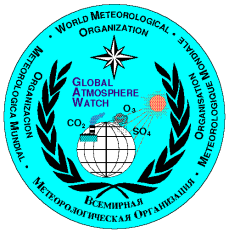

Materials Science & Technology

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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 09/3

Submitted to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GLOBAL GAW STATION MACE HEAD IRELAND, DECEMBER 2009

Submitted by
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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The fifth system and performance audit at the Global GAW station Mace Head was conducted by WCC-Empa[1] from 15 thru 17 December 2009 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The Mace Head (MHD) atmospheric research station is coordinated by the School of Physics, NUI, Galway.

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], and May 2005 [*Zellweger, et al.*, 2005].

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr Gerry Spain	NUI, Galway, station manager
Dr Simon O'Doherty	University of Bristol

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

This report is distributed to the GAW country contact (Mr Eoin Moran, Met Éireann), the MHD station manager, and the World Meteorological Organization (WMO) in Geneva. The report including executive summaries will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

The Mace Head research station (53.32°N 9.89°W) is located on the west coast of Ireland. The location is offering westerly exposure to the North Atlantic ocean (clean sector, 180 degrees through west to 300 degrees) and the opportunity to study atmospheric composition under northern hemispheric background conditions as well as European continental emissions when the winds favour transport from that region. It is 88 km west of Galway city (population approximately 60,000) which is the nearest major conurbation. The main Atlantic shipping routes are over 150 km away, while the transatlantic air corridors are over 80 km away. There are three small islands offshore which are within the clean sector, but these are uninhabited and do not appear to influence any of the measurements made at the site. The meteorological records show that on average, over 60% of the air masses arrive at the station via the clean sector. These air masses are ideal for carrying out background aerosol and trace gas measurements. Significant pollution events also occur at the site when European continental air masses, generally originating from an easterly direction, reach Mace Head. The Mace Head research station is uniquely positioned for resolving these different air masses, and for comparative studies of their constituents and characteristics.

Mace Head contributes to a number of international research networks, including the Advanced Global Atmospheric Gases Experiment (AGAGE), the Atmospheric/Ocean Chemistry Experiment (AEROCE), Tropospheric Ozone Research (TOR, a EUROTRAC project), Budget of Ozone over the Atlantic (BOA) and the NOAA/ESRL co-operative flask sampling network.

[1] WMO/GAW 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, one at ~300m and two at ~90m from the shore (~50m from high water), 23m and 10m aluminium walk-up towers and a converted cargo container laboratory. Other ancillary constructions include a 10 m meteorological tower and platforms for the positioning of sampling equipment. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

Station Management and Operation

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

Air Inlet System

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.

Surface Ozone Measurements

Ozone measurements at MHD are part of the UK Automatic Urban and Rural Network (AURN) network (http://aurn.defra.gov.uk) run by the Department for Environment, Food and Rural Affairs (DEFRA).

Instrumentation. A TEI 49C ozone analyzer was installed in March 2003 and is currently used at the station for continuous surface ozone measurements. The instrument is adequate for its intended purpose.

Standards. No ozone standard is available at the site. The instrument are audited (compared) approximately every 3 months and serviced every 6 months. DEFRA currently contracts auditing (every 3 months) to AEA Technology (http://www.aeat.co.uk) and servicing (every 6 months) to Air Monitors Ltd (http://www.airmonitors.co.uk).

Recommendation 1 (, 2010-2011)**
It should be considered to have an ozone standard available at the site for periodic instrument checks and calibrations.

Intercomparison (Performance Audit). Two comparisons were made during the audit. The first comparison was made with unchanged instrument settings. Afterwards, the instrument calibration was adjusted, and a second comparison was made. The results are summarised below and the following equations characterise the instrument bias:

TEI 49C #77086-385 (BKG -0.7 ppb, SPAN 1.028): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.58 ppb) / 1.0081 (1a)

TEI 49i #77086-385 (BKG -0.2 ppb, SPAN 1.020): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.02 ppb) / 1.0000 (1b)

The results of these comparisons are presented in Figure 1.

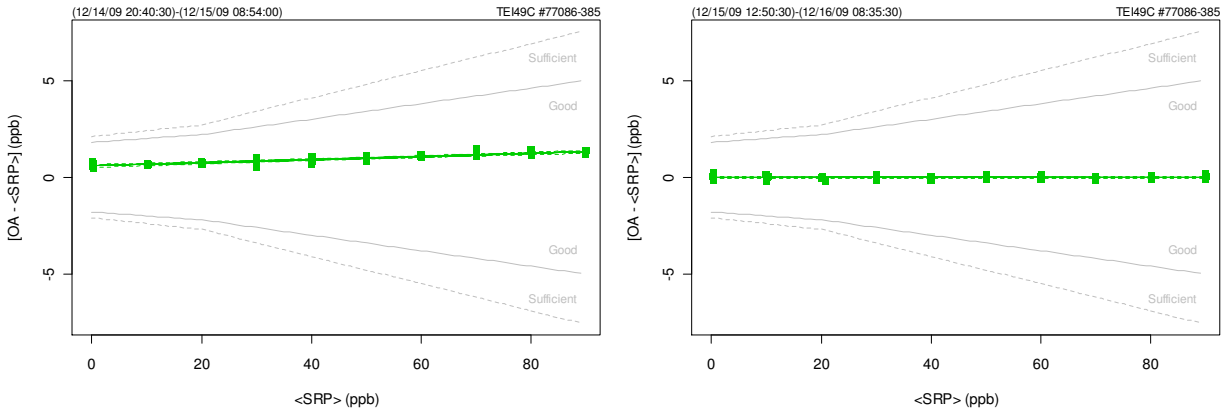

Figure 1. Bias of the MHD TEI 49C analyser with respect to the SRP as a function of mole fraction. The left panel shows the comparison before the adjustment of the calibration, the right panel after the adjustment. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

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 2005.

Instrumentation. Mace Head is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2. The instrumentation is adequate for the intended purpose, although the linearity of the system changed over time. Therefore, it should be considered to set-up a back-up measurement system such as a GC/FID with methanizer.

Recommendation 2 (*, 2011)
WCC-Empa recommends the setup of GC/FID/methanizer system to provide a backup for the CO measurements. Such a system could additionally be used for CO_2 measurements.

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). In addition, other commercial standards are available which are occasionally used to verify the response function of the GC. A full calibration of the instrument using flasks (CSIRO) is performed at irregular intervals.

Recommendation 3 (*, 2010-2011)**
A set of three or more NOAA/ESRL carbon monoxide laboratory standards should be available at MHD for a direct link to the WMO/GAW calibration scale and for the verification of the instrument response function.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the instrument with randomised carbon monoxide concentrations from traveling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 2:

RGA-3 #090189-010(MHD):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] - 1.2 ppb) / 1.006 (2)

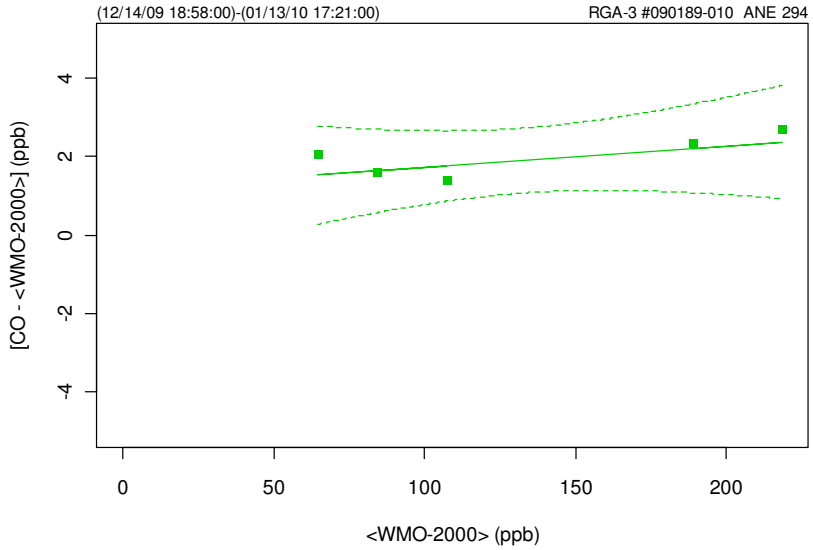

Figure 2. Bias of the Mace Head carbon monoxide instrument (RGA-3) with respect to the WMO-2000 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands.

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 2005. During the audit, a Picarro G-1301 owned by the Irish EPA was tested at the station for future measurements of CO_2 and CH_4; however, these data are not yet considered as GAW data.

Recommendation 4 (*, ongoing)
Data of the Picarro instrument should be compared with the GC/FID instrument and should also be made available for GAW purposes.

Instrumentation. A CARLE GC system with FID detector is used for methane measurements. This system has been audited by WCC-Empa in 2005 [*Zellweger, et al.*, 2005] and has not changed since then.

Standards. The station is equipped with laboratory and working standards. Mace Head CH_4 measurements are referenced to the Tohoku University methane scale by the use of stainless steel cylinders provided by Scripps Institution of Oceanography (SIO).

Recommendation 5 (*, 2010-2011)**
At least one, preferably a set of three or more NOAA/ESRL methane laboratory standards should be available at MHD for a direct link to the WMO/GAW calibration scale.

Intercomparison (Performance Audit). The comparison involved repeated measurements of WCC-Empa traveling standards with the MHD instrument. No significant deviations between the Mace Head instrument and WCC-Empa were found. The following equation characterises the instrument bias (cf. Figure 3):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 1.00028 (3)

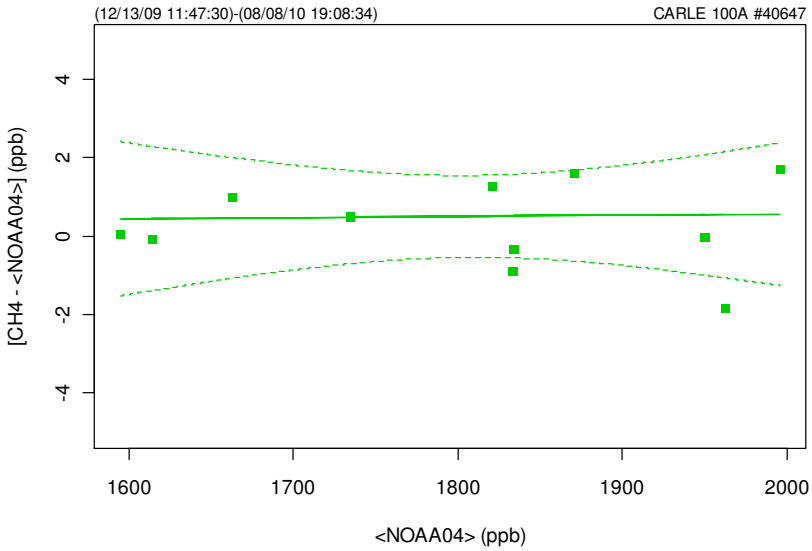

Figure 3. Bias of the Mace Head methane GC with respect to the NOAA04 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression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

It can be seen from Figure 3 that the MHD measurements meet the WMO/GAW recommendation of ±2 ppb [*WMO*, 2009a]; and the repeatability of the MHD GC instrument reached values that are comparable to the best GC/FID instruments.

Nitrous Oxide Measurements

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).

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).

Recommendation 6 (*, 2010-2011)**
A set of three or more NOAA/ESRL nitrous oxide laboratory standards should be available at MHD for a direct link to the WMO/GAW calibration scale and for the verification of the instrument response function.

Recommendation 7 (*, 2010-2011)**
The continuation of the non-linearity checks using one working standards at different pressure levels should be considered.

Intercomparison (Performance Audit). The comparison involved repeated measurements of WCC-Empa traveling standards with the MHD instrument. The N_2O mole fractions of the TS were assigned by the WCC-N_2O in 2007/2008, and have not been re-calibrated since then. The best agreement was found for mole fractions of ambient air or lower; a slightly higher deviations was observed for higher mole fractions. The MHD N_2O measurements do therefore not significantly deviate from the GAW reference (NOAA-2006 mole fraction scale). The following equation characterises the instrument bias (cf. Figure 9):

Unbiased N_2O mixing ratio (ppb): X_{N2O} (ppb) = (N_2O) / 1.00116 (4)

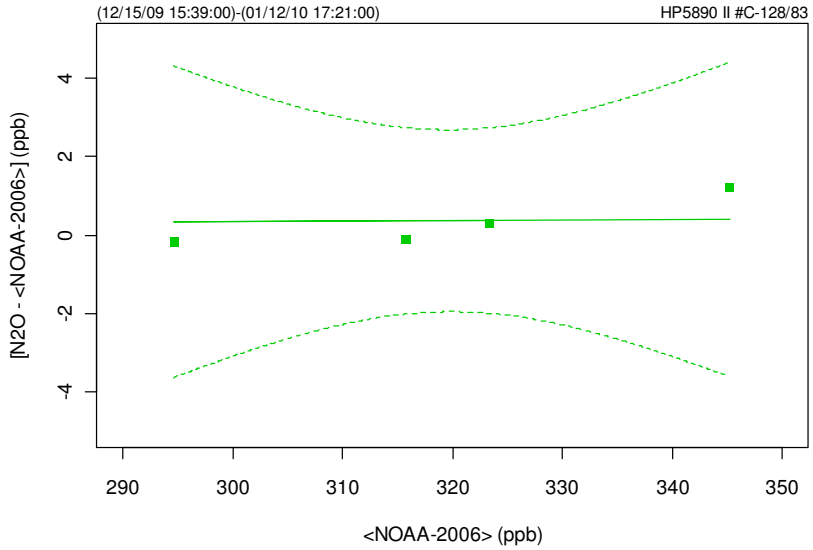

Figure 4. Bias of the Mace Head N_2O GC with respect to the NOAA-2006 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Data Acquisition and Management

Ozone data are digitally acquired using run custom programmed software under Linux. One minute averages are automatically acquired from the TEI internal data logger, including all available ancillary instrument parameters, and are stored for further data treatment. Carbon monoxide and greenhouse gas data are acquired on the AGAGE GC control software package developed at SIO. All the chromatograms are stored and automatically transferred twice daily via internet to the main database at SIO. Remote access is possible through the internet.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone (2004 – 2008), methane (1987 – 2009), carbon monoxide (1994 – 2009) and nitrous oxide (1987 – 2009) have been submitted by NUI, Galway (ozone) and AGAGE (other gases).

Recommendation 8 (, ongoing)**
Data of the GC systems have been submitted as event data; it should be considered to submit these data as hourly aggregates.

Recommendation 9 (, 2010)**
Ozone data acquired before 2004 has not been submitted to WDCGG. It is recommended to review and submit these data. Data submission should be made with a maximum delay of one year.

Conclusions

The Global GAW station Mace Head carries out a comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the MHD station an important contribution to the GAW programme. All assessed measurements were of high quality.

Summary Ranking of Mace Head Station

System Audit Aspect	Adequacy[#]	Comment
Access	(5)	Year-round access possible
Facilities		
Laboratory and office space	(4)	Limited space at the gas lab
Air Conditioning	(4)	
Power supply	(5)	
Internet access	(5)	
General Management and Operation		
Organisation	(4)	Irish EPA Picarro analyser should be part of GAW
Competence of staff	(5)	
Air Inlet System	(4)	Each system uses own inlet
Instrumentation		
Ozone	(5)	TEI49C
Carbon monoxide	(4)	RGA-3, becoming old
Methane	(4)	Carle GC/FID, relatively poor re-peatability
Nitrous Oxide	(5)	HP 5890II
Other gases*	(5)	CO_2, SF_6, CFCs, HCFCs
Aerosol parameters*	(5)	Comprehensive programme
Flask sampling	(5)	NOAA/ESRL programme
Meteo	(5)	
Standards		
Ozone	(2)	Basic checks by private company every three months
Carbon monoxide	(4)	No direct link to WMO scale
Methane	(4)	No direct link to WMO scale
Nitrous Oxide	(4)	No direct link to WMO scale
Data Management		
Data acquisition	(5)	
Data processing	(5)	
Data submission	(4)	O_3 prior 2004 not yet submitted

[#]0: inadequate thru 5: adequate; *refer to GAWSIS (www.empa.ch/gaw/gawsis) for a complete overview of measured parameters.

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Dübendorf, November 2010

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

APPENDIX

Global GAW Station Mace Head

Site description

The Atmospheric Research Station at Mace Head located at the west coast of Ireland is unique in Europe, offering westerly exposure to the North Atlantic ocean (clean sector, 180 degrees through west to 300 degrees) and the opportunity to study atmospheric composition under Northern Hemispheric background conditions as well as European continental emissions when the winds favour transport from that region. For more information, see the previous audit reports [*Zellweger, et al*., 2002; 2005]. Detailed information is available from the station web site (http://www.macehead.org) and from GAWSIS (http://gaw.empa.ch/gawsis).

Measurement Programme

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

Table 1. Measurement Programme at the MHD Station

Parameter*	**Current Instrument**	**Data Coverage (%)#**		
		<12 m	<3 y	Overall
Aerosol				
OC/EC, PM10	Filter sampling + combustion + IC			
CCN concentration	Twomey			
Backscattering coefficient	Nephelometry, integrating			
Light absorption coefficient	Aethalometer			
Light scattering coefficient	Nephelometry, integrating			
Mass concentration	Thermo-optical (Sunset Labs)			
Mass concentration TSP	Continuous gravimetry			
Multiwavelength optical depth	Sun-tracking photometry			
Number concentration	CPC			
Number size distribution	OPC and DMPS			
Total carbon (coarse), PM10	Thermo-optical (Sunset Labs)			
Ozone				
Surface ozone	UV absorption (TEI 49C)	> 99	> 99	> 99
Greenhouse Gas				
CFCs, HCFCs, CCL_4, SF_6, SO_2F_2	GC-ECD and MS, AGAGE			
CH_4	GC-FID	94	96	93
CO_2	Non-dispersive IR (NDIR)			
N_2O	GC-ECD	90	90	89
Reactive Gas				
C_2HCl_3, CH_2Cl_2, CH_3Br, CH_3Cl, $CHCl_3$	GC-MS, AGAGE			
CO and H_2	GC-HgO reduction/UV absorption	90	92	91
Flask Sampling				
VOC, CFCs, HCFs, CO_2, CH_4, CO, H_2, SF_6, CO_2 isotopes	NOAA/GMD flask sampling programme	> 70	> 80	> 90
Radio Nuclide				
Radon [Rn-222]	Adsorption - scintillation counting			
Solar radiation				
UV Broadband	UV radiometry			
Meteo				
PTU, wind speed + direction				

* Refer to GAWSIS for more details

Missing information about data coverage: information was not available, but general high data availabilities (>90%) are expected for most parameters.

Ozone, Carbon Monoxide, Methane and Nitrous Oxide Distributions at Mace Head

The monthly and yearly distributions for surface ozone (one hourly mean values), carbon monoxide, methane and nitrous oxide (GC injections every 40 min) are shown in Figure 5.

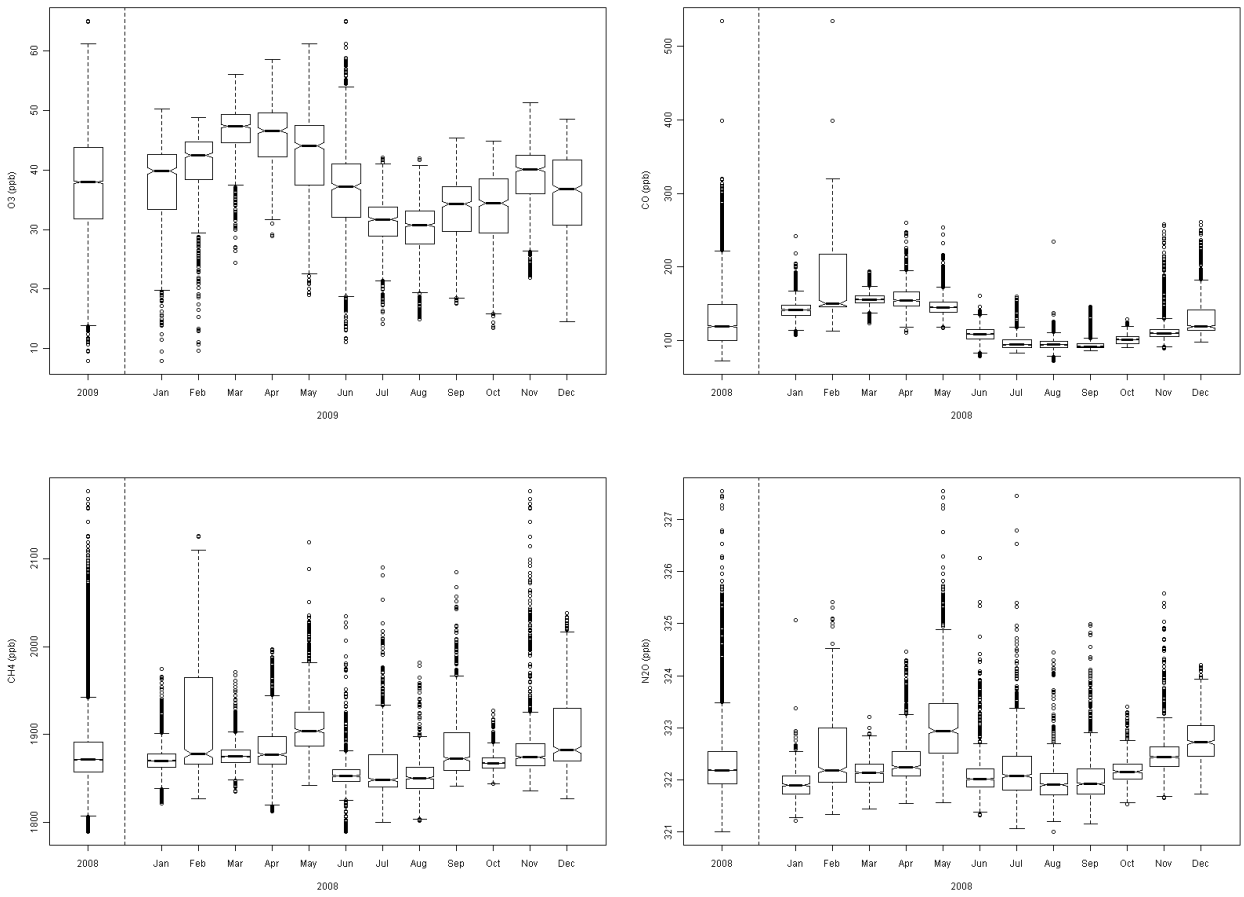

Figure 5. Yearly and monthly box plots for surface ozone (1-hourly aggregates), carbon monoxide, methane and nitrous oxide (GC injections every 30 minutes). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organisation and Contact Persons

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

Surface Ozone Measurements

Surface ozone measurements started in 1987 at the Mace Head site, and continuous one-hourly time series are available since then; however, only data of the current instrument which is at the site since 2003 has been submitted to WDCGG. The whole measurement set-up remained unchanged since the last audit by WCC-Empa [*Zellweger, et al.*, 2005]. All comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Instrumentation

The station is equipped with one ozone analyzer (TEI 49C). Instrumental details for the ozone analyzer (OA) are summarised in Table 2 below. The instrumentation has not changed since the last WCC-Empa audit.

Standards

No ozone standard is available at the site. However, the instrument is checked every three months with a travelling standard by a private company (AEA Technology), contracted by the UK AURN. However, the acceptable maximum bias during these checks is large (5%), and they can not be considered as calibrations (cf. recommendation 1).

Operation and Maintenance

The station is usually visited on working days (Monday to Friday), and the instrument is checked for general operation. Preventive maintenance of the instruments includes regular checks of several instrument parameters (flow rates, pressure and temperature readings, intensities etc.). The measurement cells are cleaned every 6 months, and the instrument is protected with an inlet filter. The filter is changed at least monthly, but earlier in case of pollution events. No automatic zero and span checks are performed.

Data Acquisition and Data Transfer

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005]. 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.

Data Submission

At the time of the audit only ozone data of the year 2004 have been submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA. The period covering 2005 to 2008 was submitted during the audit, but data submission of earlier years is still pending.

Documentation

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

Comparison of Ozone Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included comparisons of the traveling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyzer.

Table 2. Experimental details of the ozone comparison.

Transfer standard (TS)	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
MHD ozone analyzer (OA)	Model, S/N	TEI 49C #77086-385
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = -0.7; COEFF = 1.028 (before adjustment) BKG = -0.2; COEFF = 1.020 (after adjustment)
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm (WCC-Empa)
Connection between instruments		Ca. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS and OA	One minute aggregates from digital output (custom designed LabView programme of WCC-Empa)
Pressure readings at beginning of comparison (hPa)	Ambient	1027.0 (WCC reference)
	TS	1026.9, no adjustments were made
	TEI 49C	1028.8, no adjustments were made
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90
Duration per level (min)		15
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		5 runs (2009-12-14/15, initial calibration settings) 8 runs (2009-12-15/16, new calibration settings)

Setup and Connections

Table 2 details the experimental setup during the comparison of the transfer standard with the station analyzers. The data used for the evaluation was recorded by the WCC-Empa data acquisition system as indicated.

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison as described elsewhere [Klausen, et al., 2003]. The results are shown in Table 3 (initial calibration settings) and Table 4 (new calibration settings). All results refer to the calibration factors as given in Table 2 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyzer (OA) values.

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the initial comparison of the MHD ozone analyzer (OA) TEI 49C #77086-385 with the WCC-Empa transfer standard (TS).

DateTime (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2009-12-14 20:45	1	0	0.23	0.74	0	0.20	0.06	0.51	NA
2009-12-14 21:00	1	30	30.01	30.91	0	0.20	0.12	0.90	2.99
2009-12-14 21:15	1	90	90.01	91.29	0	0.09	0.07	1.28	1.43
2009-12-14 21:30	1	80	79.97	81.34	0	0.09	0.06	1.37	1.72
2009-12-14 21:45	1	60	59.97	61.04	0	0.09	0.09	1.07	1.78
2009-12-14 22:00	1	20	20.03	20.83	0	0.08	0.08	0.80	3.99
2009-12-14 22:15	1	40	40.00	40.87	0	0.12	0.06	0.87	2.17
2009-12-14 22:30	1	70	69.98	71.43	0	0.11	0.09	1.45	2.08
2009-12-14 22:45	1	10	10.19	10.88	0	0.41	0.10	0.69	6.75
2009-12-14 23:00	1	50	50.04	51.08	0	0.08	0.08	1.04	2.08
2009-12-14 23:15	2	0	0.20	0.82	0	0.27	0.08	0.62	NA
2009-12-14 23:30	2	20	20.01	20.78	0	0.19	0.11	0.77	3.85
2009-12-14 23:45	2	80	80.02	81.13	0	0.12	0.07	1.11	1.39
2009-12-15 00:00	2	90	90.01	91.24	0	0.06	0.12	1.23	1.36
2009-12-15 00:15	2	40	39.98	40.92	0	0.09	0.06	0.95	2.37
2009-12-15 00:30	2	60	59.98	61.10	0	0.07	0.09	1.12	1.86
2009-12-15 00:45	2	10	10.12	10.84	0	0.27	0.10	0.72	7.15
2009-12-15 01:00	2	70	69.99	71.09	0	0.13	0.11	1.10	1.58
2009-12-15 01:15	2	30	30.02	30.65	0	0.10	0.10	0.62	2.08
2009-12-15 01:30	2	50	50.04	51.02	0	0.12	0.06	0.98	1.97
2009-12-15 01:45	3	0	0.07	0.93	0	0.23	0.07	0.86	NA
2009-12-15 02:00	3	30	30.03	31.01	0	0.09	0.06	0.97	3.24
2009-12-15 02:15	3	50	50.01	51.01	0	0.13	0.09	1.00	2.00
2009-12-15 02:30	3	10	9.97	10.73	0	0.19	0.06	0.76	7.58
2009-12-15 02:45	3	90	90.01	91.37	0	0.07	0.10	1.36	1.51
2009-12-15 03:00	3	60	60.00	61.17	0	0.09	0.07	1.17	1.95
2009-12-15 03:15	3	20	20.01	20.72	0	0.10	0.06	0.71	3.56
2009-12-15 03:30	3	80	79.99	81.05	0	0.08	0.08	1.06	1.33
2009-12-15 03:45	3	70	70.02	71.19	0	0.13	0.07	1.17	1.68
2009-12-15 04:00	3	40	39.97	40.67	0	0.14	0.12	0.70	1.76
2009-12-15 04:15	4	0	0.20	0.97	0	0.19	0.05	0.77	NA
2009-12-15 04:30	4	30	29.98	30.49	0	0.11	0.06	0.51	1.69
2009-12-15 04:45	4	90	89.98	91.22	0	0.10	0.06	1.25	1.39
2009-12-15 05:00	4	80	80.02	81.26	0	0.09	0.07	1.23	1.54
2009-12-15 05:15	4	60	59.99	61.00	0	0.12	0.08	1.00	1.67
2009-12-15 05:30	4	20	20.00	20.78	0	0.16	0.09	0.78	3.91
2009-12-15 05:45	4	40	40.01	41.07	0	0.09	0.09	1.06	2.64
2009-12-15 06:00	4	70	70.00	71.09	0	0.14	0.08	1.09	1.56
2009-12-15 06:15	4	10	10.09	10.78	0	0.27	0.14	0.69	6.88
2009-12-15 06:30	4	50	49.99	51.09	0	0.11	0.08	1.09	2.19
2009-12-15 06:45	5	0	0.18	0.90	0	0.17	0.08	0.71	NA
2009-12-15 07:00	5	20	19.99	20.85	0	0.20	0.11	0.86	4.31
2009-12-15 07:15	5	80	80.01	81.26	0	0.08	0.12	1.25	1.56
2009-12-15 07:30	5	90	90.01	91.10	0	0.06	0.07	1.09	1.22
2009-12-15 07:45	5	40	39.99	40.83	0	0.15	0.05	0.85	2.11
2009-12-15 08:00	5	60	60.00	61.11	0	0.14	0.10	1.11	1.85
2009-12-15 08:15	5	10	9.97	10.62	0	0.18	0.09	0.65	6.52
2009-12-15 08:30	5	70	70.00	71.04	0	0.08	0.06	1.03	1.48
2009-12-15 08:45	5	30	29.99	31.02	0	0.12	0.11	1.03	3.44
2009-12-15 09:00	5	50	49.97	50.79	0	0.08	0.07	0.82	1.65

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

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the final comparison of the MHD ozone analyzer (OA) TEI 49C #77086-385 with the WCC-Empa transfer standard (TS).

DateTime (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2009-12-15 12:55	1	0	0.27	0.57	0	0.22	0.05	0.29	NA
2009-12-15 13:10	1	30	29.98	29.85	0	0.22	0.13	-0.13	-0.43
2009-12-15 13:25	1	90	90.01	89.98	0	0.13	0.13	-0.03	-0.03
2009-12-15 13:40	1	80	79.99	80.00	0	0.12	0.05	0.01	0.02
2009-12-15 13:55	1	60	60.01	59.98	0	0.11	0.06	-0.03	-0.04
2009-12-15 14:10	1	20	19.97	19.93	0	0.12	0.08	-0.04	-0.18
2009-12-15 14:25	1	40	40.01	40.01	0	0.11	0.06	0.00	0.00
2009-12-15 14:40	1	70	70.00	69.92	0	0.11	0.10	-0.08	-0.11
2009-12-15 14:55	1	10	10.32	10.43	0	0.38	0.14	0.12	1.12
2009-12-15 15:10	1	50	49.99	50.08	0	0.13	0.09	0.09	0.19
2009-12-15 15:25	2	0	0.17	0.29	0	0.28	0.03	0.13	NA
2009-12-15 15:40	2	20	19.98	19.98	0	0.17	0.06	0.00	0.02
2009-12-15 15:55	2	80	80.03	79.92	0	0.13	0.10	-0.11	-0.14
2009-12-15 16:10	2	90	90.01	89.96	0	0.11	0.16	-0.06	-0.06
2009-12-15 16:25	2	40	40.02	40.06	0	0.28	0.10	0.03	0.08
2009-12-15 16:40	2	60	60.02	60.14	0	0.09	0.08	0.12	0.20
2009-12-15 16:55	2	10	9.94	10.13	0	0.13	0.08	0.20	1.98
2009-12-15 17:10	2	70	70.01	70.00	0	0.05	0.08	0.00	-0.01
2009-12-15 17:25	2	30	29.96	30.06	0	0.20	0.13	0.10	0.33
2009-12-15 17:40	2	50	49.99	50.12	0	0.14	0.08	0.13	0.26
2009-12-15 17:55	3	0	0.23	0.22	0	0.25	0.06	-0.01	NA
2009-12-15 18:10	3	30	30.00	29.99	0	0.12	0.05	-0.01	-0.03
2009-12-15 18:25	3	50	49.98	50.08	0	0.09	0.14	0.10	0.20
2009-12-15 18:40	3	10	10.03	10.09	0	0.14	0.07	0.06	0.57
2009-12-15 18:55	3	90	89.99	89.86	0	0.05	0.07	-0.13	-0.14
2009-12-15 19:10	3	60	59.99	59.91	0	0.15	0.05	-0.09	-0.14
2009-12-15 19:25	3	20	20.03	20.11	0	0.13	0.04	0.08	0.39
2009-12-15 19:40	3	80	80.00	80.06	0	0.13	0.10	0.06	0.07
2009-12-15 19:55	3	70	69.99	69.97	0	0.12	0.07	-0.02	-0.03
2009-12-15 20:10	3	40	40.00	39.94	0	0.11	0.11	-0.06	-0.14
2009-12-15 20:25	4	0	0.18	0.32	0	0.21	0.05	0.13	NA
2009-12-15 20:40	4	30	30.02	29.92	0	0.12	0.08	-0.10	-0.32
2009-12-15 20:55	4	90	90.03	90.05	0	0.14	0.10	0.02	0.02
2009-12-15 21:10	4	80	80.01	80.08	0	0.09	0.10	0.07	0.08
2009-12-15 21:25	4	60	60.03	59.93	0	0.08	0.06	-0.10	-0.16
2009-12-15 21:40	4	20	20.02	19.95	0	0.24	0.06	-0.06	-0.31
2009-12-15 21:55	4	40	40.01	39.97	0	0.18	0.09	-0.04	-0.10
2009-12-15 22:10	4	70	70.01	69.96	0	0.08	0.07	-0.05	-0.08
2009-12-15 22:25	4	10	10.02	10.03	0	0.19	0.05	0.01	0.12
2009-12-15 22:40	4	50	50.03	50.01	0	0.08	0.07	-0.01	-0.03
2009-12-15 22:55	5	0	0.34	0.25	0	0.21	0.05	-0.08	NA
2009-12-15 23:10	5	20	20.02	19.98	0	0.15	0.09	-0.04	-0.20
2009-12-15 23:25	5	80	80.00	79.93	0	0.05	0.06	-0.06	-0.08
2009-12-15 23:40	5	90	90.01	89.81	0	0.15	0.07	-0.20	-0.22
2009-12-15 23:55	5	40	39.99	39.84	0	0.17	0.07	-0.15	-0.38
2009-12-16 00:10	5	60	59.97	59.89	0	0.11	0.08	-0.08	-0.13
2009-12-16 00:25	5	10	10.05	9.90	0	0.23	0.07	-0.15	-1.50
2009-12-16 00:40	5	70	70.03	70.01	0	0.12	0.12	-0.02	-0.03
2009-12-16 00:55	5	30	30.02	30.08	0	0.12	0.12	0.06	0.21
2009-12-16 01:10	5	50	50.02	50.01	0	0.08	0.05	-0.01	-0.03
2009-12-16 01:25	6	0	0.22	0.17	0	0.31	0.04	-0.05	NA
2009-12-16 01:40	6	30	29.99	30.11	0	0.15	0.07	0.12	0.39
2009-12-16 01:55	6	50	49.99	49.83	0	0.09	0.07	-0.15	-0.30

DateTime (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2009-12-16 02:10	6	10	10.15	10.22	0	0.19	0.10	0.06	0.64
2009-12-16 02:25	6	90	90.00	89.94	0	0.12	0.08	-0.06	-0.06
2009-12-16 02:40	6	60	59.98	59.83	0	0.11	0.09	-0.15	-0.25
2009-12-16 02:55	6	20	19.98	19.99	0	0.08	0.09	0.01	0.04
2009-12-16 03:10	6	80	80.00	79.97	0	0.12	0.07	-0.03	-0.04
2009-12-16 03:25	6	70	69.97	69.84	0	0.13	0.07	-0.13	-0.19
2009-12-16 03:40	6	40	40.00	39.99	0	0.14	0.13	0.00	-0.01
2009-12-16 03:55	7	0	0.23	0.32	0	0.12	0.07	0.09	NA
2009-12-16 04:10	7	30	29.99	30.06	0	0.15	0.11	0.07	0.23
2009-12-16 04:25	7	90	90.00	89.94	0	0.09	0.07	-0.07	-0.07
2009-12-16 04:40	7	80	80.00	79.85	0	0.12	0.12	-0.15	-0.19
2009-12-16 04:55	7	60	60.03	59.89	0	0.07	0.12	-0.14	-0.23
2009-12-16 05:10	7	20	20.72	20.53	0	0.90	0.31	-0.19	-0.91
2009-12-16 05:25	7	40	39.99	39.98	0	0.10	0.10	-0.01	-0.02
2009-12-16 05:40	7	70	69.99	69.85	0	0.18	0.11	-0.14	-0.20
2009-12-16 05:55	7	10	10.15	10.16	0	0.37	0.10	0.01	0.06
2009-12-16 06:10	7	50	50.00	49.89	0	0.11	0.07	-0.11	-0.22
2009-12-16 06:25	8	0	0.33	0.23	0	0.16	0.07	-0.10	NA
2009-12-16 06:40	8	20	20.02	19.97	0	0.20	0.11	-0.04	-0.21
2009-12-16 06:55	8	80	79.98	79.98	0	0.08	0.07	0.00	0.00
2009-12-16 07:10	8	90	89.98	90.15	0	0.14	0.10	0.16	0.18
2009-12-16 07:25	8	40	39.99	39.91	0	0.13	0.10	-0.07	-0.18
2009-12-16 07:40	8	60	59.95	60.00	0	0.18	0.08	0.05	0.08
2009-12-16 07:55	8	10	10.10	10.20	0	0.29	0.11	0.11	1.05
2009-12-16 08:10	8	70	69.99	69.80	0	0.14	0.09	-0.19	-0.27
2009-12-16 08:25	8	30	30.00	30.14	0	0.09	0.10	0.15	0.50
2009-12-16 08:40	8	50	49.95	49.87	0	0.11	0.09	-0.08	-0.16

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

Figure 6 show the regression residuals of the ozone analyzers with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

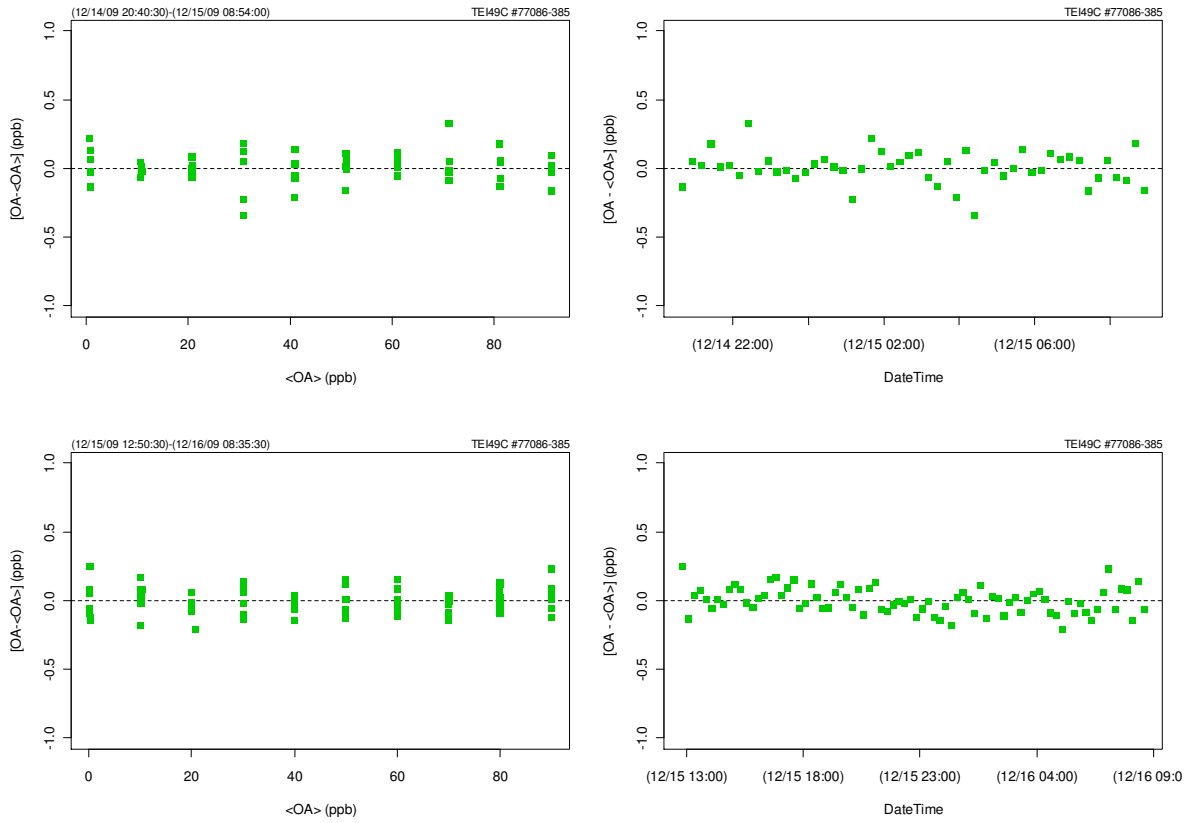

Figure 6. Regression residuals of the ozone comparisons as a function of concentration (left panel) and time (right panel) Upper panel: initial calibration settings; lower panel: new calibration settings.

Based on these comparison results, unbiased ozone volume mixing ratios X_{O3} and an estimate for the remaining combined standard uncertainty u_{O3} can be computed from the one-minute data [OA] using equation (1) [*Klausen, et al.*, 2003].

TEI 49C #77086-385 (BKG -0.7 ppb, SPAN 1.028):

$$X_{O3}\ (\text{ppb}) = ([OA] - 0.58\ \text{ppb}) / 1.0081$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.29\ \text{ppb}^2 + 2.66\text{e-}05 * X_{O3}^2) \qquad (1a)$$

TEI 49C #77086-385 (BKG -0.2 ppb, SPAN 1.020):

$$X_{O3}\ (\text{ppb}) = ([OA] + 0.02\ \text{ppb}) / 1.0000$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.28\ \text{ppb}^2 + 2.60\text{e-}05 * X_{O3}^2) \qquad (1b)$$

Conclusions

The ozone measurements at MHD agreed well compared to the WCC-Empa travelling standard. The calibration settings were slightly adjusted during the audit.

Carbon Monoxide Measurements

Carbon monoxide measurements started in 1989 at Mace Head using a gas chromatograph with a mercuric oxide detector, and a complete time series is available since then. The system has not changed since the last audit by WCC-Empa in 2005 [*Zellweger, et al.*, 2005]. The audit comprised comparison of five traveling standards covering the mole fraction range from approx. 60 to 220 ppb carbon monoxide in air. All comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

Unchanged since the last WCC-Empa audit [*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 summarized in Table 6. Instrumental details are also described in *Prinn et al.* [2000].

Standards and Calibration

The station is equipped with laboratory and working standards. Mace Head CO measurements are referenced to the CSRIO94 carbon monoxide scale by the use of stainless steel cylinders provided by Scripps Institution of Oceanography (SIO). The laboratory standards in use at MHD did not change since the last audit by WCC-Empa, and available standards are listed in the WCC-Empa report 05/2 [*Zellweger, et al.*, 2005]. In addition, other commercial standards are available which are occasionally used to verify the response function of the GC. A full calibration of the instrument using flasks (CSIRO) is performed at irregular intervals. Table 5 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.

Table 5. History of SIO working standards at the MHD station as of December 2009

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	155.17	1882.69	322.37	514.27	2009-05-21	

Operation and Maintenance

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Data Acquisition and Data Transfer

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Data Treatment

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Data Submission

At the time of the audit, data of the in-situ carbon monoxide measurements covering the period from March 1994 to March 2009 have been submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG) by the AGAGE science team. The data was submitted as event data (individual GC injections) and monthly averages.

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 Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included comparisons of the traveling standards at Empa before and after the comparison of the analyzer. Details of the traceability of the traveling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 6.

Setup and Connections

The RGA-3 instrument was compared by direct measurements of traveling standards. Details of this experiment are shown in Table 6. The data used for the evaluation was recorded by the MHD data acquisition system.

Table 6. Experimental details of the carbon monoxide comparison (RGA-3 instrument).

Traveling standard (TS)		WCC-Empa Traveling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 080820_FA02785 / 64.56 / 0.74 2 / 080814_FA02466 / 84.50 / 0.52 3 / 080820_FA02686 / 107.37 / 0.55 4 / 070927_FF21167 / 188.88 / 0.99 5 / 070927_FF17309 / 218.52 / 1.17
Field instrument	Model, S/N	RGA3, S/N 090189-010
	Principle	GC with HgO Reduction Detector Pre-column: Unibeads 1S 60/80 Analytical column: Mole sieve 5Å 60/80 Carrier: Synthetic air – Sofnocat - Mole sieve, 20 ml/min Column temp. 105°C, Detector temp. 265°C Sample loop 1 ml Sample air dried with Nafion dryer
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Duration per level (min)		Injections every 80 min; total 9-17 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (2009-12-14 to 2010-01-13)

Results - MHD RGA-3 system

The GC system was compared using WCC-Empa traveling standards. Each level was injected between 9 and 17 times. This resulted in a maximum of 17 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 7).

Table 7. CO aggregates computed from single injections for each level and repetition during the comparison of the MHD RGA-3 analyser (AL) with WCC-Empa traveling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12/14/09 19:00:00)	070927_FF17309	218.52	1.17	221.22	0.30	9	2.69	1.23
(12/15/09 01:50:00)	070927_FF21167	188.88	0.99	191.23	0.42	9	2.35	1.24
(01/11/10 18:00:00)	080814_FA02466	84.50	0.52	86.09	0.04	11	1.59	1.88
(01/08/10 23:40:00)	080820_FA02686	107.37	0.55	108.77	0.10	17	1.41	1.31
(01/13/10 17:20:00)	080820_FA02785	64.56	0.74	66.62	0.05	11	2.06	3.19

Figure 7 shows the regression residuals of the RGA-3 instrument plotted against time and mole fraction. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of concentration dependence (right panel) in the residuals indicates linearity of the instrument.

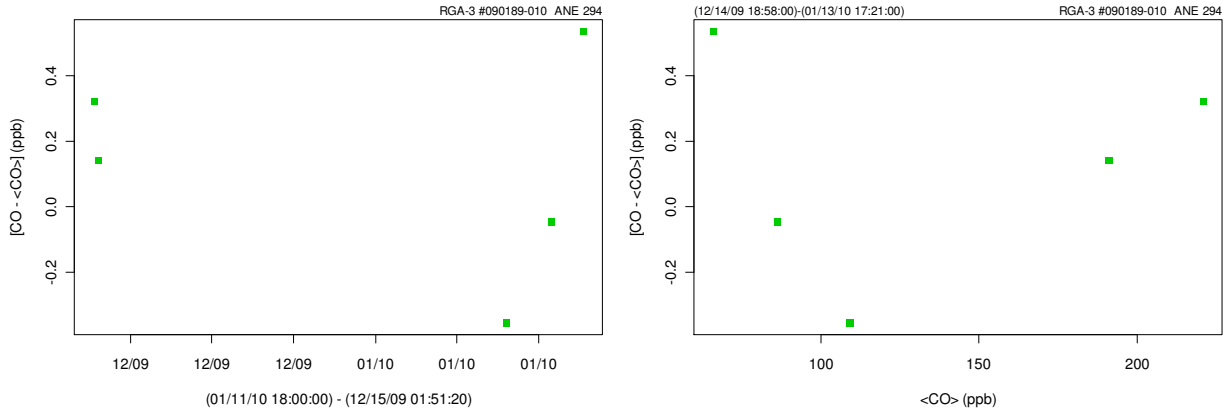

Figure 7. Regression residuals of the MHD RGA-3 based on the comparison with traveling standards. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

Based on these comparison results, unbiased carbon monoxide volume mole fractions X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed using equation (2a) for the MHD RGA-3 system.

$$X_{CO}\ (\text{ppb}) = ([CO] - 1.2\ \text{ppb}) / 1.006$$

$$u_{CO}\ (\text{ppb}) = \text{sqrt}\ (0.7\ \text{ppb}^2 + 6.87\text{e-}05 * X_{CO}^2) \quad (2)$$

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

Changes made to the instruments

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

Conclusions

Good agreement was found between WCC-Empa traveling standards and the Mace Head CO gas chromatographic instrument (RGA-3). The deviations between WCC-Empa and MHD are significantly smaller compared to previous audits, which is a result of improved calibration procedures.

Methane Measurements

Methane measurements started at MHD in 1987, and a complete time series is available since then. The system has not changed since the last audit by WCC-Empa in 2005 [*Zellweger, et al.*, 2005]. The audit comprised comparison of 11 traveling standards covering the mole fraction range from approx. 1600 to 2000 ppb methane in air. All comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Instrumentation

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005]. Instrument details are summarised in Table 8.

Standards and Calibration

The SIO working standard is used for methane calibrations at MHD. Refer to Table 5 for a history of working standards used at the station.

Operation and Maintenance

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Data Acquisition and Data Transfer

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2005].

Data Treatment

Peak integration is performed automatically, and two consecutive working tank signals are used to calculate the ambient air concentration. Peak height is used for data evaluation, and a linear fit through zero is used as a calibration function.

Data Submission

At the time of the audit, data of the in-situ methane measurements covering the period from January 1987 to March 2009 have been submitted to the GAW World Data Centre for Greenhouse Gases at JMA (World Data Centre for Greenhouse Gases, WDCGG) by the AGAGE science team. The data was submitted as event data (individual GC injections) and monthly averages.

Documentation

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

Comparison of Methane Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included comparisons of the traveling standards at Empa before and after the comparison of the analyzer. Details of the traceability of the traveling standard to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 8 below.

Setup and Connections

Table 8 shows details of the experimental setup during the comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the MHD data acquisition system, and no further corrections were applied.

Table 8. Experimental details of the methane comparison.

Traveling standard (TS)		WCC-Empa Traveling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 070808_FA02786 / 1595.36 / 0.19 2 / 071122_FF31496 / 1614.18 / 0.18 3 / 070927_FF21167 / 1663.49 / 0.24 4 / 080814_FA02466 / 1734.70 / 0.21 5 / 070927_FF17309 / 1820.81 / 0.21 6 / 050701_FA02464 / 1833.29 / 0.24 7 / 050701_FA02505 / 1834.07 / 0.28 8 / 080820_FA02686 / 1870.75 / 0.23 9 / 071122_FA01477 / 1950.26 / 0.24 10 / 080820_FA02785 / 1962.41 / 0.23 11 / 050415_FA02470 / 1995.60 / 0.27
Field instrument	Model, S/N	CARLE 100A, S/N 40647
Connection of TS to field instrument		TS were connected to the sample selection valve of the MHD system
Data Acquisition		Station data acquisition
Number of injections		Injections every 80 min; total 7-23 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (2009-12-13 to 2010-01-13)

Results

Each TS was injected between 7 to 23 times, which resulted in a maximum of 23 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 9).

Table 9. CH_4 aggregates computed from single injections (mean and standard deviation of mean) for each level during the comparison of the MHD methane analyzer with the WCC-Empa traveling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12/13/09 11:47:30)	050415_FA02470	1995.61	0.27	1997.33	2.08	14	1.72	0.09
(12/14/09 18:58:00)	070927_FF17309	1820.81	0.21	1822.08	1.99	9	1.28	0.07
(12/15/09 01:51:20)	070927_FF21167	1663.49	0.24	1664.47	1.20	9	0.98	0.06
(12/15/09 15:39:00)	050701_FA02505	1834.07	0.28	1833.73	1.42	7	-0.34	-0.02
(12/16/09 17:39:00)	071122_FF31496	1614.18	0.18	1614.10	1.23	7	-0.08	-0.01
(12/17/09 05:39:00)	071122_FA01477	1950.26	0.24	1950.23	2.08	7	-0.02	0.00
(01/06/10 23:18:00)	050701_FA02464	1833.29	0.24	1832.38	1.43	14	-0.91	-0.05
(01/08/10 19:08:34)	080820_FA02686	1870.75	0.23	1872.34	3.19	23	1.60	0.09
(01/10/10 01:17:28)	080814_FA02466	1734.70	0.21	1735.20	3.25	19	0.50	0.03
(01/12/10 16:41:00)	070808_FA02786	1595.36	0.19	1595.39	0.86	10	0.03	0.00
(01/13/10 17:21:00)	080820_FA02785	1962.41	0.23	1960.55	1.10	11	-1.86	-0.09

Figure 8 shows the regression residuals of the Carle-3800 GC plotted against time and concentration. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of concentration dependence (right panel) in the residuals indicates linearity of the instrument.

Based on the comparison results, unbiased methane volume mixing ratios of the CARLE 100A analyzer X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed from the single injection comparison data using equation (3).

$$X_{CH4}\ (\text{ppb}) = (CH_4) / 1.00028$$

$$u_{CH4}\ (\text{ppb}) = \text{sqrt}\ (3.5\ \text{ppb}^2 + 4.29\text{e-}08 * X_{CH4}^2) \qquad (3)$$

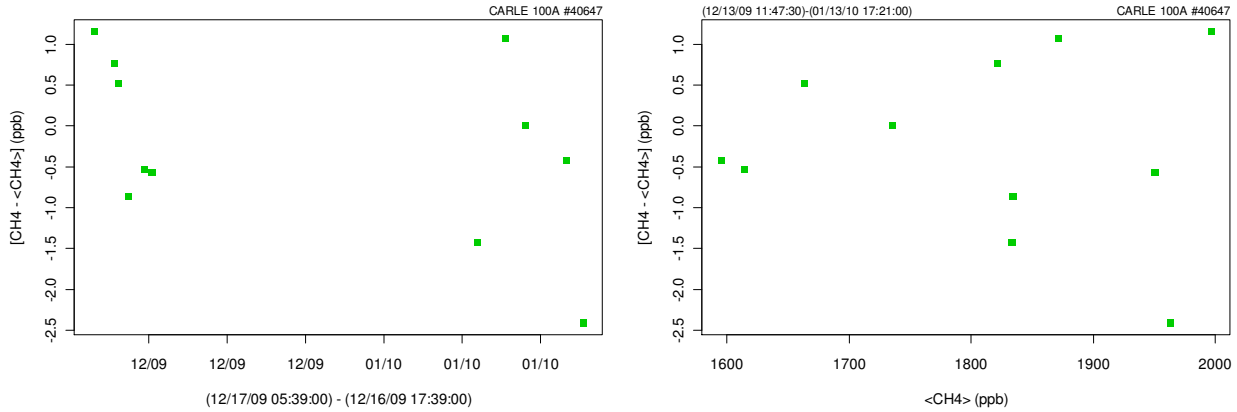

Figure 8. Regression residuals of the MHD methane GC. Points represent averages of valid single injections. Left panel: time dependence; Right panel: concentration dependence.

Conclusions

No significant deviations between Mace Head and WCC-Empa were found. The good result of the comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. Therefore no further technical recommendations are made by WCC-Empa. The repeatability of the Mace Head GC was good, with an average standard deviation of 0.10% (15-31 injections). The best GC-FID systems at GAW stations reach average standard deviations between 0.05 and 0.10%.

Nitrous Oxide Measurements

Nitrous oxide measurements started at MHD in 1987 as part of the AGAGE programme. Besides N_2O are large number of other greenhouse gases is measured. A continuous N_2O time series of is available from MHD since the start in 1987. Details of the measurement setup can be found on the AGAGE website (http://agage.eas.gatech.edu/instruments-gcmd.htm).

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

The same air inlet system as for methane is used nitrous oxide. A detailed description of the inlet system can be found in Prinn et al. [2000]. The air inlet system is adequate for analyzing N_2O concerning materials and residence time.

Instrumentation

A HP 5800 II GC with an ECD detector is used for the measurements of N_2O. A detailed description of the analytical set-up can be found in Prinn et al. [2000].

Standards and Calibration

MHD is equipped with only one standard for N_2O measurements. The current standard as well as previously used tanks are listed in Table 5. The linearity of the ECD was checked weekly up until recently by injecting samples of working standard at a number of pressures from sub-ambient to super-ambient. Knowing the pressure, temperature and volume of the injections allowed the calculation of the response function, which was determined for the range of +10 ppb / -15ppb of the working standard. In the whole record for Mace Head there was only one pollution event in 1996 which was outside this range. Currently, these non-linearity checks have been suspended after about 15 years because the linearity of the ECD was pretty constant over time.

Operation and Maintenance

A detailed SOP is available, and a weekly check list with engineering parameters and chromatogram status is filled in. The carrier and calibration gas consumption is routinely checked.

Data Acquisition and Data Transfer

The data acquisition consists of a workstation and the "AGAGE GC control" software package developed at SIO. All the chromatograms are stored and automatically transferred twice daily via internet to the main database at SIO. Peak integration is carried out both for area and height but peak height is used for the final data set.

Data Submission

At the time of the audit, data of the in-situ N_2O measurements covering the period from January 1987 to March 2009 have been submitted to the GAW World Data Centre for Greenhouse Gases at JMA (World Data Centre for Greenhouse Gases, WDCGG) by the AGAGE science team. The data was submitted as event data (individual GC injections) and monthly averages.

Documentation

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

Comparison of Nitrous Oxide Measurements

The travelling standards used for the comparison were calibrated by WCC-N_2O in April 2008. Since then, no re-calibrations have been made. Details of the traceability of the traveling standard to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 8 below.

Setup and Connections

Table 8 shows details of the experimental setup during the comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the MHD data acquisition system, and no further corrections were applied.

Table 10. Experimental details of the N_2O comparison.

Traveling standard (TS)		WCC-Empa* Traveling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level Cylinder Reference* std dev 1 070808_FA02786 294.44 0.05 2 050701_FA02505 315.61 0.05 3 071122_FA01477 323.63 0.10 4 071122_FF31496 346.41 0.07
Field instrument	Model, S/N	HP 5800 II C-128/83
Connection of TS to field instrument		TS were connected to the sample selection valve of the MHD system
Data Acquisition		Station data acquisition
Number of injections		Injections every 80 min; total 7-11 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (2009-12-15 to 2010-01-12)

* Mixing ratios were assigned by the WCC-N_2O

Results

Each TS was injected between 7 to 11 times, which resulted in a maximum of 11 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 9).

Table 11. N_2O aggregates computed from single injections (mean and standard deviation of mean) for each level during the comparison of the MHD methane analyzer with the WCC-Empa traveling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12/15/09 15:39:00)	050701_FA02505	315.73	0.30	315.61	0.05	7	-0.12	-0.04
(12/16/09 17:39:00)	071122_FF31496	345.21	0.23	346.41	0.07	7	1.20	0.35
(12/17/09 05:39:00)	071122_FA01477	323.34	0.19	323.63	0.10	7	0.29	0.09
(01/12/10 17:21:00)	070808_FA02786	294.61	0.23	294.44	0.05	11	-0.17	-0.06

The deviations between WCC-Empa TS calibrated by WCC-N_2O and MHD were within 0.3 ppb and not significant for ambient or lower N_2O mole fractions. The average deviation of these TS meets the recommendations (comparability of ±0.1 ppb) made by WMO [*WMO*, 2009b]; however, individual measurements slightly exceed these recommendations. Slightly larger deviations were found for the highest TS, which was above the calibrated range of the instrument.

Figure 9 shows the regression residuals of the HP-5800 II GC plotted against time and concentration. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of concentration dependence (right panel) in the residuals indicates linearity of the instrument.

Based on the comparison results, unbiased N_2O volume mixing ratios of the HP-5800 II GC X_{N2O} and an estimate for the remaining combined standard uncertainty u_{N2O} can be computed from the single injection comparison data using equation (4).

$$X_{N2O}\ (\text{ppb}) = (N_2O) / 1.00116$$

$$U_{N2O}\ (\text{ppb}) = \text{sqrt}\ (0.37\ \text{ppb}^2 + 2.09\text{e-}06 * X_{N2O}^2) \qquad (4)$$

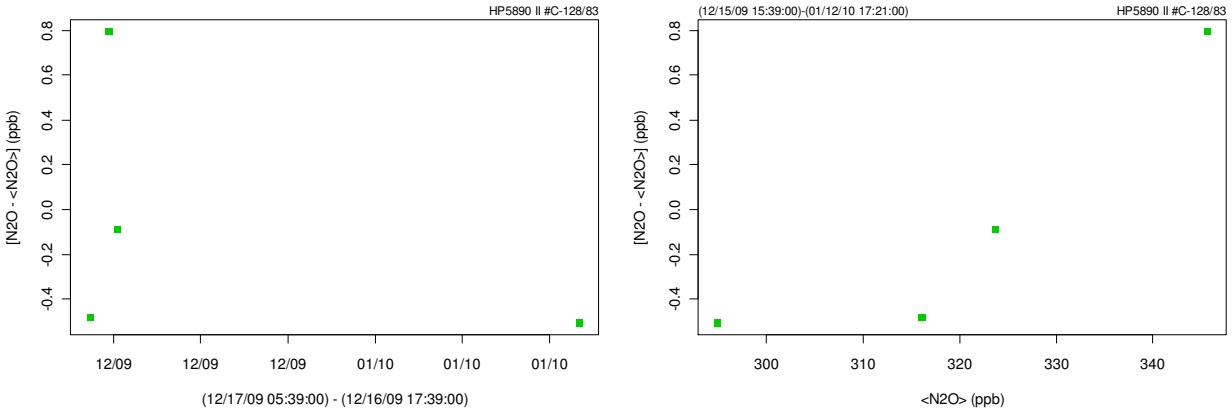

Figure 9. Regression residuals of the MHD nitrous oxide GC. Points represent averages of valid single injections. Left panel: time dependence; Right panel: concentration dependence.

Conclusions

Slightly larger deviations than the WMO recommendations [*WMO*, 2009b] of 0.1 ppb were found between the Mace Head measurements and WCC-Empa traveling standard for the mole fraction range of approximately 295 to 325 ppb N_2O. A significantly larger bias was observed for higher mole fractions outside the calibrated range of the instrument. WCC-Empa recommends that the MHD nitrous oxide measurements are assessed by the WCC-N_2O.

WCC-Empa Traveling Standards

Ozone

The WCC-Empa traveling standard (TS) was compared with the Standard Reference Photometer before and after use during the field audit. Details of these comparisons at the Empa calibration laboratory are summarised in Table 12, the comparison data is given in Table 13.

Table 12. Experimental details of the comparison of traveling standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Traveling standard (TS)	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (2009-10-26) 3 runs after return of TS (31 2010-02-03)

Table 13. 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)
2009-10-26	1	0	-0.20	0.33	-0.18	0.21
2009-10-26	1	140	145.09	0.18	144.89	0.30
2009-10-26	1	30	31.66	0.22	31.56	0.33
2009-10-26	1	60	62.04	0.18	61.90	0.34
2009-10-26	1	190	196.20	0.34	196.70	0.25
2009-10-26	1	30	94.14	0.21	94.12	0.24
2009-10-26	1	0	-0.10	0.27	-0.05	0.13
2009-10-26	2	0	-0.13	0.31	-0.14	0.24
2009-10-26	2	190	197.73	0.28	197.84	0.21
2009-10-26	2	90	94.19	0.25	93.81	0.33
2009-10-26	2	140	144.23	0.18	144.40	0.31
2009-10-26	2	60	62.01	0.46	62.15	0.27
2009-10-26	2	30	31.69	0.15	31.92	0.36
2009-10-26	2	0	0.05	0.24	-0.08	0.30
2009-10-26	3	0	0.05	0.34	-0.05	0.21
2009-10-26	3	60	62.01	0.32	62.15	0.21
2009-10-26	3	90	94.07	0.25	94.26	0.23
2009-10-26	3	140	144.21	0.19	144.56	0.36
2009-10-26	3	30	31.80	0.27	31.58	0.08
2009-10-26	3	190	195.30	0.29	195.45	0.30
2009-10-26	3	0	0.07	0.19	-0.09	0.17
2010-02-03	4	0	0.21	0.24	-0.02	0.24
2010-02-03	4	60	62.87	0.49	62.64	0.31
2010-02-03	4	30	32.11	0.45	32.16	0.27
2010-02-03	4	140	145.65	0.32	145.81	0.24
2010-02-03	4	190	197.33	0.27	197.47	0.29
2010-02-03	4	90	94.45	0.28	94.75	0.19
2010-02-03	4	0	0.08	0.20	-0.02	0.26
2010-02-03	5	0	0.02	0.24	-0.03	0.27
2010-02-03	5	90	94.91	0.36	94.77	0.25
2010-02-03	5	30	32.32	0.37	32.34	0.33
2010-02-03	5	190	197.93	0.23	198.05	0.29
2010-02-03	5	60	62.36	0.18	62.35	0.10
2010-02-03	5	140	144.84	0.64	145.08	0.15
2010-02-03	5	0	0.11	0.17	0.34	0.23
2010-02-03	6	0	0.12	0.31	0.25	0.31
2010-02-03	6	140	145.88	0.28	145.89	0.13
2010-02-03	6	60	62.70	0.15	62.73	0.19
2010-02-03	6	90	94.29	0.18	94.62	0.11
2010-02-03	6	190	197.12	0.22	197.26	0.20
2010-02-03	6	30	32.48	0.44	32.13	0.19
2010-02-03	6	0	0.06	0.13	0.01	0.15

[#]the level is only indicative.

The traveling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 10). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (equation 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [*Klausen, et al.*, 2003]).

$$X_{TS}\ (\text{ppb}) = ([TS] + 0.06\ \text{ppb}) / 1.0013$$

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

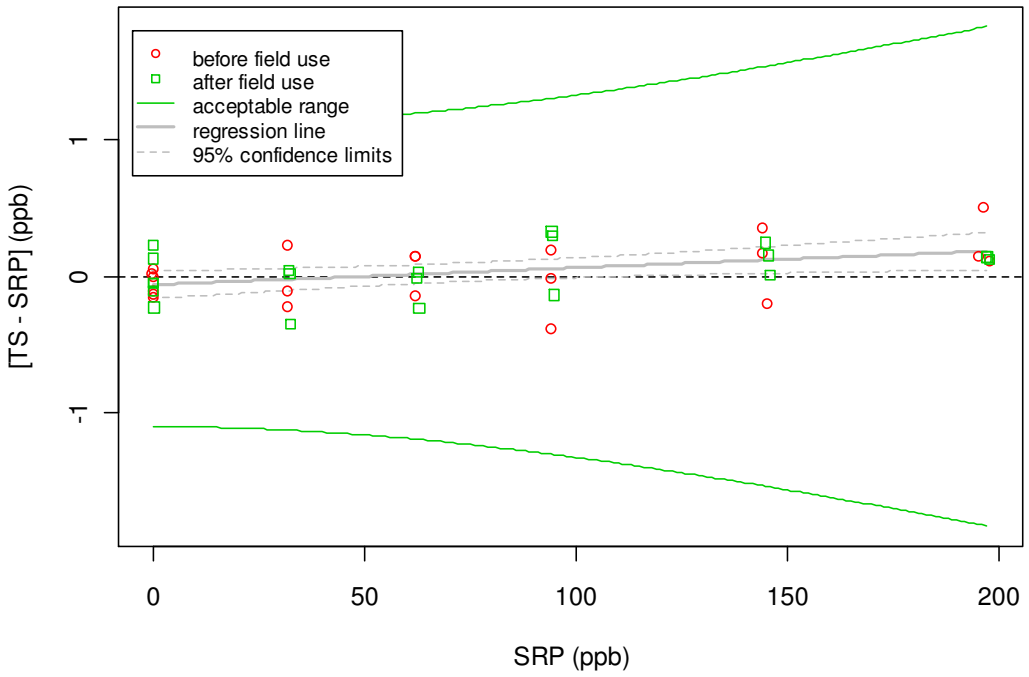

Figure 10. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL by way of traveling standards. The scale was transferred to the traveling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. Details are given in Table 14 and Table 15.

Table 14. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the traveling standard (TS) used during the field comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale is based on one specific cylinders, CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Traveling standard - cylinders		Carbon monoxide cylinders for direct comparisons. (cf. Table 15)
Connection between instruments		Ca. 2 meter 1/16” stainless steel tubing.
Range (ppb)		65 – 220 ppb cf. Table 15
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 15. Calibration of the carbon monoxide traveling standards with the WCC-Empa reference before and after the audit.

dte	070927_FF17309	sd	070927_FF21167	sd	080814_FA02466	sd	080820_FA02686	sd	080820_FA02785	sd
2009-11-20	218.2	0.7	188.7	0.8	84.3	0.3	107.3	0.6	64.1	0.4
2010-02-02			189.1	0.8	84.7	0.5	107.4	0.5		
2010-02-03	218.8	0.7							65.0	0.7

No significant drift was observed over the period of the audit. The average of the two measurements was used for the evaluation of the audit results.

Methane

WCC-Empa refers to the WMO/GAW methane scale (hereafter: NOAA04 scale) [*Dlugokencky, et al.*, 2005] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 16). The scale was transferred to the traveling standards using a Picarro G1301 analyser. Details of the traveling standards are given in Table 17.

Table *16*. NOAA/ESRL CH_4 laboratory standards at WCC-Empa. The uncertainty represents the measured standard deviation.

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

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

Table 17. Calibration of the methane traveling standards with the WCC-Empa reference (Average mole fraction in ppb ± sd (n = 10)).

dte	070927_FF17309	sd	070927_FF21167	sd	080814_FA02466	sd	080820_FA02686	sd	080820_FA02785	sd	050701_FA02464	sd	050701_FA02505	sd	071122_FF31496	sd	071122_FA01477	sd	070808_FA02786	sd	050415_FA02470	sd
2009-11-20	**1820.8**	0.1	**1663.6**	0.1	**1734.7**	0.1	**1870.9**	0.1	**1962.4**	0.1	**1833.4**	0.0	**1834.2**	0.0	**1614.2**	0.1	**1950.3**	0.1	**1595.3**	0.1	**1995.7**	0.1
2010-02-02			**1663.4**	0.1	**1734.6**	0.1	**1870.7**	0.1			**1833.2**	0.1	**1833.9**	0.1							**1995.5**	0.1
2010-02-03	**1820.7**	0.1							**1962.3**	0.1					**1614.2**	0.1	**1950.2**	0.1	**1595.4**	0.1		
2010-02-11	**1820.9**	0.1			**1734.8**	0.1	**1870.7**	0.0	**1962.5**	0.1												

Nitrous Oxide

WCC-Empa refers to the WMO/GAW nitrous oxide scale (hereafter: NOAA-2006 scale) [*Hall, et al.*, 2007]. The TS used during this audit have been calibrated by the WCC-N_2O in April 2008. The standards have not been recalibrated after the audit.

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

Ozone Audit Executive Summary (MHD)

0.1	Station Name:	Mace Head
0.2	GAW ID:	MHD
0.3	Coordinates/Elevation:	53.32583°N 9.89945°W (5 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-12-14 to 2009-12-16
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Gerry Spain
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(1.0013 \pm 0.0010) \times [SRP] - (0.06 \pm 0.15)$
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C #77086-385
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG = -0.7; COEFF = 1.028
1.5.4	Calibration at start of audit (ppb):	$[OA] = (1.008 \pm 0.001) \times [SRP] + (0.58 \pm 0.06)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] - 0.58) / 1.008$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.29\ ppb^2 + 2.66e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	BKG = -0.2; COEFF = 1.020
1.5.8	Calibration after audit (ppb):	$[OA] = (1.000 \pm 0.000) \times [SRP] - (0.02 \pm 0.06)$
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	$X = ([OA] + 0.02) / 1.000$
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.60e\text{-}5 \times X^2)^{1/2}$
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 09/3

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

GAW World Calibration Centre for Carbon Monoxide
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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 9.89945°W (5 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2009-12-14 to 2010-01-13	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Gerry Spain	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	080820_FA02785 080814_FA02466 080820_FA02686 070927_FF21167 070927_FF17309	64.56±0.74 ppb 84.50±0.52 ppb 107.37±0.55 ppb 188.88±0.99 ppb 218.52±1.17 ppb
1.5	CO Reference:	WMO-2000	
1.5.1	Model:	RGA3, S/N 090189-010	
1.5.2	Range of calibration:	64 – 220 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	$CO = (1.0055 \pm 0.0067) \times X + (1.2 \pm 0.8)$	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 1.2) / 1.0055$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (0.7\ ppb^2 + 6.89e\text{-}05 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	NA	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged	
1.6	Comments:	Gas chromatograph, main instrument	
1.7	Reference:	WCC-Empa Report 09/3	

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 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 9.89945°W (5 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2009-12-13 to 2010-01-13	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Gerry Spain	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02786	1595.36±0.19 ppb
		071122_FF31496	1614.18±0.18 ppb
		070927_FF21167	1663.49±0.24 ppb
		080814_FA02466	1734.70±0.21 ppb
		070927_FF17309	1820.81±0.21 ppb
		050701_FA02464	1833.29±0.24 ppb
		050701_FA02505	1834.07±0.28 ppb
		080820_FA02686	1870.75±0.23 ppb
		071122_FA01477	1950.26±0.24 ppb
		080820_FA02785	1962.41±0.23 ppb
		050415_FA02470	1995.60±0.27 ppb
1.5	CH_4 analyzer [CA]		
1.5.1	Model:	CARLE 100A, S/N 40647	
1.5.2	Range of calibration:	1595 –1995 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00028 \pm 0.00018) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00028$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (3.5\ ppb^2 + 4.29e\text{-}08 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/3	

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

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LIST OF ABBREVIATIONS

a.s.l.	above sea level
CCL	Central Calibration Laboratory
DAQ	Data Acquisition System
GAW	Global Atmosphere Watch
GC	Gas Chromatograph
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyzer
MHD	Mace Head GAW Station
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Traveling Standard
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation