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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

WCC-EMPA REPORT 02/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION MACE HEAD

IRELAND, AUGUST 2002

Submitted by

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

EMPA Dübendorf, Switzerland

Contents:

EMPA is accredited as a calibration laboratory for ozone measuring instruments in accordance with EN SN 45'001

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S	SWISS CALIBRATION SERVICE		

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Mace Head from 21. to 26. August 2002 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. This is the third audit by WCC-EMPA. Previous audits were made in 1996 (for O_3) and 1998 (for O_3 and CH_4). The results of the third audit can be summarised as follows:

System Audit of the Observatory

The Mace Head global GAW station offers excellent facilities for atmospheric research and measurement campaigns. Spacious laboratories are available in the laboratory buildings.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and main ozone instrument of the station, demonstrated good agreement between the station analyser and the transfer standard. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range from 10 to 100 ppb (Figure 1).

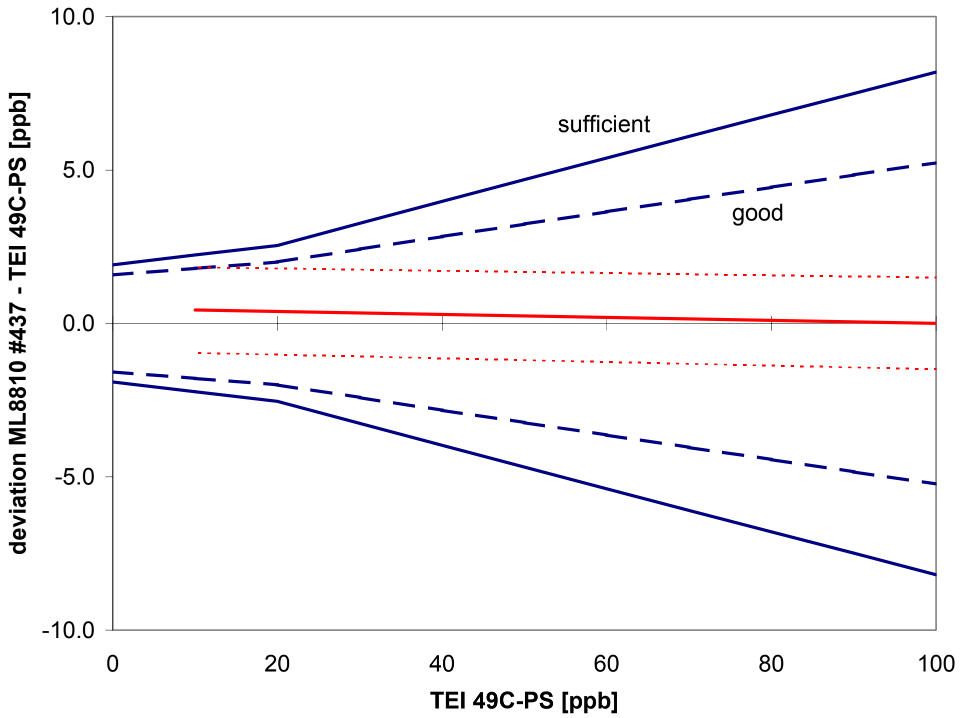

Figure 1: Inter-comparison of the ML8810 #437 field instrument with the WCC transfer standard

The inter-comparison confirmed the results of the WCC-EMPA audit from 1998, and only minor recommendations were made by WCC-EMPA concerning ozone measurements. However, due to the rather poor stability of the ozone analyser, a replacement of the 15-year old instrument should be considered.

Audit of the Carbon Monoxide Measurement

The results of the inter-comparisons between the five WCC-EMPA transfer standards and the RGA-3 system of the Mace Head station showed a difference of 8.4 to 11.4 ppb in the concentration range of 70 to 310 ppb. Part of the significant differences could be explained by the recent revision of the CMDL scale, but further investigation is needed to re-solve the problem of differences between the scales.

Audit of the Methane Measurement

The results of the inter-comparisons between the eight WCC-EMPA transfer standards and the GC system of the Mace Head station showed good agreement over a concentration range of 1630 to 2010 ppb. The deviation was within ±0.4 %. No further recommendations are suggested by WCC-EMPA concerning methane measurements.

Conclusions

All measurements of the audited parameters (O_3, CO, CH_4) at Mace Head were performed at a high level. The whole system from the air inlet to the instrumentation, including maintenance and data handling, is operated with great care. The staff involved in measurements and data evaluation is highly motivated and experienced.

A replacement of the station ozone analyser should be considered to improve the data quality. Discrepancies between different carbon monoxide scales remains still a unsolved problem where further investigation is needed.

The station offers an excellent infrastructure for atmospheric research and measurement campaigns.

Dübendorf, 4. June 2003 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Station Mace Head** is part of Ireland's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory at Mace Head is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters.

The air pollution and environmental technology section of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the GAW **World Calibration Center** (WCC) for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a co-ordinated quality assurance programme 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, Gerard Spain, and the principal investigator, Peter Simmonds, a **system and performance audit** at the Mace Head observatory was conducted by WCC-EMPA between 21. and 26. August 2002.

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 ozone audit was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the ozone inter-comparison have been developed by EMPA based on WMO-GAW Report No. 97 (WCC-EMPA Report 98/5, "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements", July 2000, available on request from EMPA or downloadable from www.empa.ch/gaw). The present audit report is distributed to the station manager and the World Meteorological Organization in Geneva.

Staff involved in the audit

Mace Head	Prof. Dr. Peter Simmonds	contacts, general program
	Gerard Spain	contacts, general program, technical assistance at the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
QA/SAC Switzerland	Dr. Jörg Klausen	assistant auditor

Previous audits at the GAW station Mace Head:

- October 1996 by WCC-EMPA for surface ozone
- May 1998 by WCC-EMPA for surface ozone and carbon monoxide

3. Global GAW Site Mace Head, Ireland

3.1. Description of the Site

The Atmospheric Research Station at Mace Head (53°19'33"N 9°53'58"W, 5 m a.s.l.) is located on the west coast of Ireland, County Galway. The site offers excellent exposure to the North Atlantic with a clean air sector from 180 to 300°. The nearest major conurbation which is 90 km 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 rocks and vegetation which consists mainly of grasses and sedges. There are three small islands offshore which are within the clean air sector, and are uninhabited.

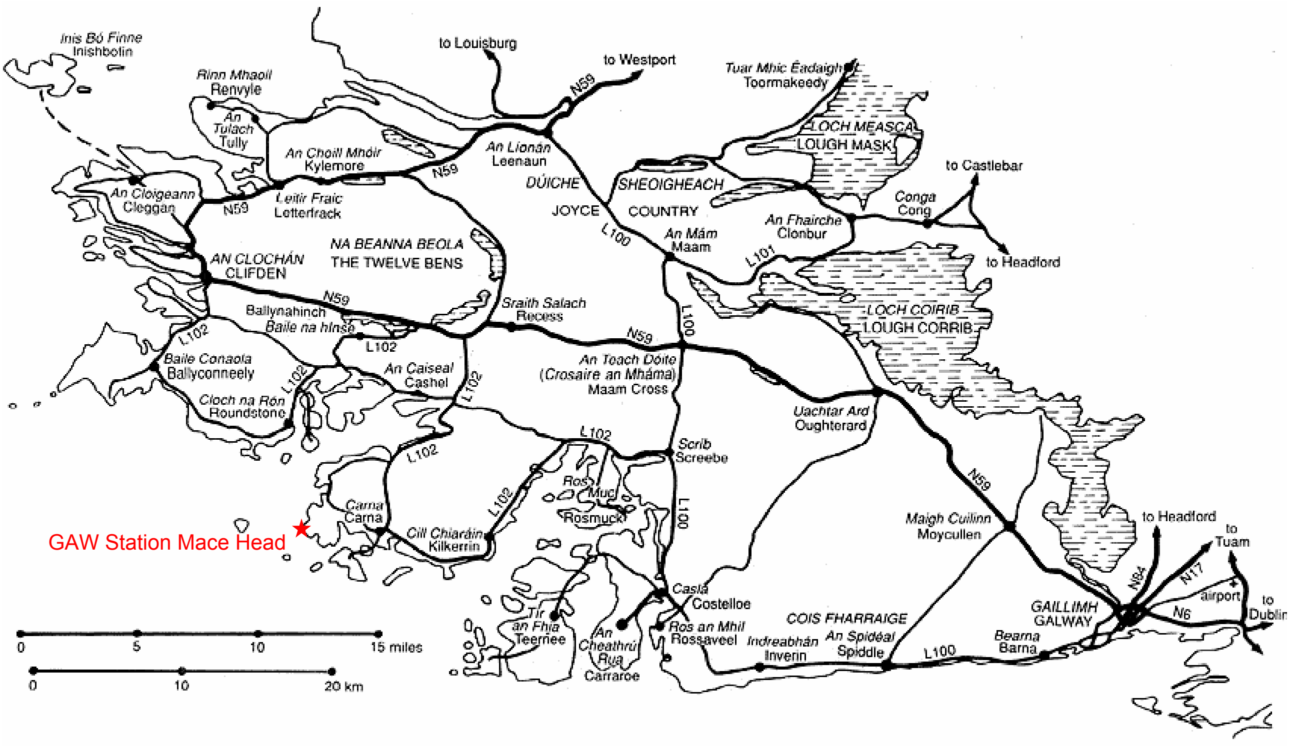

Figure 2: Map of Connemara with the location of the station at Mace Head (from www.connemara.com)

