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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 05/2

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION MACE HEAD

IRELAND, MAY 2005

Submitted by

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WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
Empa Dübendorf, Switzerland

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Empa is accredited as a calibration laboratory for ozone measuring instruments in accordance with ISO/IEC 17025

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1 EXECUTIVE SUMMARY

A system and performance audit was conducted at the Global Atmosphere Watch station Mace Head from 22. to 26. May 2005 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa). The results of the third WCC-Empa audit can be summarized as follows:

1.1 System Audit of the Observatory

The Mace Head global GAW station is an ideal platform for atmospheric research and provides excellent facilities for measurement campaigns.

1.2 Audit of the Ozone Measurements

The station ozone analyzer was replaced following a recommendation of the last WCC-Empa audit in 2002. The old instrument was decommissioned and the new analyser was inter-compared with the travelling standard of WCC-Empa. The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the ozone instrument of the station, demonstrated good agreement between the station analyzer and the transfer standard. The recorded differences fulfilled the assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1).

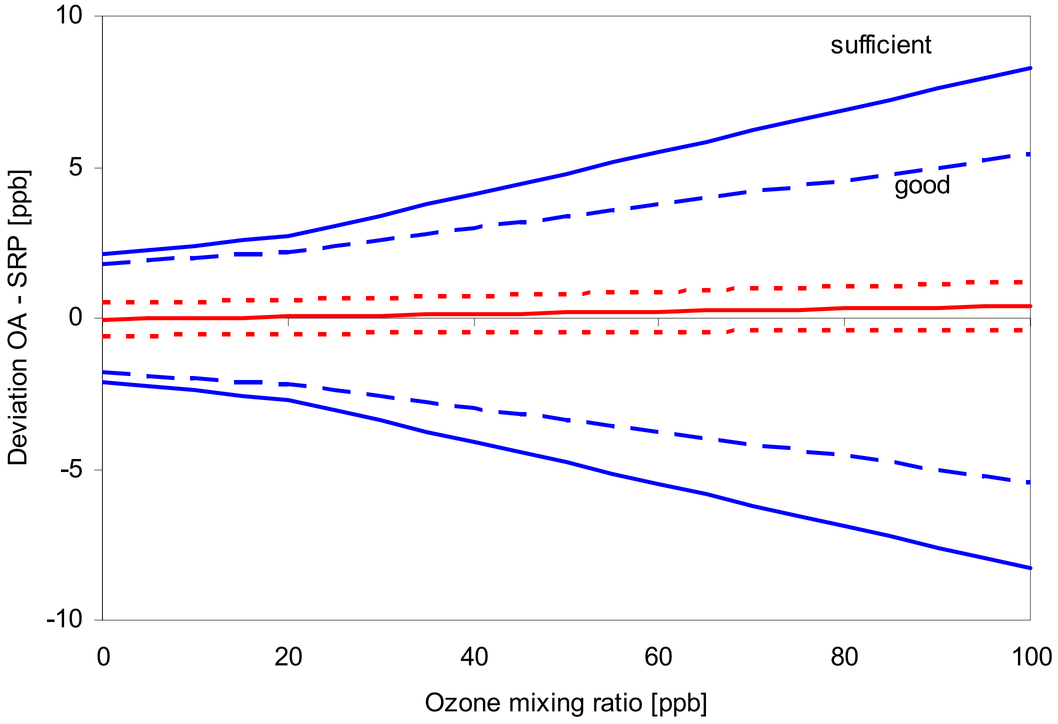


Figure 1: Inter-comparison of instrument TEI 49C #77086-385

Due to the good results of the inter-comparison, only minor recommendations were made by WCC-Empa. An executive summary of the surface ozone audit results is given in Appendix V

1.3 Audit of the Carbon Monoxide Measurements

The results of the WCC-Empa audit in 2002 showed relatively large deviations between WCC-Empa and Mace Head. Only part of the differences could be explained by inconsistencies and uncertainties of the CO scale. It was concluded by WCC-Empa that further investigations are needed to solve this issue. Consequently, the aim of the current audit was to resolve the inconsistencies of the audit in 2002. It was found during this audit that a blank correction was applied in the automatic data evaluation which was no longer appropriate. The result of the recalculation neglecting the blank correction is shown in Figure 2. These results still include the non-linearity correction. The Mace Head values excluding the blank correction are on average 3.8% lower compared to WCC-Empa, which compares well with the differences between the NOAA-CMDL WMO-88 and WMO-2000 scales. WCC-Empa refers to the NOAA-CMDL WMO-2000 scale but calibration standards at lower concentrations (below 200 ppb CO) are determined using a higher concentration standard on a UV-Fluorescence instrument. Inconsistencies within the two CO scales explain most of the observed differences.

The audit showed that frequent linearity and blank checks are necessary for accurate measurements with the RGA-3 system. The frequency of these checks should be increased at Mace Head.

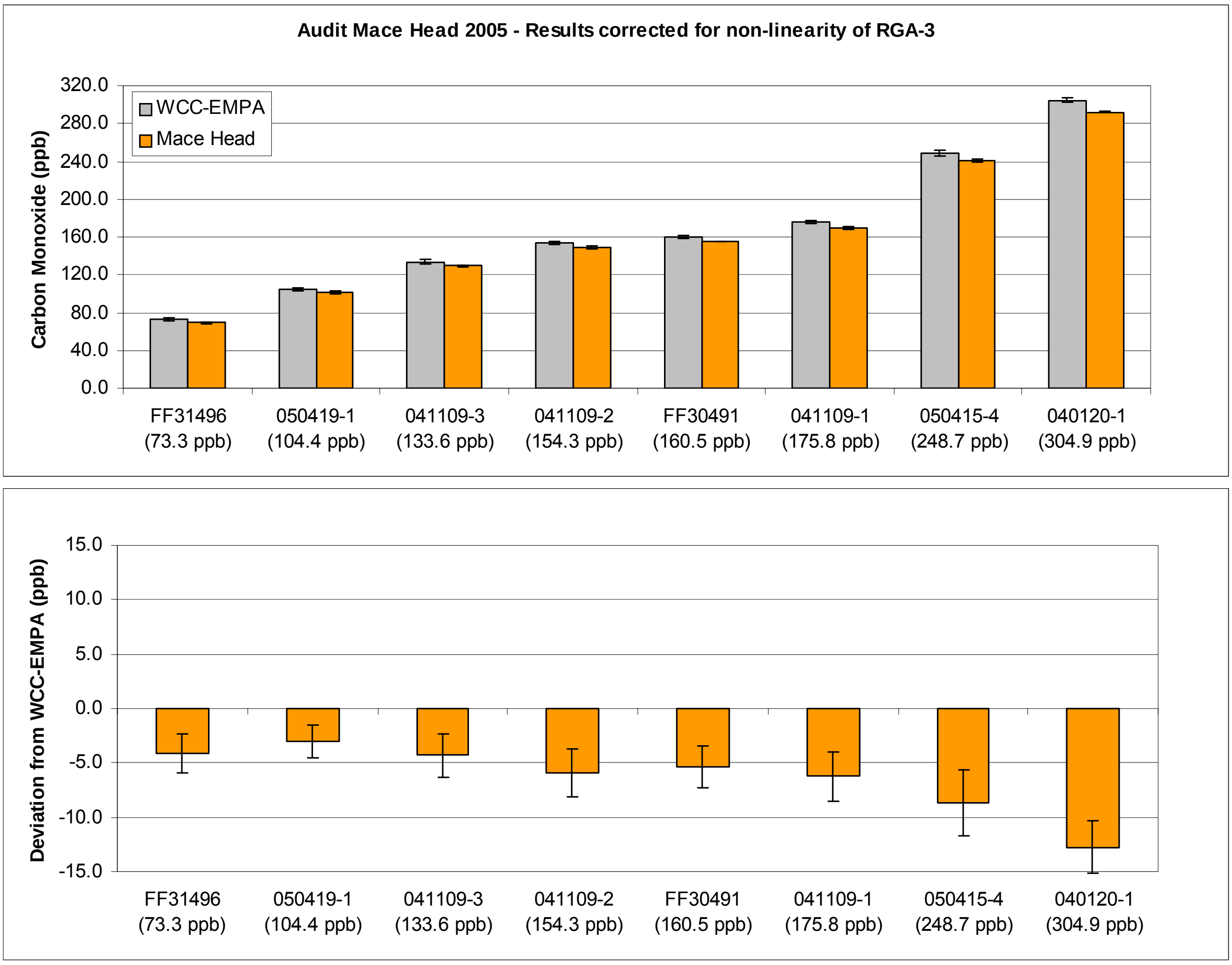


Figure 2: Upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mace Head (orange) with the correction for the non-linearity of the RGA-3 applied.
Lower panel: deviation of the Mace Head station from the reference.
The error bars represent the 95% confidence interval.

1.4 Audit of the Methane Measurements

The results of the inter-comparisons between the eight WCC-Empa travelling standards and the GC system of Mace Head showed good agreement over the concentration range of 1750 to 1990 ppb (Figure 3). The audit results at Mace Head are good when compared to methane audits conducted by WCC-Empa at other GAW sites. The station instrument also showed reasonable repeatability. Due to the good results no technical recommendations are made by WCC-Empa.

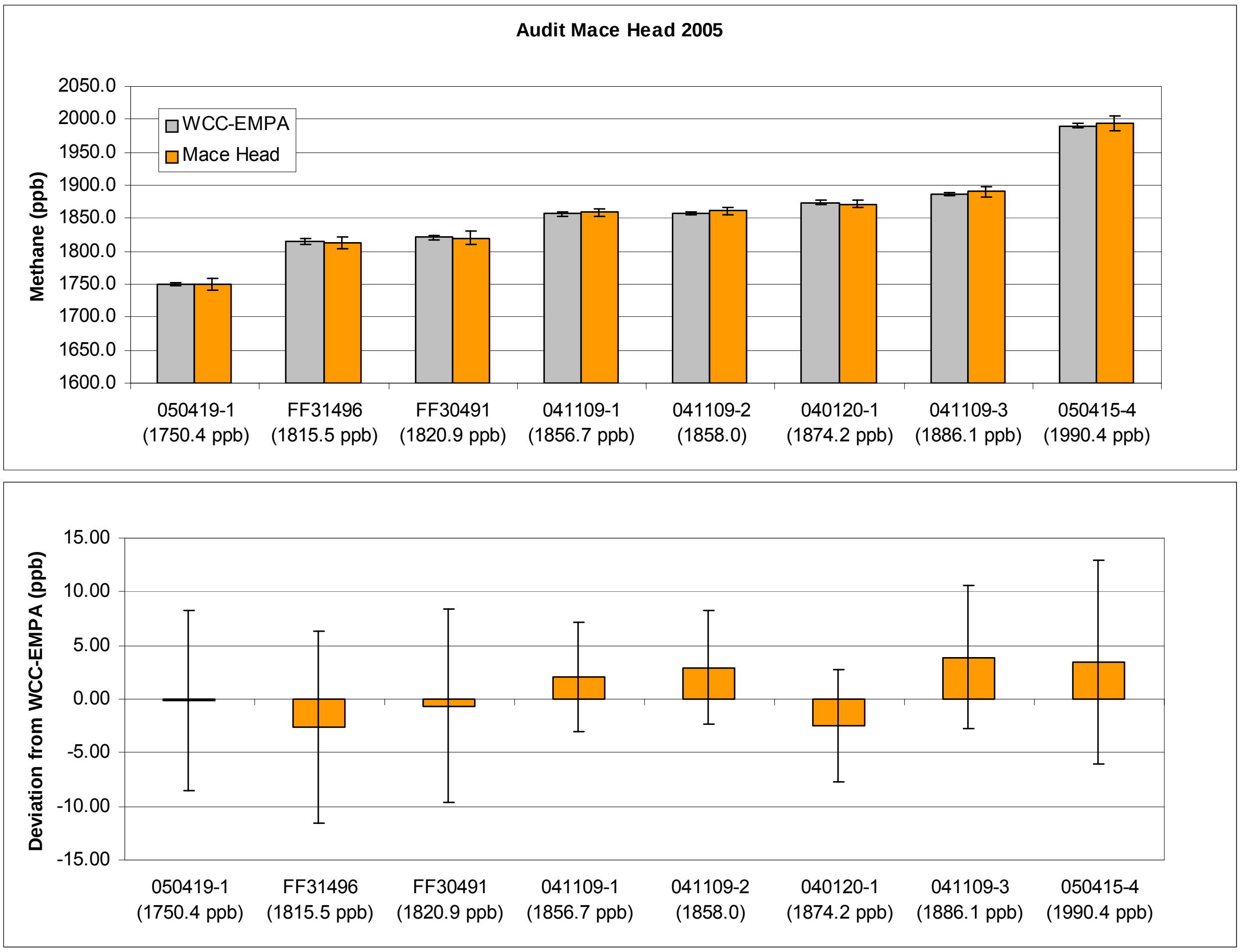


Figure 3: Upper panel: concentrations of the WCC transfer standards (grey) measured with the GC system of Mace Head (orange).
Lower panel: deviation of Mace Head from the reference.
The error bars represent the 95% confidence interval.

1.5 Data Submission

Data submission to the GAW World Data Centres is one of the obligations of stations participating in the GAW program. To date only part of the data has been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Ozone data has not yet been submitted, carbon monoxide is available for the period 03/1994 to 12/1999, and methane is available from 01/1987 to 09/2003.

1.6 Conclusions

The global GAW station Mace Head is an established monitoring site within the GAW program. Several decades of high quality data series exist for many parameters. The Mace Head site also provides a good platform for extensive atmospheric research studies.

The results of the inter-comparisons for surface ozone, carbon monoxide and methane showed good agreement between WCC-Empa and the station instruments for ozone, carbon monoxide and methane. However, the CO instrument needs to be more frequently checked for linearity and blank values. The blank correction that was applied was found to be no longer valid.

The analysis of the WCC-Empa transfer standards at the Mace Head station for CO resulted in lower values for the concentrations between 70 and 300 ppb when compared to the WCC-Empa reference scale. Differences observed between Mace Head and WCC-Empa at lower CO concentrations are attributable to uncertainties within the CO scale provided by CMDL.

Data submission to the WDCGG needs to be improved. WCC-Empa cannot offer future audits until data submission is improved.

Dübendorf, 18. October 2005

Empa Dübendorf, WCC-Empa

Project leader | Head of the laboratory

Dr. C. Zellweger | Dr. B. Buchmann

2 INTRODUCTION

The global GAW station Mace Head is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters of the atmosphere. The observatory is maintained by the National University of Ireland (NUI), Galway.

The Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa) was assigned by the WMO to operate the **GAW World Calibration Centre (WCC)** for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a coordinated quality assurance program for this part of GAW. The detailed goals and tasks of the WCC concerning surface ozone are described in the GAW report No. 104. System and performance audits at global GAW stations are conducted regularly based on mutual agreement about every two to four years.

In agreement with the station manager, Mr. Gerard Spain (NUI), a system and performance audit was conducted at the global GAW station Mace Head, Ireland, from 22. - 26. May 2005.

The scope of the audit was the whole measurement system in general and surface ozone, carbon monoxide and methane measurements in particular. The entire system from the air inlet to the data processing and the quality assurance was reviewed during the audit procedure. The assessment criteria for the ozone inter-comparison have been developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003]. The present audit report is distributed to the GAW station Mace Head and the World Meteorological Organization in Geneva.

Staff involved in the audit

NUI	Mr. Gerard Spain	contacts, general program and technical assistance at the observatory
WCC-Empa	Dr. Christoph Zellweger Dr. Martin Steinbacher	lead auditor

Previous audits at the GAW station Mace Head:

October 1996 (O_3), May1998 (O_3 and CO) and August 2002 (O_3, CO and CH_4) by WCC-Empa

3 GLOBAL GAW SITE MACE HEAD, IRELAND

3.1 Site description

Mace Head Research Station (53°19'33"N 9°53'58"W, 5 m a.s.l.) is located on the west coast of Ireland, County Galway (Figure 4). The site offers excellent exposure to the North Atlantic (clean air sector, 180° through west to 300°). The nearest major conurbation approximately 90 km to the east of Mace Head is Galway, a city with a population of approximately 65000 inhabitants. 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 facilities at the site consist of three laboratory buildings, two aluminium walk-up towers, (20 m and 10 m) and a converted cargo container office. The two shore laboratories (Figure 5), ca. 90 m from the shore, house gas and aerosol measurement equipment. The cottage laboratory, ca. 300 m from the shore primarily houses equipment for measurement of meteorological and solar radiation parameters.

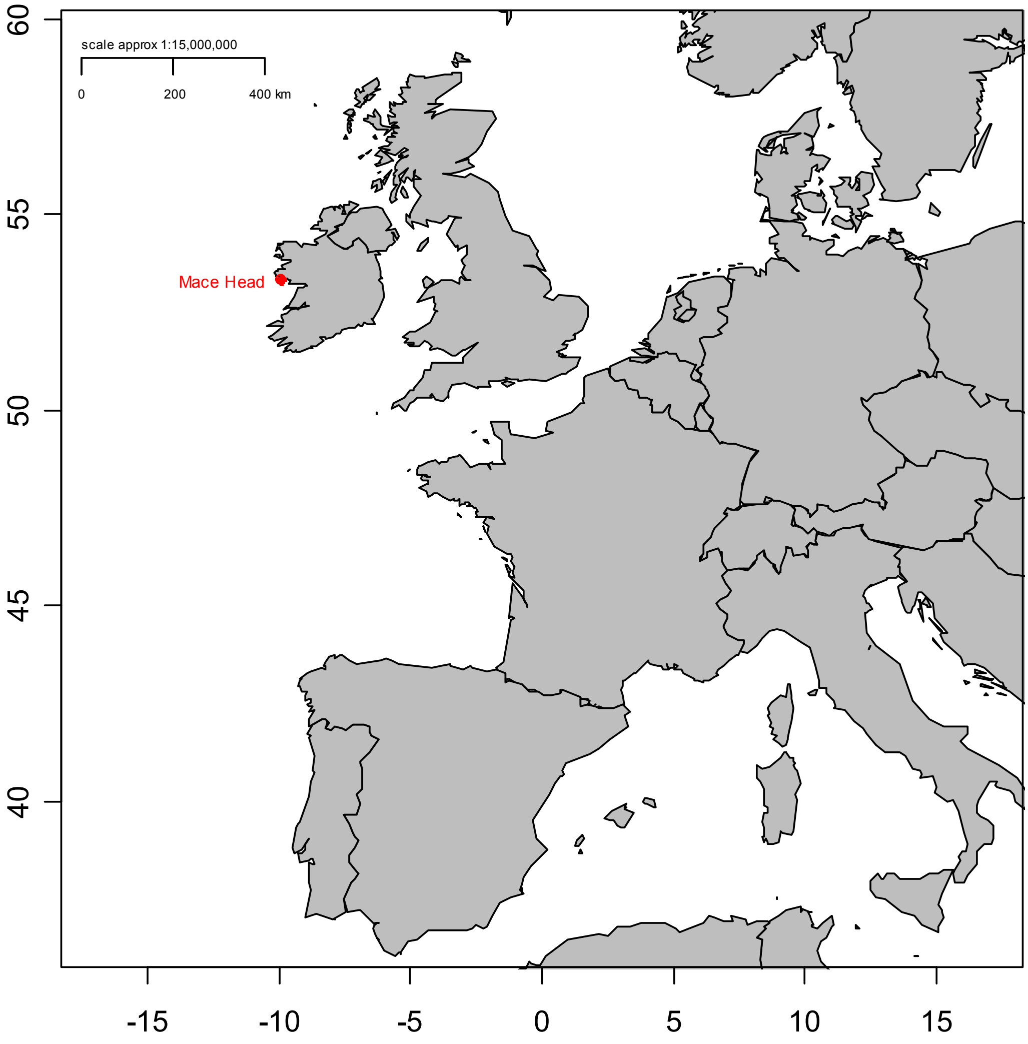


Figure 4: Location of Mace Head

Figure 5: Mace Head observatory

3.2 Ozone, carbon monoxide and methane levels at Mace Head

The frequency distributions of one hourly mean values for surface ozone, carbon monoxide and methane are shown in Figures 6 to 8.

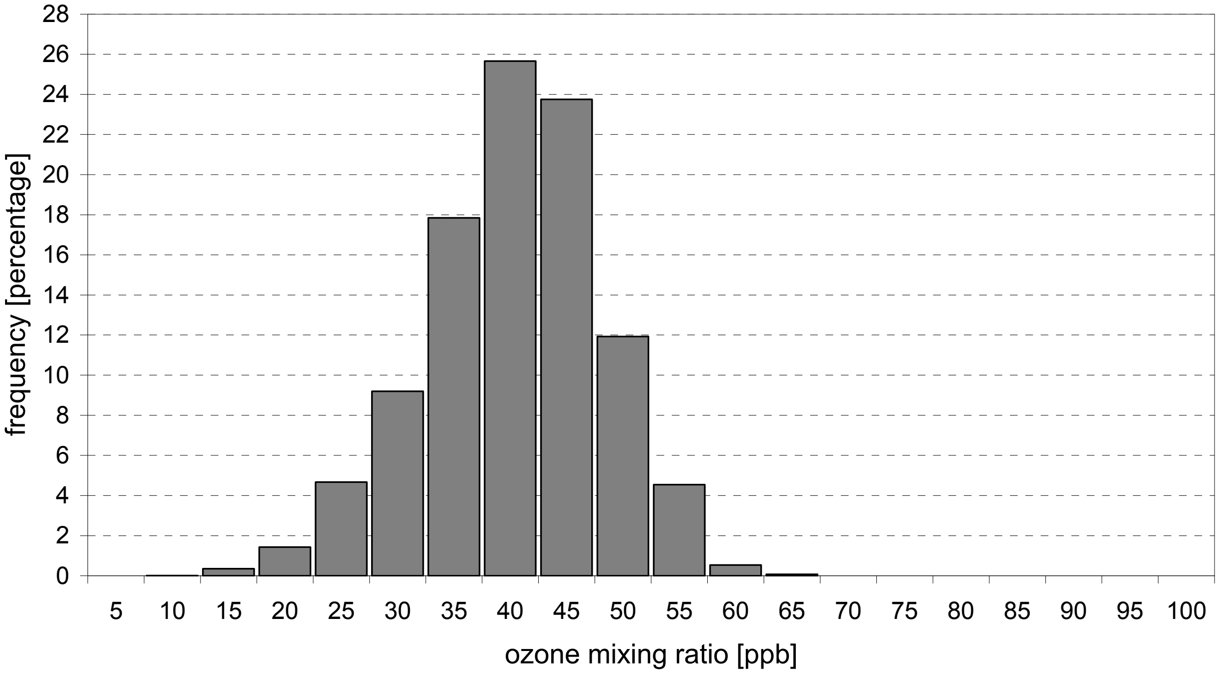


Figure 6: Frequency distribution of hourly ozone mixing ratios (ppb) at Mace Head for the year 2004. Data availability 98.3%.

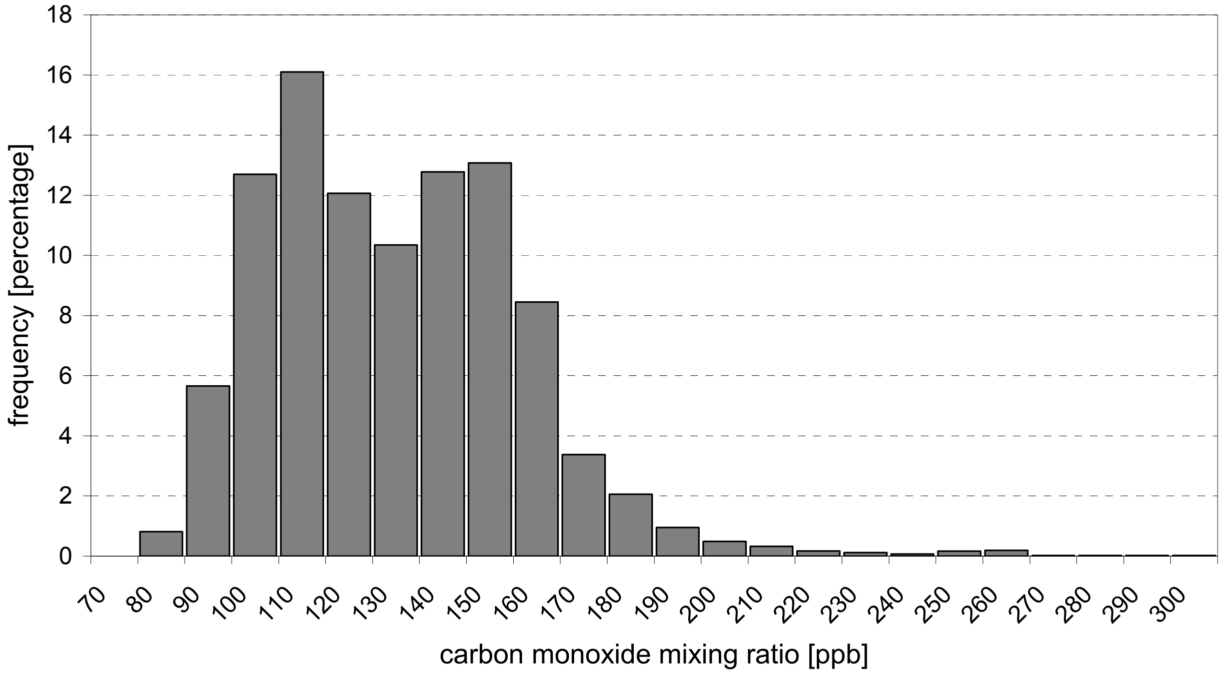


Figure 7: Frequency distribution of hourly carbon monoxide mixing ratios (ppb) at Mace Head for the year 2004 (preliminary data). Data availability 78.9%.

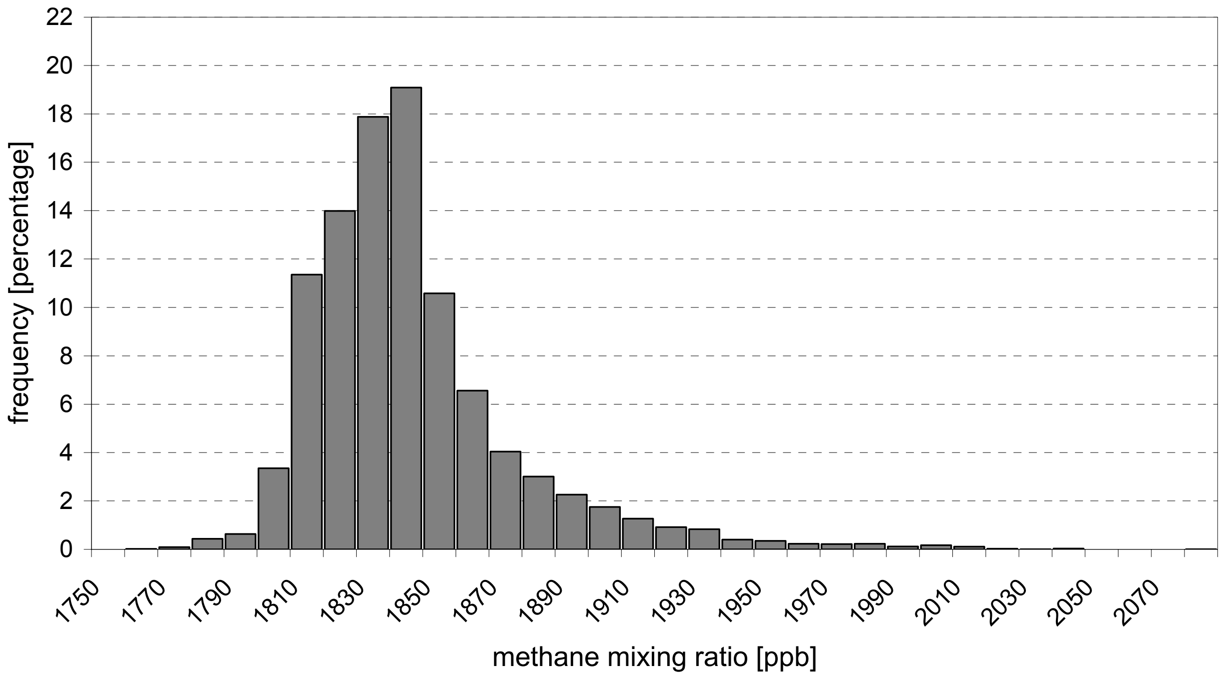


Figure 8: Frequency distribution of hourly methane ratios (ppb) at Mace Head for the year 2004. Data availability 79.2%.

3.3 Mace Head Staff

The GAW station Mace Head is approximately one hour drive from the National University of Ireland in Galway. During working days the station is visited by the station operator. Table 1 shows the staff responsible as of May 2005. In addition further experiments are run by different institutions, and information about the measurement programme and staff is available on the web (GAWSIS, www.empa.ch/gaw/gawsis; Mace Head homepage, http://macehead.nuigalway.ie).

Table 1: Staff responsible for the GAW station Mace Head (May 2005)

Name	**Position and duty**
Prof. S. Gerard Jennings	Primary station contact, measurement leader (aerosol)
Prof. Dr. Peter G. Simmonds	Consultant, PI Greenhouse and reactive gases
Mr. Gerard Spain	Station manager, measurement leader (trace gases)

4 SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE

The WCC-Empa in 2002 showed a good agreement between Mace Head and WCC-Empa, but the instrument showed a relatively poor stability and a non-linear response near zero. It was therefore recommended to replace the MonitorLabs ML8810 instrument after the audit in 2002. This recommendation resulted in a replacement with a new TEI49C in 2003, and the old instrument was decommissioned.

4.1 Monitoring Set-up and Procedures

4.1.1 Air Inlet System

The air inlet was moved a few meters since the last audit and is now mounted on the tower between the two lab buildings. The change is not expected to influence the ozone measurements.

Sampling-location: approx. 4.5 m above ground on the tower between the laboratories.

Sample inlet:

Rain protection: The Inlet is protected against rain and snow by an inverted Teflon cup.
Inlet-filter: Teflon inlet filter before analyser, exchanged monthly or when dirty.
Sample line: PFA. Length = 6 m, i.d. = 4 mm. Flow rate approx. 1 litre per minute.

Residence time in the sampling line: approx. 4 s

Materials as well as the residence time of the inlet system are adequate for surface ozone measurements.

4.1.2 Instrumentation

Ozone Analyser

Surface ozone measurements are made with a TEI 49C ozone analyser. Instrumental details can be found in Table 2. The instrument is installed in the first floor of the air-conditioned laboratory, and is protected from direct sunlight.

Ozone Calibrator

No ozone calibrator is available at the site. However, inter-comparisons with an NPL traceable transfer standard are made every three months by an external company (www.netcen.co.uk).

Table 2: Ozone instrument at Mace Head

Manufacturer	Thermo Electron Corp.
Model / Serial No.	TEI 49C / 77086-385
Method	UV absorption
At Mace Head	Since March 2003
Cal. before audit	BKG -0.7, Span 1.028
Cal. after audit	No change
Analogue output	0-10 V (not used)
Digital output	RS-232

Operation and Maintenance

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.

4.1.3 Data Handling

Data Acquisition and –transfer

The data acquisition is made via RS-232 interface using a free software package (http://sourceforge.net/projects/sjinn) run 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.

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 Ozone data have not yet been submitted to the data centre for surface ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG). As a result of the audit submission will take place during 2005 and surface ozone data of 2004 was submitted in September 2005.

Documentation

Electronic station and instrument logbooks are available. The notes are up to date and describe all important events. All instrument manuals are available at the site.

Comment

The frequent instrument checks and the up-to-date electronic logbook support the quality of the data. No change of the current practice is suggested.

4.2 Inter-comparison of the Ozone Instrument

4.2.1 Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode to warm up for more than 24 hours. During this stabilisation time the transfer standard and the PFA tubing connections to the instrument were conditioned with 300 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 9 the experimental set-up during the audit. No modifications of the ozone analyzers which could influence the measurements were made for the inter-comparisons.

The audit procedure included a direct inter-comparison of the WCC-Empa transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at Empa. The results are shown in Appendix II.

Table 3: Experimental details of the ozone inter-comparison

reference	Empa: TEI 49C-PS #5409-300 transfer standard
field instruments	TEI 49C #77086-385
ozone source	WCC: TEI 49C-PS, internal generator
zero air supply	Empa: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition systems	Data was acquired using a LabView programme via the RS-232 interface. 30 s averages were stored.
pressure transducer readings	Ambient Pressure: 1003.0 hPa TEI 49C-PS (WCC): adjusted to 1003.9 hPa TEI 49C #77086-385: 1003.9 hPa, not adjusted
concentration range	0 - 100 ppb
number of concentrations	5 + zero air at start and end
approx. concentration levels	10 / 20 / 30 / 50 / 90 ppb
sequence of concentration	random
averaging interval per concentration	5 minutes
number of runs	3 runs on 23 May 2005
connection between instruments	about 1.5 meter of 1/4" PFA tubing

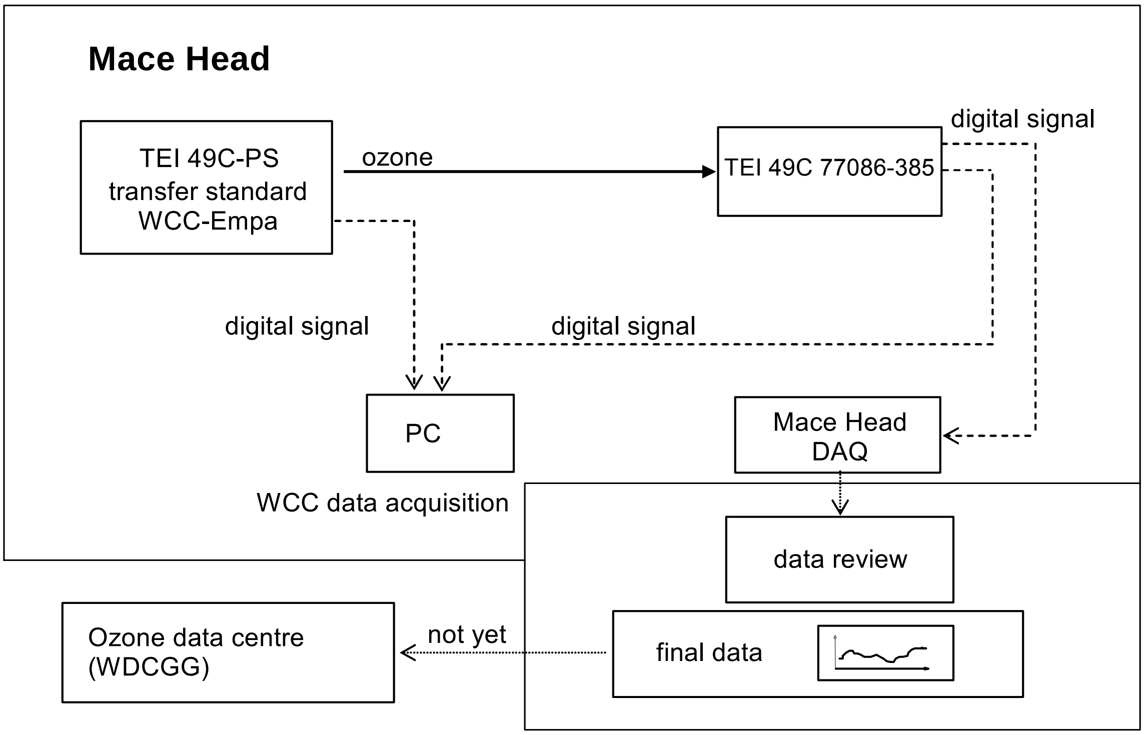


Figure 9: Experimental set up for the ozone inter-comparison

4.2.2 Results

The assessment of the inter-comparison was done according to [*Klausen, et al.*, 2003]. The results shown below refer to the calibration factors as given in Table 2.

Ozone Analyzer

The results comprise the inter-comparison between the TEI 49C #77086-385 field instrument and the WCC transfer standard TEI 49C-PS, carried out on 23 May 2005.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 4. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

Figures 10 and 11 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 10 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 11 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 12).

The data used for the evaluation was recorded by the WCC-Empa data acquisition system. The raw data was treated according to the usual station method, and no further corrections were applied to the data.

Table 4: Inter-comparison of the ozone field instrument TEI 49C #77086-385

run index	WCC TEI 49C-PS conc.	s_d	TEI 49C #77086-385 conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.12	0.19	0.31	0.09	0.19	
2	9.73	0.09	9.83	0.14	0.10	1.01
3	49.82	0.13	49.89	0.31	0.07	0.14
4	29.87	0.19	30.13	0.21	0.25	0.85
5	20.03	0.13	20.02	0.24	-0.01	-0.07
6	89.90	0.08	90.15	0.19	0.26	0.28
7	0.18	0.04	0.25	0.10	0.07	
8	0.19	0.08	0.21	0.18	0.03	
9	49.97	0.06	50.09	0.08	0.11	0.23
10	10.04	0.08	10.11	0.06	0.06	0.63
11	89.91	0.06	90.12	0.13	0.21	0.23
12	20.01	0.07	19.97	0.08	-0.03	-0.17
13	29.95	0.08	30.04	0.08	0.09	0.29
14	0.20	0.06	0.14	0.04	-0.06	
15	0.08	0.05	0.01	0.17	-0.07	
16	89.93	0.08	90.19	0.16	0.25	0.28
17	19.99	0.08	20.01	0.09	0.02	0.12
18	49.94	0.05	49.99	0.18	0.04	0.09
19	9.99	0.10	10.09	0.09	0.10	0.99
20	29.95	0.08	30.05	0.12	0.10	0.33
21	0.17	0.07	0.15	0.07	-0.02	

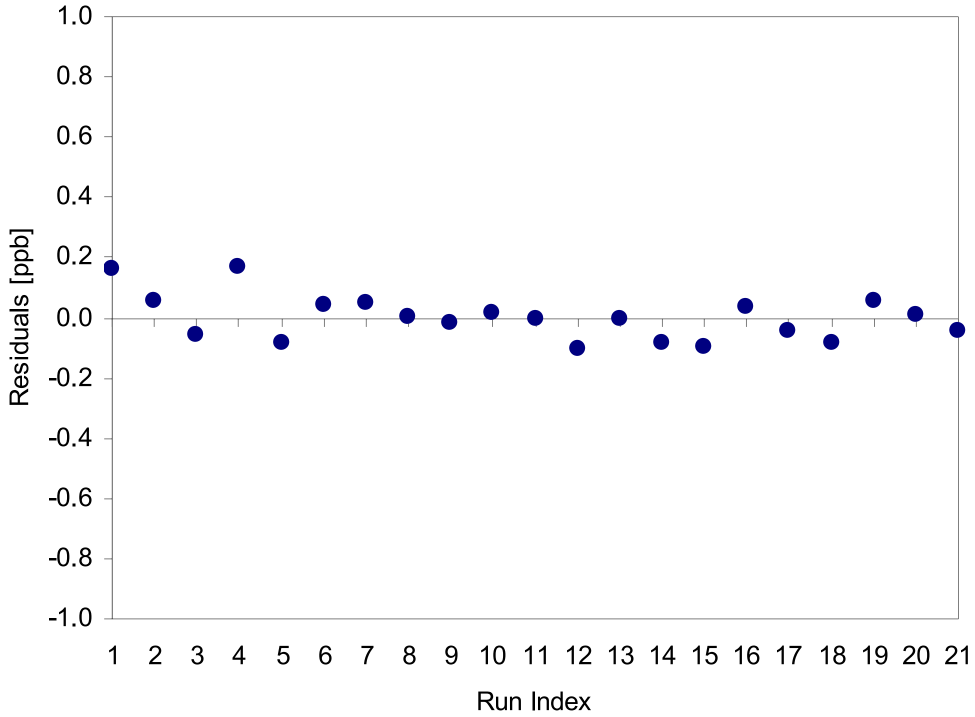


Figure 10: Residuals to the linear regression function (TEI 49C #77086-385) vs. the run index (time dependence)

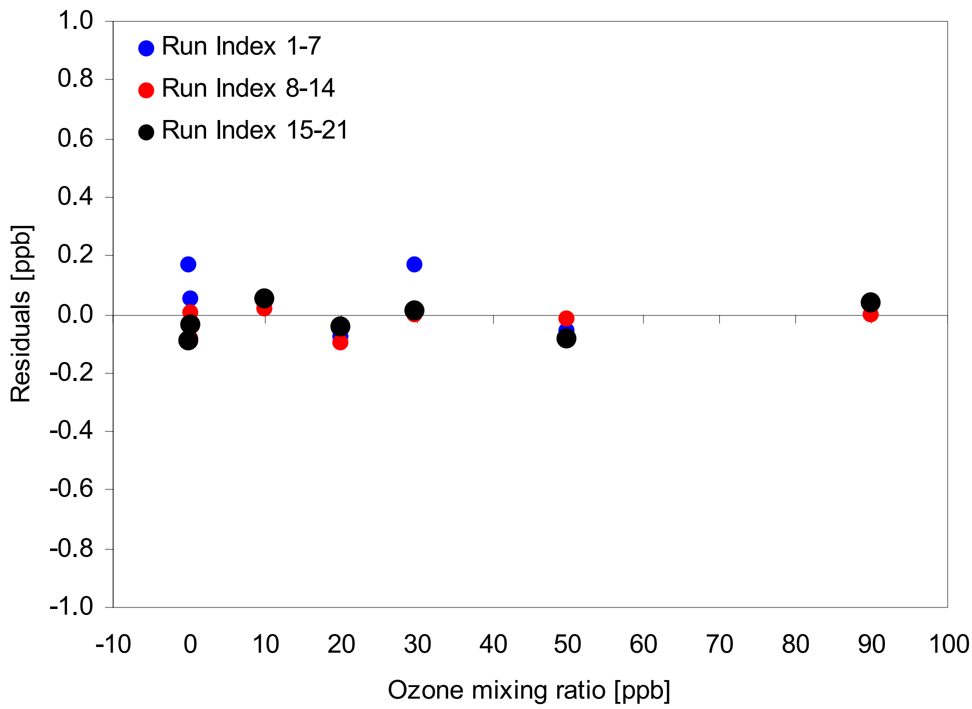


Figure 11: Residuals to the linear regression function (TEI 49C #77086-385) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of [*Klausen, et al.*, 2003]. The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

TEI 49C #77086-385:

$$\text{Unbiased } O_3 = (\text{TEI 49C} + 0.04) / 1.0045$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49C = O_3 mixing ratio in ppb, determined with TEI 49C #77086-385

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.55 \text{ ppb})^2 + (0.00612 \text{ x } C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 12 shows the deviation of the TEI 49C #77086-385from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

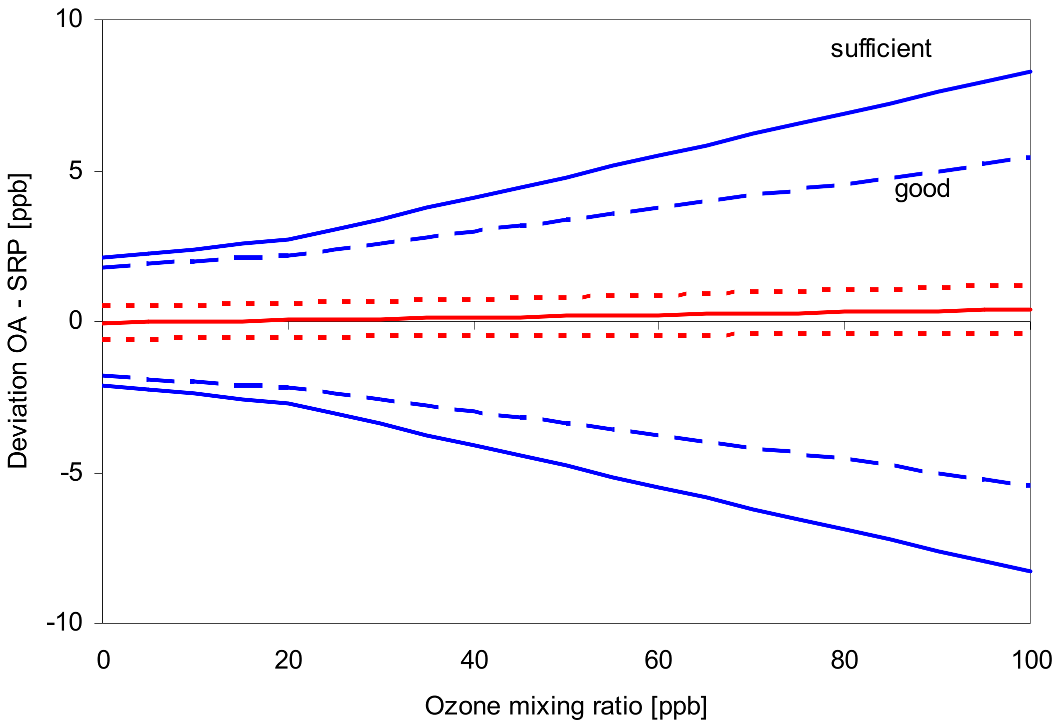


Figure 12: Inter-comparison of instrument TEI 49C #77086-385

Comment

The ozone concentrations observed at Mace Head (2004) ranged between 23.8 and 50.1 ppb (5-and 95-percentile of 60 min mean values). The main ozone analyzer and the station calibrator of Mace Head fulfil the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3 Recommendation for Surface Ozone Measurements

Due to the good inter-comparison results only the following recommendations are made by WCC-Empa for surface ozone measurements at Mace Head:

- Ozone loss in the inlet line should be checked regularly.
- Submission of the surface ozone data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly recommended. Data submission is one of the obligations of a GAW station and particularly Global GAW stations should act as role models..

5 SYSTEM AND PERFORMANCE AUDIT FOR CARBON MONOXIDE

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 was not changed since the last audit by WCC-Empa in 2002.

5.1 Monitoring Set-up and Procedures

5.1.1 Air Inlet System for CO and CH_4

Sampling-location: at the 10 m level of the 23 m tower between the two laboratory buildings

Inlet description: 15 m long stainless steel tube (1/4'') - pump and overflow (~6 l/min)

For most of the time the air is vented after the pump but 90 seconds before an injection a solenoid valve is activated, so that approximately 110 ml / min (corresponding to 50 mbar overpressure in the sample loop) flows through a 7 µm SS-filter, a Nafion dryer, the 1ml sample loop and a flow regulator valve to the RGA-3 instrument.

Residence time in the sampling line: approx. 2 s

The inlet systems, including all parts and materials are adequate for the analysis of CO (and CH_4).

5.1.2 Instrumentation

An RGA-3 GC-system of Trace Analytical Inc. is used as an in-situ CO analyser. Instrumental details are listed in Table 5.

Table 5: Carbon monoxide gas chromatograph at Mace Head

Manufacturer	Trace Analytical Inc.
Model, S/N	RGA3, S/N 090189-010 ANE 294
At Mace Head since	since 1989
Method	GC / HgO Detector
Loop size	1 ml
Columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
Carrier gas	ambient air – AADCO - Sofnocat - Mole sieve - Dryerite - GC, 20 ml/min
Operating temperatures	Detector: 265 °C, Column: 105 °C
Analogue output	0 - 1 V
Calibration interval	every 40 min (working standard)
Instrument's specials	8 seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate loop pressure with ambient pressure

Operation and Maintenance

Analysis: Injections are made every 20 minutes, alternating between working standard and ambient air.

Weekly checks: RGA-3 test points
chromatogram / peak width / CO-retention time
cylinder pressures

A linearity check with a dilution system is performed when significant changes of the instrument are made (e.g. replacement of the mercury bed).

Gas Standards

The standard CO scale, to which the Mace Head CO measurements are referenced, is based on a set of three stainless steel cylinders provided by Scripps Institution of Oceanography (SIO) and calibrated against the Australian CSIRO scale. Furthermore other gas standards are available at the site which are occasionally used to verify the response function of the RGA-3. A full calibration using flasks from CSIRO is performed at irregular intervals. Table 6 gives an overview of all CO cylinders available at the site.

Table 6: Station CO cylinders

Cylinder #	Description	Conc. [ppb]	Scale
J-081	Working standard provided by SIO	171.4	CSIRO
G-050	Station standard; Cape Grim real air standard	63.0	CSIRO
G-055*	Station standard; Cape Grim real air standard	172.6	CSIRO
H-54	Future station standard; Mace Head real air standard	131.2	CSIRO
H-55	Future station standard; Mace Head real air standard	138.4	CSIRO
49177	Commercial standard (BOC); CO in synthetic air	364.0	Mace Head assigned
55604	Commercial standard (BOC); CO in synthetic air	~600.0	Mace Head assigned
CLM 005557	NIST SRM CO in Air	1003.6	NIST

*cylinder is known to be drifting

5.1.3 Data Handling

Data Acquisition and –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 Treatment

The responsibility for data review and data management is split between the station operator, the data reviewer at the University of Bristol, and the SIO. In a first step, the station operator plots the data and examines the chromatograms. Comments and notes are made in electronic log files. These comments contain e.g. calibration notes or remarks on events that might have influenced the data. After this pre-selection, the data reviewer applies flags to the data based mainly on the station operators logs but also flagging data which appears suspect. To get the final results, the raw data (every single chromatogram) is recalculated by applying the appropriate calibration function. This function is evaluated from the pre- and post-analysis of the working standard cylinder at SIO. During the 6-monthly meetings of the AGAGE members the data is further discussed regarding scientific aspects.

Data Submission

Carbon monoxide data have been submitted to the GAW data centre for greenhouse gases (WDCGG) at JMA but with unacceptable delay. By May 2005 data from March 1994 to December 1999 was available at the WDCGG.

5.1.4 Documentation

Logbooks

An electronic logbook is available for the carbon monoxide instrument. The notes are up-to-date and describe all important events.

5.2 Inter-comparison of the in-situ Carbon Monoxide Analyzer

5.2.1 Experimental Procedure

The eight transfer standards of WCC-Empa (concentration range approx. 70-300 ppb CO) were stored in the same room as the CO measurement system to equilibrate over night. The transfer standards were calibrated against the CMDL WMO-2000 scale [*Novelli, et al.*, 2003] at Empa before the audit (Appendix III). Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected and analysed six times in the period 19 to 23 May 2005. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the measurement leader during the audit. The experimental details are summarized in Table 7.

Table 7 Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA3, S/N 090189-010 ANE 294
reference:	WCC-Empa transfer standards
data acquisition system:	Station data acquisition
approx. concentration levels:	70 to 300 ppb
injections per concentration:	6

5.2.2 Results

The CO concentrations determined by the RGA-3 field instrument for the eight WCC-Empa transfer standards are shown in Table 8 (data as it was calculated by the AGAGE software, i.e. blank and non-linearity correction were applied) and Table 9 (same data but without the blank correction).

For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 13 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (reference) for the non-linearity and blank corrected data; the result of the data without blank correction is presented in Figure 14.

The WCC TS were calibrated before and after the audit against the CMDL scale (Reference: CMDL CA02854, 295.5 pbb) with an Aerolaser AL5001. The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at Mace Head. The data of the RGA-3 field instrument were re-processed during the audit and are based on calibration of the instrument against the reference standards available at the site.

Table 8: Carbon monoxide inter-comparison results (correction for non-linearity and blank of RGA-3 applied)

No.	**WCC standard**	**Mace Head analysis (RGA-3, Peak Height, non-linearity and blank corrected data)**				
	conc. ± 1σ	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	73.4 ± 0.9	65.9	0.2	6	-7.5	-10.1
2	104.4 ± 0.7	99.1	0.3	6	-5.3	-5.0
3	133.6 ± 1.0	127.9	0.3	6	-5.7	-4.2
4	154.3 ± 0.9	147.6	0.7	6	-6.7	-4.3
5	160.5 ± 1.0	154.6	0.2	6	-5.9	-3.7
6	175.8 ± 1.1	169.5	0.5	6	-6.3	-3.6
7	248.7 ± 1.4	242.3	0.6	6	-6.4	-2.6
8	304.9 ± 1.1	296.1	0.6	6	-8.8	-2.9

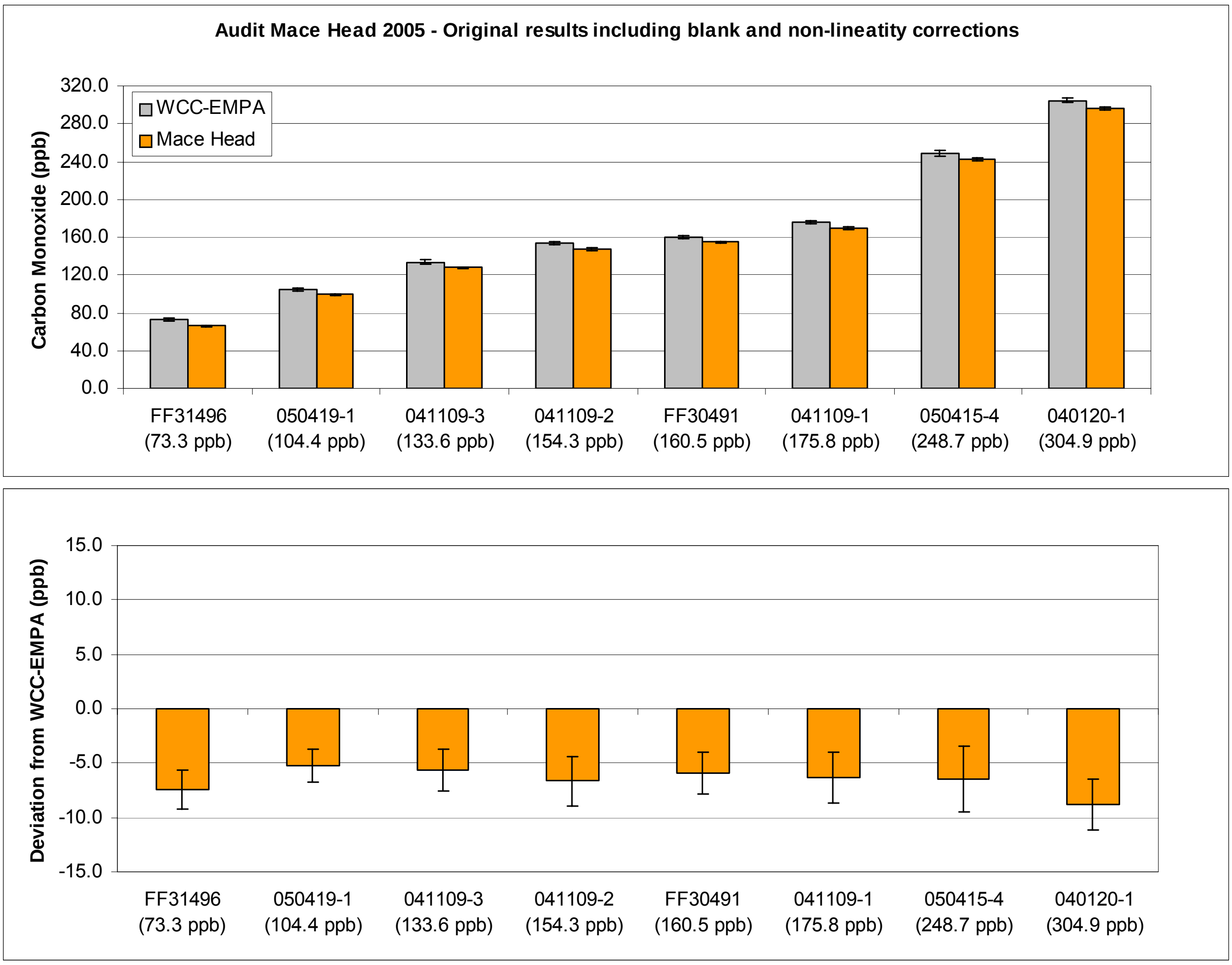


Figure 13: Upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mace Head (orange) with corrections for non-linearity and blank value of the RGA-3 applied.
Lower panel: deviation of the Mace Head station from the reference.
The error bars represent the 95% confidence interval.

The above result was automatically calculated by the AGAGE software using the following equation:

C_HT = (Cstd + blank) * R_HT – blank

where

C_HT: final CO concentration based on peak height (ppb)

Cstd: CO concentration of the working standard (here 171.37 ppb)

blank: blank value in ppb (here 5.5 ppb)

R_HT: calibration factor including a correction for the non-linearity of the RGA-3.

It was realised that the blank correction by the AGAGE software imposed an additional error into the measurement because the RGA-3 did not show a blank value during the audit. Re-calculation setting the blank to zero resulted in much more consistent data, which are shown in Table 9 and Figure 14.

Table 9: Carbon monoxide inter-comparison results (corrected for non-linearity of RGA-3, blank set to zero)

No.	**WCC standard**	**Mace Head analysis (RGA-3, Peak Height, non-linearity corrected data; blank set to zero)**				
	conc. ± 1σ	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	73.4 ± 0.9	69.2	0.2	6	-4.1	-5.6
2	104.4 ± 0.7	101.3	0.3	6	-3.0	-2.9
3	133.6 ± 1.0	129.3	0.3	6	-4.3	-3.2
4	154.3 ± 0.9	148.3	0.7	6	-5.9	-3.8
5	160.5 ± 1.0	155.1	0.2	6	-5.4	-3.4
6	175.8 ± 1.1	169.5	0.5	6	-6.3	-3.6
7	248.7 ± 1.4	240.0	0.6	6	-8.7	-3.5
8	304.9 ± 1.1	292.2	0.6	6	-12.7	-4.2

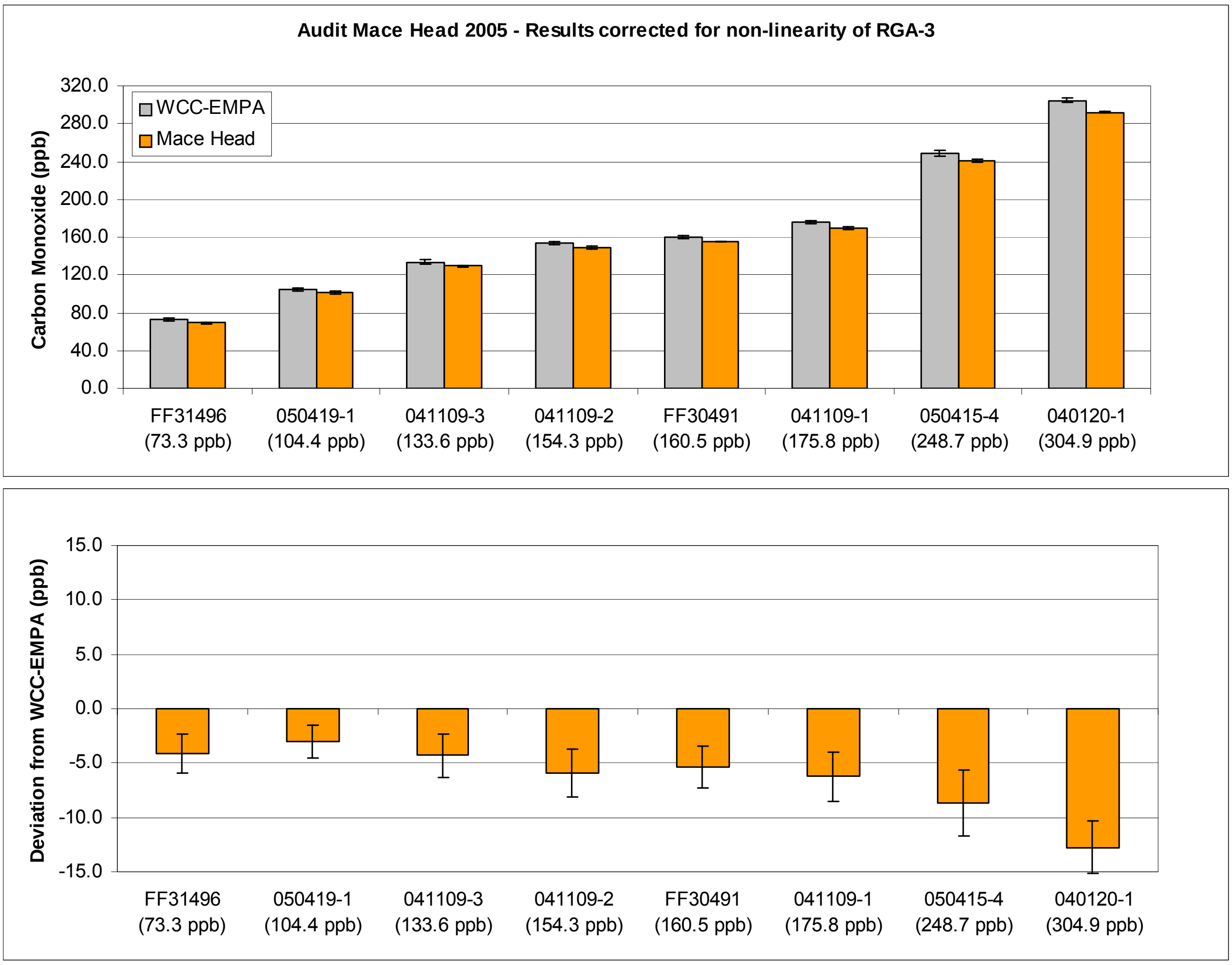


Figure 14: Upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mace Head (orange) with the correction for the non-linearity of the RGA-3 applied.
Lower panel: deviation of the Mace Head station from the reference.
The error bars represent the 95% confidence interval.

The results without the blank correction show a clear linear relationship between WCC-Empa and Mace Head. A scatter plot of Mace Head data vs. WCC-Empa assigned values including a linear fit is shown in Figure 15. The residuals of the linear regression are shown in Figure 16.

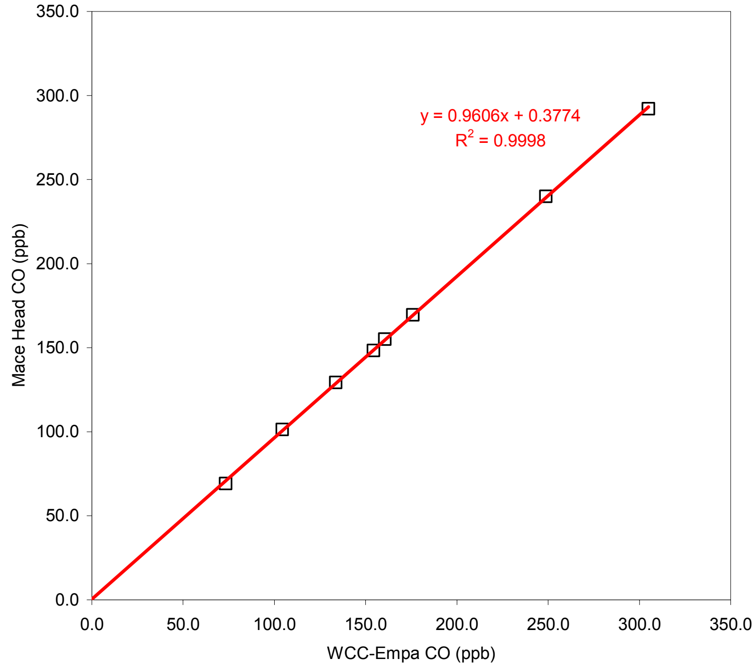


Figure 15: Line fit plot of Mace Head results (non-linearity corrected; no blank correction) vs. WCC-Empa

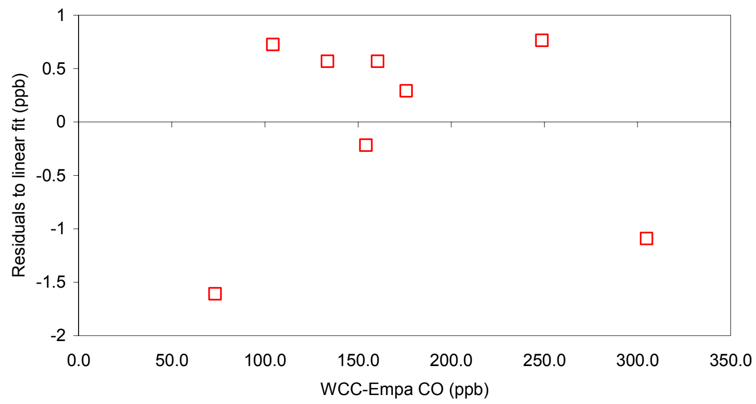


Figure 16: Residuals of linear regression (see above figure)

The Mace Head values excluding the blank correction are on average 3.8% lower compared to WCC-Empa, which compares well with the differences between the NOAA-CMDL WMO-88 and WMO-2000 scales.

5.3 Mace Head CO Standards analysed by WCC-Empa

In addition to the above measurements, WCC-Empa analysed the available station CO standards with an Aerolaser AL5001 instrument. Table 10 gives an overview of the analysed standards including measurement results.

Table 10: Mace Head CO cylinders analysed by WCC-Empa

Cylinder #	Assigned Conc. [ppb]	Scale	Mace Head measured (no blank correction.)	WCC-Empa measured	Deviation from WCC [ppb]	Deviation from WCC [%]
J-081	171.4	CSIRO	171.4	177.6	-6.2	-3.6
G-050	63.0	CSIRO	66.4	67.7	-1.3	-1.9
G-055*	172.6	CSIRO	172.6	180.2	-7.6	-4.4
H-54	131.2	CSIRO	132.5	136.9	-4.4	-3.4
H-55	138.4	CSIRO	139.4	143.4	-4.0	-2.8
49177	364.0	Mace Head	357.5	375.1	-17.5	-4.9
55604	~600.0	Mace Head	593.6	613.4	-19.8	-3.3
CLM 005557	1003.6	NIST	941.8	966.8	-25.1	-2.7

*cylinder is known to be drifting

Cylinders G-050 and G-055 were also measured by WCC-Empa in 2002 at CSIRO, Australia. The results were as follows:

G-050: CSIRO 63.8 ± 0.6 ppb, WCC-Empa 67.0 ± 0.8 ppb (1σ, N = 73)

G-055: CSIRO 160.7 ± 0.9 ppb, WCC-Empa 166.1 ± 1.1 ppb (1σ, N = 91)

G-050 seems to have good stability, but G-055 shows a significant upward drift for CO of approximately 5 ppb per year.

5.4 Ambient Air Measurements at Mace Head with RGA-3 and Aerolaser AL5001

Ambient air measurements using the Aerolaser 5001 of WCC-Empa were performed between 23. and 26. May 2005 at Mace Head. Figure 17 shows the concentrations measured with both the AL and the RGA-3 instruments. Data shown for the RGA-3 instrument is non-linearity corrected data and does not include a blank correction. Averaging time was 30 seconds for the Aerolaser, and single injections were made with the RGA-3 instrument every 40 or 80 minutes. Corresponding 5 minute average Aerolaser values are also shown in Figure 17.

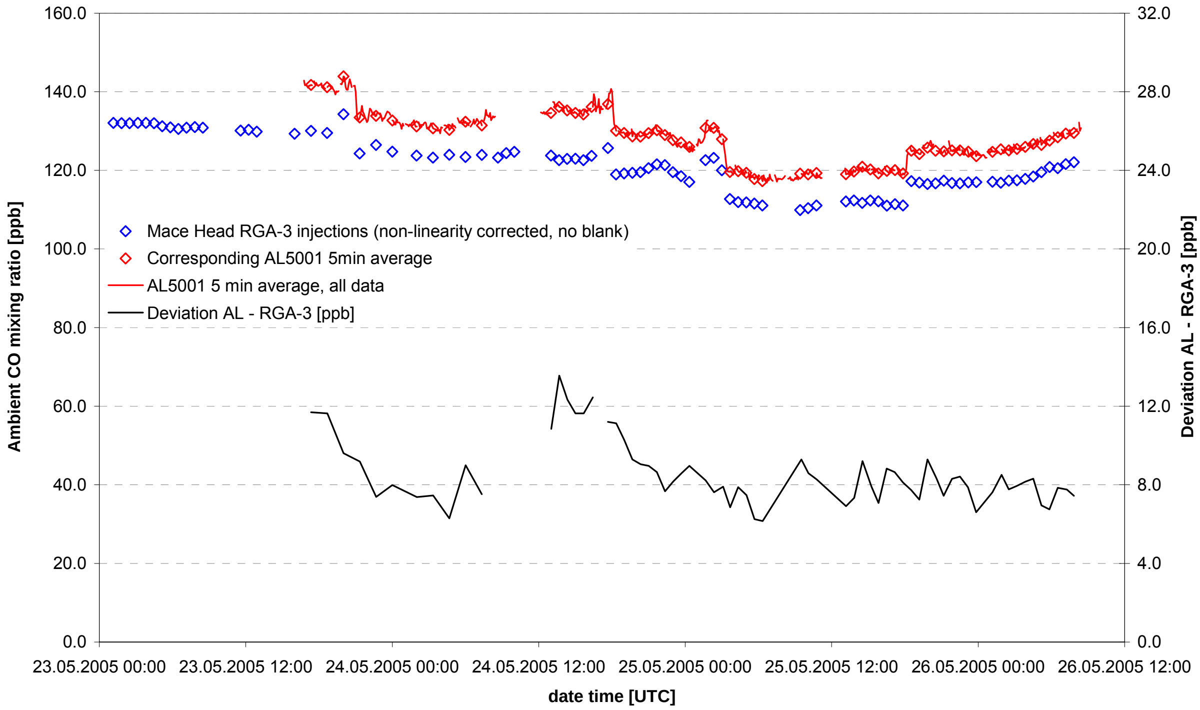


Figure 17: Ambient air measurements at Mace Head with the Aerolaser 5001 (WCC-Empa) and RGA-3 (station instrument). RGA-3 injections were made every 40 or 80 minutes, and corresponding 5 min averages of the AL instrument are shown.

It can be seen from Figure 17 that the CO concentration remained relatively constant throughout most of the time period. WCC-Empa and Mace Head measurements showed a clear linear relationship, with a slope of 0.933 (intercept set to zero, R^2=0.93). Generally lower concentrations (average 6.7%) were found with the RGA-3 instrument. This is slightly lower compared to the inter-comparison of the WCC-Empa transfer standards (lower findings of Mace Head between 2.9 and 5.6%) and also lower compared to the measurements of the Mace Head station standards with the AL5001 (station standards 1.9 to 4.6% lower compared to WCC-Empa measurements).

5.5 Discussion of the Inter-comparison Results

The following conclusions can be made from the inter-comparison results:

a) Analysis of WCC-Empa travelling standards by Mace Head

The inter-comparison showed that the blank correction which was still implemented is no longer appropriate. Re-evaluation of the data omitting the blank correction resulted in values which are lower by 2.9 to 5.6% compared to WCC-Empa. This difference may to a large extent be explained by scale differences. WCC-Empa refers to the revised NOAA-CMDL CO scale (WMO-2000) [*Novelli, et al.*, 2003]. The WMO-2000 scale is by approximately 2.7% higher compared to WMO-88 for concentrations higher than 190 ppb CO; larger deviations exist for lower concentrations.

The analysis of the WCC-Empa transfer standards by the Mace Head station resulted in lower values (-12.7 to -3.0 ppb or -2.9 to -5.6%) for concentrations between 70 and 300 ppb compared to the reference. The revision and uncertainty of the CO scale explains therefore most of the observed differences between Mace Head and WCC-Empa. If the concentration of J-081 is set to 177.6 ppb (WMO-2000 value measured by WCC-Empa), the deviations become significantly lower (+0.03 to -2.72%).

The inter-comparison also showed that the correction of the non-linearity applied by the station software improved the results. However, this correction may still be improved if a higher number of standards are injected in more frequent intervals (see Recommendations, next section).

b) Analysis of Mace Head station standards by WCC-Empa

The results confirmed the analysis of the WCC-Empa travelling standards. Again, lower values between 1.9 and 4.6% were measured by Mace Head compared to WCC-Empa, which can be explained mostly by scale differences.

c) Ambient air measurements by WCC-Empa and Mace Head

Ambient air measurement also confirmed the findings of the inter-comparisons of the travelling and station standards. However, a slightly larger difference was found which cannot be fully explained.

5.6 Recommendation for Carbon Monoxide Measurements

The major issue that was identified by WCC-Empa was an inappropriate correction of the data due to changed instrument response. Therefore, WCC-Empa strongly suggests that the linearity and instrument blanks are more often assessed, e.g. in three monthly intervals.

WCC-Empa recommendations concerning CO measurements at Mace Head are summarized below:

- Blank and linearity checks should be done frequently (e.g. three monthly). As a consequence of the audit this is already done automatically on monthly intervals for two span levels and the blank. It is planned to extend the number of automatically injected span gases. Five or more span levels are necessary to fully characterise the response function of the RGA-3 system.
- If a blank is detected, the reason should be assessed. Detectable blank values should not be present in a well operating RGA-3 system.
- Previous data needs to be corrected considering the changing instrument response over time.
- Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly encouraged. Data submission is one of the obligations of a GAW station. Submission delays of more than one year are unacceptable.

6 SYSTEM AND PERFORMANCE AUDIT FOR METHANE

Continuous methane measurements became operational at Mace Head in 1987. The annual average CH_4 concentration at Mace Head has increased from approx. 1760 ppb in 1987 to 1850 ppb in 2003.

6.1 Monitoring Set-up and Procedures

6.1.1 Air Inlet System for CH_4

Inlet: same as for Carbon Monoxide (see 5.1.1)

6.1.2 Instrumentation

A CARLE 100A gas chromatograph with an FID detector is used for ambient methane measurements at Mace Head. Instrument details are summarised in Table 11.

Table 11: Gas chromatograph for methane at the Mace Head station

Instrument	CARLE 100A, S/N 40647
at Mace Head since	November 1994
method	GC / FID Detector
sample loop	4.5 ml
column	Molecular sieve 5Å
carrier gas	N_2 99.999%
operating temperatures	Column: 60°C
calibration interval	working standard every 40 min
instrument specials	8 seconds before injection, the flow through the loop is stopped to equilibrate pressure.

Operation and Maintenance

Analysis: Injections are made every 20 minutes, alternating between working standard and ambient air.

Weekly checks are made for tank pressures, temperatures, flow rates, and retention times. Further measures are taken when something unusual is observed.

CH_4 Measurement Scale

The same working standard as for CO measurements is used. The CH_4 concentrations are provided by Scripps Institution of Oceanography (SIO) and re-calibrated after the return of the standard. The current cylinder (J-081) was assigned a CH_4 concentration of 1846.09 ppb. No additional CH_4 standards are available at the site.

6.1.3 Data Handling

Data Acquisition and –transfer

See Section 5.1.3.

Data Treatment

See Section 5.1.3.

Data Submission

Data have been submitted to the GAW data centre for greenhouse gases (WDCGG) at JMA. At the time of the audit submitted data span the period from 01/1987 to 09/2003.

6.1.4 Documentation

Logbooks

An electronic logbook is available for the methane instrument. The notes are up-to-date and describe all important events.

Standard Operation Procedures (SOPs)

The instrument manual is available at the site.

Comment

The frequent instrument checks and the up-to-date logbook support the quality of the data. No change of the current practice is suggested.

6.2 Inter-Comparison of in-situ Methane Measurements

6.2.1 Experimental Procedure

The eight transfer standards of the WCC (approx. concentration range 1750 - 1990 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate over night. The transfer standards were calibrated against CMDL laboratory standards (CA05316, CA04462, CA04580) at WCC-Empa before the audit (see Appendix IV). Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected 5 to 6 times and analyzed between 19 and 23 May 2005. No modifications of the GC system were made for the inter-comparison. The station software acquired the data. The data (mean values and standard deviations) was processed during the audit. The experimental details are summarized in Table 12.

Table 12: Experimental details of the methane inter-comparison

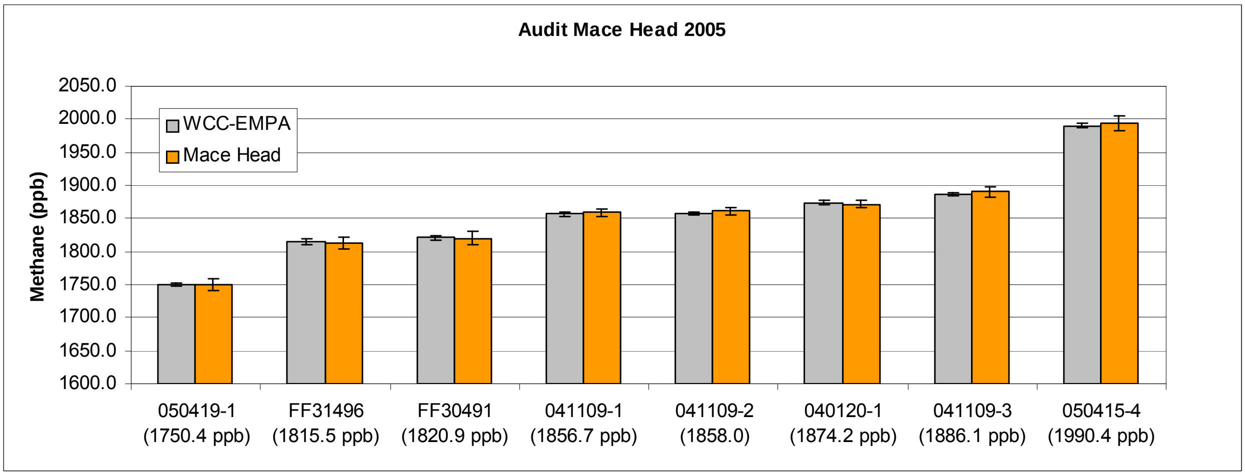
field instrument:	CARLE 100A, S/N 40647
Reference:	8 WCC-Empa transfer standards
data acquisition system:	Station GC control software
approx. concentration levels:	concentration range approx. 1750 – 1990 ppb
Injections per concentration:	5 to 6

6.2.2 Results of the Methane Inter-comparison

The results of the inter-comparison between the CARLE 100A field instrument and the five WCC transfer standards are shown in Table 13. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 18 shows the absolute differences (ppb) between the measurements of the CARLE 100A GC and the WCC transfer standards (TS) (reference). The transfer standards were analysed before and after the audit. The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at Mace Head. The data from the CARLE 100A field instrument were reprocessed during the audit and are based on the comparison with the station standard.

Table 13: Methane inter-comparison measurements at Mace Head

No.	WCC standard	Mace Head analysis (CARLE 100A GC-FID, Peak Height)				
	conc. ± 1σ	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1750.4 ± 1.1	1750.2	4.0	6	-0.2	-0.01
2	1815.5 ± 2.1	1812.9	3.9	6	-2.6	-0.15
3	1820.9 ± 1.5	1820.2	4.2	6	-0.7	-0.03
4	1856.7 ± 1.4	1858.7	2.0	6	2.0	0.11
5	1858.0 ± 1.2	1860.9	2.3	6	2.9	0.16
6	1874.2 ± 1.4	1871.7	2.2	6	-2.5	-0.13
7	1886.1 ± 1.2	1890.0	3.1	6	3.9	0.21
8	1990.4 ± 1.3	1993.8	4.4	6	3.4	0.17



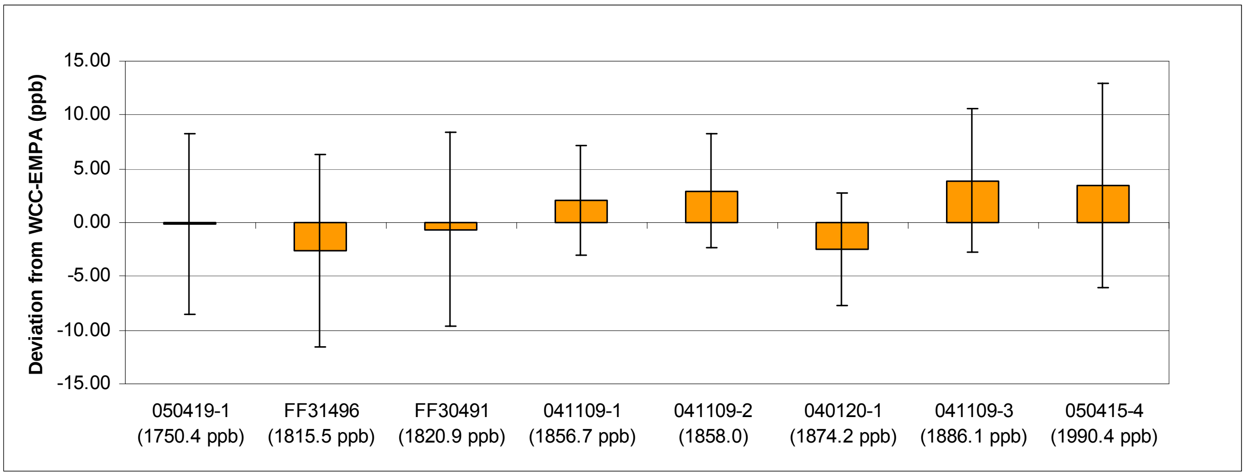


Figure 18: Upper panel: concentrations of the WCC transfer standards (grey) measured with the GC system of Mace Head (orange).
Lower panel: deviation of Mace Head from the reference.
The error bars represent the 95% confidence interval.

The repeatability of multiple injections was sufficiently good, with an average standard deviation of 0.18% of six injections. This value is comparable to the results of the audit by WCC-Empa in 2002 (0.16%). The best instruments at GAW stations reach a repeatability of approximately 0.05%.

Comment

The CH_4 inter-comparison between WCC-Empa and Mace Head agreed very well in the concentration range between 1750 and 1990 ppb methane. The deviation from the transfer standards is less than 0.2 %.

6.3 Recommendation for Methane Measurements

The good result of the inter-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.

Methane data were submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA, and data until the September 2003 were available at the WDC by the time of the audit. It is recommended that data submission continues with maximum delay of one year.

7 REFERENCES

Hofer, P., et al. (2000), Traceability, Uncertainty and Assessment Criteria of Surface Ozone Measurements, 19 pp, WCC-EMPA Report 98/5, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf, Switzerland.

Klausen, J., et al. (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res.-Atmos.*, *108*, 4622, doi:4610.1029/2003JD003710.

Novelli, P. C., et al. (2003), Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, *J. Geophys. Res.-Atmos.*, *108*, 4464, doi:4410.1029/2002JD003031.

Press, W. H., et al. (1995), *Numerical Recipes in C: The Art of Scientific Computing*, 994 pp., Cambridge University Press, Cambridge, U.K.

APPENDIX

I. Empa Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The UV absorption is proportional to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 19. One gas stream flows through a pressure regulator to the reference solenoid valve to become the zero reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. After the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS then determines the ozone concentration for each cell and outputs the average concentration.

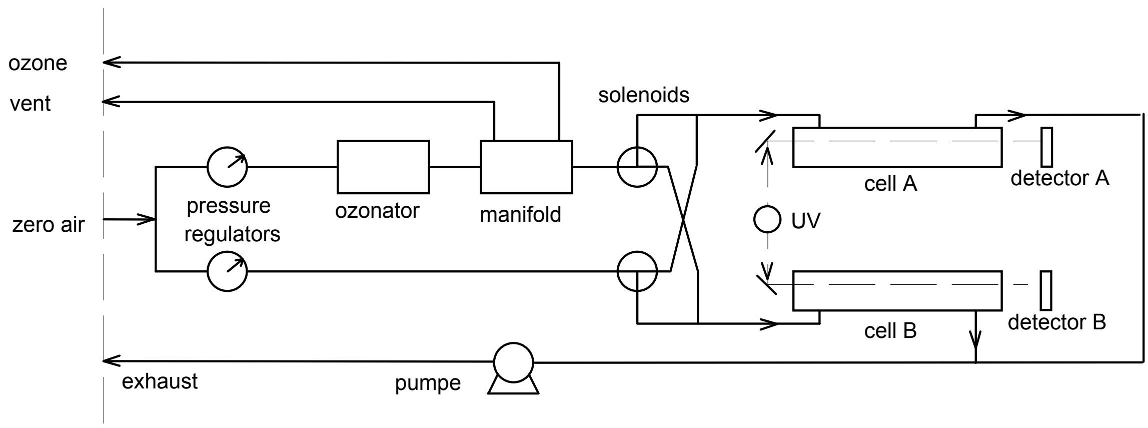


Figure 19: Flow schematic of TEI 49C-PS

II. Stability of the Transfer Standard TEI 49C-PS

To exclude errors that might result from transportation of the transfer standard, the TEI 49C PS #54509-300 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this inter-comparison at the Empa calibration laboratory are summarized in Table 14 and Figure 20.

Table 14: Inter-comparison procedure SRP - TEI 49C-PS

pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 140 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurized air - zero air generator (CO catalyst, Purafil, charcoal, filter)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

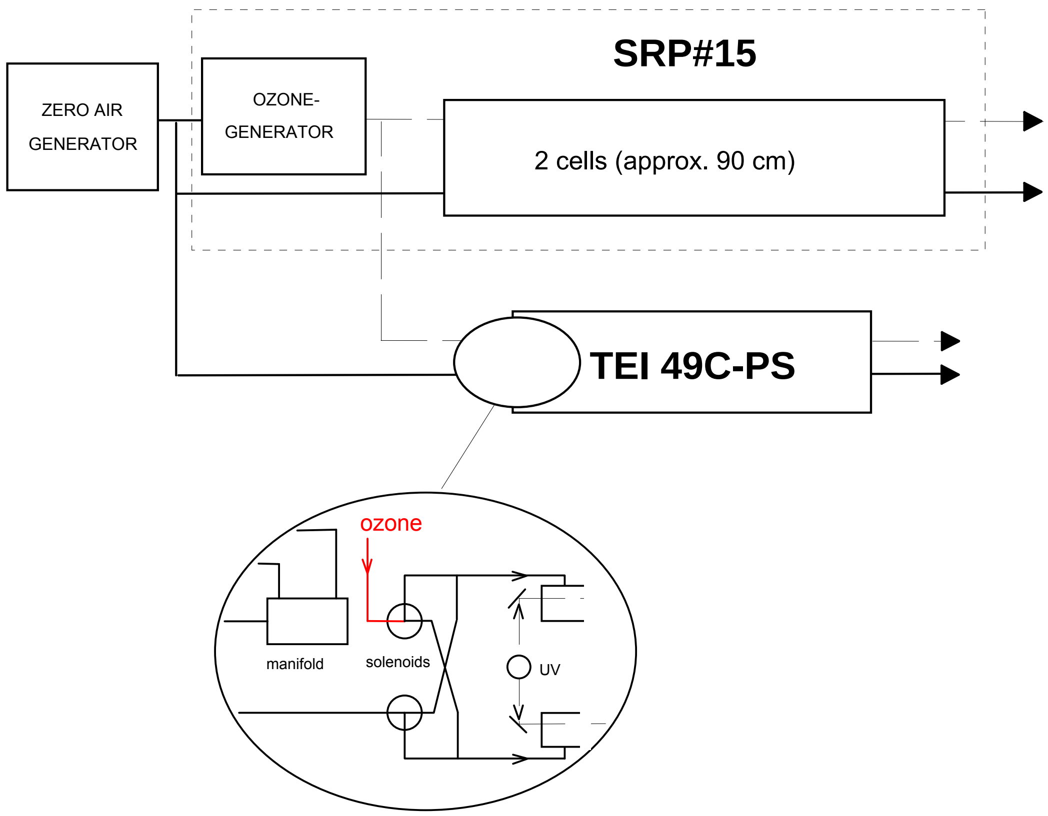


Figure 20: Instruments set up SRP -TEI 49C-PS

The transfer standard fulfilled the criteria given in [*Klausen, et al.*, 2003], which means that neither intercept nor slope were different from 0 and 1,respectively, on the 95% confidence level.

Figure 21 shows the deviation of the transfer standard from SRP#15 before and after the audit. The maximum allowed deviation is also shown in this figure. The regression statistics between the WCC-Empa transfer standard and SRP#15 were calculated using the procedure `fitexy` given in [*Press, et al.*, 1995]. The following relationship was found for the pooled data of the inter-comparisons before and after the audit:

TEI 49C-PS #54509-300 = 1.0024 x SRP#15 – 0.07 ppb

This relationship was used for the calculation of the unbiased ozone concentrations.

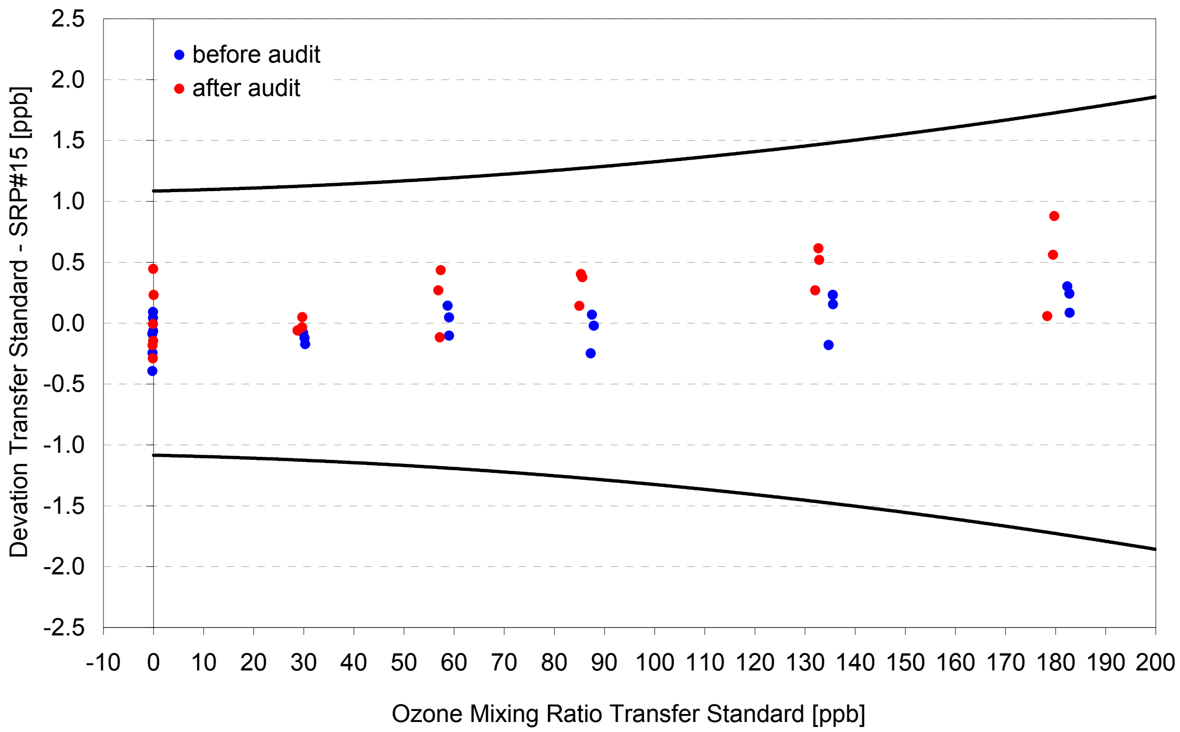


Figure 21: Deviation of the WCC-Empa transfer standard from SRP#15 before and after the audit

III. WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at the WCC are listed in Table 15:

The CO scale of the CMDL was revised in 2000 (Novelli et al., 2003). WCC-Empa refers to the **revised** scale (WMO-2000). The WCC-Empa transfer standards used during the audit are listed in Table 16.

Table 15: CMDL CO Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Standard (Gas Cylinders)	CMDL WMO-88 scale*	CMDL revised scale**	WCC-Empa assigned***	Cylinder
CMDL Laboratory Standard	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	56.3 ± 1.0 ppb	CA03209
CMDL Laboratory Standard	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	108.6 ± 1.1 ppb	CA02803
CMDL Laboratory Standard		129.8 ± 1.3 ppb	131.7 ± 1.3 ppb	CA05373
CMDL Laboratory Standard	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	153.9 ± 1.5 ppb	CA03295
CMDL Laboratory Standard	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	295.5 ± 3.0 ppb	CA02854

*** Certificates from 5.8.97 (97.6, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)**
** Revised scale (by P. Novelli), re-calibrated at CMDL, 23.01.01; Certificate from 15.4.04 (129.8 ppb)
*** WCC-Empa assigned valued based on calibrations with CA02854

Table 16: CO transfer standards of the WCC (average of calibrations from April 05 and June 05 with measured standard deviation).

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL WMO-2000 scale CA02854) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	73.1 ± 0.8 ppb	73.5 ± 1.0 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	104.1 ± 0.7 ppb	104.6 ± 0.7 ppb	050419-1
WCC Transfer Standard (6 l cylinder)	133.2 ± 1.0 ppb	134.0 ± 0.9 ppb	041109-3
WCC Transfer Standard (2 l cylinder)	154.5 ± 1.0 ppb	154.0 ± 0.8 ppb	041109-2
WCC Transfer Standard (6 l cylinder)	160.5 ± 1.0 ppb	160.5 ± 0.9 ppb	FF30491
WCC Transfer Standard (6 l cylinder)	175.8 ± 1.1 ppb	175.8 ± 1.0 ppb	041109-1
WCC Transfer Standard (6 l cylinder)	247.3 ± 1.4 ppb	250.1 ± 1.4 ppb	050415-4
WCC Transfer Standard (6 l cylinder)	304.9 ± 1.1 ppb	304.9 ± 1.0 ppb	040120-1

IV. WCC Methane Reference

The methane reference scale maintained by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CH_4 in the atmosphere. This CH_4 reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The CMDL standards used at WCC-Empa are listed in Table 17. The WCC-Empa transfer standards (Table 18) are traced back to the CMDL standards shown below.

Table 17: CMDL CH_4 Standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

CMDL Standard	Methane [ppb]*	Cylinder
CMDL Laboratory Standard (basis for WCC)	1691.6 ± 0.30 ppb	CA05316
CMDL Laboratory Standard (basis for WCC)	1795.1 ± 0.19 ppb	CA04462
CMDL Laboratory Standard (basis for WCC)	1882.0 ± 0.24 ppb	CA04580

* Certificates from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316)

Table 18: WCC-Empa CH_4 transfer standards (average of calibrations from April 05 and June 05). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards CA05316, CA04462 and CA04580)		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	1750.2 ± 1.1 ppb	1750.5 ± 1.1 ppb	050419-1
WCC Transfer Standard (6 l cylinder)	1815.0 ± 2.4 ppb	1816.5 ± 0.8 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	1820.5 ± 1.5 ppb	1821.2 ± 1.5 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	1857.4 ± 1.1 ppb	1856.0 ± 1.7 ppb	041109-1
WCC Transfer Standard (2 l cylinder)	1858.7 ± 1.0 ppb	1857.2 ± 1.4 ppb	041109-2
WCC Transfer Standard (2 l cylinder)	1872.8 ± 0.9 ppb	1875.5 ± 1.3 ppb	040120-1
WCC Transfer Standard (6 l cylinder)	1884.9± 0.9 ppb	1887.2 ± 1.1 ppb	041109-3
WCC Transfer Standard (6 l cylinder)	N/A*	1990.4 ± 1.5 ppb	050415-4

* Analysis of 050415-4 prior to audit invalid because of stability problems.

V. Ozone Audit Executive Summary

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

Ozone Audit Executive Summary

0.1	Station Name:	Mace Head
0.2	GAW ID:	
0.3	Coordinates/Elevation:	53.326°N, 9.899°W (5 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1	Date of Audit: 22. -26. May 2005	
1.2	Auditors:	Dr. C. Zellweger and Dr. M. Steinbacher
1.3	Station staff involved in audit:	Mr. Gerry Spain
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS S/N: 54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0024±0.0010) × [SRP] - (0.07±0.11)
1.6	Ozone Analyzer [OA]	
1.6.1	Model:	TEI 49C S/N 77086-385
1.6.2	Coefficients prior to audit	BKG -0.7, Span 1.028
1.6.3	Coefficients during and after audit	BKG -0.7, Span 1.028
1.6.4	Range of calibration:	0 – 100 ppb
1.6.5	Calibration before audit (ppb):	[OA] = (1.0021±0.0034) × [TS] + (0.02±0.13)
1.6.6	Calibration after audit (ppb):	[OA] = (1.0021±0.0034) × [TS] + (0.02±0.13)
1.6.7	Unbiased ozone concentration (ppb):	C = ([OA] + 0.05) / 1.0045
1.6.8	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.55 \text{ ppb})^2 + (0.0061 \times C)^2\}^{1/2}$
1.7	Comments:	
1.8	Reference:	EMPA-WCC Report 05/2