the Mace Head GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide measurements in particular. The ozone assessment was made according to the method developed by WCC-Empa and QA/SAC Switzerland (Klausen et al., 2003).

The report is distributed to all involved institutes, the Irish GAW Country Contact 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 Mace Head Research Station is located on the west coast of Ireland, County Galway. The site offers excellent exposure to the North Atlantic (clean air sector, 180° through west to 300°). The nearest major conurbation is Galway city, approximately 60 km to the east of Mace Head, with a population of approximately 75000. The hilly area around Mace Head is wet and boggy with a lot of exposed rock and vegetation which consists mainly of grasses and sedges. There are three small uninhabited islands offshore which are within the clean air sector. The location is adequate for the intended purpose. Year-round access to MHD is possible by car.

Further information is available from GAWSIS (http://gaw.empa.ch/gawsis) and the station web site (http://macehead.org).

[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 Facilities

The facilities at the site consist of three laboratory buildings, two aluminium walk-up towers, (20m and 10m) and a converted cargo container office. The two shore laboratories, ca. 90m (5masl) from the shore, house gas and aerosol measurement equipment. The cottage laboratory, ca. 300m (21masl) from the shore primarily houses equipment for measurement of atmospheric structure, meteorological and solar radiation parameters. The MHD research station is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Station Management and Operation

The Mace Head Atmospheric Research Facility is managed and operated by the School of Physics, National University of Ireland, Galway. The station is usually visited on working days by the station operator.

Air Inlet Systems

The air inlet systems were not changed since the last audit. Each instrument has its own air inlet system or inlet line. The design of these systems is adequate for its intended purpose, which also has been confirmed by the parallel measurements of CO, CH_4 and CO_2 during the current audit.

Surface Ozone Measurements

Surface ozone measurements started in 1987 at the Mace Head site, and continuous one-hourly time series are available since then.

Instrumentation. The station is equipped with one ozone analyser (TEI 49C) based on the UV absorption. The instrumentation is fully adequate for its intended purpose.

Standards. No ozone standard is available at the site; however, 3-monthly comparisons are made by an external company. These comparisons serve as a quality check and are not considered for adjusting calibration settings.

Recommendation 1 (*, minor, 2014)
The current practice should be continued. Adjustments of the calibration settings should never be made based upon the 3-monthly comparisons. It further should be considered to purchase an ozone standard for periodic instrument checks and calibrations.

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

TEI 49C #77086-385 (Offset -0.2 ppb, Slope 1.020):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.28 ppb) / 1.0012 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.44 ppb^2 + 2.69e-05 * X_{O3}^2) (1b)

The result of the comparison is further illustrated in the below figure.

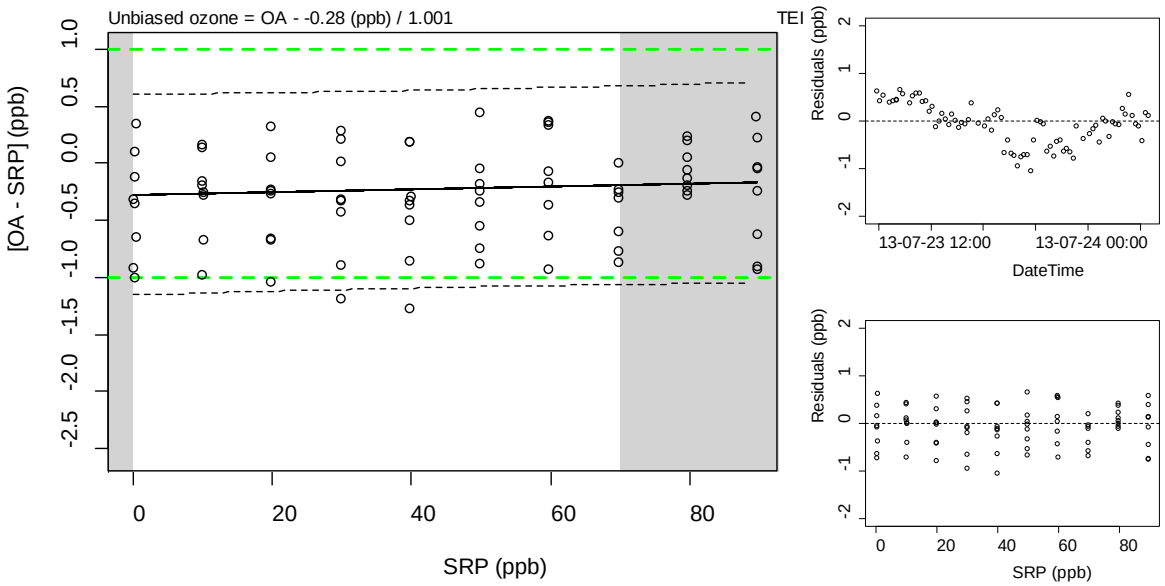

Figure 1. *Left: Bias of the MHD ozone analyser (TEI 49C #77086-385) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The white area represents the mole fraction range relevant for MHD, whereas the green lines 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 TEI 49C #77086-385 ozone analyser is in good calibration and the bias is within the WMO/GAW DQOs for the relevant mole fraction range. However, the instrument noise and stability was found to be worse compared to other TEI 49C instruments and also compared to the last audit in 2009. The instrumentation at MHD is adequate for ozone measurements.

Recommendation 2 (, important, 2014)**
The reason for the slight degradation of stability and repeatability of the instrument compared to the last audit needs to be explored. Due to the age of the analyser, a replacement should be considered.

Carbon Monoxide Measurements

On-going measurement of carbon monoxide at Mace Head commenced in 1989, and continuous data series are available since then. Carbon monoxide measurements at Mace Head are made using GC with HgO detector technique. The system has not significantly changed since the last audit by WCC-Empa in 2009.

Instrumentation. Mace Head is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2.

Standards. The station is equipped with laboratory and working standards, which are mainly stainless steel cylinders provided by Scripps Institution of Oceanography (SIO). In addition, other commercial standards are available which are occasionally used to verify the response function of the RGA-3. A full calibration of the instrument using flasks (filled and provided by CSIRO) is performed at irregular intervals.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MHD instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. However, some of the WCC-Empa TS contained H_2 levels which significantly exceeded ambient mole fractions. The following equations characterise the instrument bias, and the results are further illustrated in Figure 2 with respect to the WMO GAW DQOs (WMO, 2011, 2010):

RGA-3 #090189-010:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 2.9) / 1.1011 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (4.5 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

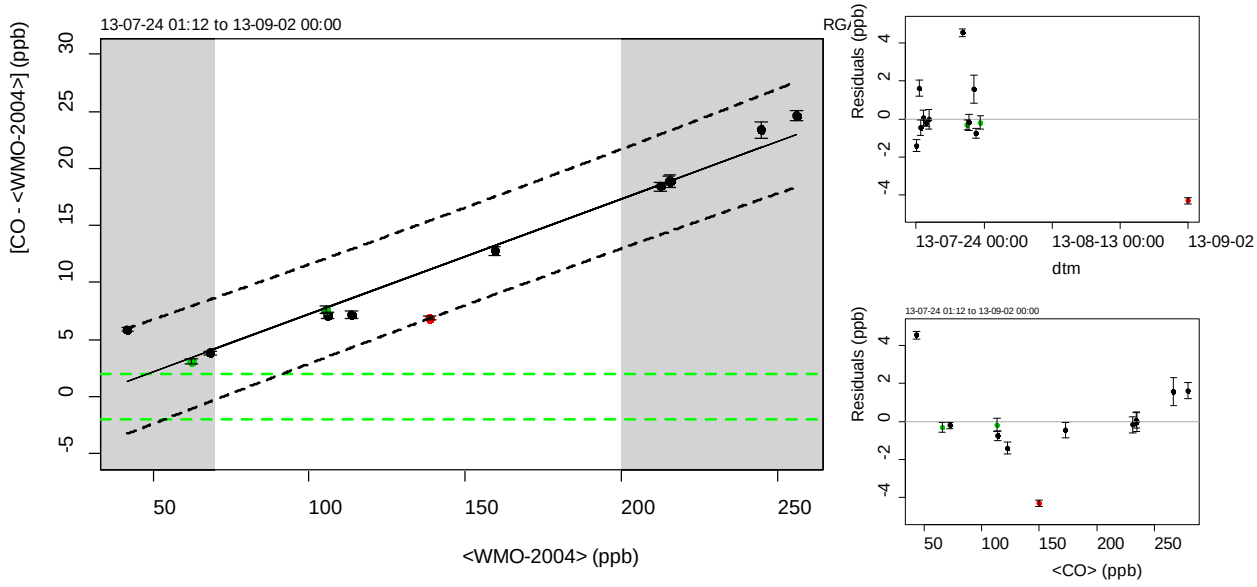

Figure 2. *Left: Bias of the MHD RGA-3 carbon monoxide instrument with respect to the WMO2004 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for MHD, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. Point colour: green: cylinder with <2000 ppb H_2, black: >3000 ppb H_2, red: J-066 (low H_2). 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:

A significant bias between the WCC-Empa and MHD CO measurements was found. Some WCC-Empa TS contained high mole fraction of H_2, which complicated the identification of the reason of the bias. However, no clear relationship between the H_2 level of the TS and the bias was observed. The bias was then also confirmed by a SIO tank that was analysed at Empa after the audit and shipped to MHD. Again, the MHD results were significantly higher but less pronounced compared to the measurements carried out during the audit. A further indication that the bias is real is the fact that the comparison with the WCC-Empa travelling instrument (results see further below) showed also a bias of the same magnitude. Consequently, the reason of the bias needs to be found, and the following recommendations are made:

Recommendation 3 (*, important, 2014)**
The reason for the bias between the MHD and the WCC-Empa CO values needs to be identified. A re-assessment of the calibration function (linearity) of the RGA-3 system is strongly recommended.
Recommendation 4 (, important, 2014)**
It should be considered to purchase a set of NOAA/ESRL CO standards for calibration purposes.

Methane Measurements

On-going measurement of methane at Mace Head commenced in 1987, and continuous data series are available since then. Methane measurements at Mace Head are made using GC with FID detector technique. The system has not significantly changed since the last audit by WCC-Empa. In addition, two Cavity Ringdown Spectrometers (CRDS) were installed at the station. One of the instruments belongs to the Irish EPA (G1301), and the second instrument is operated by the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) (G2301).

Instrumentation. CARLE GC system with FID detector, Picarro G1301 (humid measurements), Picarro G2301 (dry measurements).

Standards. GC/FID: See carbon monoxide. CRDS: Four laboratory standards from Deuste-Steininger, which were calibrated against the WMO-X2004 methane and the WMO-X2007 carbon dioxide scales at MPI-BGC, are available at MHD. These standards are used manually for calibrations of both CRDS instruments approx. once per month. Furthermore, a working standard is available for frequent checks. Currently the system measures ambient air for 660 min, followed by 20 min WS measurement.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MHD 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 following equation characterises the instrument bias. The result is further illustrated in Figure 3 to Figure 5 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (green lines) (WMO, 2011, 2009).