Ozone-, Carbon Monoxide and Methane Levels at Mace Head

The frequency distribution of 60 minute mean values of O_3, CO and CH_4 for 2001 are shown in Figure 3 to 5.

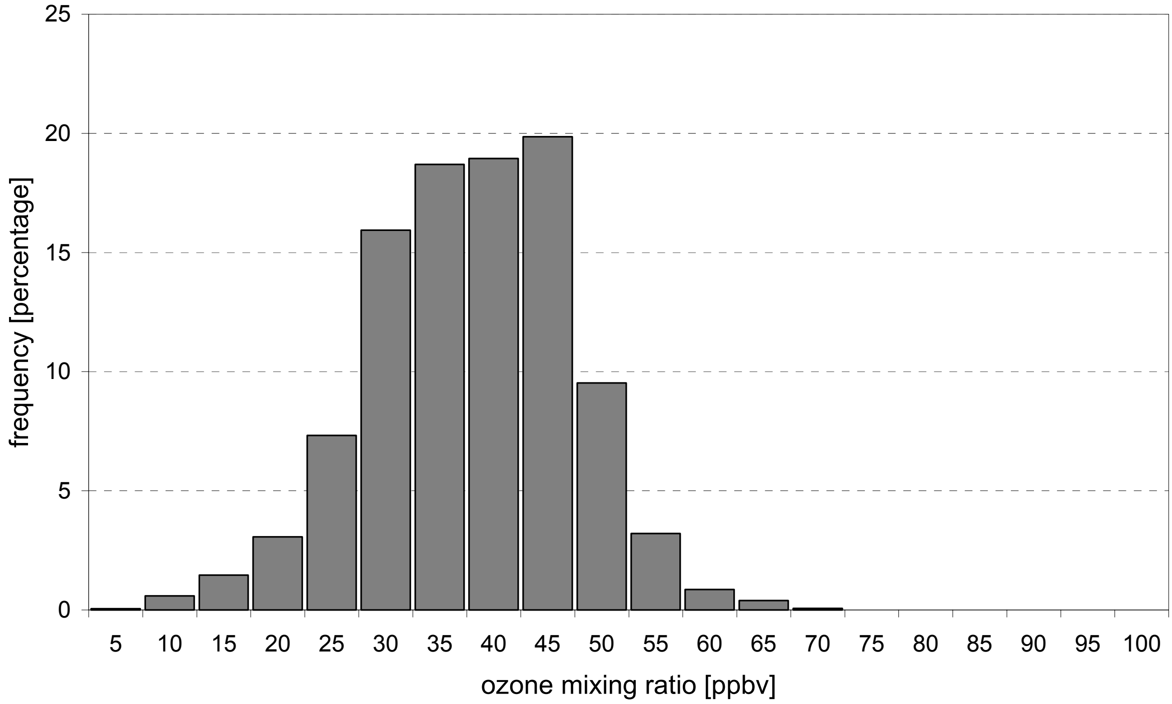

Figure 3: Frequency distribution of the 60 minutes mean ozone mixing ratio (2001) at Mace Head. Availability of data: 99.6%.

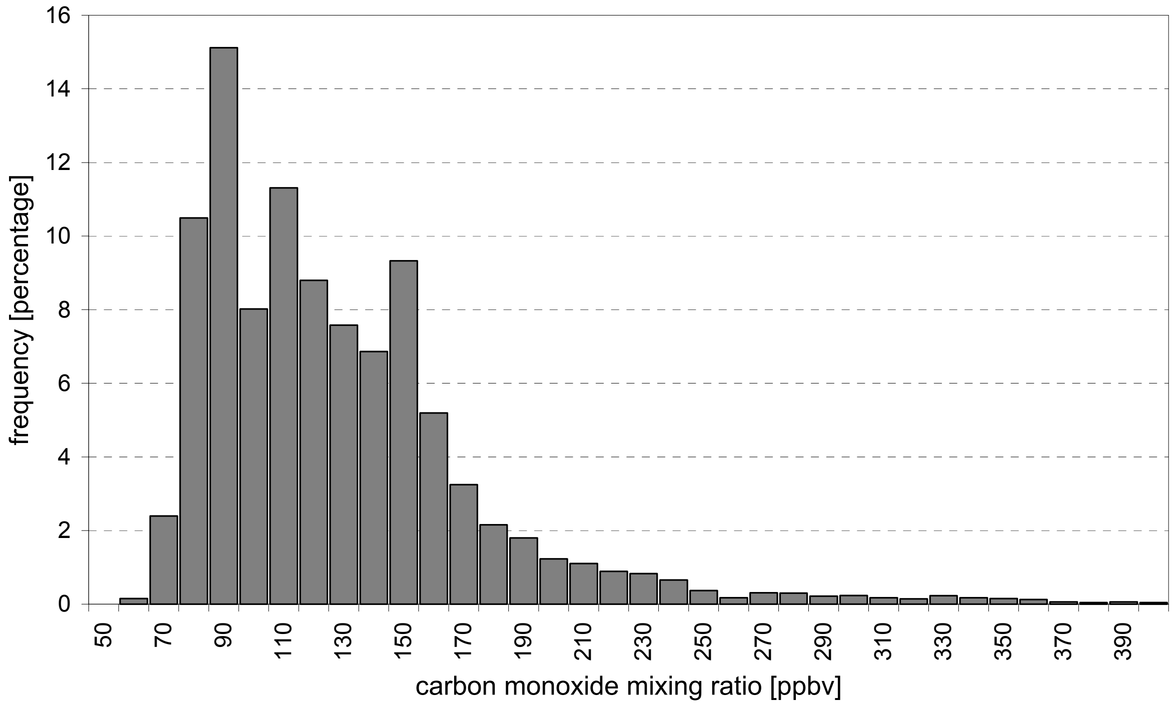

Figure 4: Frequency distribution of the mean carbon monoxide mixing ratio (2001) at Mace Head (injections every 40 minutes). Availability of data: 74.4%.

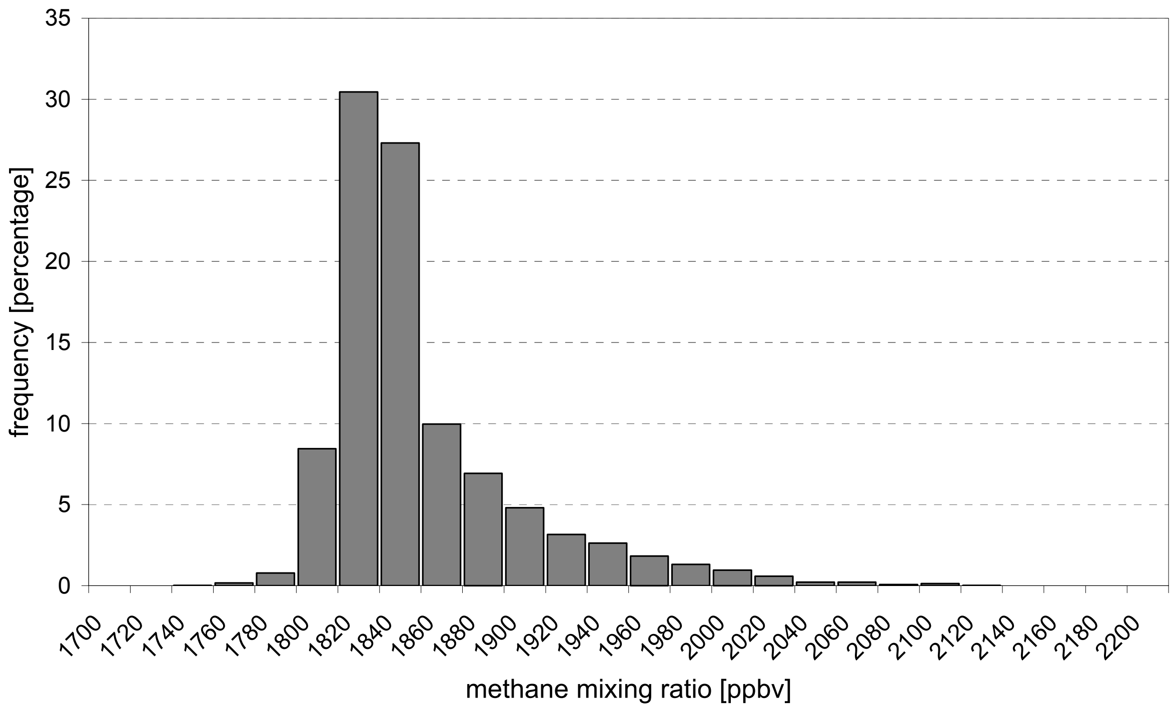

Figure 5: Frequency distribution of the mean methane mixing ratio (2001) at Mace Head (injections every 40 minutes). Availability of data: 77.4%.

3.2. Description of the Observatory

The facilities at the site consist of three laboratory buildings, one 300 m and two ~90 m from the shore, a 23 m aluminium walk-up tower and a converted 20 ft cargo container office (see Figure 6).

Comment

- The Mace Head GAW station offers spacious laboratories which meet all requirements for the measurement of air pollutants.

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Mace Head (as of August 2002)

Name	**Position and duty**
Peter G. Simmonds	Principal investigator / consultant
Gerard Spain	Station manager, atmospheric chemist
Duncan Brown	Station operator

Figure 6: View of the main laboratory buildings at the Mace Head GAW station with the 10- and 23 m towers.

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

No changes of the ozone instrument set-up were made since the last audit of WCC-EMPA in 1998.

4.1.1. Air Inlet System

Sampling-location: 3 m above ground and 1.2 meters from the wall on the seaward side of the two story laboratory building.

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 = 4.5 m, i.d. = 4 mm. Flow rate 1.4 liters per minute.

Residence time in the sampling line: approx. 3 s

Comment

The PFA tube was clean and free of dust. Materials as well as residence time of the inlet system are adequate for trace gas measurements in particular with regard to minimal loss of ozone.

4.1.2. Instrumentation

Ozone Analyser

A Monitor Labs 8810 ozone analyser is in use at the Mace Head station (Table 2). The instrument is installed inside the laboratory and is protected from direct sunlight. The laboratory is air-conditioned to 20°C.

Table 2: Ozone analyser at the Mace Head Research Station

Type	ML 8810 #437
Method	UV absorption
at Mace Head	since 1989
Range	0-500 ppb
Analog output	0-1 V
Instrument specials	internal ozone/ zero air generator

Ozone Calibrator

No ozone calibrator is available at the site. However, calibrations are performed every 3 months with a transfer standard of the National Physical Laboratory (NPL) at the site.

Operation and Maintenance

Preventive instruments maintenance includes several instrument checks (flow rate, pressure and temperature readings, lamp voltage), and adjustment of the pressure transducer is made when necessary. The instrument cells are cleaned yearly. Inlet filters are exchanged monthly or when dirty.

A full instrument calibration is done every three months by NPL.

4.1.3. Data Handling

Data Acquisition and –transfer

The data acquisition system consists of an ADC circuit board and a computer. One minute average values are stored. Back-ups of this raw data are made in regular intervals.

Data Treatment

The raw data as it was collected from the data acquisition is inspected by the station operator (time series plot, check with instrument log book). The data is corrected according to the calibrations with the NPL transfer standard for every three-months period using the calibration results before and after this period.

Data Submission

Ozone data have not been submitted to the former GAW data centre at NILU, but submission to the recently established WDC for surface ozone at JMA is planned.

4.1.4. Documentation

Logbooks

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

Standard Operation Procedures (SOPs)

The manual for the instrument is 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 for warming up for 13 hours. During this stabilisation time the transfer standard and the PFA tubing connections to the instrument were conditioned with 250 ppb ozone for 40 minutes. Afterwards, three comparison runs between the field instrument and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 7 the experimental set-up during the audit. No modifications of the ozone analyser which could influence the measurements were made for the inter-comparisons.

The audit procedure included a direct inter-comparison of the TEI 49C-PS WCC 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:	WCC: TEI 49C-PS #54509-300 transfer standard
field instrument:	ML 8810 #437
ozone source:	WCC: TEI 49C-PS, internal ozone generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellows pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	16-channel ADC with acquisition software
pressure transducer readings:	TEI 49C-PS (WCC): 1017.9 hPa adjusted to ambient pressure (1022.9 hPa) before the inter-comparison. ML 8810 #437: 1015.7 hPa (no adjustment made)
concentration range	0 - 100 ppb
number of concentrations:	5 plus zero air at start and end
approx. concentration levels:	10 / 20 / 30 / 50 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on 22. August 2002
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

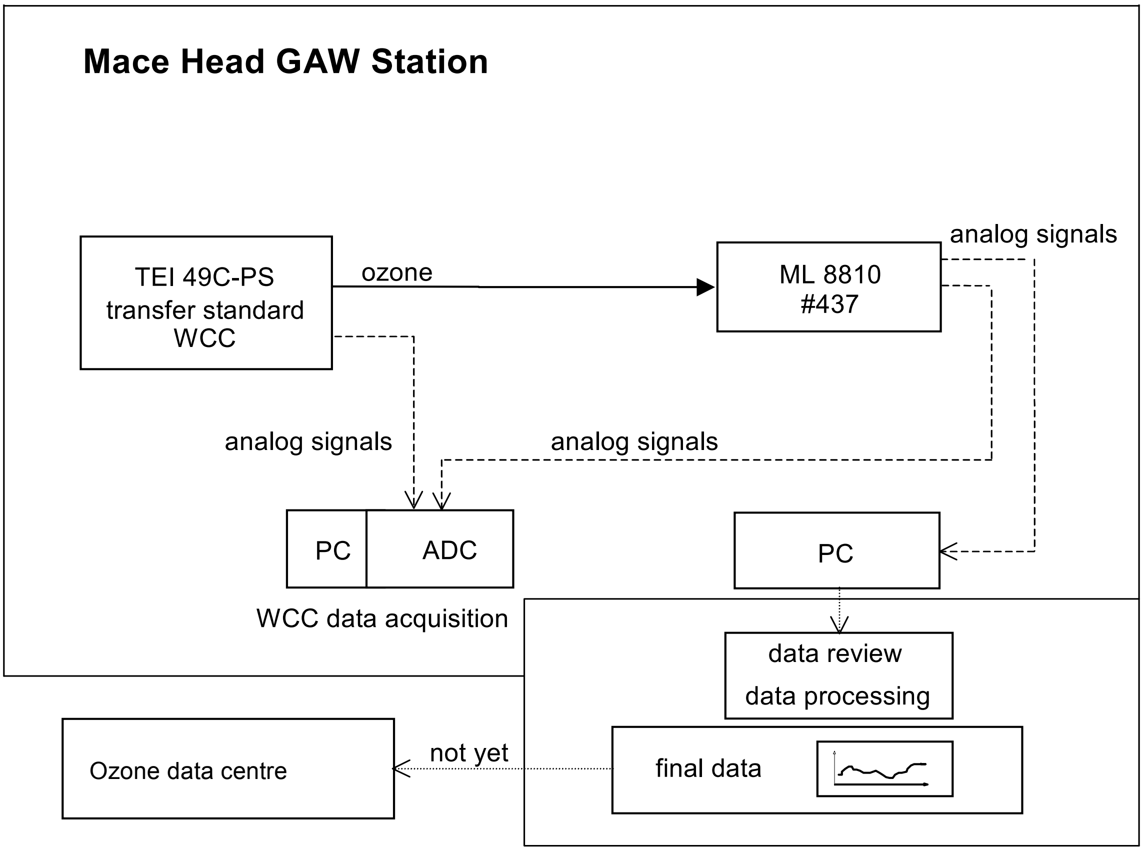

Figure 7: Experimental set up for the ozone inter-comparison

4.2.2. Results

Ozone Analyser

The results comprise the inter-comparison between the ML8810 #437 field instrument and the WCC transfer standard TEI 49C-PS, carried out on 22. August 2002.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Table 4. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 8 and 9 show the residuals of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The residuals versus the run index are shown in Figure 8 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 9 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 10).

The data used for the evaluation was recorded by both EMPA and Mace Head data acquisition systems. This raw data was treated according to the usual station method based on the last inter-comparison with the NPL transfer standard. Corresponding to this procedure, the ozone concentration was calculated from the raw voltage reading of the ML8810 by the following equation (based on the inter-comparison with NPL from 15.08.02):

ML8810 O_3 [ppb] = (Analog Output [mV] –2.0175) / 2.0339

The non-linearity of the ML8810 in the low concentration range is a well know problem. The zero points are shown in Table 4, but were excluded for the further interpretation of the inter-comparison result. The problem of non-linearity close to the zero point was recognised during the first audit by WCC-EMPA in 1996. Due to the fact that ozone concentrations below 5 ppb are almost never observed at Mace Head, the accuracy at low concentrations is of minor importance.

Table 4: Inter-comparison of the ozone field instrument

	TEI 49C-PS		**ML 8810 #437**			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
	0.3	0.13	1.9	0.92	1.6	
1	10.0	0.10	10.3	2.19	0.3	2.6%
2	30.0	0.11	29.2	1.41	-0.8	-2.7%
3	90.0	0.12	89.6	1.84	-0.5	-0.5%
4	20.1	0.11	20.0	1.89	-0.1	-0.3%
5	50.0	0.12	49.6	1.58	-0.4	-0.8%
	0.2	0.13	2.2	0.91	2.0	
	0.2	0.16	2.5	1.69	2.3	
6	90.1	0.13	89.0	1.60	-1.1	-1.2%
7	50.1	0.13	50.5	1.48	0.5	0.9%
8	10.1	0.08	10.5	1.37	0.4	3.5%
9	20.1	0.14	21.3	1.39	1.2	5.8%
10	30.1	0.08	29.1	1.43	-1.0	-3.3%
	0.2	0.13	1.9	1.47	1.7	
	0.3	0.07	2.6	1.30	2.3	
11	30.0	0.10	29.1	1.00	-0.9	-2.9%
12	10.0	0.12	11.2	1.13	1.1	11.3%
13	49.9	0.16	50.4	1.12	0.5	1.0%
14	20.1	0.08	20.2	2.04	0.2	0.8%
15	90.0	0.13	89.8	1.96	-0.2	-0.2%
	0.3	0.14	3.1	1.00	2.8	

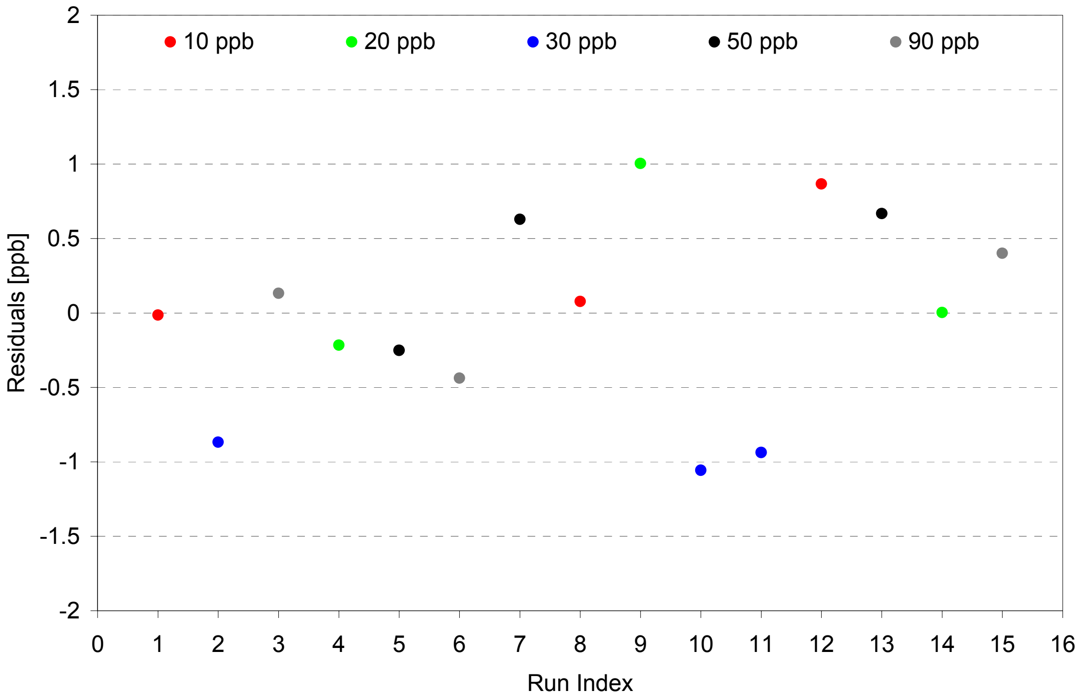

Figure 8: Residuals to the linear regression function (ML8810 #437) vs the run index (time dependence)

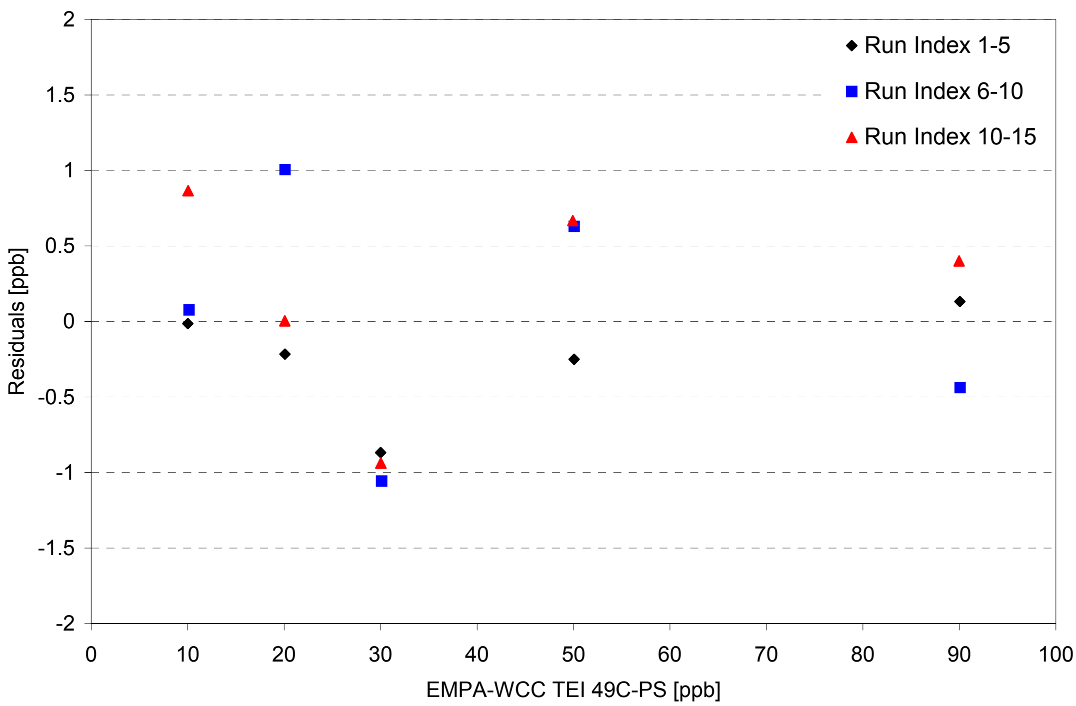

Figure 9: Residuals to the linear regression function (ML8810 #437) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the ML8810 #437 field instrument with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 10-100 ppb ozone) is:

ML8810 #437:

$$\text{ML8810 \#437} = 0.989 \times \text{TEI 49C-PS} + 0.39 \text{ ppb}$$

ML8810 #437= O3 mixing ratio in ppb, determined with ML8810 #437

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.006	(f = 13) f = degree of freedom
	- offset S_b in ppb	0.30	(f = 13)
	- residuals in ppb	0.48	(n = 15)

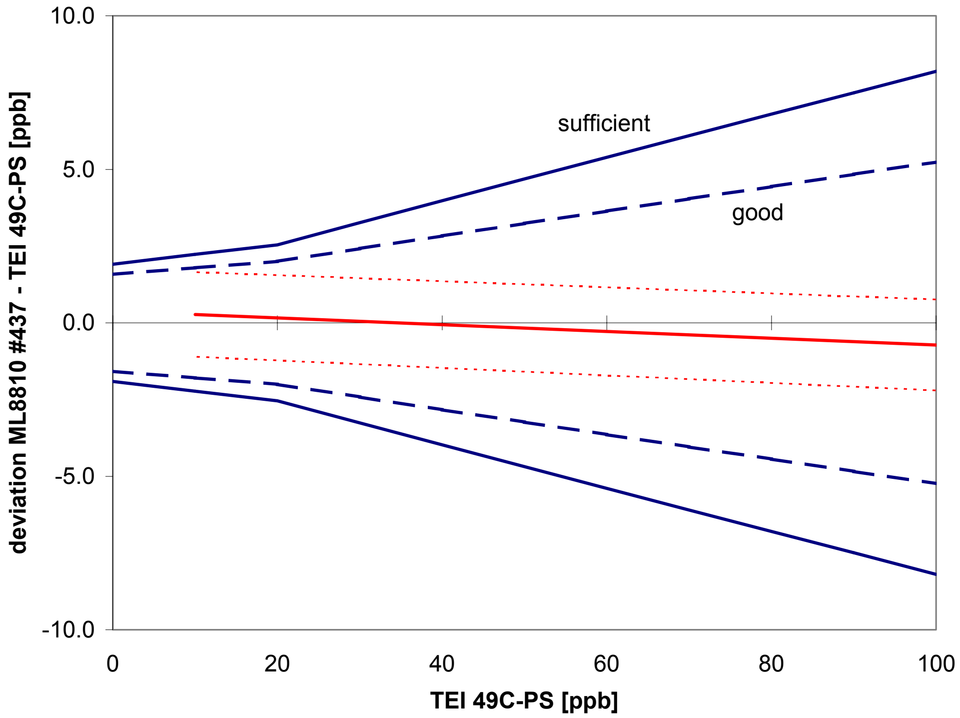

Figure 10: Inter-comparison of instrument ML8810 #437

Comment

The ozone concentrations observed at Mace Head (2001) ranged between 20 and 50 ppb (5- and 95-percentile of 60 min mean values). The ML8810 fulfils the assessment criteria of “good” over the tested range between 10 and 100 ppb ozone. However, the instrument was very unstable, which caused the large prediction interval in Figure 10. The problem of insufficient stability was also recognised during the audit of 1996, but a re-location of the instrument to the present location improved the instrument stability during the 1998 audit. The analyser is now 15 years old, and a replacement should be considered.

4.3. Recommendation for the Ozone Measurements

The ML8810 ozone instrument at Mace Head fulfils the assessment criteria as "good" over the tested range of 10 to 100 ppb. However, the instrument is very unstable. Considering the age of the instrument and the linearity problem in the low concentration range, a replacement of the monitor by a more modern model should be considered.

Submission of the ozone data to the recently established GAW data centre for surface ozone at JMA is encouraged.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Mace Head in 1989 and a continuos time series is available since then. A first audit for carbon monoxide measurements was conducted by WCC-EMPA in 1998.

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-fritte, 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

Comment

The inlet system is adequate for analysing CO and CH_4 concerning materials and residence time.

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

instrument	Trace Analytical Inc.
model, S/N	RGA3, S/N 090189-010 ANE 294
at Mace Head	since 1989
configuration	E-001 (Trace Analytical terminology)
method	GC / HgO Detector
loop	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
analog 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

Gas Standards

Table 6 shows the gas standards that are used for the verification of the measurements. A cylinder calibrated against the Australian CSIRO scale is available at the site to serve as a working standard. This working standard is exchanged every 6 to 8 months, and re-calibrated after use. The working standard is injected alternating with ambient air every 20 minutes. The other standards available at the site are used less frequent, e.g. for linearity checks. Traceability to the CMDL scale is not given.

Table 6: Station CO cylinders

Gas cylinder	Description	Conc. [ppb]
J-062	Working standard provided by SIO, calibrated against CSIRO Australia standards	147.3
G-050	CSIRO Australia, Cape Grim, real air standard	59.0
G-055	CSIRO Australia, Cape Grim, real air standard	134.0
No. 49177	Synthetic air standard , verified with NDIR (365 ppb) and CSIRO (364 ppb)	365.0
No. 55604	Synthetic air standard , used for dilution purpose – linearity check, verified with NDIR	600.0
CLM 005557	Scott Speciality Gases, NIST SRM certified, verified with NDIR, synthetic air	1003.6

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).

Comment

- CO analysis by GC followed by mercury reduction detection is a sophisticated method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision. Unfortunately, the detectors are not perfectly linear.

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 Scripps Institution of Oceanography (SIO). All the chromatograms are stored and automatically transferred twice daily via modem/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 of data reviewing 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 practically oriented 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 factor. This parameter is evaluated from the pre- and post-analysis of the working standard cylinder at SIO. During 6-monthly meetings of the AGAGE members the data is further discussed regarding scientific aspects and is finalised.

Data Submission

For scientific reasons data have been submitted to different teams. To date only a few monthly mean values (until 1993) have been submitted to the GAW WDC for greenhouse gases in Tokyo.

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.

Standard Operation Procedures (SOPs)

The manual for the instrument 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.

5.2. Inter-comparison of the in-situ Carbon Monoxide Analyser

5.2.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CO measurements until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CO audits.

The five transfer standards of the WCC (concentration range 70-310 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 scale at EMPA before and after 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 between 8 and 12 times in the period from 22. to 26. August 2002. No modifications of the RGA-3 carbon monoxide analyser were made for the inter-comparison. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the station operators during the audit. The experimental details are summarised 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:	AGAGE GC control software
approx. concentration levels:	70 to 310 ppb
injections per concentration:	8 to 12

5.2.2. Results

The CO concentrations determined by the RGA-3 field instrument for the five WCC transfer standards are shown in Table 8. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 11 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (conventional true value). The WCC TS were calibrated before and after the audit against the CMDL scale (Reference: CMDL CA02854, 295.5 pbb) with the 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 injection of the transfer standards at Mace Head. The data of the RGA-3 field instrument were processed during the audit by the station operators and are based on calibration of the instrument against the working standard available at the site.

Table 8: Carbon monoxide inter-comparison measurements at Mace Head

No.	WCC standard	Mace Head analysis (RGA-3, Peak Height)				
	conc. ± 1σ (N)	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	71.6 ± 0.8 (107)	60.7	0.3	9	-10.9	-15.2
2	75.5 ± 0.9 (109)	64.1	1.3	8	-11.4	-15.1
3	99.2 ± 1.1 (110)	89.7	0.7	10	-9.5	-9.6
4	159.8 ± 0.7 (142)	151.4	0.8	12	-8.4	-5.3
5	310.3 ± 1.4 (134)	320.5	8.5	9	10.2	3.3

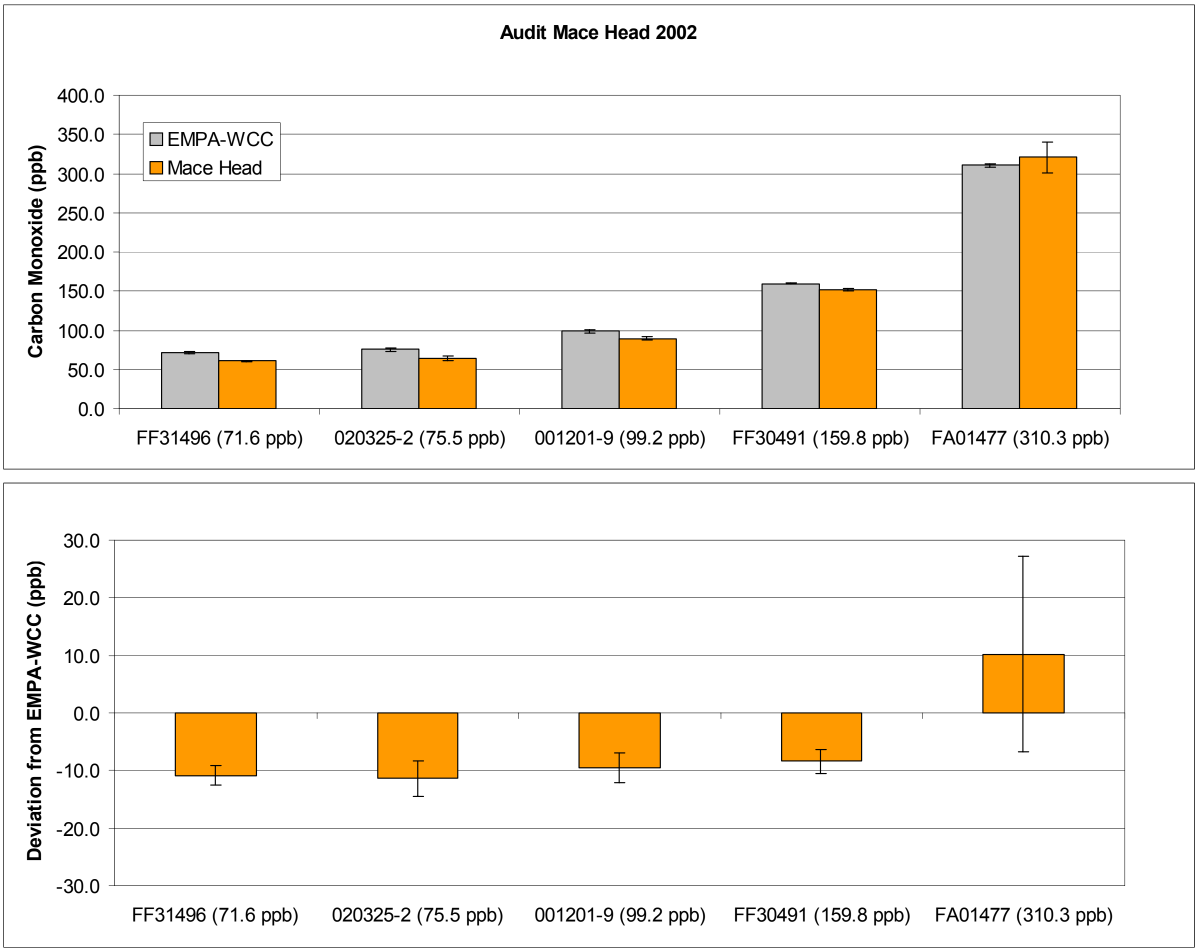

Figure 11: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mace Head (orange). lower panel: deviation of the Mace Head station from the conventional true value. The error bars represent the 95% confidence interval.

5.3. Discussion of the Inter-comparison Results

Concentrations < 200 ppb

The analysis of the WCC-EMPA transfer standards by the station resulted in significantly lower values (8.4 to 11.4 ppb) for the concentrations below 160 ppb compared to the conventional true value. The transfer standards of WCC-EMPA are traceable to the CMDL scale (see Appendix III). This scale was revised by Paul Novelli in 2000, and significant corrections were made. All transfer standards of WCC-EMPA were calibrated using the 194.7 ppb and 295.5 ppb CMDL CO standards with an Aerolaser AL5001 CO instrument. Measurements of the lower WCC-EMPA CMDL standards using the above standards as a reference also result in higher findings (2.6 to 3.9 ppb) in comparison to the CMDL certificates.

During the audit in 1998, WCC-EMPA referred to the “old” CMDL scale. The results were then significantly better in comparison to WCC-EMPA. Considering the changes of the CMDL scale and the fact that WCC-EMPA calibrations using the 194.7 ppb and 295.5 ppb CMDL standards result in higher concentrations compared to CMDL, the results of this audit reflect mainly the change of the CO scale. However, the differences between WCC-EMPA and Mace Head are high, and further investigation is needed to re-solve this problem.

Concentrations > 300 ppb

The WCC-EMPA transfer standard with approx. 300 ppb CO was the same as during the 1998 audit. Using the new CMDL scale, a value of 310.3 ppb was assigned by WCC-EMPA for this cylinder (old scale 1998: 297.8 ppb). Analysis by Mace Head resulted in 320.5 ± 8.5 ppb (1σ) (1998: 294.0 ± 0.6 ppb). Although a small drift of the CO concentration in the cylinder can not be excluded, a significant difference is observed between the 1998 and 2002 audits.

5.4. Recommendation for Carbon Monoxide Measurements

Since the major problem for the CO measurements seems to be the uncertainty of the CO scale, WCC-EMPA can only make minor recommendations, which can be summarised as follows:

- Continuation of the measurements at Mace Head using various standards for calibrations and consistency checks is encouraged.
- The RGA instrument used at Mace Head seems to show a rather linear response for concentrations up to 160 ppb. Linearity checks with the dilution system and other standards for concentrations up to 300 ppb are encouraged.
- Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended as soon as the issue of the CO scale is solved.

5.4. Changes after the audit

A full re-calibration of the system was planned for the time after the audit. However, until the date of the finalisation of the present report, no new CO values have been reported to WCC-EMPA. It is expected that part of the differences found between WCC-EMPA and Mace Head should disappear after this re-calibration.

6. System-and Performance Audit for Methane

Methane measurements became operational at Mace Head in 1987. The average CH_4 concentration measured at Mace Head increased from approx. 1760 ppb to over 1840 ppb since then. Since such a long time series is available from Mace Head, the continuation of these measurements at Mace Head is of great importance.

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)

Comment

The inlet system is adequate for analysing CH_4 concerning materials and residence time.

6.1.2. Analytical System

Gas chromatograph

A CARLE 100A gas chromatograph with an FID detector is used for ambient methane measurements at Mace Head. Instrument details are summarised in Table 9.

Table 9: 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: 61°C
calibration interval	working standard every 40 min
instrument specials	8 seconds before injection, the flow through the loop is stopped to equilibrate pressure.

Gas Standards

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-062) was assigned with a CH_4 concentration of 1826.29 ppb. No additional CH_4 standards are available at the site.

Operation and Maintenance

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

6.1.3. 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 modem/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 of data reviewing 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 daily 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 practically oriented 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 factor. This parameter is evaluated from the pre- and post-analysis of the working standard cylinder at SIO. During 6-monthly meetings of the AGAGE members the data is further discussed regarding scientific aspects and is finalised.

Data Submission

Data are submitted to the GAW World Data Centre for Greenhouse Gases at JMA.

6.1.4. Documentation

Logbooks

An electronic logbook is available for the methane GC. 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

Since no Standard Operation Procedure (SOP) has been established for CH_4 measurements until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CH_4 audits.

The five transfer standards of the WCC (approx. concentration range 1630 - 2010 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate for 12 hours. The transfer standards were calibrated against CMDL laboratory standards (CA04462, CA04580) at EMPA before and after 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 12 times and analysed between 22. and 26. August 2002. No modifications of the GC system were made for the inter-comparison. The data was acquired by the station software. This data (mean values and standard deviations) was processed during the audit by the station operator. The experimental details are summarised in Table 10.

Table 10: Experimental details of the methane inter-comparison

field instrument:	CARLE 100A, S/N 40647
reference:	5 WCC-EMPA transfer standards
data acquisition system:	AGAGE GC control software
approx. concentration levels:	concentration range approx. 1630 – 2010 ppb
injections per concentration:	5 to 12

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 11. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 12 shows the absolute differences (ppb) between the measurements of the CARLE 100A GC and the WCC transfer standards (TS) (conventional true value). 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 working standard.

Table 11: Methane inter-comparison measurements at Mace Head

No.	**WCC standard**	**Mace Head analysis** (CARLE 100A **GC-FID, Peak Height)**				
	conc. ± 1σ (N)	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1633.1 ± 5.9 ppb (14)	1634.9	3.0	7	1.8	0.1
2	1725.4 ± 3.8 ppb (20)	1729.7	5.4	5	4.3	0.2
3	1817.0 ± 3.7 ppb (19)	1820.2	0.6	8	3.2	0.2
4	1820.7 ± 4.3 ppb (19)	1822.0	3.4	12	1.3	0.1
5	2006.8 ± 2.6 ppb (20)	2014.8	1.5	7	8.0	0.4

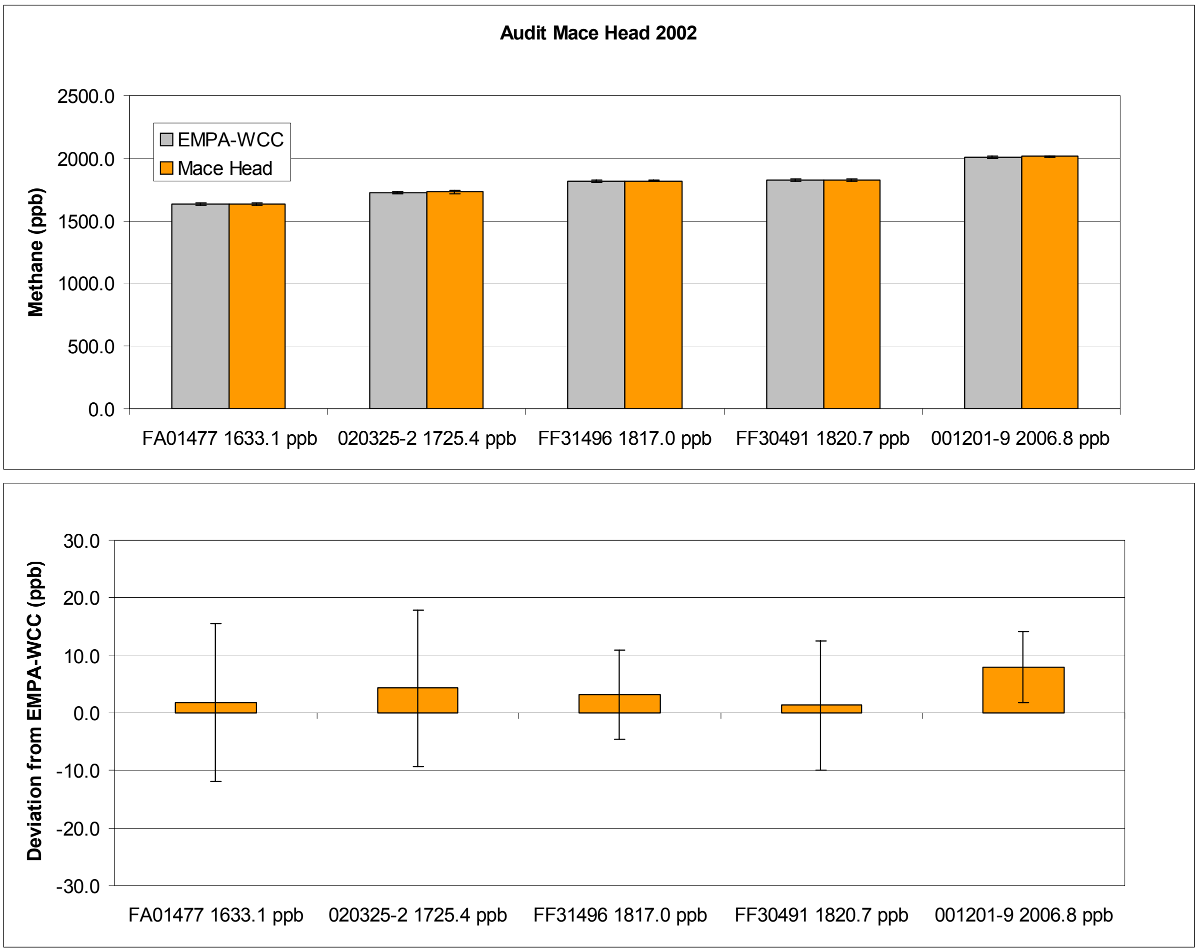

Figure 12: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix IV) measured with the GC system of Mace Head (orange).
lower panel: deviation of Mace Head from the conventional true value.
The error bars represent the 95% confidence interval.

Comment

The CH_4 concentrations of the WCC-EMPA transfer standards as obtained with the Mace Head field instrument agrees very well with the conventional true value in the concentration range between 1630 and 2010 ppb methane. The deviation from the transfer standards is less than 0.4 %. Thus, the Mace Head methane measurements can be considered to be fully traced to the GAW reference standards.

6.3. Recommendation for the Measurement of Methane

The good result of the inter-comparison measurements show that the whole measurement system, beginning at the air inlet and ending at the data treatment is appropriate for the measurement of methane. Therefore no further technical recommendations are made by the WCC.

7. Conclusions

The global GAW station Mace Head is a well-established site within the GAW programme, and long time series of high quality exist for ozone, carbon monoxide, methane and other parameters. An excellent platform for extensive atmospheric research is available at the site.

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 and methane, but a replacement of the ozone analyser should be considered due to its rather poor stability.

The results of the CO inter-comparison showed significant differences between WCC-EMPA and Mace Head. Part of this can be explained by the recent revision of the CO scale by CMDL. However, further investigation is needed to re-solve this problem.

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 13. 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.

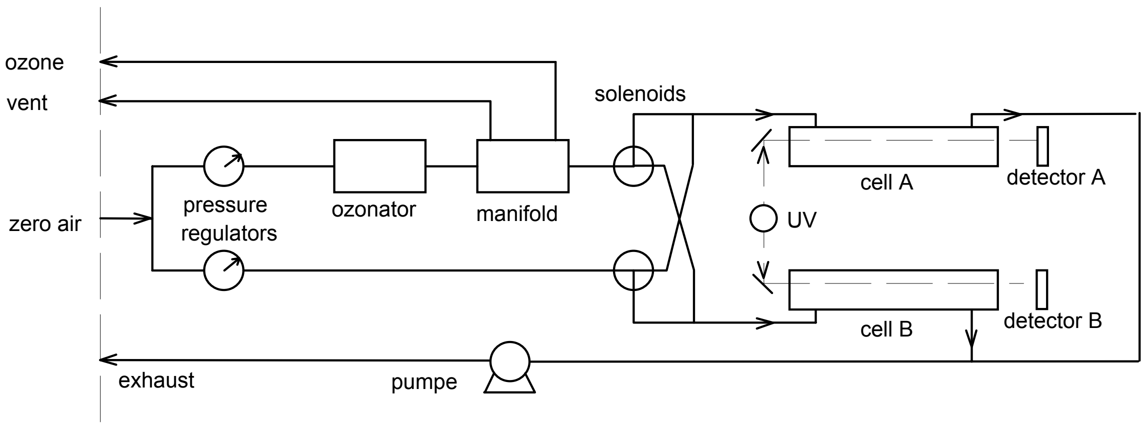

Figure 13: Flow schematic of TEI 49C-PS

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 summarised in Table 12 and Figure 14.

Table 12: 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:	Pressurised air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

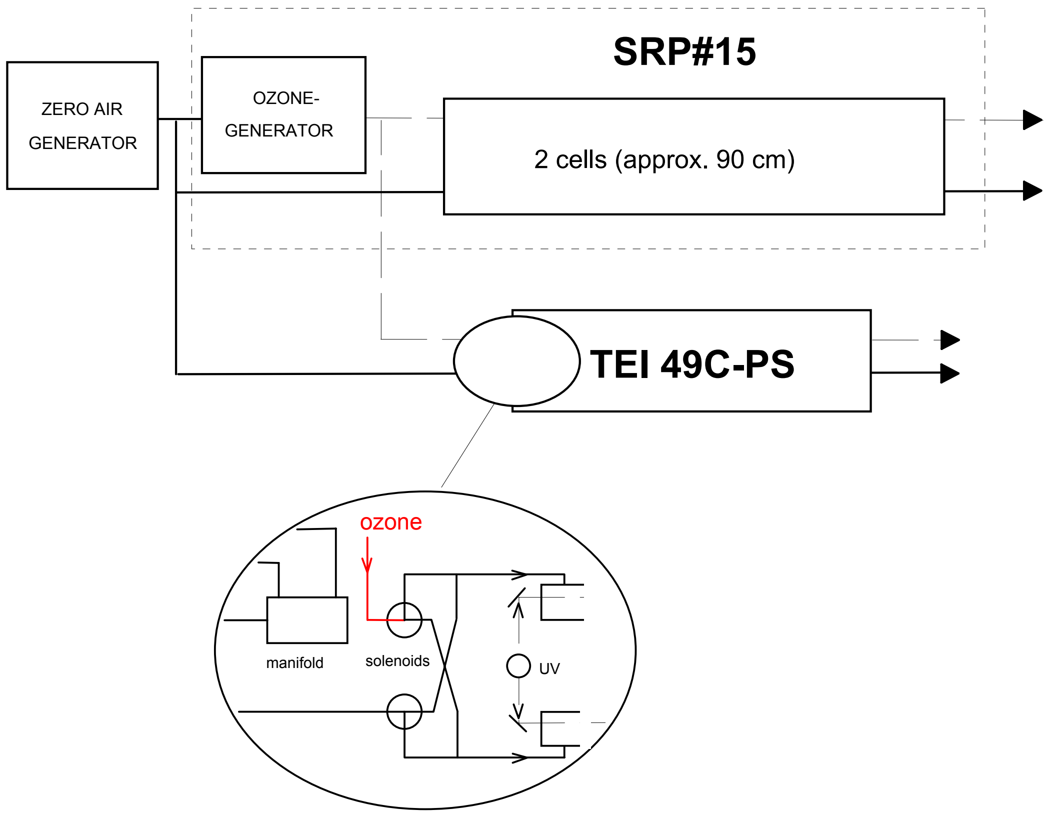

Figure 14: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard was thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the WCC-O_3 (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to approximately $\pm$(1 ppb + 0.5%).

Figures 15 and 16 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. The results show that the EMPA transfer standard fulfilled the recommended criteria for the period of the audit, including transportation.

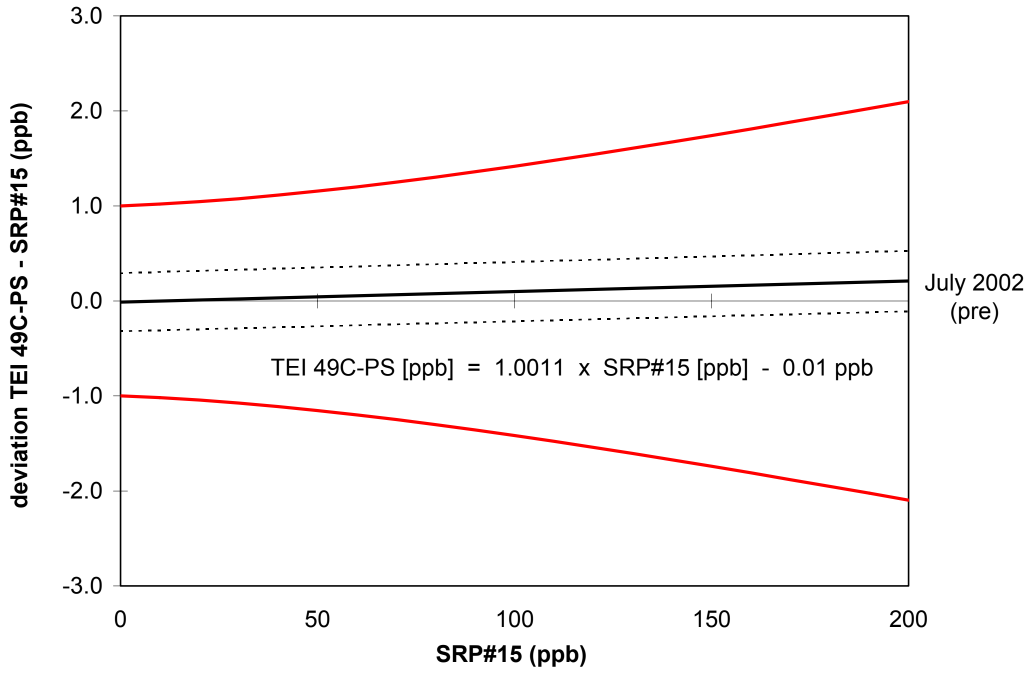

Figure 15: Transfer standard before audit

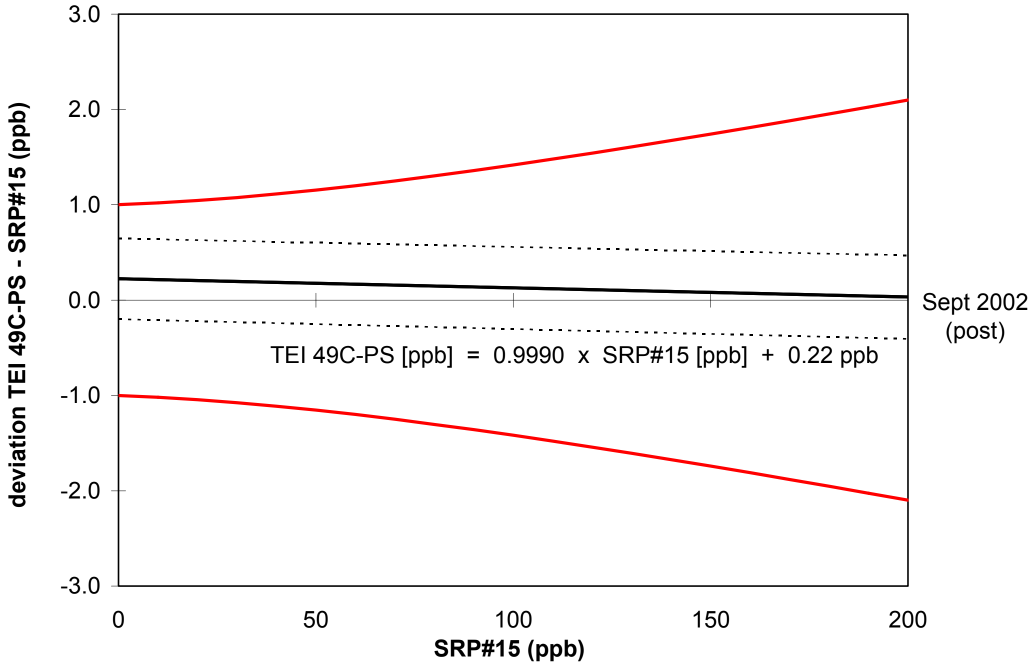

Figure 16: Transfer standard after audit

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 programme. The standards used at the WCC are listed in Table 13:

The CO scale of the CMDL was recently revised. WCC-EMPA refers to the **new** scale. The WCC-EMPA transfer standards used during the audit are listed in Table 14.

Table 13: 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 old scale*	CMDL new scale**	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard (")	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	CA02854

* Certificates from 5.8.97 (97.6, 189.3, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)
** Revised scale (by P. Novelli), re-calibrated at CMDL, 23.01.01

Table 14: CO transfer standards of the WCC (average of calibrations from July 02 and September 02). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL new scale CA02854) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	71.1 ± 0.7 ppb	72.1 ± 0.4 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	75.0 ± 0.9 ppb	76.0 ± 0.5 ppb	020325-2
WCC Transfer Standard (2 l cylinder)	98.4 ± 0.6 ppb	99.9 ± 0.8 ppb	001201-9
WCC Transfer Standard (6 l cylinder)	159.5 ± 0.7 ppb	160.1 ± 0.6 ppb	FF30491
WCC Transfer Standard (6 l cylinder)	308.9 ± 1.7 ppb	311.6 ± 1.0 ppb	FA01477

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 programme. The CMDL standards used at the WCC are listed in Table 15. The WCC-EMPA transfer standards (Table 16) are traced back to the CMDL standards shown below.

Table 15: CMDL CH_4 Standards at the WCC. 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)	1795.1 ± 0.19 ppb	CA04462
CMDL Laboratory Standard (")	1882.0 ± 0.24 ppb	CA04580

* Certificates from 13.09.2000

Table 16: WCC CH_4 transfer standards (average of calibrations from July 02 and September 02). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards CA04462 and CA04580)		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	1631.7 ± 5.5 ppb	1634.5 ± 6.3 ppb	FA01477
WCC Transfer Standard (2 l cylinder)	1723.0 ± 2.6 ppb	1727.7 ± 3.5 ppb	020325-2
WCC Transfer Standard (2 l cylinder)	1816.4 ± 2.7 ppb	1817.5 ± 4.6 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	1821.3 ± 2.7 ppb	1819.9 ± 5.6 ppb	FF30491
WCC Transfer Standard (6 l cylinder)	2005.3 ± 2.7 ppb	2008.3 ± 1.2 ppb	001201-9