CARLE GC/FID:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 4.0) / 0.99772 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (2.2 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

Picarro G1301 (EPA):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 8.2) / 0.99543 (3c)

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

Picarro G2301 (LSCE):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 11.9) / 0.99372 (3e)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.1 ppb^2 + 1.30e-07 * X_{CH4}^2) (3f)

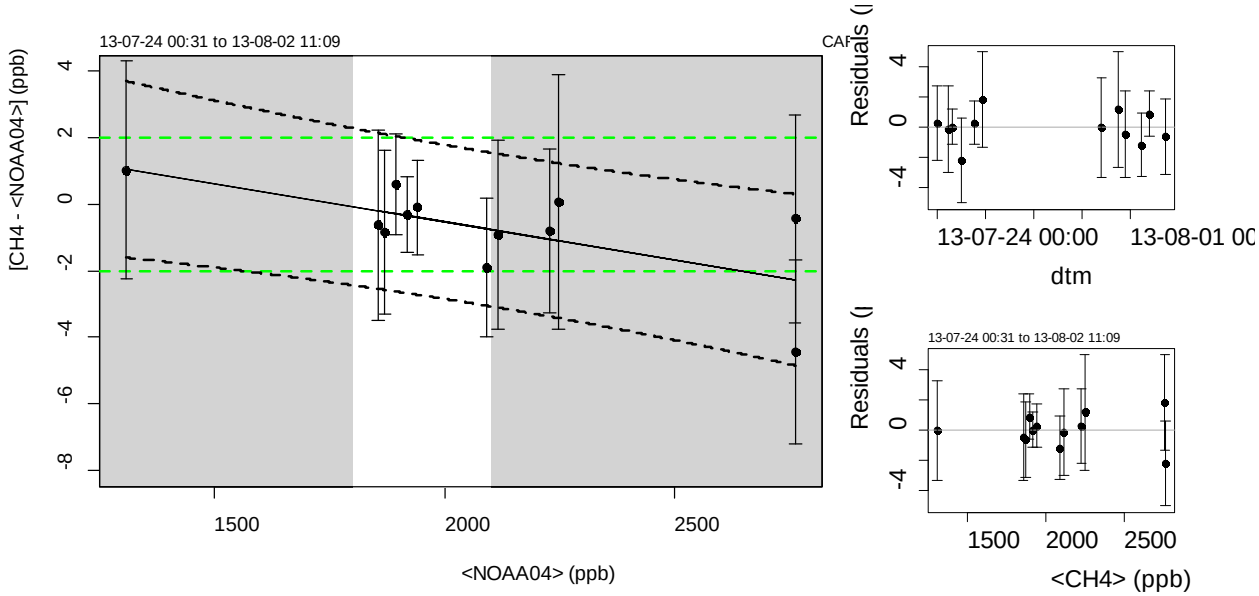

Figure 3. *Left: Bias of the CARLE GC/FID methane instrument (MPI-BGC) with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for MHD, whereas the green lines correspond to the DQOs. Each point represents the average of data 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).*

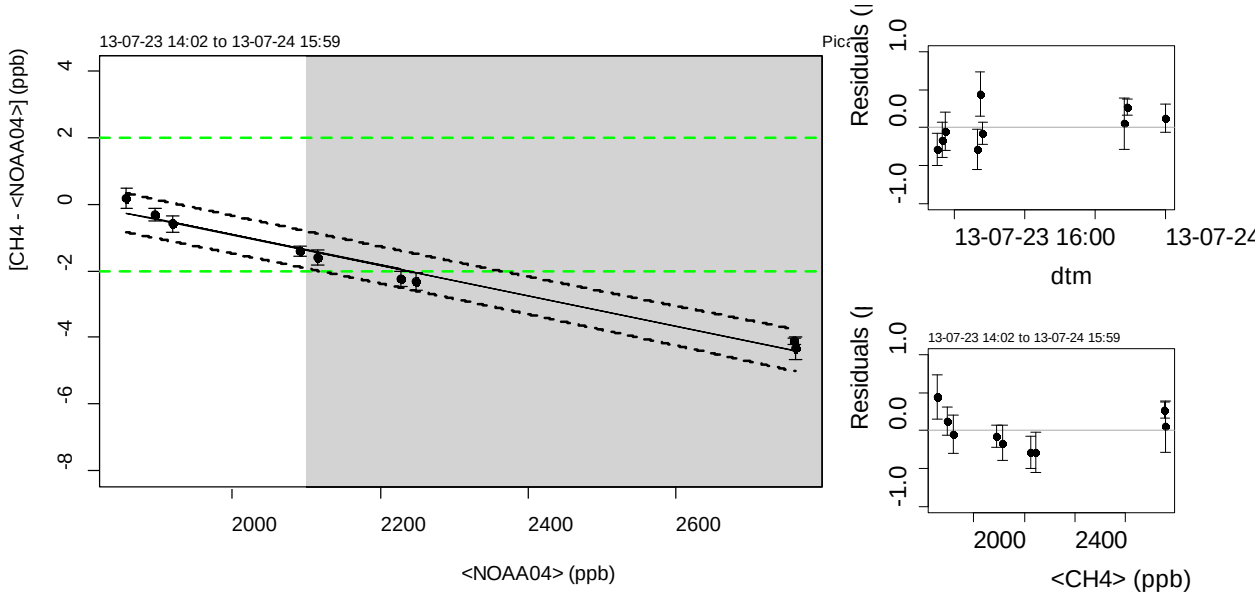

Figure 4. *Same as above for the Picarro G1301 analyser.*

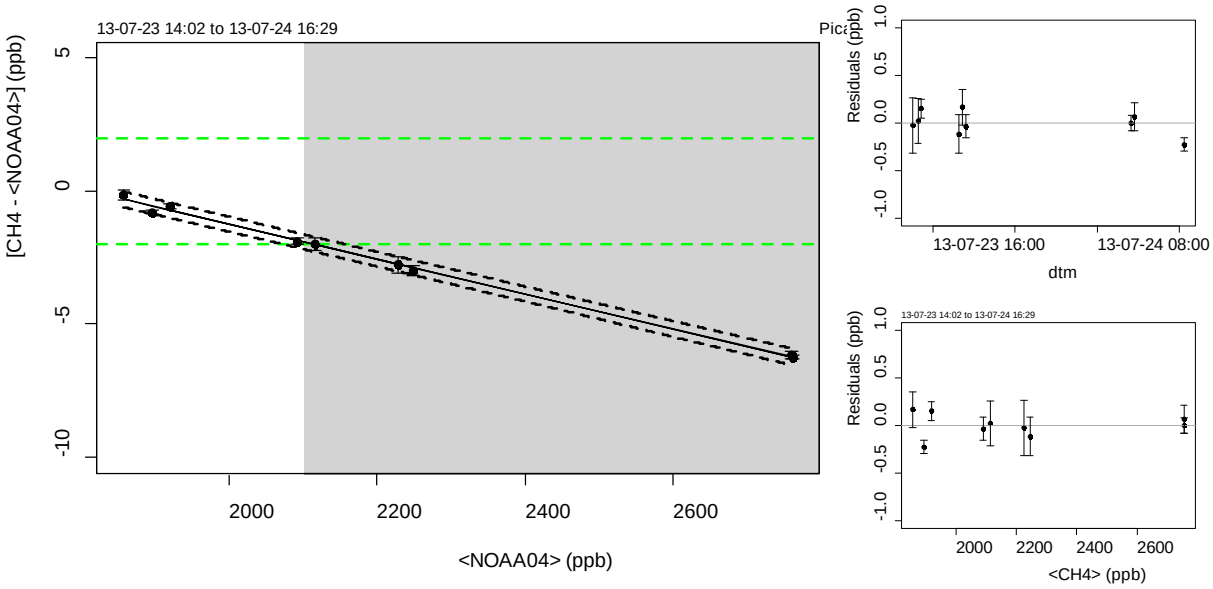

Figure 5. *Same as above for the Picarro G2301 analyser.*

The results of the comparisons can be summarised as follows:

Agreement within the WMO/GAW DQOs of ±2 ppb was found in the relevant mole fraction range of methane for all three instruments. A significantly higher uncertainty is associated with the GC/FID measurements. Furthermore, these measurements have a significantly smaller temporal coverage compared to the continuous CRDS measurements. In this light the value of the GC/FID instrument is questionable, and decommission of the instrument could be considered, since the CRDS analysers provide more accurate methane numbers with lower uncertainties.

> **Recommendation 5 (*, minor, 2014)**
> *Redundant measurements with independent analytical techniques further improve the quality of a measurement system. However, the GC/FID technique has significantly larger measurement uncertainties compared to the CRDS systems, and continuation of the GC/FID measurements could consequently be re-considered.*

A clear linear relationship between the MHD bias and the mole fraction of the WCC-Empa TS was observed, which is indicating a bias in the calibration standards.

> **Recommendation 6 (**, important, 2014)**
> *The mole fraction dependant bias between MHD and WCC-Empa is indicating a small deviation in one or more of the MHD methane standards. It is recommended to purchase a set of NOAA/ESRL methane standards to establish a direct link to the WMO/GAW CCL.*

Carbon Dioxide Measurements

Continuous measurements of CO_2 at MHD commenced in 1992, and continuous data is available since then.

Instrumentation. Initial measurements were made using NDIR technique (Licor 6262, Siemens Ultramat 5F). In 2009, measurements with CRDS (Picarro G1301) commenced, and the NDIR system was finally replaced by another CRDS instrument (Picarro G2301) in March 2011. The Picarro G1301 is owned by the Irish EPA, and the G2301 is owned and operated by LSCE. The sample air of the Picarro G2301 is dried with a Nafion drier, whereas the Picarro G1301 measures humid air followed

by a correction of water vapour interference. The instrumentation is adequate for the measurement of CO_2.

Standards. A set of 4 laboratory standards (10L aluminium cylinders, Deuste Steininger) is available at the station. The standards have been calibrated by MPI-BGC (Armin Jordan). In addition, a working standard is available.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MHD 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 two Picarro instruments. 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 (green lines) (WMO, 2011).

Picarro G1301 (EPA):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.90) / 0.99785 (4a)

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

Picarro G2301 (LSCE):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 1.16) / 0.99725 (4c)

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

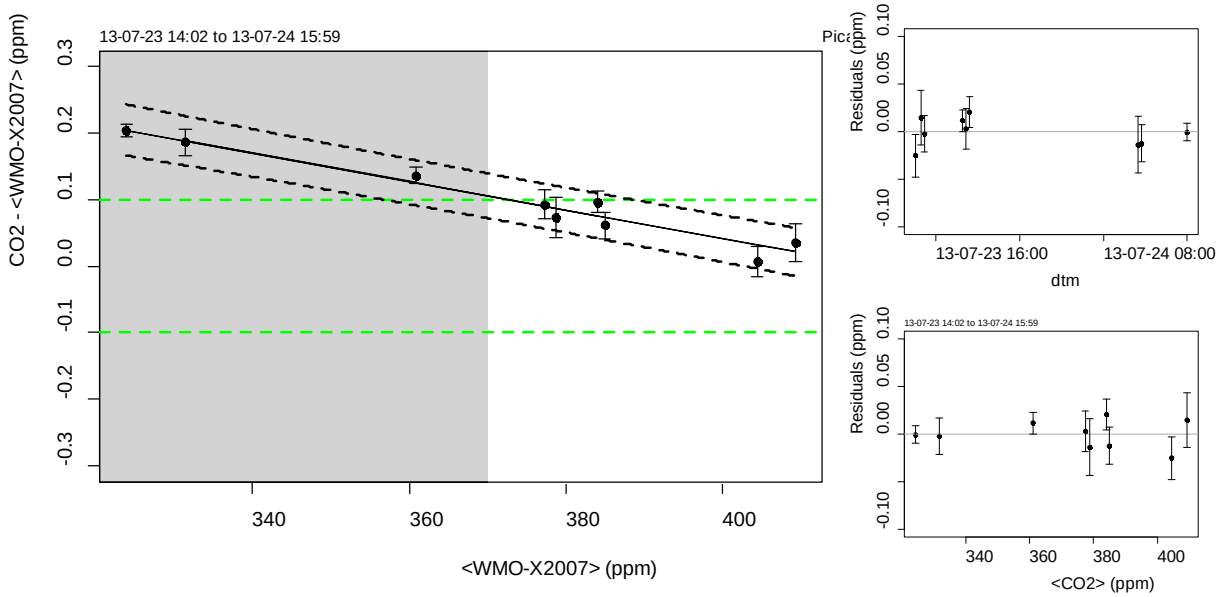

Figure 6. *Left: Bias of the MHD Picarro G1301 analyser (EPA) with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for MHD, whereas the green lines correspond to the DQOs. Each point represents the average of data at 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).*

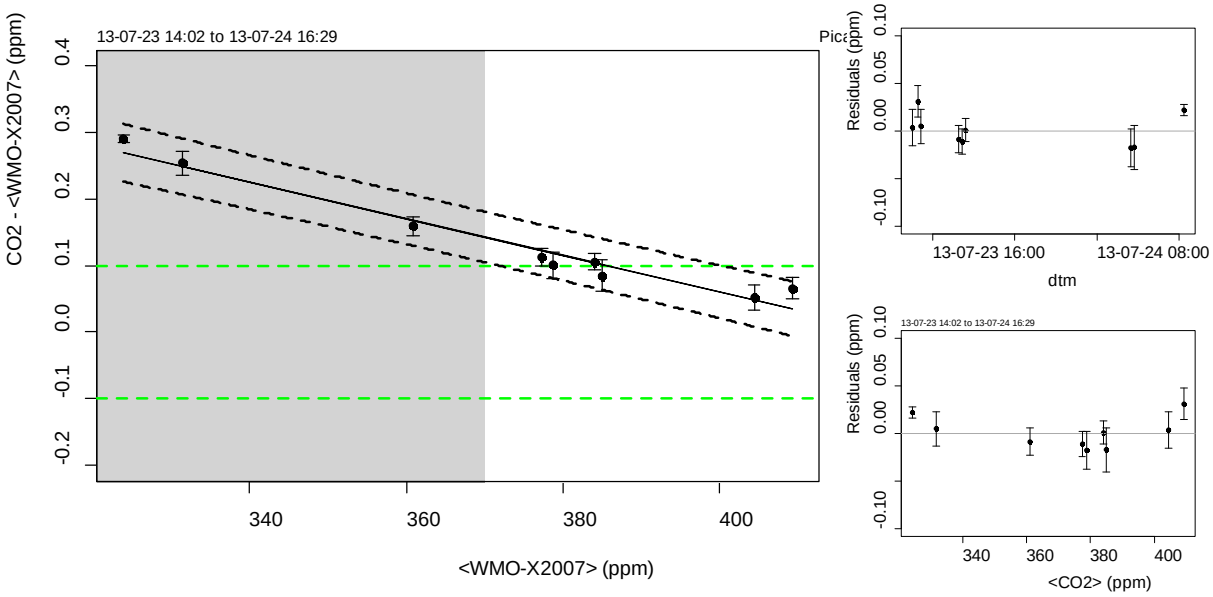

Figure 7. *Same as above for the Picarro G2301 (LSCE).*

The results of the comparison can be summarised as follows:

The results of the TS comparison agreed well within the WMO/GAW DQOs in the relevant mole fraction range above 370 ppm CO_2. However, both instruments exhibited a clear linear relationship between the bias and the CO_2 mole fraction, indicating that one or more of the MHD CO_2 standards have a slight offset. The small positive bias was also confirmed by the parallel measurements of ambient air between MHD and WCC-Empa. This is indicating that the whole measurement set-up including the inlet system and data processing is fully appropriate.

Recommendation 7 (, important, 2014)**
The mole fraction dependant bias between MHD and WCC-Empa is indicating a small deviation in one or more of the MHD carbon dioxide standards. It is recommended to purchase a set of NOAA/ESRL methane standards to establish a direct link to the WMO/GAW CCL.

Nitrous Oxide Measurements

Nitrous oxide measurements started at MHD in 1987 as part of the AGAGE programme, and N_2O time series are available since then.

Instrumentation. HP 5800 II S/N C-128/83 with ECD detector. Details of the measurement setup can be found on the AGAGE website (http://agage.eas.gatech.edu/instruments-gcmd.htm). The instrumentation is adequate for the measurement of N_2O.

Standards. The station is equipped with laboratory and working standards. Mace Head N_2O measurements are referenced to the SIO-2005 nitrous oxide scale by the use of stainless steel cylinders provided by Scripps Institution of Oceanography (SIO).

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the MHD instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 2 with respect to the WMO GAW DQOs (WMO, 2011, 2009):

HP 5800 II:

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O + 0.38) / 1.0004 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.01 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

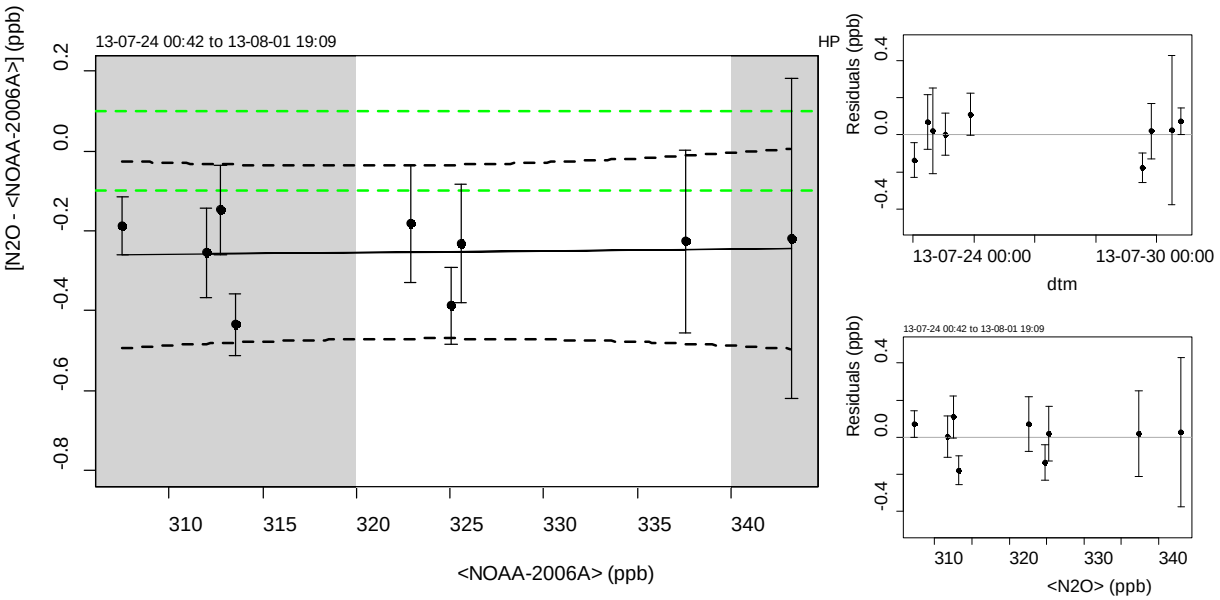

Figure 8. *Left: Bias of the MHD HP 5800 II nitrous oxide instrument with respect to the WMO-2006A reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for MHD, whereas the green lines correspond to the DQOs. Each point represents the average of data 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).*

The results of the comparisons can be summarised as follows:

The MHD results were on average 0.25 ppb lower compared to the WCC-Empa assigned numbers. This is in very good agreement with the results of the audit carried out by the WCC-N_2O in September 2012, where an average bias of 0.29 ppb (MHD lower) was found. The recommendations of the audit by WCC-N_2O to re-assess the calibration function and the change to the WMO-X2006A calibration scale should therefore be implemented.

Parallel Measurements of Ambient Air

The audit included parallel measurements of CO, CH_4 and CO_2 with a WCC-Empa travelling instrument (TI) (CRDS, Picarro G2401). The TI was running from 24 July through 26 August 2013. The TI was connected to an independent inlet system, which was set-up during a FTIR comparison made by the University of Heidelberg. The air sampled with the WCC TI was not dried. To account for the effect of water vapour a correction function as described by Rella et al. (2013) was applied to the WCC-Empa Picarro data. Instead of the original Picarro G2401 pump unit, another pump (KNF, type N 920 AP.29.18) was used. For CH_4 and CO_2, the Picarro G2401 was calibrated every 40 h using one working standard, and two additional tanks were used as target cylinders. The average of all three WCC-Empa cylinders was used for the CO calibration of the TI. Based on the measurements of the working standards, 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 <0.05 ppm for CO_2. The following figures show the results of the ambient air comparisons.

Carbon monoxide:

Figure 9 shows the comparison of the RGA-3 instrument (MHD) with the WCC-Empa Picarro G2401. One minute data of the TI and single injections of the RGA-3 are shown. The bias between the two instruments shows significant variation, which most likely can be attributed to instrument drift and noise. The average bias of approx. 6 ppb between the TI and the RGA-3 measurements corresponds well to the deviation found in the comparison of the travelling standards. If the correction function (2a) is applied to the MHD RGA-3 data, the agreement significantly improves with an average bias of -0.61±1.81 ppb, which is illustrated in Figure 10. The fact that both the comparison of the travelling standards and side-by-side ambient air measurements resulted in the same bias is indicating that the calibration of the RGA-3 has changed since the last audit.

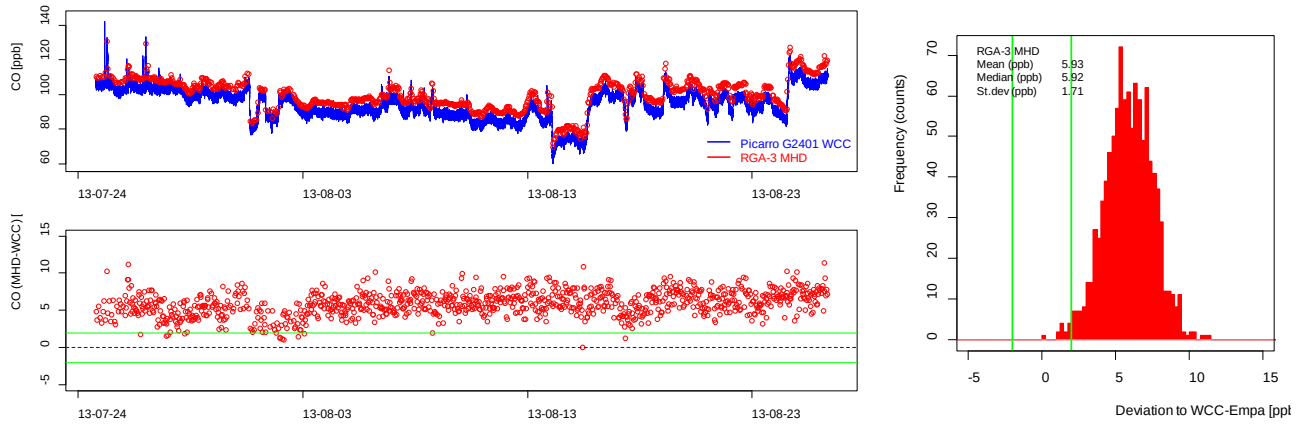

Figure 9. *Upper left panel: CO time series measured at MHD with the Picarro G2401 travelling instrument (1-min averages) and the RGA-3 analyser (individual injections) of MHD. Lower left panel: Deviation of the MHD system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

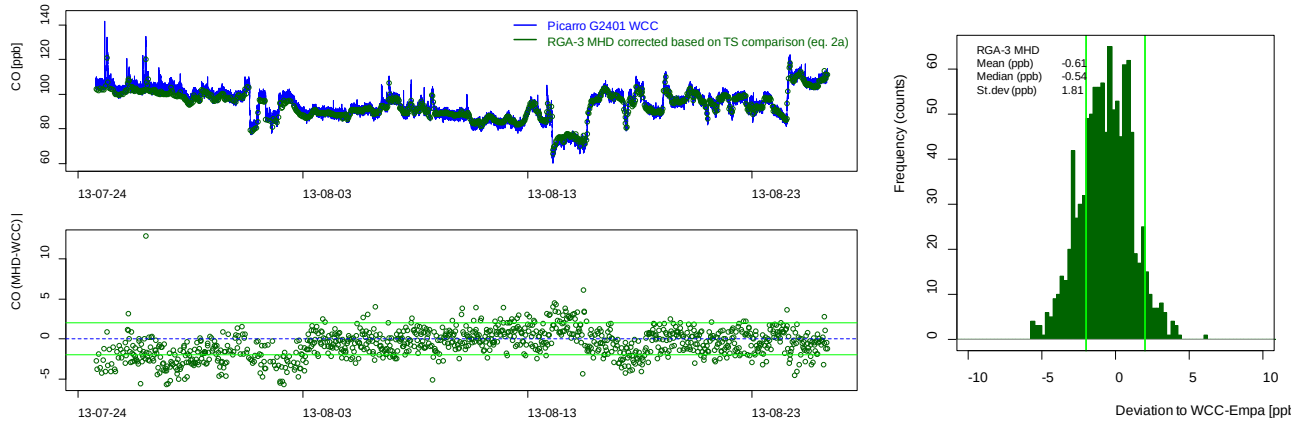

Figure 10. *Same as above but MHD RGA-3 data corrected based on TS comparison with equation (2a).*

Recommendation 8 (, important, 2014)**
A careful re-assessment of the RGA-3 calibration function (linearity) is required.

Methane:

The following figures show the comparison of the MHD methane instruments with the WCC-Empa TI. It can be seen that the average bias was small and within the WMO/GAW DQOs for all instruments; however, the GC-FID system shows, as expected, significantly more scatter in the observed bias. It also can be seen that CRDS instruments can be operated without drying of the sample air. No difference was found between the Picarro G1301 (with drying system) and the MHD Picarro G2301 and the WCC Picarro G2401 (both without sample drying). The results of the methane ambient air comparison confirmed the results of the TS comparisons for the GC/FID system, whereas a slight positive offset was found for the two Picarro instruments during the parallel measurements in contrast to the results of the TS comparisons.

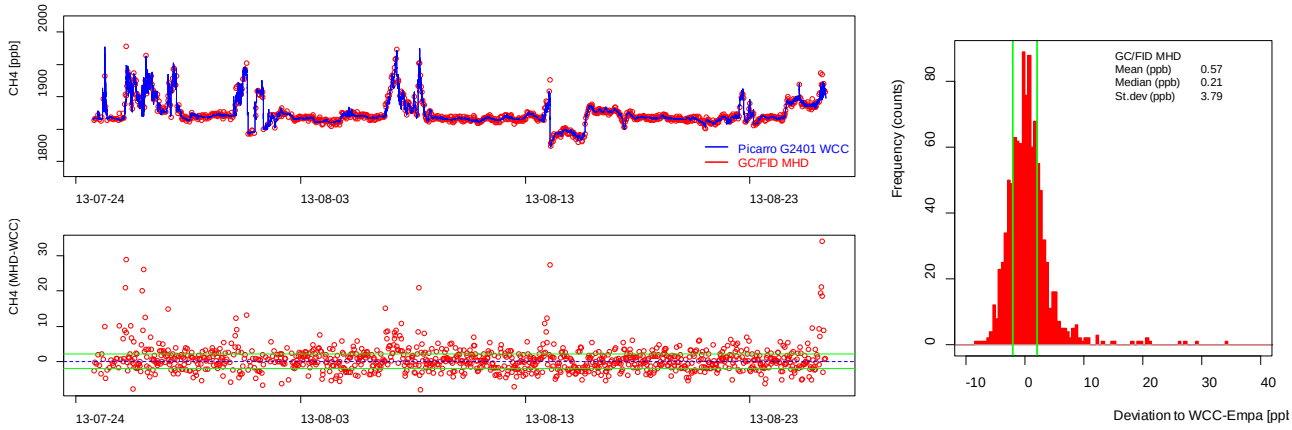

Figure 11. *Upper left panel: CH_4 time series measured at MHD with the Picarro G2401 travelling instrument (1-min averages) and the CARLE GC/FID system (individual injections). Lower left panel: Deviation of the MHD system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

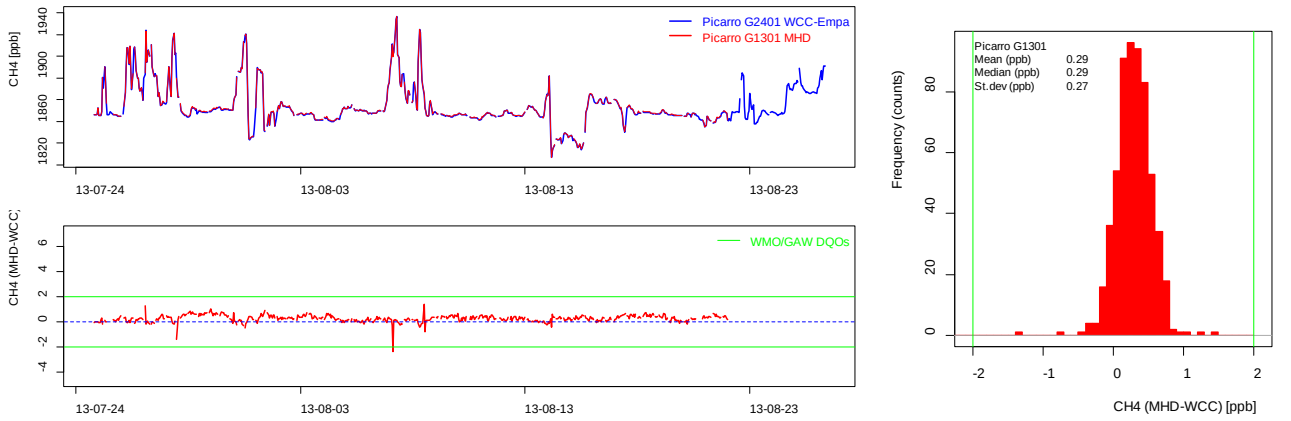

Figure 12. *Upper left panel: CH_4 time series (hourly averages) measured at MHD with the Picarro G2401 travelling instrument and the Picarro G1301 analyser. Both instruments were measuring himid air, and a water vapour correction was applied. Lower left panel: Deviation of the MHD system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

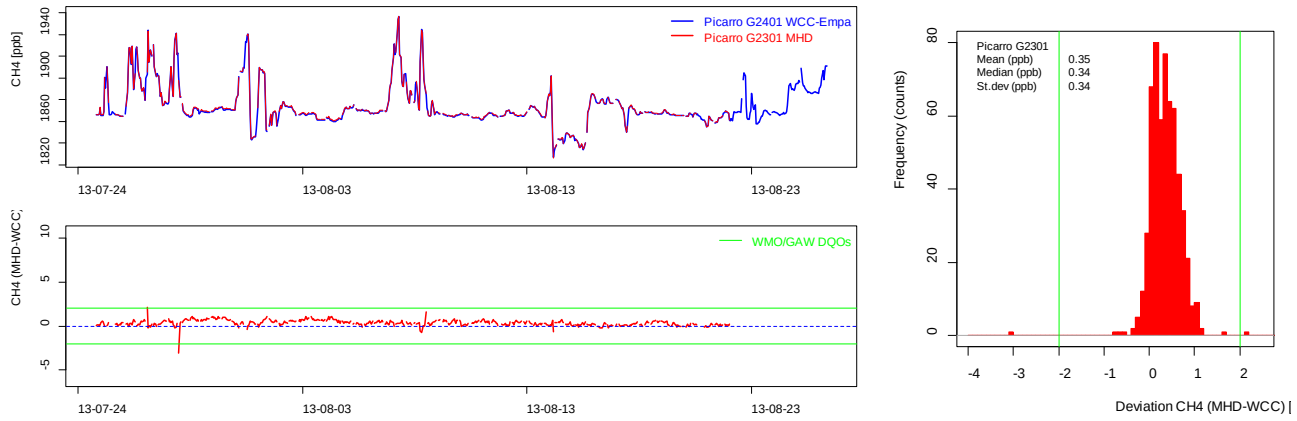

Figure 13. *Same as above for the Picarro G2301 of MHD. The sample air of the Picarro G2301 was dried, whereas a water vapour correction was applied to the Picarro G2401.*

Recommendation 9 (*, minor, future data use)
Both ambient air and travelling standard comparisons showed that the CRDS methane data is more accurate compared to the GC/FID system. The CRDS data should therefore be considered as the main methane data set of MHD since the installation of these instruments.

Carbon dioxide:

Figure 14 and Figure 15 show the comparison of the Picarro G1301 and G2301 analysers with the WCC-Empa TI. The Picarro G1301 CO_2 measurements were on average by 0.13±0.04 ppm higher compared to the WCC-Empa TI, and the Picarro G2301 was 0.07±0.04 ppm higher. This is in very good agreement with the results of the performance audit, which indicated a bias of approx. 0.06 to 0.08 ppm at CO_2 mole fractions of 390 ppm. Therefore, the observed bias can most likely be attributed to differences in the calibration standards. A bias in the same order of magnitude was also observed during the FTIR comparison of the University of Heidelberg (Vardag et al., 2014).

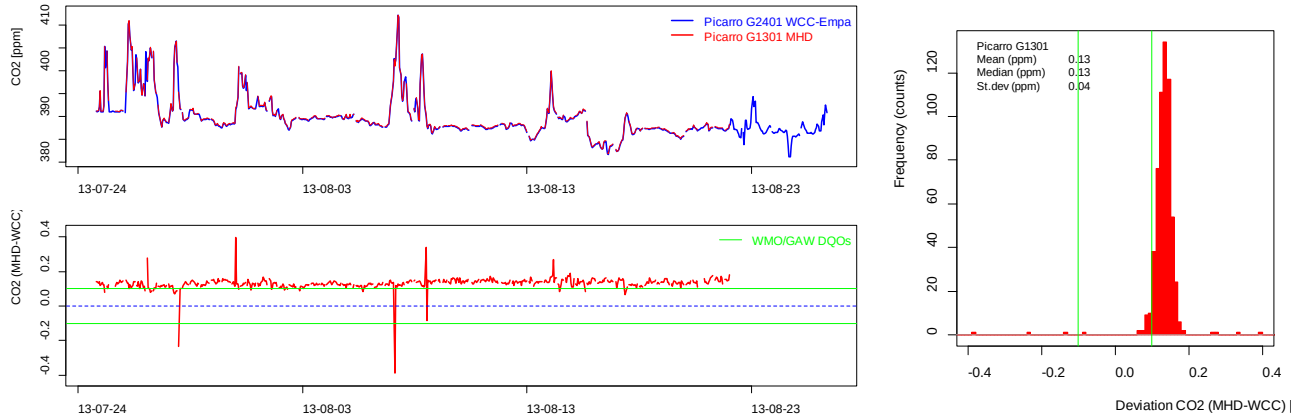

Figure 14. *Upper left panel: CO_2 time series (hourly averages) measured at MHD with the Picarro G2401 travelling instrument and the Picarro G1301 (both instruments measuring humid air). Lower left panel: Deviation of the MHD system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

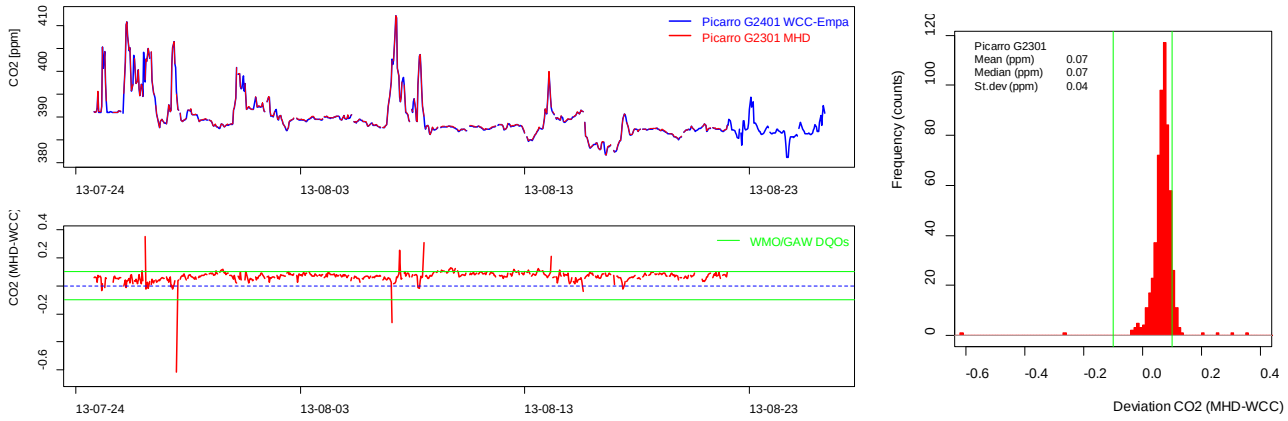

Figure 15. *Same as above for the Picarro G2301 of MHD (with drying system) and the Picarro G2401 travelling instrument (humid air).*

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

Different contributors are submitting data of the MHD station to the World Data Centre for Greenhouse Gases (WDCGG). For the parameters of the audit scope, in-situ data for CO (1994-2012), N_2O and CH_4 (both 1987-2012) was submitted to WDCGG by AGAGE at the time of the audit. CO_2 data (1992-2011) has been submitted by LSCE, and O_3 data (2004-2008) has been submitted by NUI at the time of the audit. Picarro CH_4 and CO_2 data have not been submitted.

Recommendation 10 (, important, ongoing)**
It was already recommended after the last audit in 2009 that ozone data should be submitted; however, no submissions occurred since then. 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.

Recommendation 11 (, important, ongoing)**
GAWSIS entries need to be regularly updated by the MHD station manager. Currently, the CRDS instruments are not listed in GAWSIS.

Conclusions

The Global GAW station Mace Head comprises a very comprehensive set of measurements and participates in many international programmes. The combination of long-term measurements, the large number of measured parameters and the location of the site make the MHD station a very important contribution to the GAW programme. The assessed parameters were mostly of high quality; however, an issue with the calibration of the CO system needs further attention.

Continuation of the Mace Head measurement series and the scientific collaboration with external partners is highly recommended.

Summary Ranking of the Mace Head GAW Station

System Audit Aspect	Adequacy[#]	Comment
Access	(5)	All year access possible
Facilities		
Laboratory and office space	(4)	Adequate but limited space, some refurbishing recommended
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully functional
Power supply	(5)	Reliable power supply
General Management and Operation		
Organisation	(5)	Well established cooperation among different partners
Competence of staff	(5)	Highly experienced staff
Air Inlet System	(5)	Fully adequate individual inlets
Instrumentation		
Ozone	(5)	Adequate instrumentation
CO (RGA-3)	(3)	Potential calibration issues
CH_4 (GC/FID)	(3)	Poor repeatability
N_2O (GC/ECD)	(4)	Relatively poor repeatability
CO_2/CH_4 (CRDS)	(5)	State of the art instrumentation
Standards		
Ozone	(2)	3-monthly checks by contractor
CO, CH_4, N_2O (GC)	(4)	SIO traceable
CH_4, CO_2, (CRDS)	(4)	Traceability to WMO via MPI-BGC
Data Management		
Data acquisition	(5)	Adequate systems
Data processing	(5)	Experienced staff
Data submission (AGAGE)	(5)	Submitted until 2012
Data submission (MHD)	(1)	No data submitted after 2008
Data submission (LSCE)	(3)	CRDS data not yet submitted

[#]0: inadequate thru 5: adequate.

Dübendorf, September 2014

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

APPENDIX

Global GAW Station Mace Head

Site description and measurement programme

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

http://macehead.org/
http://gaw.empa.ch/gawsis/reports.asp?StationID=53

Organisation and Contact Persons

The programme of the MHD atmospheric research station is coordinated by the School of Physics at NUI, Galway. Besides NUI Galway's own research activities, a large number of institutes are using the MHD facilities as a platform for their research programmes. An overview of the organisation is available from the MHD web site (http://www.macehead.org).

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The ozone laboratory at MHD is air conditioned to approx. 20°C.

Air Inlet System

No change since the WCC-Empa audit in 2005 (Zellweger et al., 2005).

Instrumentation

One ozone analyser (TEI 49C). Instrumental details are summarised in Table 1.

Standards

No ozone standard is available at the site. Checks using an ozone standard are made by a contractor every 3 months. These checks have qualitative character and are not used to calibrate the MHD instrument.

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri) by the station operator.
Zero / Span check:	None.
Calibration/checks with standard:	Usually every 3 months by external contractor. No adjustments of calibration settings.
Inlet filter exchange:	Monthly, earlier in case of pollution events.
Other (cleaning, leak check etc.):	Instrument is serviced by an external contractor every 6 months (cell cleaning, leak checking, any necessary parts changed and comparison vs a travelling standard to confirm correct operation).

Data Acquisition and Data Transfer

Unchanged since the WCC-Empa audit in 2005 (Zellweger et al., 2005). Custom made system running under Linux. One-minute averages including additional instrument status information are stored. Remote access to the data is possible through internet.

Data Treatment

The data is reprocessed on a monthly basis. All data is visually inspected before a validated data set is created.

Documentation

Electronic station and instrument logbooks were available at the site. The information was 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	TEI 49C #77086-385
Principle	UV absorption
Range	0-1 ppm
Settings	Offset = -0.2; Span = 1.020
Pressure readings (mmHg)	Ambient 755.4, OA 756.5, 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. 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 Tables (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 MHD ozone analyser (OA) TEI 49C #77086-385 with the WCC-Empa travelling standard (TS) before adjustment of the calibration factors.

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-07-23 11:50	1	0	0.42	0.68	0.20	0.08	0.26	NA
2013-07-23 12:05	1	40	40.04	39.99	0.15	0.08	-0.05	-0.1
2013-07-23 12:20	1	60	60.03	60.06	0.07	0.07	0.03	0.0
2013-07-23 12:50	1	90	90.01	89.82	0.13	0.09	-0.19	-0.2
2013-07-23 13:05	1	80	80.00	79.86	0.14	0.12	-0.14	-0.2
2013-07-23 13:20	1	10	10.06	10.10	0.18	0.09	0.04	0.4
2013-07-23 13:20	1	30	30.00	30.01	0.18	0.06	0.01	0.0
2013-07-23 13:35	1	50	50.01	50.18	0.10	0.10	0.17	0.3
2013-07-23 13:50	1	20	20.00	20.15	0.08	0.06	0.15	0.8
2013-07-23 14:20	2	0	0.25	0.26	0.20	0.05	0.01	NA
2013-07-23 14:35	2	30	30.02	30.11	0.16	0.08	0.09	0.3
2013-07-23 14:50	2	90	89.98	89.97	0.10	0.13	-0.01	0.0
2013-07-23 15:05	2	60	60.01	60.08	0.11	0.08	0.07	0.1
2013-07-23 15:20	2	10	10.04	10.05	0.18	0.10	0.01	0.1
2013-07-23 15:35	2	40	40.03	39.99	0.14	0.09	-0.04	-0.1
2013-07-23 15:50	2	70	70.03	69.69	0.10	0.11	-0.34	-0.5
2013-07-23 16:05	2	20	19.97	19.85	0.20	0.12	-0.12	-0.6
2013-07-23 16:20	2	50	49.98	49.37	0.12	0.11	-0.61	-1.2
2013-07-23 16:35	2	80	80.02	79.45	0.13	0.13	-0.57	-0.7
2013-07-23 16:50	3	0	0.30	0.08	0.20	0.06	-0.22	NA
2013-07-23 17:05	3	50	50.01	49.55	0.17	0.13	-0.46	-0.9
2013-07-23 17:20	3	90	90.02	89.36	0.07	0.10	-0.66	-0.7
2013-07-23 17:35	3	60	59.99	59.61	0.10	0.03	-0.38	-0.6
2013-07-23 17:50	3	10	10.15	9.76	0.32	0.14	-0.39	-3.8
2013-07-23 18:05	3	40	40.01	39.41	0.08	0.08	-0.60	-1.5
2013-07-23 18:20	3	70	70.00	69.43	0.09	0.10	-0.57	-0.8
2013-07-23 18:35	3	30	29.99	29.48	0.14	0.16	-0.51	-1.7
2013-07-23 18:50	3	20	20.00	19.61	0.20	0.09	-0.39	-2.0
2013-07-23 19:05	3	80	80.00	79.82	0.09	0.11	-0.18	-0.2
2013-07-23 19:35	4	0	0.20	-0.21	0.20	0.03	-0.41	NA
2013-07-23 20:05	4	40	40.01	39.44	0.16	0.06	-0.57	-1.4
2013-07-23 20:20	4	60	59.97	59.50	0.07	0.09	-0.47	-0.8
2013-07-23 20:35	4	30	30.01	29.38	0.11	0.11	-0.63	-2.1
2013-07-23 20:50	4	90	90.00	89.54	0.09	0.08	-0.46	-0.5
2013-07-23 21:05	4	80	79.98	79.65	0.10	0.15	-0.33	-0.4
2013-07-23 21:20	4	10	9.95	9.63	0.28	0.08	-0.32	-3.2
2013-07-23 21:35	4	50	49.99	48.84	0.14	0.13	-1.15	-2.3
2013-07-23 21:50	4	20	19.98	19.15	0.16	0.08	-0.83	-4.2
2013-07-23 22:05	4	70	69.97	68.75	0.14	0.14	-1.22	-1.7
2013-07-23 22:20	5	0	0.34	-0.76	0.23	0.14	-1.10	NA
2013-07-23 22:35	5	30	30.02	28.63	0.15	0.07	-1.39	-4.6
2013-07-23 22:50	5	90	90.00	88.65	0.11	0.18	-1.35	-1.5
2013-07-23 23:05	5	60	60.04	58.80	0.09	0.21	-1.24	-2.1
2013-07-23 23:20	5	10	10.03	8.93	0.23	0.12	-1.10	-11.0
2013-07-23 23:35	5	40	40.02	38.50	0.15	0.16	-1.52	-3.8

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-07-23 23:50	5	70	70.02	69.08	0.08	0.14	-0.94	-1.3
2013-07-24 00:05	5	20	20.00	19.60	0.11	0.09	-0.40	-2.0
2013-07-24 00:20	5	50	50.00	49.48	0.06	0.16	-0.52	-1.0
2013-07-24 00:35	5	80	80.03	79.41	0.10	0.11	-0.62	-0.8
2013-07-24 00:50	6	0	0.20	-0.81	0.30	0.15	-1.01	NA
2013-07-24 01:05	6	50	49.99	48.96	0.10	0.23	-1.03	-2.1
2013-07-24 01:20	6	90	89.98	88.66	0.08	0.09	-1.32	-1.5
2013-07-24 01:35	6	60	60.00	59.05	0.09	0.16	-0.95	-1.6
2013-07-24 01:50	6	10	10.30	9.50	0.41	0.18	-0.80	-7.8
2013-07-24 02:05	6	40	39.98	38.89	0.08	0.14	-1.09	-2.7
2013-07-24 02:20	6	70	69.97	68.85	0.04	0.22	-1.12	-1.6
2013-07-24 02:35	6	30	30.00	28.91	0.19	0.18	-1.09	-3.6
2013-07-24 02:50	6	20	20.00	18.79	0.11	0.13	-1.21	-6.0
2013-07-24 03:05	6	80	79.95	79.29	0.18	0.19	-0.66	-0.8
2013-07-24 03:35	7	0	0.47	-0.27	0.19	0.05	-0.74	NA
2013-07-24 04:05	7	40	40.04	39.29	0.13	0.11	-0.75	-1.9
2013-07-24 04:20	7	60	60.01	59.33	0.10	0.13	-0.68	-1.1
2013-07-24 04:35	7	30	30.02	29.49	0.14	0.15	-0.53	-1.8
2013-07-24 04:50	7	90	90.02	88.98	0.09	0.11	-1.04	-1.2
2013-07-24 05:05	7	80	80.00	79.49	0.08	0.14	-0.51	-0.6
2013-07-24 05:20	7	10	10.19	9.79	0.31	0.16	-0.40	-3.9
2013-07-24 05:35	7	50	50.03	49.22	0.10	0.14	-0.81	-1.6
2013-07-24 05:50	7	20	19.99	19.56	0.09	0.13	-0.43	-2.2
2013-07-24 06:05	7	70	69.99	69.38	0.09	0.14	-0.61	-0.9
2013-07-24 06:20	8	0	0.24	-0.20	0.16	0.11	-0.44	NA
2013-07-24 06:35	8	30	30.00	29.81	0.20	0.12	-0.19	-0.6
2013-07-24 06:50	8	90	89.99	89.53	0.13	0.07	-0.46	-0.5
2013-07-24 07:05	8	60	59.99	60.03	0.14	0.14	0.04	0.1
2013-07-24 07:20	8	10	9.98	9.69	0.26	0.12	-0.29	-2.9
2013-07-24 07:35	8	40	40.06	39.53	0.08	0.11	-0.53	-1.3
2013-07-24 07:50	8	70	69.97	69.33	0.08	0.11	-0.64	-0.9
2013-07-24 08:05	8	20	19.99	19.16	0.22	0.16	-0.83	-4.2
2013-07-24 08:20	8	50	49.99	49.67	0.10	0.19	-0.32	-0.6

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

Unchanged since the WCC-Empa audit in 2005 (Zellweger et al., 2005).

Instrumentation

Mace Head is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2. Instrumental details are listed in Table 4, and further details of the setup are given by *Prinn et al.* (2000).

Standards

The station is equipped with laboratory and working standards. Mace Head CO measurements are referenced to the CSIRO94 carbon monoxide scale by the use of stainless steel cylinders provided by Scripps Institution of Oceanography (SIO). Table 3 gives details of the SIO working standards used since 1994 at MHD. All working standards contain natural air with less than 30 ppm H_2O, calibrated against the SIO reference scales. A full calibration of the instrument using flasks (CSIRO) is performed at irregular intervals but hasn't been done since the last audit by WCC in 2009.

Table 3. SIO CO standards at MHD as of July 2013.

Standard	CO (ppb)	CH_4 (ppb)	N_2O (ppb)	H_2 (ppb)	start of use	end of use
G-024	54.12	1695.82	309.37	506.84	1994-02-17	1994-06-08
G-028	39.50	1674.37	309.99	523.69	1994-06-08	1994-10-22
G-032	42.44	1681.31	309.83	517.54	1994-10-22	1995-05-01
G-036	52.85	1699.11	310.95	530.23	1995-05-01	1995-08-31
G-037	40.68	1686.13	310.83	540.22	1995-08-31	1996-01-22
G-041	52.77	1706.21	310.23	513.74	1996-01-22	1996-06-06
J-007	155.75	1813.74	312.27	523.59	1996-06-06	1996-12-02
J-012	199.25	1830.36	312.66	526.40	1996-12-02	1997-06-09
J-016	148.14	1814.58	312.27	516.20	1997-06-09	1997-09-24
J-020	175.45	1832.82	312.53	534.87	1997-09-24	1998-05-14
J-025	180.54	1837.73	314.09	505.90	1998-05-14	1999-02-03
J-030	166.96	1840.31	313.65	512.00	1999-02-03	1999-09-09
J-035	181.40	1839.65	313.83	514.92	1999-09-09	2000-02-22
J-046	167.36	1859.49	316.12	524.47	2000-02-22	2001-01-31
J-052	152.73	1848.35	316.11	544.26	2001-01-31	2001-10-12
J-058	161.41	1856.27	316.16	529.60	2001-10-12	2002-05-31
J-062	153.82	1849.75	316.23	554.70	2002-05-31	2003-02-16
J-067	153.93	1850.63	316.24	538.92	2003-02-16	2003-10-15
J-071	162.47	1848.12	318.30	525.31	2003-10-15	2004-06-18
J-076	171.35	1868.06	318.32	521.79	2004-06-18	2004-12-22
J-081	173.37	1868.02	318.26	521.81	2004-12-22	2005-07-25
J-087	163.25	1851.20	319.24	501.45	2005-07-25	2006-01-25
J-091	163.46	1851.34	319.24	502.30	2006-01-25	2006-08-31
J-097	166.08	1861.45	320.08	483.79	2006-08-31	2007-04-30
J-101	113.84	1810.62	320.84	528.14	2007-04-30	2008-01-02
J-108	156.16	1857.32	320.92	505.82	2008-01-02	2008-09-23
J-116	161.78	1888.57	322.19	489.72	2008-09-23	2009-05-21
J-120	153.48	1882.51	322.35	526.77	2009-05-21	2010-02-18
J-128	153.91	1882.43	322.25	516.17	2010-02-18	2010-11-07
J-137	152.01	1876.29	323.12	514.94	2010-11-07	2011-08-22
J-144	119.35	1859.70	325.29	515.40	2011-08-22	2012-06-22
J-151	131.59	1873.31	325.35	550.54	2012-06-22	2013-02-08
J-158	128.79	1873.33	325.21	549.58	2013-02-08	2013-10-07
J-166	138.73	1883.39	325.06	531.93	2013-10-07	2014-07-29
J-174	124.04	1885.02	326.321	530.36	2014-07-29	

Operation and Maintenance

Check for general operation: Daily (Mon – Fri) by the station operator. Once per week additional checks (RGA-3 test points, chromatogram, peak width, CO-retention times, and cylinder pressures) are made. The RGA linearity is also irregularly checked using flasks (CSIRO) or vs a dilution system

Other (cleaning, leak check etc.): As required.

Data Acquisition and Data Transfer

No change since the last audit in 2009. The RGA-3 as well as the CH_4/N_2O GC: data of the gas chromatograph systems 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.

Data Treatment

Unchanged since the WCC-Empa audit in 2005 (Zellweger et al., 2005).

Documentation

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

Comparison of the Carbon Monoxide Analyser

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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 16 below.

Setup and Connections

Table 4 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the MHD data acquisition system.

Table 4. Experimental details of MHD 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 MHD (AL)	
Model, S/N	RGA-3 #090189-010
Principle	HgO reduction gas detector
Drying system	PERMAPURE Nafion drier
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports

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.

Table 5. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the RGA-3 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 (%)
(13-07-24 01:12:16)	120803_FA02783	113.6	0.3	120.8	0.3	11.0	7.2	6.3
(13-07-24 11:25:00)	120823_FA02789	256.3	0.2	280.9	0.4	6.0	24.6	9.6
(13-07-24 15:25:00)	120719_FA02782	159.5	0.1	172.3	0.4	6.0	12.8	8.0
(13-07-25 01:26:55)	110512_FB03374	215.3	0.3	234.2	0.4	11.0	18.9	8.8
(13-07-25 13:08:00)	100204_FA02464	68.3	0.1	72.1	0.2	6.0	3.8	5.6
(13-07-25 21:08:00)	110512_FB03350	215.6	0.6	234.5	0.5	6.0	18.9	8.8
(13-07-30 19:41:20)	080814_FA02488	41.9	0.3	47.8	0.2	6.0	5.9	14.0
(13-07-31 12:34:40)	100212_FA02773	62.2	0.6	65.3	0.3	6.0	3.1	5.0
(13-07-31 19:38:00)	120718_FB03377	212.5	0.4	230.9	0.4	6.0	18.4	8.7
(13-08-01 11:48:17)	130423_FF30491	244.8	0.1	268.2	0.7	7.0	23.4	9.6
(13-08-01 19:09:00)	110511_FB03384	106.0	0.4	113.1	0.3	6.0	7.1	6.7
(13-08-02 11:09:00)	080820_FA02686	105.6	0.2	113.2	0.4	6.0	7.6	7.2
(13-09-02 00:00:00)	J-166	138.7	0.2	145.6	0.2	2.0	6.8	4.9

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

GC/FID: Same as for carbon monoxide.

Picarro:

Each Picarro instrument has its own direct inlet line to the top of the MHD tower.

Location of air intake: Top of 20 m tower, extended by poles. Sampling height approx. 23 m. Inlet tube is ½ inch Synflex 1300. Total length approx. 30 m, flow rate 2 l/min.

Inlet protection: Protection against rain water / snow / insects.

Instrument connection: Instruments are directly connected to the ½ inch Synflex tubing with approx. 3 m ¼ inch Synflex-1300. Flow rate approx. 200 ml/min.

Inlet filter: Swagelok particle filters (40 and 7 µm).

Residence time: Approx. 70 s

Instrumentation

Currently three independent CH_4 measurements are carried out at Mace Head using a GC/FID system and two CRDS instruments. Instrumental details are listed in Table 6.

Standards

GC/FID: see carbon monoxide.

CRDS: Currently, four laboratory standards from Deuste-Steininger, which were calibrated against the WMO-X2004 methane and WMO-X2007 carbon dioxide scales at MPI-BGC, are available at MHD. These standards are used manually for calibrations of both Picarro instruments approx. once

per month. Furthermore, a working standard is available for frequent checks. Currently the system measures ambient air for 660 min, followed by 20 min WS measurement.

Operation and Maintenance

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

Other (cleaning, leak check etc.): As required.

Data Acquisition and Data Transfer

Same as for carbon monoxide (GC/FID). The CRDS instruments are using the internal data acquisition system.

Data Treatment

Final data processing is made at LCSE for the Picarro instruments according to ICOS standards.

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, 2007a) 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 6 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 6. 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 16.	
Station Analysers (OA)	
Model, S/N	CARLE GC/FID
Principle	GC/FID
Drying system	Nafion dryer
Model	Picarro G1301
Principle	CRDS
Drying system	Cryogenic trap -50°C
Model	Picarro G2301
Principle	CRDS
Drying system	None
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port (GC/FID)

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 7. CH_4 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the CARLE GC/FID (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 (%)
(13-07-24 00:31:40)	120803_FA02783	2228.22	0.14	2227.43	2.47	12	-0.78	-0.04
(13-07-24 11:25:00)	120823_FA02789	2115.41	0.10	2114.49	2.85	6	-0.92	-0.04
(13-07-24 15:25:00)	120719_FA02782	1919.19	0.07	1918.89	1.15	6	-0.30	-0.02
(13-07-25 00:45:00)	110512_FB03374	2762.16	0.12	2757.72	2.78	10	-4.43	-0.16
(13-07-25 13:08:00)	100204_FA02464	1941.83	0.11	1941.74	1.41	6	-0.09	0.00
(13-07-25 21:08:00)	110512_FB03350	2760.59	0.11	2760.16	3.14	6	-0.43	-0.02
(13-07-30 19:41:20)	080814_FA02488	1309.77	0.04	1310.81	3.29	6	1.04	0.08
(13-07-31 12:34:40)	100212_FA02773	2247.86	0.04	2247.95	3.83	6	0.09	0.00
(13-07-31 19:38:00)	120718_FB03377	1856.64	0.15	1856.01	2.85	6	-0.63	-0.03
(13-08-01 11:48:17)	130423_FF30491	2091.60	0.07	2089.70	2.08	7	-1.90	-0.09
(13-08-01 19:09:00)	110511_FB03384	1894.98	0.10	1895.59	1.50	6	0.61	0.03
(13-08-02 11:09:00)	080820_FA02686	1870.85	0.05	1870.02	2.47	6	-0.83	-0.04

Table 8. Same as above for the Picarro G1301 instrument.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(13-07-23 18:33:00)	100212_FA02773	2247.86	0.04	2245.53	0.27	4	-2.33	-0.10
(13-07-23 14:54:00)	120719_FA02782	1919.19	0.07	1918.61	0.25	4	-0.59	-0.03
(13-07-23 14:02:15)	120803_FA02783	2228.22	0.14	2225.98	0.22	4	-2.24	-0.10
(13-07-23 14:34:00)	120723_FA02789	2115.41	0.10	2113.81	0.23	4	-1.60	-0.08
(13-07-24 11:39:00)	110512_FB03350	2760.59	0.11	2756.47	0.11	4	-4.12	-0.15
(13-07-24 11:19:00)	110512_FB03374	2762.16	0.12	2757.82	0.34	4	-4.34	-0.16
(13-07-23 18:53:00)	120718_FB03377	1856.64	0.15	1856.83	0.30	4	0.19	0.01
(13-07-24 15:59:00)	110511_FB03384	1894.98	0.10	1894.68	0.18	3	-0.30	-0.02
(13-07-23 19:13:00)	130423_FF30491	2091.60	0.07	2090.20	0.15	4	-1.40	-0.07

Table 9. Same as above for the Picarro G2301 instrument.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(13-07-24 11:39:00)	110512_FB03350	2760.59	0.11	2755.25	0.15	4	-5.34	-0.19
(13-07-23 18:33:00)	100212_FA02773	2247.86	0.04	2245.54	0.20	4	-2.32	-0.10
(13-07-23 14:54:00)	120719_FA02782	1919.19	0.07	1919.19	0.10	4	0.00	0.00
(13-07-23 14:02:15)	120803_FA02783	2228.22	0.14	2226.12	0.29	4	-2.10	-0.09
(13-07-23 14:34:00)	120723_FA02789	2115.41	0.10	2114.06	0.23	4	-1.35	-0.06
(13-07-24 11:19:00)	110512_FB03374	2762.16	0.12	2756.70	0.08	4	-5.46	-0.20
(13-07-23 18:53:00)	120718_FB03377	1856.64	0.15	1857.06	0.19	4	0.41	0.02
(13-07-24 16:29:00)	110511_FB03384	1894.98	0.10	1894.76	0.07	4	-0.22	-0.01
(13-07-23 19:13:00)	130423_FF30491	2091.60	0.07	2090.36	0.12	4	-1.24	-0.06

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

See methane (Picarro instruments).

Comparison with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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

See methane (Picarro instruments).

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 10. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Picarro G1301 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 (%)
(13-07-23 14:02:15)	120803_FA02783	404.38	0.03	404.39	0.02	4	0.01	0.00
(13-07-23 14:34:00)	120723_FA02789	409.31	0.02	409.35	0.03	4	0.04	0.01
(13-07-23 14:54:00)	120719_FA02782	331.43	0.02	331.62	0.02	4	0.19	0.06
(13-07-23 18:33:00)	100212_FA02773	360.89	0.01	361.03	0.01	4	0.14	0.04
(13-07-23 18:53:00)	120718_FB03377	377.30	0.05	377.39	0.02	4	0.09	0.02
(13-07-23 19:13:00)	130423_FF30491	384.00	0.03	384.10	0.02	4	0.10	0.03
(13-07-24 11:19:00)	110512_FB03374	378.73	0.03	378.80	0.03	4	0.07	0.02
(13-07-24 11:39:00)	110512_FB03350	384.93	0.01	384.99	0.02	4	0.06	0.02
(13-07-24 15:59:00)	110511_FB03384	323.94	0.03	324.14	0.01	3	0.20	0.06

Table 11. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Picarro G2301 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 (%)
(13-07-24 11:39:00)	110512_FB03350	384.93	0.01	385.01	0.02	4	0.08	0.02
(13-07-23 18:33:00)	100212_FA02773	360.89	0.01	361.05	0.01	4	0.16	0.04
(13-07-23 14:54:00)	120719_FA02782	331.43	0.02	331.68	0.02	4	0.25	0.08
(13-07-23 14:02:15)	120803_FA02783	404.38	0.03	404.43	0.02	4	0.05	0.01
(13-07-23 14:34:00)	120723_FA02789	409.31	0.02	409.38	0.02	4	0.07	0.02
(13-07-24 11:19:00)	110512_FB03374	378.73	0.03	378.83	0.02	4	0.10	0.03
(13-07-23 18:53:00)	120718_FB03377	377.30	0.05	377.41	0.01	4	0.11	0.03
(13-07-24 16:29:00)	110511_FB03384	323.94	0.03	324.23	0.01	4	0.29	0.09
(13-07-23 19:13:00)	130423_FF30491	384.00	0.03	384.11	0.01	4	0.11	0.03

Nitrous Oxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

Same as for carbon monoxide.

Instrumentation

A HP 5890 II GC is used for nitrous oxide measurements at MHD. The instrument is part of the AGAGE system and was installed in 1997. Detailed information on the system is available from the AGAGE web site (http://agage.eas.gatech.edu/instruments-gcmd.htm) Instrumental details are listed in Table 6.

Standards

One laboratory standard serving as working standard is available at the station (stainless steel Essex cylinders 34 l). This is a tertiary standard from Scripps Institution of Oceanography (SIO) and based on the SIO-2005 scale.

Operation and Maintenance

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

Other (cleaning, leak check etc.): As required.

Data Acquisition and Data Transfer

See 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, 2007a) 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 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 16.	
Station Analysers (OA)	
Model, S/N	HP 5800 II S/N C-128/83 with ECD detector
Principle	GC/ECD
Drying system	Nafion dryer
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 Table 13.

Table 13. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the HP 5800 II GC (AL) with the WCC-Empa TS (WMO-2006A N_2O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(13-07-24 00:42:47)	120803_FA02783	325.04	0.03	324.65	0.10	9	-0.39	-0.12
(13-07-24 11:25:00)	120823_FA02789	322.87	0.03	322.69	0.15	6	-0.18	-0.06
(13-07-24 15:25:00)	120719_FA02782	337.55	0.05	337.32	0.23	6	-0.23	-0.07
(13-07-25 01:25:06)	110512_FB03374	311.96	0.02	311.71	0.11	10	-0.25	-0.08
(13-07-25 21:08:00)	110512_FB03350	312.74	0.04	312.59	0.11	6	-0.15	-0.05
(13-07-31 12:34:40)	100212_FA02773	313.51	0.04	313.07	0.08	6	-0.44	-0.14
(13-07-31 19:38:00)	120718_FB03377	325.57	0.03	325.34	0.15	6	-0.23	-0.07
(13-08-01 11:48:17)	130423_FF30491	343.24	0.04	343.02	0.40	7	-0.22	-0.06
(13-08-01 19:09:00)	110511_FB03384	307.51	0.02	307.32	0.07	6	-0.19	-0.06

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 14. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 16). 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)).

$$X_{TS}\ (\text{ppb}) = ([TS] - 0.09\ \text{ppb}) / 1.0036 \quad (6a)$$

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

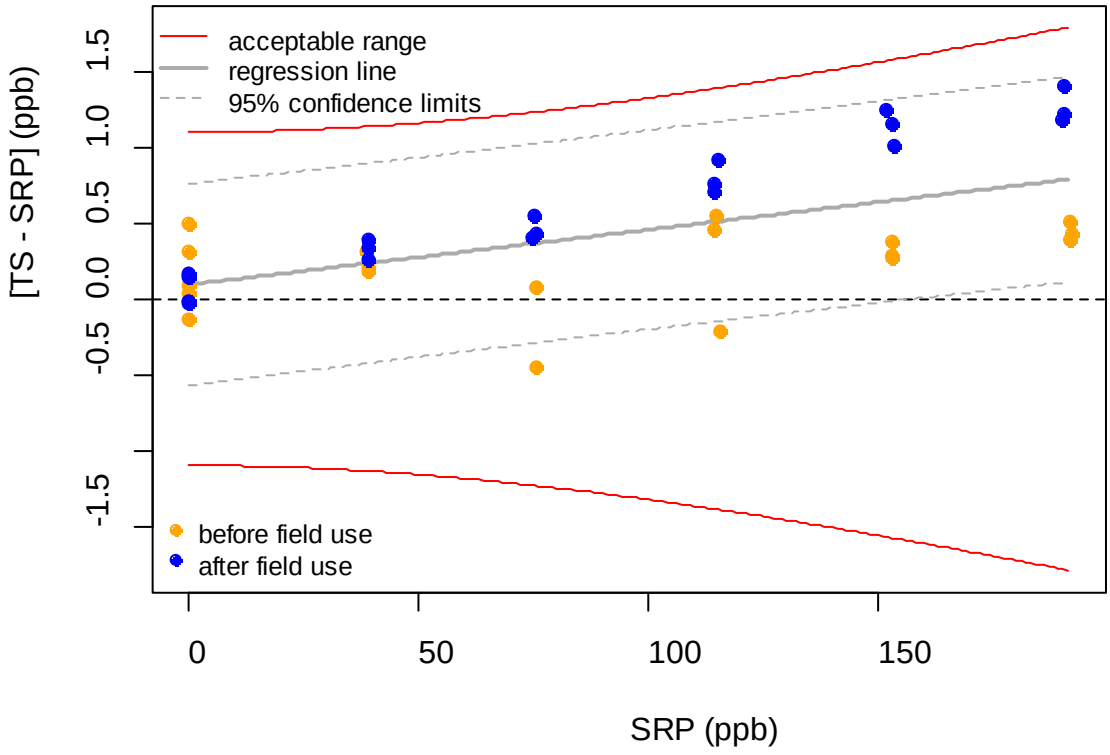

Figure 16. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

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)
2013-03-07	1	0	-0.14	0.21	-0.05	0.14
2013-03-07	1	40	38.48	0.31	38.78	0.18
2013-03-07	1	200	191.61	0.29	192.00	0.20
2013-03-07	1	120	115.34	0.35	115.13	0.17
2013-03-07	1	160	152.96	0.22	153.26	0.29
2013-03-07	1	80	75.51	0.25	75.58	0.34
2013-03-07	1	0	-0.04	0.22	-0.01	0.20
2013-03-07	2	0	-0.20	0.25	0.12	0.32
2013-03-07	2	120	114.44	0.32	114.99	0.19
2013-03-07	2	200	191.68	0.18	192.20	0.22
2013-03-07	2	40	38.91	0.22	39.11	0.34
2013-03-07	2	160	152.96	0.30	153.34	0.17
2013-03-07	2	80	75.43	0.20	75.50	0.21
2013-03-07	2	0	-0.04	0.23	0.11	0.20
2013-03-07	3	0	-0.15	0.19	0.34	0.20
2013-03-07	3	120	114.35	0.34	114.80	0.20
2013-03-07	3	200	191.83	0.33	192.26	0.18
2013-03-07	3	40	38.77	0.28	38.95	0.42
2013-03-07	3	160	152.90	0.28	153.17	0.18
2013-03-07	3	80	75.38	0.24	74.93	0.30
2013-03-07	3	0	-0.07	0.29	-0.21	0.15
2013-09-24	4	0	0.04	0.25	0.03	0.36
2013-09-24	4	40	38.96	0.17	39.29	0.26
2013-09-24	4	160	153.08	0.19	154.08	0.20
2013-09-24	4	200	190.30	0.24	191.70	0.26
2013-09-24	4	120	114.20	0.24	114.90	0.18
2013-09-24	4	80	74.94	0.12	75.49	0.30
2013-09-24	4	0	0.04	0.34	0.20	0.35
2013-09-24	5	0	0.01	0.31	0.17	0.16
2013-09-24	5	80	75.38	0.19	75.81	0.23
2013-09-24	5	40	38.87	0.16	39.12	0.23
2013-09-24	5	160	152.63	0.25	153.79	0.22
2013-09-24	5	200	189.92	0.20	191.11	0.55
2013-09-24	5	120	114.20	0.28	114.96	0.15
2013-09-24	5	0	0.03	0.19	0.01	0.31
2013-09-24	6	0	-0.03	0.21	0.12	0.26
2013-09-24	6	120	114.85	0.16	115.76	0.24
2013-09-24	6	40	38.81	0.21	39.19	0.29
2013-09-24	6	200	190.11	0.14	191.33	0.37
2013-09-24	6	80	74.81	0.18	75.21	0.20
2013-09-24	6	160	151.37	0.18	152.61	0.19
2013-09-24	6	0	0.04	0.25	0.01	0.17

[#]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-X2004 scale (Novelli et al., 2003)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004 scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

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 and N_2O: 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 17 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)	
CC339523	347.9	0.3	1854.60	0.13	322.52	0.12	396.88	0.06	350.9	0.3	1854.76	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	394.1	0.4	1981.18	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	167.2	0.3	1805.07	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)
080814_FA02488	41.90	0.30	1309.77	0.04	149.79	0.03	127.60	0.14
080820_FA02686	105.61	0.22	1870.85	0.05	172.97	0.02	130.29	0.25
100204_FA02464	68.29	0.07	1941.83	0.11	347.11	0.02	286.73	0.04
100212_FA02773	62.20	0.55	2247.86	0.04	360.89	0.01	313.51	0.04
110511_FB03384	106.01	0.41	1894.98	0.10	323.94	0.03	307.51	0.02
110512_FB03350	215.59	0.49	2760.59	0.11	384.93	0.01	312.74	0.04
110512_FB03374	215.27	0.31	2762.16	0.12	378.73	0.03	311.96	0.02
120718_FB03377	212.51	0.40	1856.64	0.15	377.30	0.05	325.57	0.03
120719_FA02782	159.53	0.14	1919.19	0.07	331.43	0.02	337.55	0.05
120723_FA02789	256.25	0.17	2115.41	0.10	409.31	0.02	322.87	0.03
120803_FA02783	113.61	0.29	2228.22	0.14	404.38	0.03	325.04	0.03
130423_FF30491	244.77	0.06	2091.60	0.07	384.00	0.03	343.24	0.04

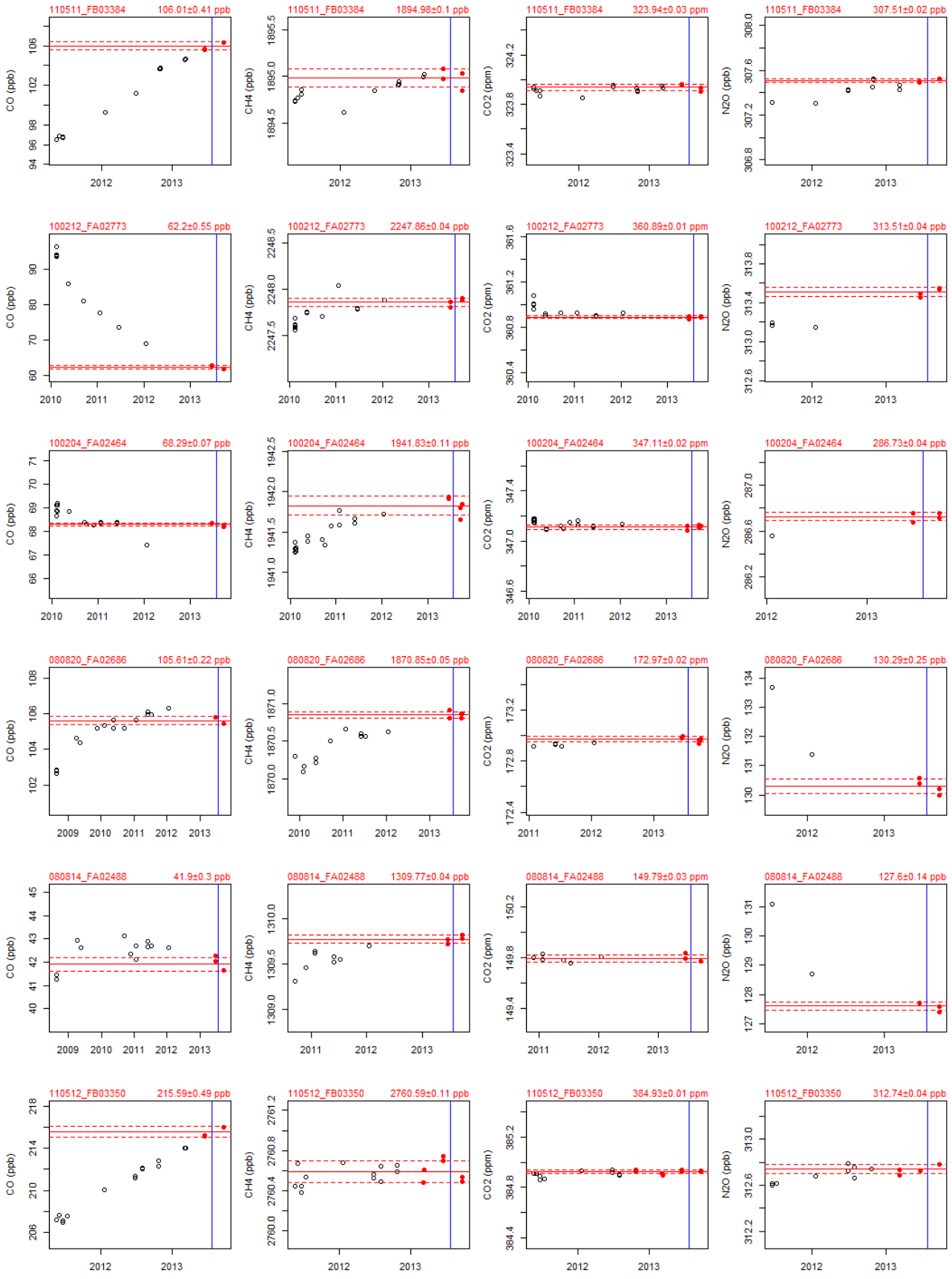

Figure 17. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

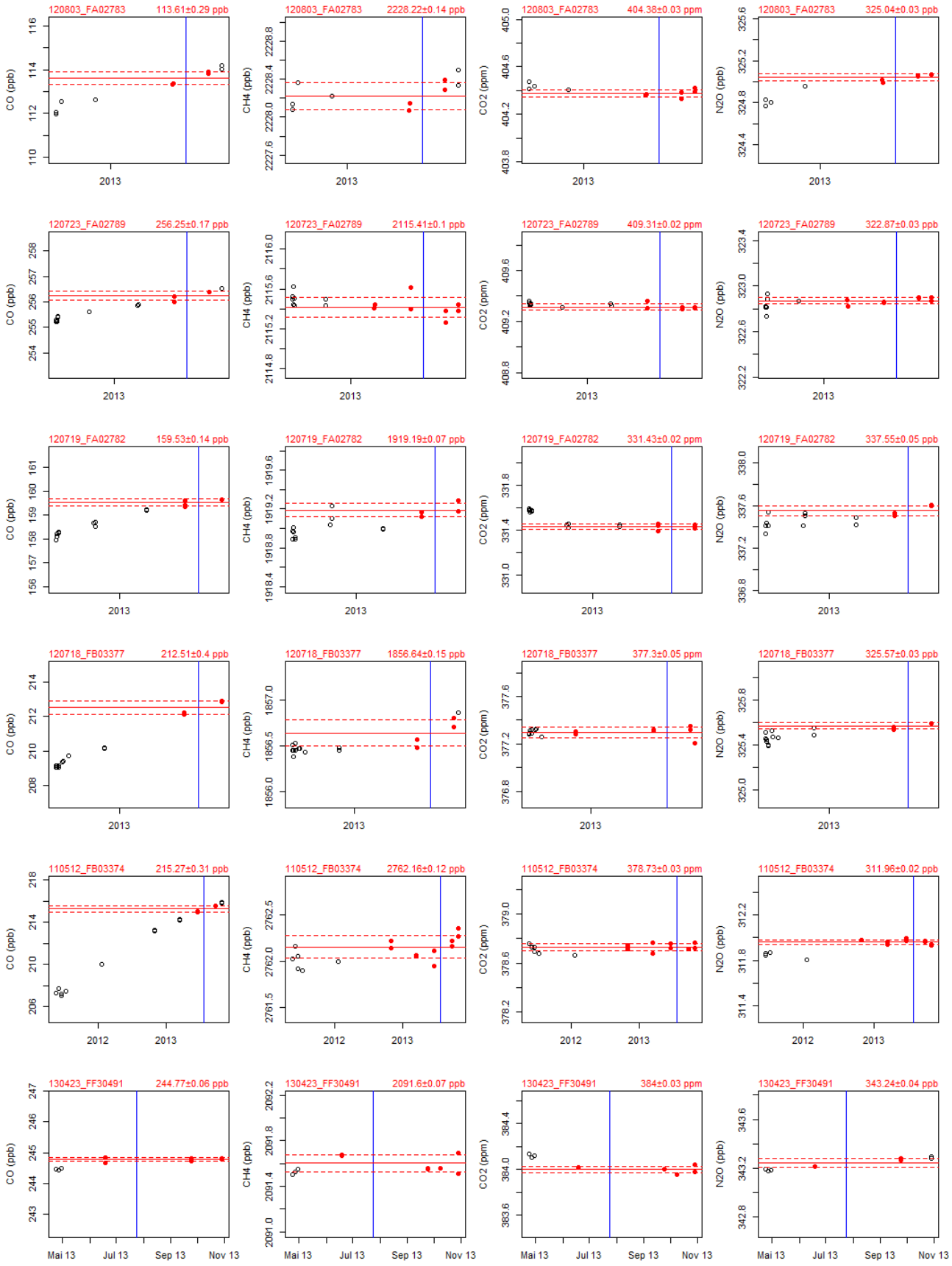

Figure 18. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

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Ozone Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2013-07-23 through 2013-07-24
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain
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):	(1.0036±0.0012) □ [SRP] + (0.09±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #77086-385
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset = -0.2; Span = 1.020
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0012±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) /1.0012
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.44 ppb^2 + 2.69e-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 13/1

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

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Carbon Monoxide Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2013-07-24 through 2013-09-02
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain
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:	RGA-3 #090189-010
1.6.2	Range of calibration:	44 – 255 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.1011±0.0081) □ X_{CO} - (2.9±1.3)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 2.9 / 1.1011
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (4.5 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:	MHD CO analyser
1.8	Reference:	WCC-Empa Report 13/1

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

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Methane Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2013-07-24 through 2013-08-02
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain
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:	CARLE GC/FID
1.6.2	Range of calibration:	1310 – 2762 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99772 \pm 0.00084) \cdot X_{CH4} + (4.0 \pm 1.8)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 4.0) / 0.99772
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (2.2 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 13/1

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

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Methane Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2013-07-23 through 2013-07-24
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS] standards	TS calibrated against the WCC-Empa laboratory
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro G1301 #163-CFADS046
1.6.2	Range of calibration:	1856 – 2762 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99543 \pm 0.00027) \cdot X_{CH4} + (8.2 \pm 0.6)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 8.2) / 0.99543
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 13/1

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

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Methane Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2013-07-23 through 2013-07-24
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS] standards	TS calibrated against the WCC-Empa laboratory
1.6	Station Analyser:	
1.6.1	Analyser Model:	Picarro G2301 #639-CFADS2122
1.6.2	Range of calibration:	1856 – 2762 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99372 \pm 0.00013) \cdot X_{CH4} + (11.9 \pm 0.3)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 11.9) / 0.99372
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.1 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 13/1

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

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Carbon Dioxide Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2013-07-23 through 2013-07-24
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain, Benoit Wastine
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 G1301 #163-CFADS046
1.6.2	Range of calibration:	324 – 410 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.99785 \pm 0.00021) \cdot X_{CO2} + (0.90 \pm 0.08)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 – 0.90) / 0.99785
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:	Owned by Irish EPA
1.8	Reference:	WCC-Empa Report 13/1

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

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Carbon Dioxide Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2013-07-23 through 2013-07-24
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain, Benoit Wastine
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 G2301 #639-CFADS2122
1.6.2	Range of calibration:	324 – 410 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	CO_2 = (0.99725±0.00024) □ X_{CO2} + (1.16±0.09)
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 – 1.16) / 0.99725
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:	Owned by LSCE
1.8	Reference:	WCC-Empa Report 13/1

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

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Nitrous Oxide Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89944°W (5 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2013-07-24 through 2013-08-01
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Gerry Spain
1.4	WCC-Empa N_2O Reference:	NOAA laboratory standards (WMO-2006A scale)
1.5	N_2O Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	HP 5800 II S/N C-128/83 with ECD detector
1.6.2	Range of calibration:	307 – 344 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$N_2O = (1.0004 \pm 0.0030) \cdot X_{N2O} - (0.38 \pm 0.97)$
1.6.5	Unbiased N_2O mixing ratio (ppb) at start of audit:	X_{N2O} (ppb) = (N_2O + 0.38) / 1.0004
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{N2O} (ppb) = sqrt (0.01 ppb^2 + 1.01e-07 * X_{N2O}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased N_2O mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 13/1

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

REFERENCES

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, Journal Of Geophysical Research-Atmospheres, 110, Article D18306, 2005.

Herzog, A., Buchmann, B., and Hofer, P.: System and Performance Audit for Surface Ozone and Carbon Monoxide, Global GAW Station Mace Head, Ireland, May 1998, WCC-Empa Report 98/3, Empa Dübendorf, Switzerland, 32 pp., 1998.

Herzog, A., Buchmann, B., and Hofer, P.: System and Performance Audit for Surface Ozone, Global GAW Station Mace Head, Ireland, October 1996, WCC-Empa Report, Empa Dübendorf, Switzerland, 21 pp., 1996.

Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, Journal of Geophysical Research-Atmospheres, 108, 4622, doi:4610.1029/2003JD003710, 2003.

Novelli, P. C., Masarie, K. A., Lang, P. M., Hall, B. D., Myers, R. C., and Elkins, J. W.: Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, Journal of Geophysical Research-Atmospheres, 108, 4464, doi:4410.1029/2002JD003031, 2003.

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., and McCulloch, A.: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, Journal of Geophysical Research-Atmospheres, 105, 17751-17792, 2000.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech., 6, 837-860, 2013.

Vardag, S. N., Hammer, S., O'Doherty, S., Spain, T. G., Wastine, B., Jordan, A., and Levin, I.: Comparisons of continuous atmospheric CH4, CO2 and N2O measurements; results of InGOS travelling instrument campaign at Mace Head, Atmos. Chem. Phys. Discuss., 14, 10429-10462, 2014.

WMO: http://www.wmo.int/pages/prog/arep/gaw/documents/GAW_194_WMO_TD_No_1553_web_low_resol.pdf, 2011.

WMO: Guidelines for Continuous Measurements of Ozone in the Troposphere, WMO TD No. 1110, GAW Report No. 209, World Meteorological Organization, Geneva, Switzerland, 2013.

WMO: Guidelines for the Measurement of Atmospheric Carbon Monoxide, GAW Report No. 192, World Meteorological Organization, Geneva, Switzerland, 2010.

WMO: Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance, GAW Report No. 185, World Meteorological Organization, Geneva, Switzerland, 2009.

WMO: Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland, 2007a.

WMO: WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, GAW Report #172, World Meteorological Organization, Geneva, Switzerland, 2007b.

Zellweger, C., Klausen, J., and Buchmann, B.: System and Performance Audit of Surface Ozone Carbon Monoxide and Methane at the Global GAW Station Mace Head, Ireland, August 2002, WCC-Empa Report 02/3, Empa, Dübendorf, Switzerland, 37 pp., 2002.

Zellweger, C., Klausen, J., and Buchmann, B.: System and Performance Audit of Surface Ozone Carbon Monoxide and Methane at the Global GAW Station Mace Head, Ireland, May 2005, WCC-Empa Report 05/2, Empa, Dübendorf, Switzerland, 44 pp., 2005.

Zellweger, C., Klausen, J., Buchmann, B., and Scheel, H. E.: System and Performance Audit of Surface Ozone,Carbon Monoxide, Methane and Nitrous Oxide at the Global GAW Station Mace Head, Ireland, December 2009, WCC-Empa Report 09/3, Dübendorf, Switzerland, 38 pp., 2009.

Zhao, C. L. and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, Journal of Geophysical Research-Atmospheres, 111, 2006.

LIST OF ABBREVIATIONS

AGAGE	Advanced Global Atmospheric Gases Experiment
AL	Analyser
BKG	Background
CCL	Central Calibration Laboratory
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DQO	Data Quality Objective
dtm	Date/Time
ECD	Electron Capture Detector
EPA	Environmental Protection Agency
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 Observation System
LS	Laboratory Standard
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
MPI-BGC	Max-Planck-Institute for Biogeochemistry
MHD	Mace Head Observatory
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
UV	Ultra Violet
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard