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 02/4

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE AT THE GLOBAL GAW STATION CAPE GRIM

AND

ASSESSMENT OF THE CARBON MONOXIDE SCALE AT CSIRO ASPENDALE

AUSTRALIA, NOVEMBER / DECEMBER 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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C SERVIZIO SVIZZERA DI TARURA
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1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Cape Grim from 26. November to 3. December 2002 by the World Calibration Centre (WCC) for surface ozone, carbon monoxide and methane. It was the first audit by WCC-EMPA at Cape Grim. Following up the audit further investigations of the carbon monoxide scale was made at CSIRO Aspendale to assess uncertainties of the carbon monoxide measurements. The results of the audit can be summarised as follows:

System Audit of the Observatory

The Cape Grim 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).

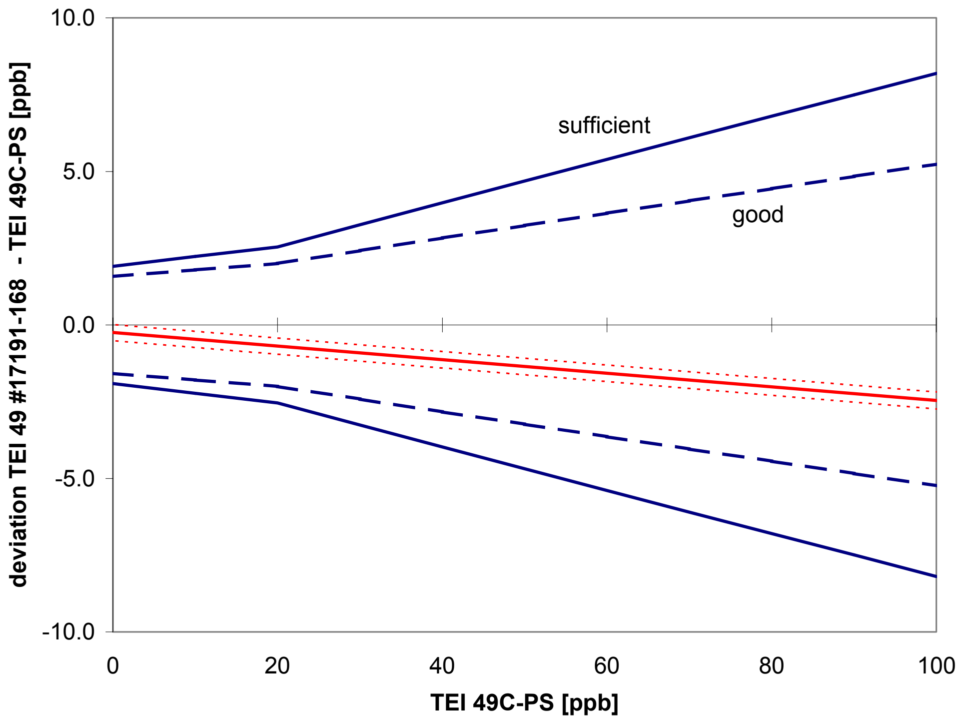

Figure 1: Inter-comparison of the TEI 49 #17191-168 field instrument with the WCC transfer standard

The lower readings of the station analyser compared to the WCC-EMPA transfer standard confirmed a comparison of the instrument performed at NIST in 1986. Since then no further comparisons of the instrument with external standards were performed. Further inter-comparisons were made with the station calibrator (TEI 49PS #AOC-10687) and the second ozone analyser (ML 9810 #327B-125). The results obtained with these instruments were similar as for the main ozone instrument, although a poorer stability was observed for the Monitor Labs instrument.

Audit of the Carbon Monoxide Measurement

The results of the inter-comparisons between the five WCC-EMPA transfer standards and the RGA/RGD-2 system of the Cape Grim station showed a difference of 1.8 to 8.8 ppb (2.8 to 5.2% lower readings of the Cape Grim analyser) in the concentration range of 35 to 230 ppb. The differences can 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 Cape Grim station showed good agreement over a concentration range of 1690 to 1950 ppb. The deviation was within ±0.1 %. No further recommendations are suggested by WCC-EMPA concerning methane measurements.

CO scale inter-comparison at CSIRO

The eight transfer standards of WCC-EMPA were also analysed at CSIRO Aspendale. Furthermore, several primary and a set of surveillance standards of CSIRO were analysed by WCC-EMPA using an Aerolaser AL5001 UV-Fluorescence instrument. A linear relationship between WCC-EMPA and CSIRO was observed, with lower findings of CSIRO of approximately 3 to 4 %.

Conclusions

All measurements of the audited parameters (O_3, CO, CH_4) at Cape Grim 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.

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

Inter-comparisons of the CO scales resulted in a linear relationship between CSIRO and WCC-EMPA. These results are a first step towards re-solving of remaining inconsistencies and uncertainties of the carbon monoxide scale.

Dübendorf, 4. November 2003 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Station Cape Grim** is part of Australia's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory at Cape Grim 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 Centre** (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 officer in charge, Dr. Neil Tindale of the Bureau for Meteorology (BOM), and the principal investigators from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Atmospheric Research, Dr. Paul Steele (CO and CH_4) and Dr. Mick Meyer (O_3), a **system and performance audit** at the Cape Grim observatory was conducted by WCC-EMPA between 26. November and 3. December 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, CSIRO and the World Meteorological Organization in Geneva.

Staff involved in the audit

Cape Grim	Dr. Neil Tindale	contacts, general program
	Laurie Porter	technical assistance at the observatory
CSIRO	Dr. Paul Steele	contacts, general program technical assistance at the observatory
	Ian Galbally	contacts, general program, technical assistance at the observatory
	Sarah Lawson	technical assistance at the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
	Dr. Stefan Reimann	assistant auditor

Previous audits at the GAW station Cape Grim:

- None

3. Global GAW Site Cape Grim, Australia

3.1. Description of the Site

The Cape Grim Baseline Air Pollution Station (CGBAPS) (40°40'56"S;144°41'18"E) is located on a cliff-top (approximate elevation 90 m a.s.l.) near the northern end of the west coast of Tasmania, overlooking the Southern Ocean. The building is on a small block surrounded by an additional 500 ha of grazing land known as the buffer zone. A small area within and next to the building is leased to a telecommunications company and its 74 m tower is used by the station. The buffer zone is surrounded by a 22,000 ha used for sheep, beef and dairy farming. From the station, the baseline sector is 190-280 degrees. Winds from this sector occur about 35 % of the time. The station is supported by an office in Smithton and laboratories in Melbourne. Further information on station specifications, site plan, and program summaries are given in the station's annual report (Baseline), available on request.

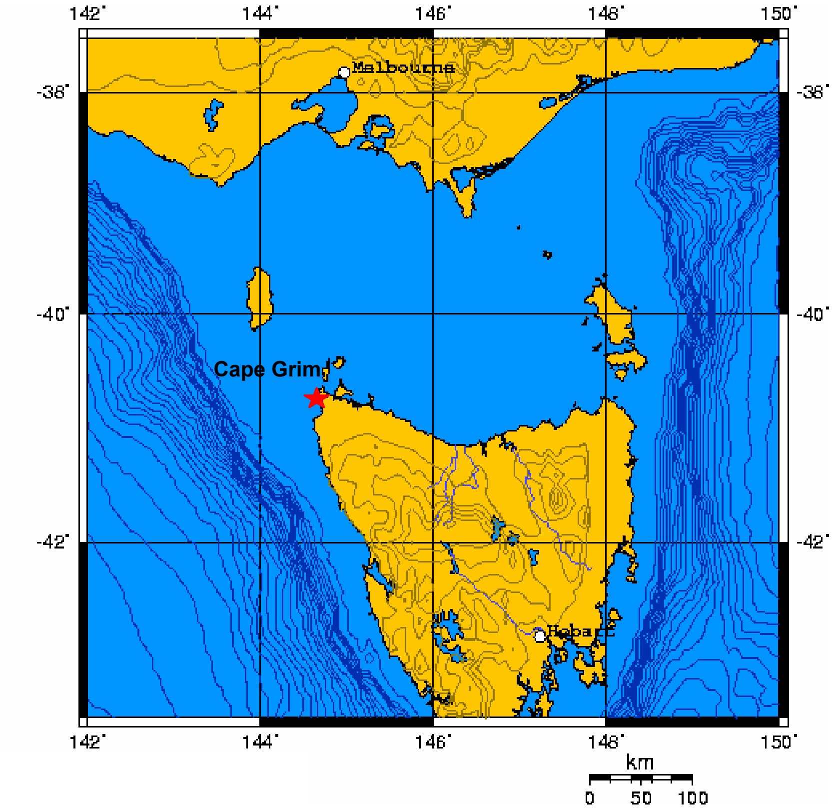

Figure 2: Map showing location of the Cape Grim station (from www.aquarius.geomar.de/omc/)

Ozone-, Carbon Monoxide and Methane Levels at Cape Grim

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

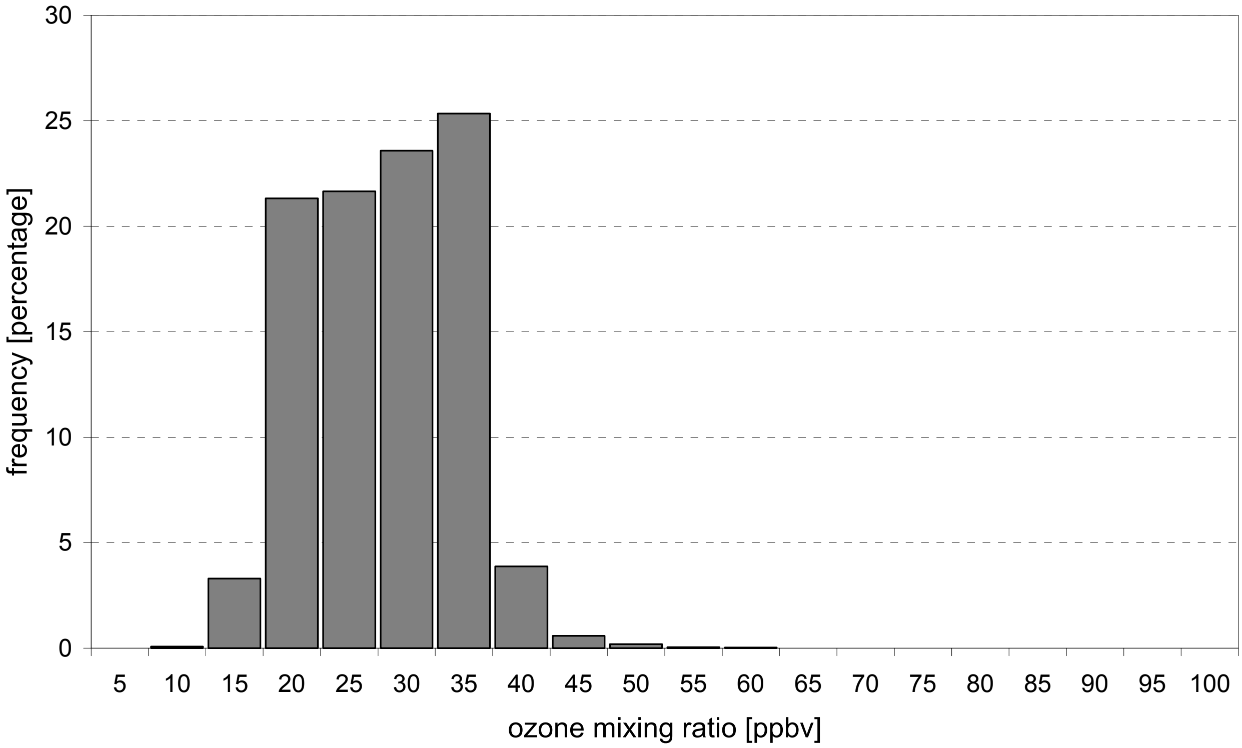

Figure 3: Frequency distribution of the 60 minutes mean ozone mixing ratio (2001) at Cape Grim. Availability of data: 90.2%.

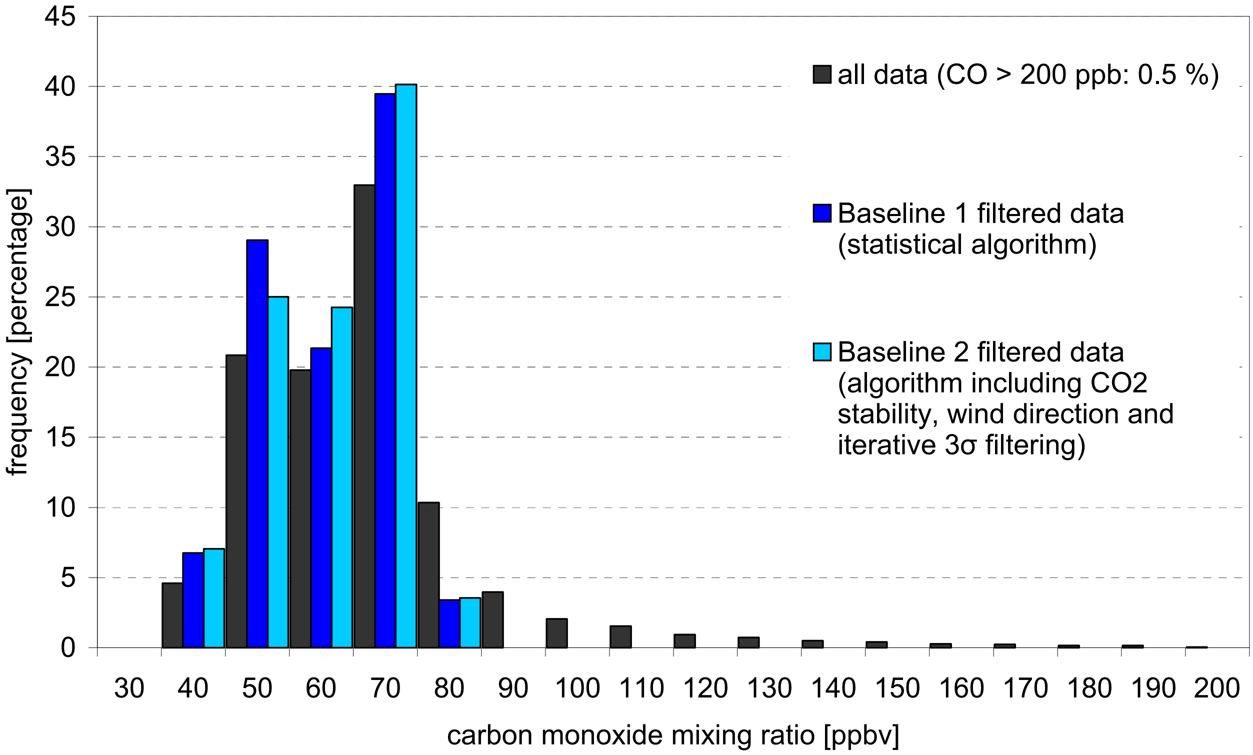

Figure 4: Frequency distribution of the mean carbon monoxide mixing ratio (2001) at Cape Grim (injections every 40 minutes). Availability of data: 74.4%.

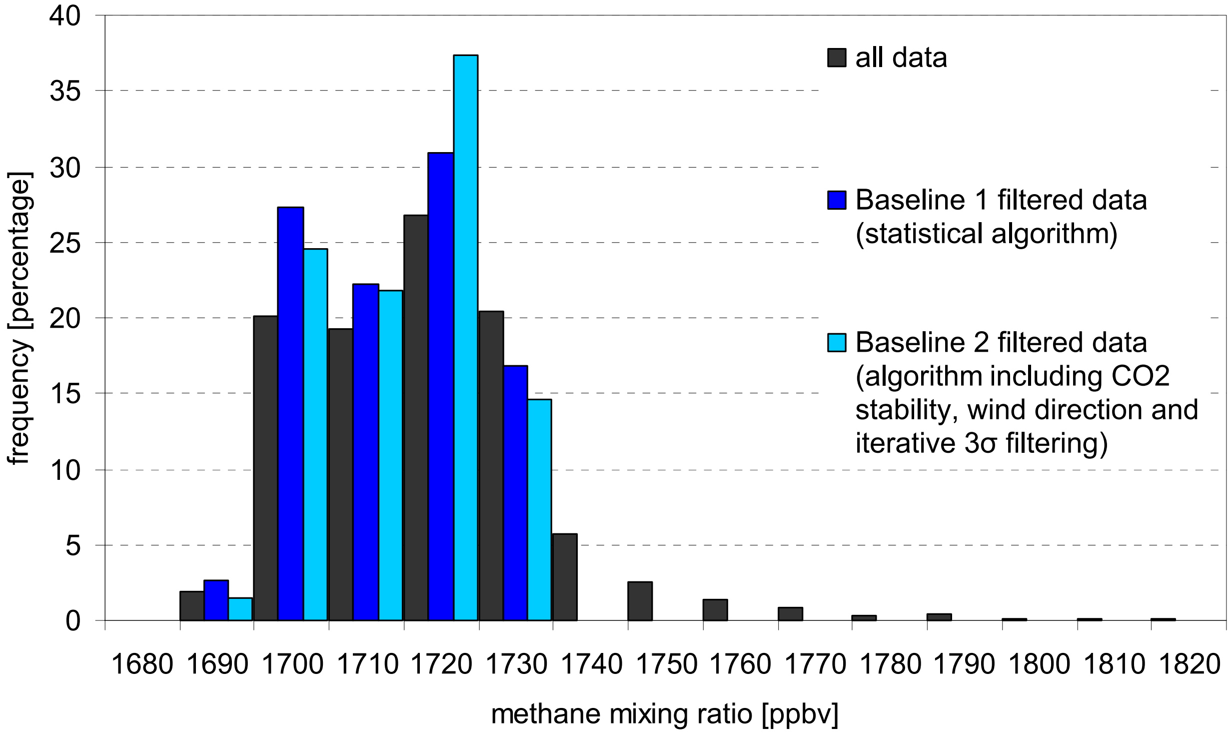

Figure 5: Frequency distribution of the mean methane mixing ratio (2001) at Cape Grim (injections every 40 minutes). Availability of data: 77.9% (for all data), 54.2% (Baseline 1), 23.4% (Baseline 2).

3.2. Description of the Observatory

The facilities at the site consist of a large laboratory building with office and living facilities (see Figure 6). The station is accessible by car. All measurements are performed in one large laboratory (Figure 7).

Comment

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

Figure 6: View of the laboratory building at the Cape Grim GAW station with the 74 m tower.

Figure 7: Laboratory at the Cape Grim GAW station.

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Cape Grim (as of December 2002)

Name	**Position and duty**
Station / Smithton Office	
Neil Tindale	Officer in Charge, Station manager
Laurie Porter	Technical Officer, Station operator
Stuart Baly	Technical Officer, Station operator
Randall Wheaton	IT Officer, Station operator
Responsibilities at CSIRO	
Ian Galbally	Ozone
Mick Meyer	Ozone
Simon Bentley	Ozone
Sarah Lawson	Ozone
Paul Steele	Carbon Monoxide and Methane
Ray Langenfelds	Carbon Monoxide and Methane
Paul Krummel	Carbon Monoxide and Methane

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

Surface ozone measurements started in April 1976 at the Cape Grim GAW station, and a complete time series is available since then. The station analyser used at the site as the main ozone instrument was installed in 1983, and upgraded in 1990.

4.1.1. Air Inlet System

Sampling-location: The inlet is mounted on top of the laboratory building and has a height of 10 m. The sampling height is 13 m above the ground or 104 m above sea level.

Sample inlet:

- Inlet dimension: length 10 m, inner diameter 15 cm, flow rate 220 lpm, stainless steel.
- Rain protection: The Inlet is protected against rain and snow by an inverted stainless steel cup. Stainless steel wires inside the cup prevent bird nestling.
- Inlet-filter: Teflon inlet filter before analyser, exchanged 1-2 times per year or when dirty.
- Sample line: PFTE. Length approx. 5 m, i.d. = 4 mm. Flow rate 3 litres per minute.

Residence time in the sampling line: approx. 50 s

Comment

The residence time in the inlet is rather long. However, the flow rate in the stainless steel part is adjusted to obtain a laminar flow through this part of the inlet. The flow rate was reduced to 220 lpm (from 730 lpm) in 1995. Before 1995, parallel measurements were performed to estimate the ozone loss in the inlet system (approx. 3%, see also section 4.1.3. data treatment). Since this loss has most likely changed with the new flow rate, it is strongly recommended to re-assess the ozone loss in the inlet system.

4.1.2. Instrumentation

Ozone Analyser

A TEI 49 ozone analyser is used as the main ozone instrument at the Cape Grim station (Table 2). Additionally, a Monitor Labs 9810 is available as a back-up instrument. The instruments are installed inside the laboratory and are protected from direct sunlight. The laboratory is air-conditioned to 21±1°C.

Table 2: Ozone analysers at the Cape Grim Research Station

Type	TEI 49 #17191-168	ML 9810B #327B-125
Settings	Offset 55, Span 500	Zero 0.000, Gain 1.193
Method	UV absorption	UV absorption
at Cape Grim	since 1983	since 1998
Range	0-1000 ppb	0-300 ppb
Analog output	0-10 V	0-1 V

Ozone Calibrator

Two ozone calibrators are available at the Cape Grim station. While a monitor 9811 calibrator was never used, frequent inter-comparisons are performed with a TEI 49PS (see Table 3).

Table 3: Ozone calibrator at the Cape Grim Research Station

Type	TEI 49PS #AOC-10687
Method	UV absorption
at Cape Grim	since 1983
Range	0-1000 ppb
Analog output	0-10 V

Operation and Maintenance

Preventive instruments maintenance includes several instrument checks. The lamp intensities and noise, the cell pressure and temperature and the pressure sensor (pump off) are checked weekly. Half-yearly to yearly maintenance include pre-maintenance calibrations, a test of the ozone monitor control system (OMCS), cleaning of sample cells, exchange of inlet filters, leak checks, and ozone loss checks in the sample lines and the OMCS. The ozone loss in the Inlet (stainless steel part) is check on irregular intervals.

4.1.3. Data Handling

Data Acquisition and –transfer

The data acquisition system consists of an ADC circuit board and a computer. One minute averages with standard deviation and minimum / maximum values are stored. Back-ups of this raw data are made in regular intervals.

Data Treatment

Data treatment involved three steps. Step 1 and 2 are performed at the Smithton office, and the data is finally reviewed and stored at CSIRO.

Step 1: Station and instrument log books deletes.

Step 2: Data correction. A maximum of two 1 minute averages is deleted when the change in the ozone concentration was bigger than 10 ppbv between two 1 minute averages. The data is flagged when the standard deviation of an hourly mean value exceeds 4 ppbv. The ozone loss of 3% in the inlet system is corrected. The zero offset is corrected using the data of the automatic zero checks. Afterwards, the data is inspected visually (time series plot, check with instrument log book).

Step 3: Final data quality check at CSIRO, data storage.

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

Logbooks are available for all instruments and the station. The notes are up to date and describe all important events.

Standard Operation Procedures (SOPs)

The manuals for the instruments 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 Instruments

4.2.1. Experimental Set-up

Inter-comparisons for all ozone instruments except the ML 9811 calibrator were made at the Cape Grim GAW station, but only the results for the TEI 49 an 49 PS are shown in this section. The results for the ML 9810 are shown in Appendix I, since this instrument is considered to be of minor importance. The WCC transfer standard TEI 49C PS (details see Appendix II-III) was operated in stand-by mode for warming up for 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 instrument and the WCC transfer standard were performed. Table 4 shows the experimental details and Figure 8 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 III.

Table 4: Experimental details of the ozone inter-comparison

reference:	WCC: TEI 49C-PS #54509-300 transfer standard
field instrument:	TEI 49 #17191-168 TEI 49PS #AOC-10687 ML 9810B #327B-125 (see Appendix I)
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): 1006.0 hPa TEI 49: 1010 hPa (no adjustment made) TEI 49PS: 1015 hPa (no adjustment made) ML 9810B: not checked
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:	for each instrument 3 x between 27. and 29. Nov 02
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

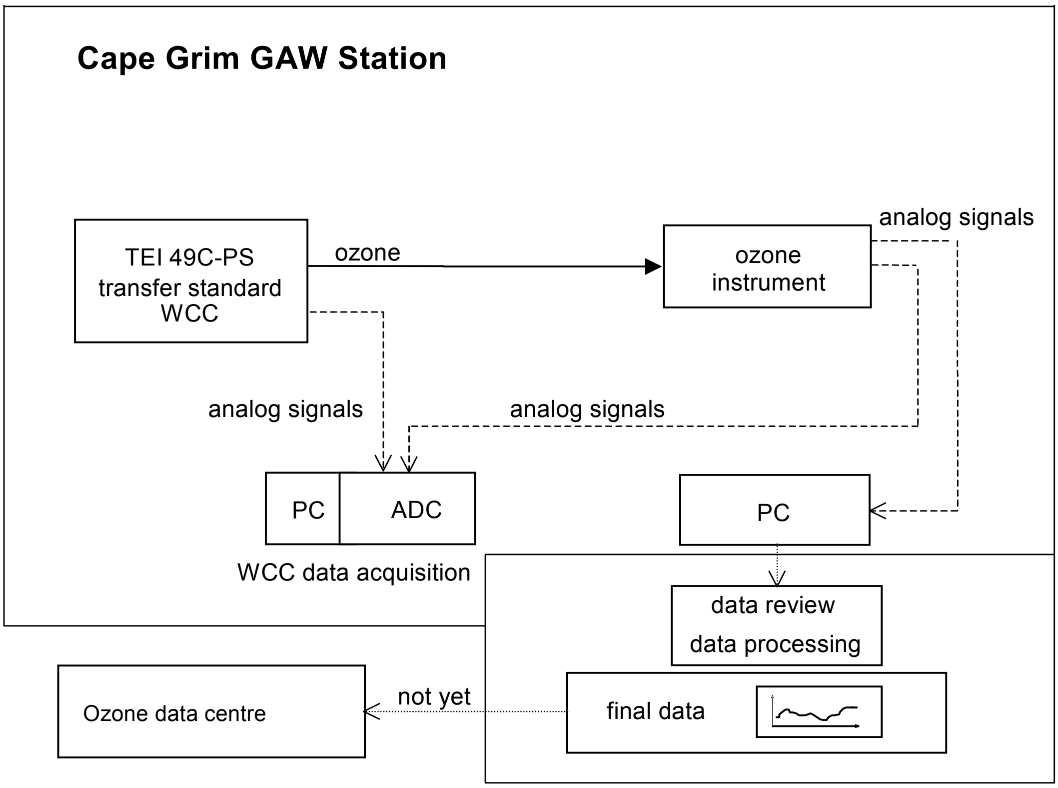

Figure 8: Experimental set up for the ozone inter-comparison. All instruments were checked separately.

4.2.2. Results

Ozone Analyser

The results comprise the inter-comparison between the TEI 49 #17191-168 field instrument and the WCC transfer standard TEI 49C-PS, carried out on 27. November 2002. Results for the Monitor Labs 9810 instrument are shown in Appendix I. This instrument is operated as a backup instrument, and data are not submitted.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Table 5. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 9 and 10 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 9 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 10 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 11).

The data used for the evaluation was recorded by both EMPA and Cape Grim data acquisition systems. This raw data was treated according to the usual station method, and a zero offset of 4.63 ppb was subtracted from all data.

Table 5: Inter-comparison of the ozone field instrument

	TEI 49C-PS		TEI 49 #17191-168			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.22	0.13	-0.21	0.37	-0.4	
2	49.95	0.08	48.71	0.17	-1.2	-2.5%
3	20.05	0.13	19.17	0.28	-0.9	-4.4%
4	89.95	0.12	87.64	0.45	-2.3	-2.6%
5	30.00	0.12	29.01	0.29	-1.0	-3.3%
6	10.13	0.08	9.74	0.31	-0.4	-3.9%
7	0.29	0.06	-0.10	0.40	-0.4	
8	0.33	0.10	-0.01	0.31	-0.3	
9	10.09	0.07	9.80	0.37	-0.3	-2.9%
10	89.89	0.13	87.55	0.29	-2.3	-2.6%
11	50.00	0.11	48.82	0.19	-1.2	-2.4%
12	30.01	0.11	28.99	0.30	-1.0	-3.4%
13	20.07	0.10	19.37	0.31	-0.7	-3.5%
14	0.30	0.07	0.05	0.34	-0.2	
15	0.29	0.11	-0.01	0.38	-0.3	
16	49.95	0.10	48.79	0.22	-1.2	-2.3%
17	19.99	0.07	19.31	0.26	-0.7	-3.4%
18	89.92	0.26	87.66	0.35	-2.3	-2.5%
19	29.97	0.33	29.05	0.25	-0.9	-3.1%
20	10.15	0.11	9.72	0.27	-0.4	-4.2%
21	0.28	0.01	0.27	0.32	0.0	

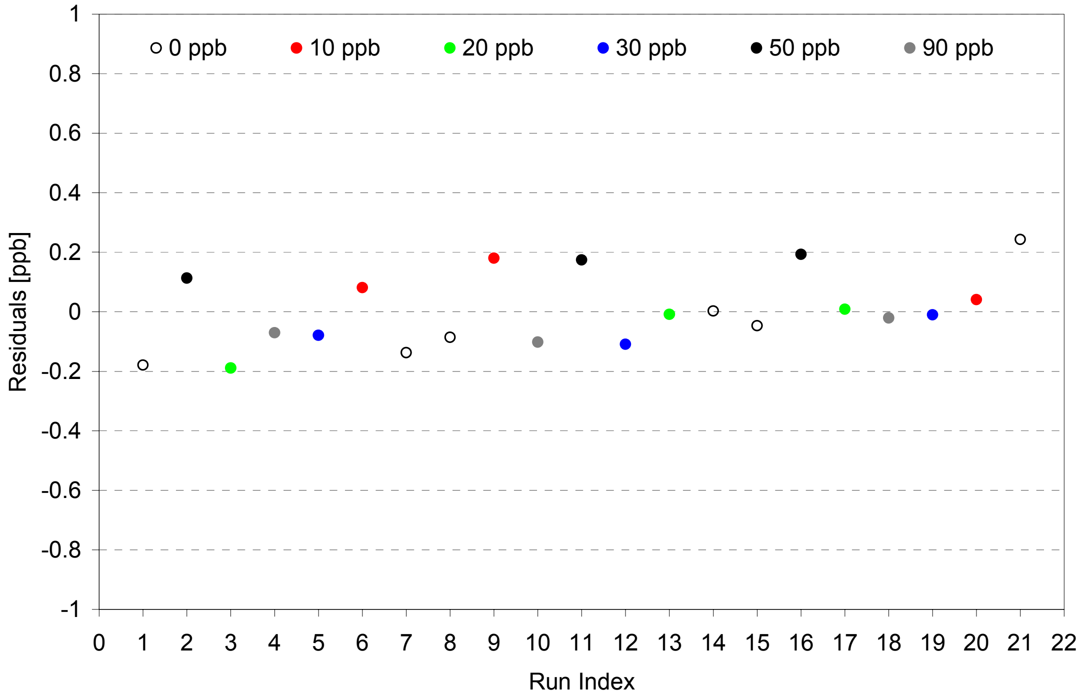

Figure 9: Residuals to the linear regression function (TEI 49 #17191-168) vs the run index (time dependence)

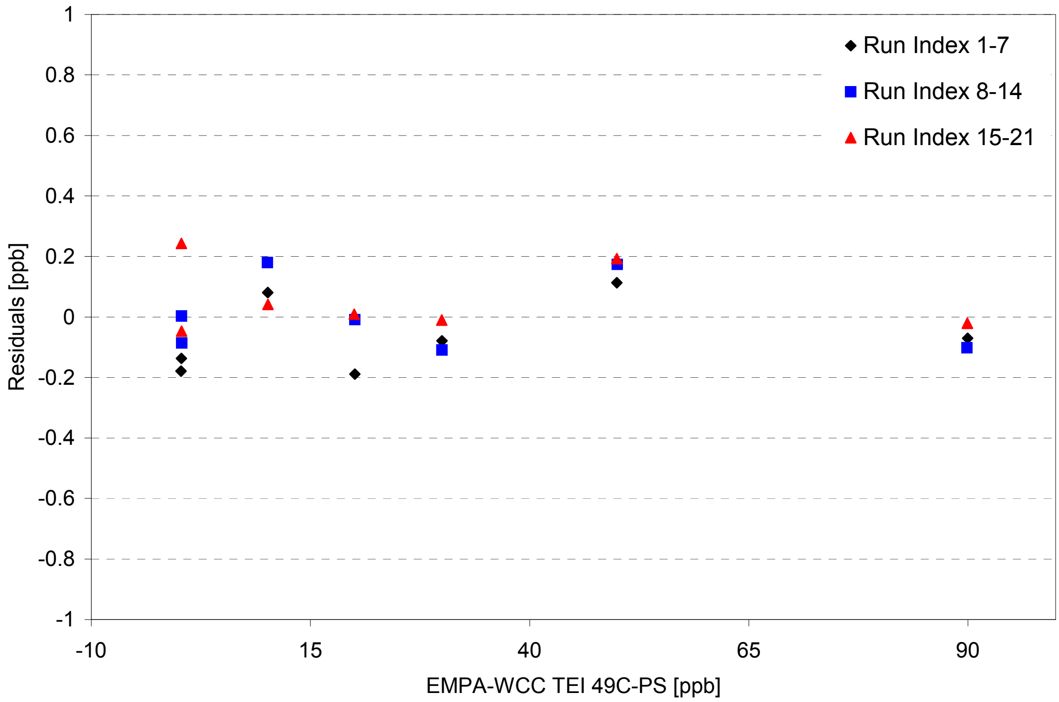

Figure 10: Residuals to the linear regression function (TEI 49 #17191-168) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI 49 #17191-168 field instrument with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 10-100 ppb ozone) is:

TEI 49 #17191-168:

TEI 49 #17191-168 = 0.978 x TEI 49C-PS - 0.25 ppb

TEI 49 #17191-168 = O3 mixing ratio in ppb, determined with TEI 49 #17191-168

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

Standard deviation of:	- slope s_m	0.001	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.04	(f = 19)
	- residuals in ppb	0.10	(n = 21)

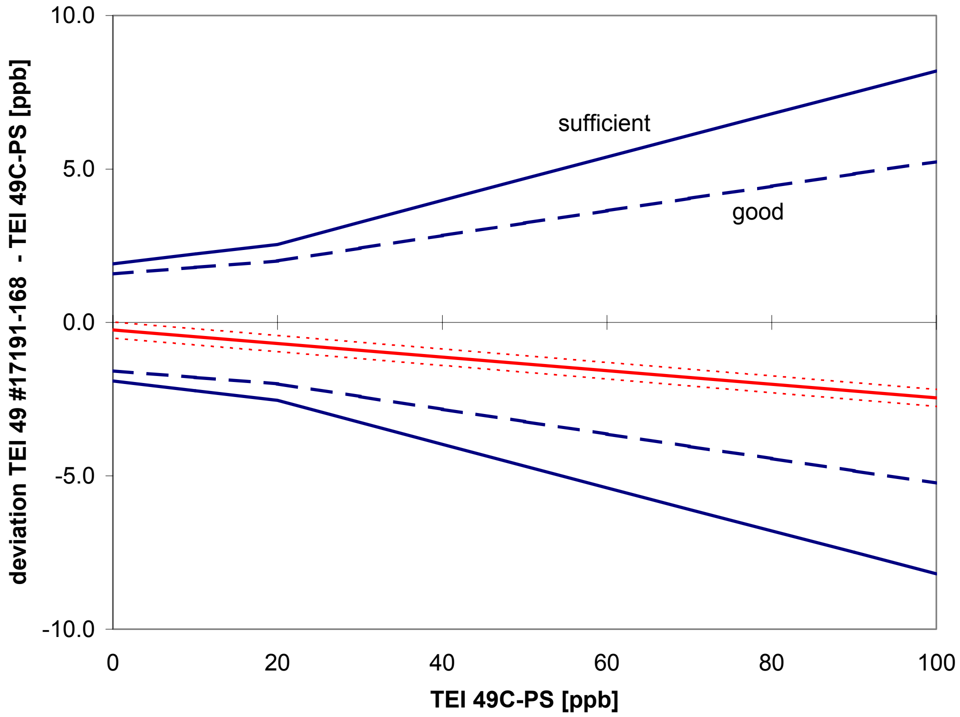

Figure 11: Inter-comparison of instrument TEI 49 #17191-168

Comment

The ozone concentrations observed at Cape Grim (2001) ranged between 15.8 and 34.9 ppb (5- and 95-percentile of 60 min mean values). The TEI 49 fulfils the assessment criteria of “good” over the tested range between 10 and 100 ppb ozone.

The relatively low readings still compare well with the first (and only) calibration of the instrument with an external standard in 1986 at the National Bureau of Standards (NBS, now NIST). The relationship between the NBS standard and the TEI 49 field instrument was:

TEI 49 #17191-168 = 0.985 x NBS - 0.01 ppb

Ozone Calibrator

The results comprise the inter-comparison between the TEI 49PS #AOC-10687 calibrator and the WCC transfer standard TEI 49C-PS, carried out on 27. December 2002.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Table 6. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 12 and 13 show the residuals of the linear regression analysis of the station calibrator compared to the EMPA transfer standard. The residuals versus the run index are shown in Figure 12 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 13 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 14).

The data used for the evaluation was recorded by both EMPA and Cape Grim data acquisition systems.

Table 6: Inter-comparison of the station ozone calibrator

	TEI 49C-PS		TEI 49PS #AOC-10687			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.30	0.09	0.03	0.25	-0.3	
2	49.84	0.08	48.07	0.33	-1.8	-3.5%
3	19.92	0.10	18.90	0.39	-1.0	-5.1%
4	89.91	0.11	87.24	0.32	-2.7	-3.0%
5	29.99	0.09	28.53	0.28	-1.5	-4.9%
6	10.06	0.11	9.12	0.28	-0.9	-9.3%
7	0.20	0.09	0.56	1.40	0.4	
8	0.24	0.16	0.02	0.23	-0.2	
9	20.02	0.12	19.15	0.22	-0.9	-4.3%
10	10.08	0.23	9.19	0.35	-0.9	-8.9%
11	89.96	0.08	87.24	0.24	-2.7	-3.0%
12	29.96	0.09	28.58	0.33	-1.4	-4.6%
13	50.00	0.07	48.19	0.35	-1.8	-3.6%
14	0.23	0.07	0.06	0.23	-0.2	
15	0.26	0.11	0.00	0.23	-0.3	
16	29.99	0.07	28.75	0.29	-1.2	-4.1%
17	89.95	0.08	87.25	0.24	-2.7	-3.0%
18	49.99	0.09	48.33	0.37	-1.7	-3.3%
19	20.04	0.11	18.96	0.24	-1.1	-5.4%
20	10.07	0.12	9.10	0.29	-1.0	-9.7%
21	0.24	0.08	0.00	0.22	-0.2	

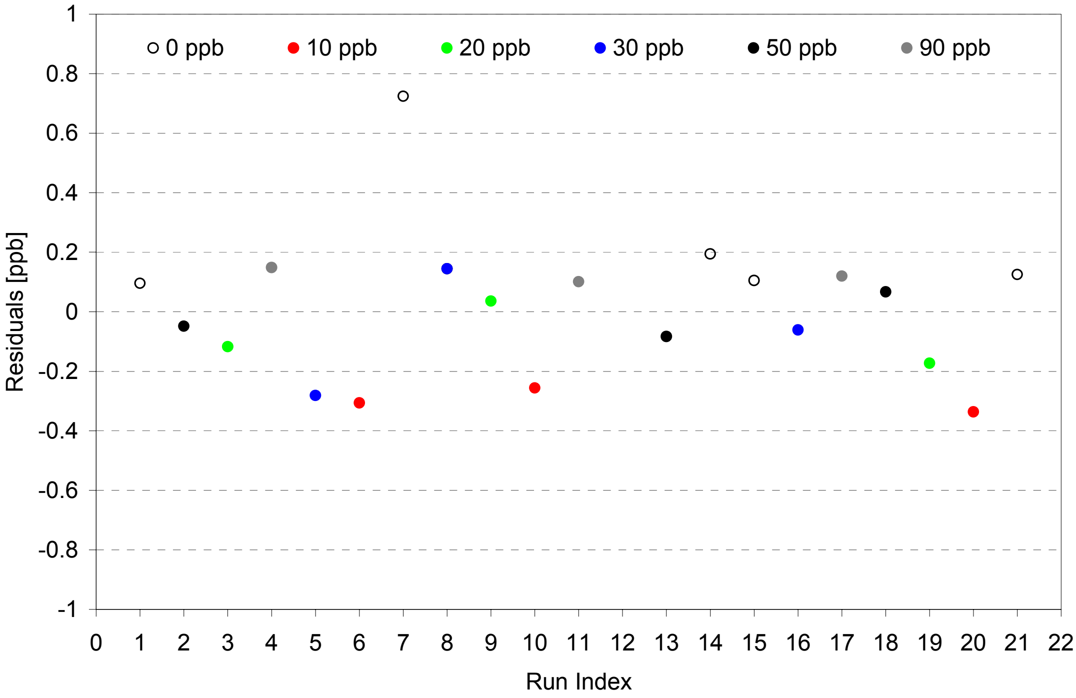

Figure 12: Residuals to the linear regression function (TEI 49PS #AOC-10687) vs the run index (time dependence)

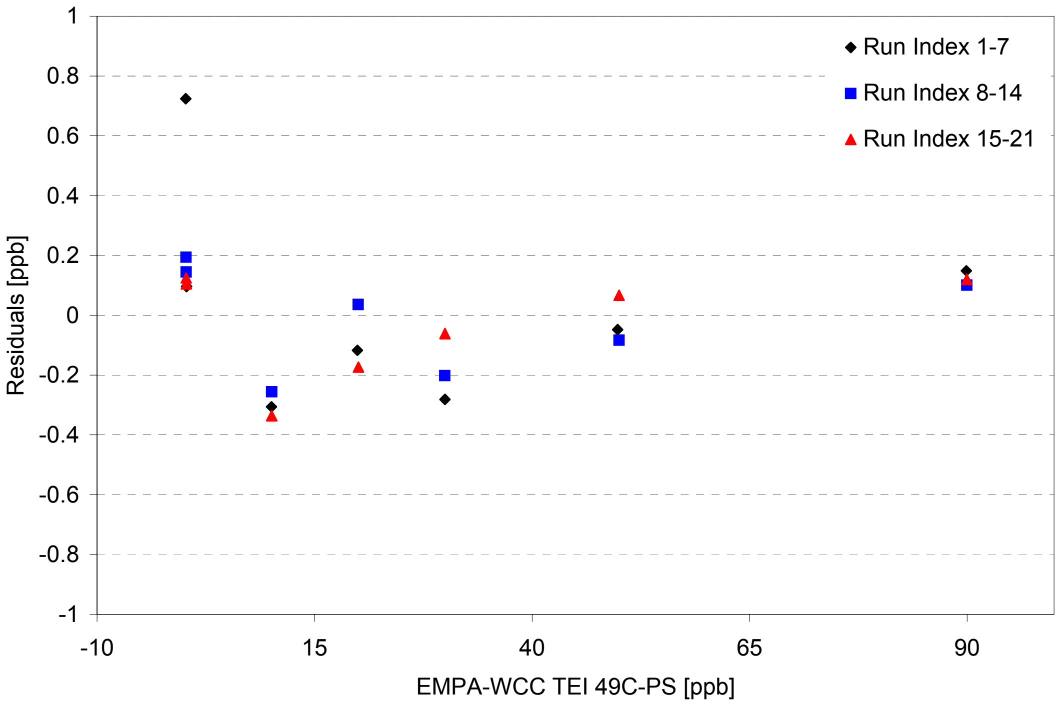

Figure 13: Residuals to the linear regression function (TEI 49PS #AOC-10687) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI 49PS #AOC-10687 station calibrator with the TEI 49C-PS transfer standard from WCC-EMPA, the resulting linear regression (for the range of 10-100 ppb ozone) is:

TEI 49PS #AOC-10687:

$$\text{TEI 49PS \#AOC-10687} = 0.973 \times \text{TEI 49C-PS} - 0.36 \text{ ppb}$$

TEI 49PS #AOC-10687 = O3 mixing ratio in ppb, determined with TEI 49PS #AOC-10687

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

Standard deviation of:	- slope s_m	0.002	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.07	(f = 19)
	- residuals in ppb	0.14	(n = 21)

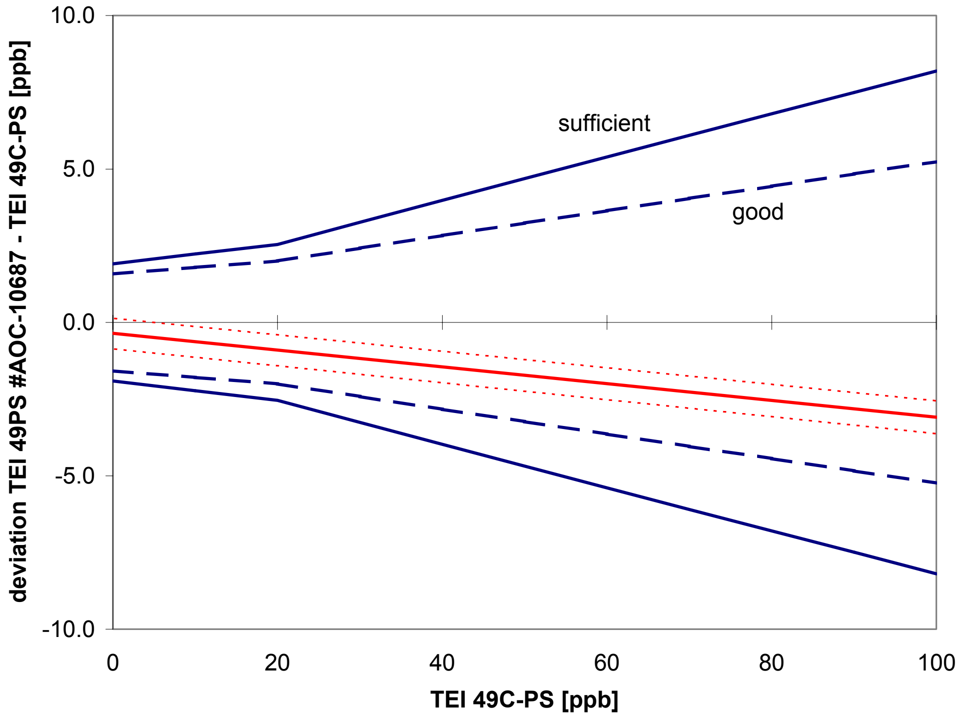

Figure 14: Inter-comparison of instrument TEI 49PS #AOC-10687

Comment

The station calibrator TEI 49PS fulfils the assessment criteria of “good” over the tested range between 10 and 100 ppb ozone. However, the observed differences are relatively large. Agreement between the station analyser and the station calibrator is good.

4.3. Recommendation for the Ozone Measurements

The following recommendations are made by WCC-EMPA to improve the quality of surface ozone measurements at the Cape Grim station:

- A replacement of the ozone analyzer and calibrator should be considered. The instruments are already 20 years old. However, since the stability of the instruments proved to be good, the replacement is not of highest priority.
- The ozone loss in the inlet line must be re-evaluated with inter-comparison measurements. The loss is used to correct the final ozone data. The flow rate changed significantly since the last assessment of the ozone loss in 1995. This is regarded as of highest priority.
- Submission of the ozone data to the GAW world data centre for greenhouse gases (WDCGG) at JMA is encouraged.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Cape Grim in 1993 and a continuous time series is available since then. This is the first audit for carbon monoxide measurements conducted by WCC-EMPA at the Cape Grim station.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO and CH_4

Sampling-location: at the 10 and 70 m levels of the 70 m tower

Inlet description:

Inlet (70m):	ca 80 m long PE tube (outer diameter 40 mm) - pump and overflow (300 l/min)
Inlet (10m):	same as for ozone
Sample line:	Stainless steel. Length approx. 5 m, i.d. = 4 mm. Flow rate 4 litres per minute. For most of the time the air is not flowing but two minutes before an injection the pump 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 2 ml sample loop and a flow regulator valve to the RGA/RGD-2 instrument.

Residence time in the sampling line: approx. 50 s (10 m), < 10 s (70 m)

Comment

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

5.1.2. Instrumentation

An RGA-2 / RGD-2 GC-system of Trace Analytical Inc. is used as an in-situ CO analyser. Instrumental details are listed in Table 7.

Table 7: Carbon monoxide gas chromatograph at Cape Grim

instrument	Trace Analytical Inc.
model, S/N	RGA2, S/N 121586-005 RGD2, S/N 041587-006
at Cape Grim	since 1996
configuration	E-001 (Trace Analytical terminology)
method	GC / HgO Detector
loop	2 ml
columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
carrier gas	ambient air – AADCO 737 - 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	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate loop pressure with ambient pressure

Gas Standards

Table 8 shows the gas standards that are used for the verification of the measurements. The 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 for a weekly check of the calibration function. A full calibration using flasks is performed approx. every three years. All standards used are calibrated against the primary scale of CSIRO Aspendale before and after their use at Cape Grim. Data are referenced to the scale maintained at CSIRO, which differs substantially from the current version of the CMDL scale (see Section 6).

Table 8: Station CO cylinders

Gas cylinder	Description	Conc. [ppb]
UAN 994812	Working standard	150.1
UAN 970259	CSIRO Australia, Cape Grim, real air standard	40.0
UAN 994991	CSIRO Australia, Cape Grim, real air standard	92.0
UAN 950243	CSIRO Australia, Cape Grim, real air standard	260.0

Operation and Maintenance

Analysis: Injections are made every 20 minutes, alternating between working standard and ambient air. Ambient air measurements alternate between the 10 and 70 m inlets.

Weekly checks: RGA/RGD-2 test points
chromatogram / peak width / CO-retention time
cylinder pressures
check of the calibration function using the four station standards (automatic)

A linearity check with a dilution standards is performed is performed every 2 to 3 years or when significant changes of the instrument are made (e.g. replacement of the mercury bed). A zero check is performed monthly.

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 and CSIRO. 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 CSIRO, 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. 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 data have not been submitted to the GAW data centre for greenhouse gases (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.

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 eight transfer standards of the WCC (concentration range 35 - 240 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 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 and analysed between 5 and 9 times in the period from 26. to 29. November 2002. No modifications of the RGA/RGD-2 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 after the audit using the calibration of the instrument with the CSIRO dilution standards (December 2002). The experimental details are summarised in Table 9.

Table 9: Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA2, S/N 121586-005 RGD2, S/N 041587-006
reference:	WCC-EMPA transfer standards
data acquisition system:	AGAGE GC control software
approx. concentration levels:	35 to 240 ppb
injections per concentration:	5 to 9

5.2.2. Results

The CO concentrations determined by the RGA/RGD-2 field instrument for the eight WCC transfer standards are shown in Table 10. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 15 shows the absolute differences (ppb) between the measurements of the RGA/RGD-2 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 injections of the transfer standards at Cape Grim. The data of the RGA/RGD-2 field instrument were processed after the audit by the station operators and are based on calibration of the instrument against dilution standards of CSIRO.

Table 10: Carbon monoxide inter-comparison measurements at Cape Grim

No.	WCC standard	Cape Grim analysis (RGA/RGD-2 , Peak Height)				
	conc. ± 1σ (N)	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	36.4 ± 1.1 (130)	35.3	0.2	5	-1.1	-2.8
2	44.3 ± 1.1 (113)	42.8	0.4	9	-1.5	-3.3
3	54.7 ± 0.8 (133)	51.8	0.6	5	-2.9	-5.2
4	72.3 ± 0.9 (175)	68.8	0.4	5	-3.6	-4.9
5	81.9 ± 1.2 (137)	78.4	0.7	8	-3.5	-4.3
6	93.8 ± 1.0 (120)	89.8	0.6	5	-4.0	-4.3
7	159.6 ± 1.3 (91)	154.5	0.6	5	-5.1	-3.2
8	233.8 ± 1.6 (112)	225.0	1.4	6	-8.8	-3.8

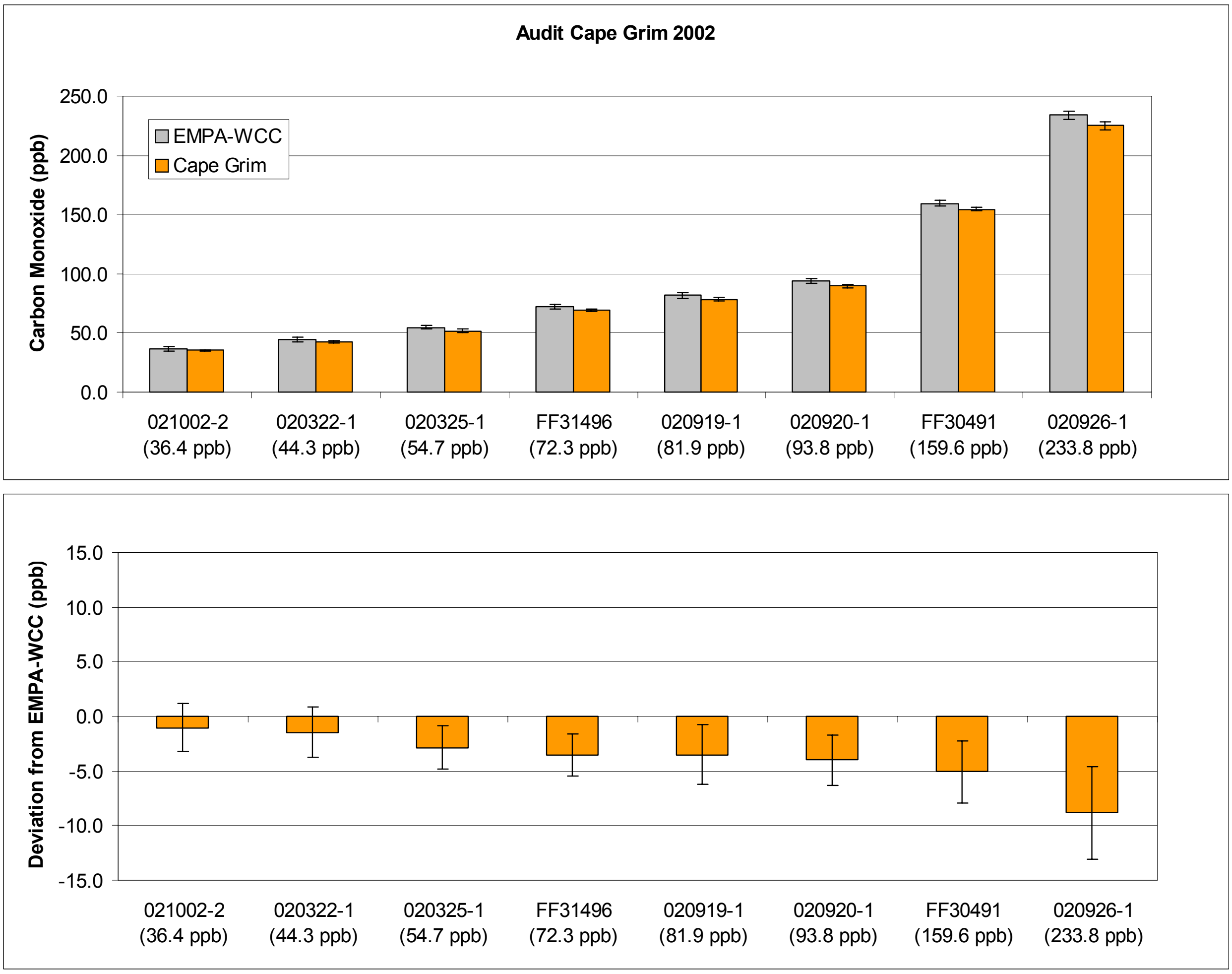

Figure 15: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Cape Grim (orange). lower panel: deviation of the Cape Grim station from the conventional true value. The error bars represent the 95% confidence interval.

5.3. Ambient air measurements at Cape Grim

Ambient air measurements using the Aerolaser 5001 of WCC-EMPA were performed between 26. and 29. November 2002 at Cape Grim. Figure 16 shows the concentrations measured with both the AL and the RGA-3 instruments. Averaging time was 30 seconds for the Aerolaser, and single injections were made with the RGA-3 instrument every 80 minutes. Corresponding 3 minute averages are also shown for the AL instrument.

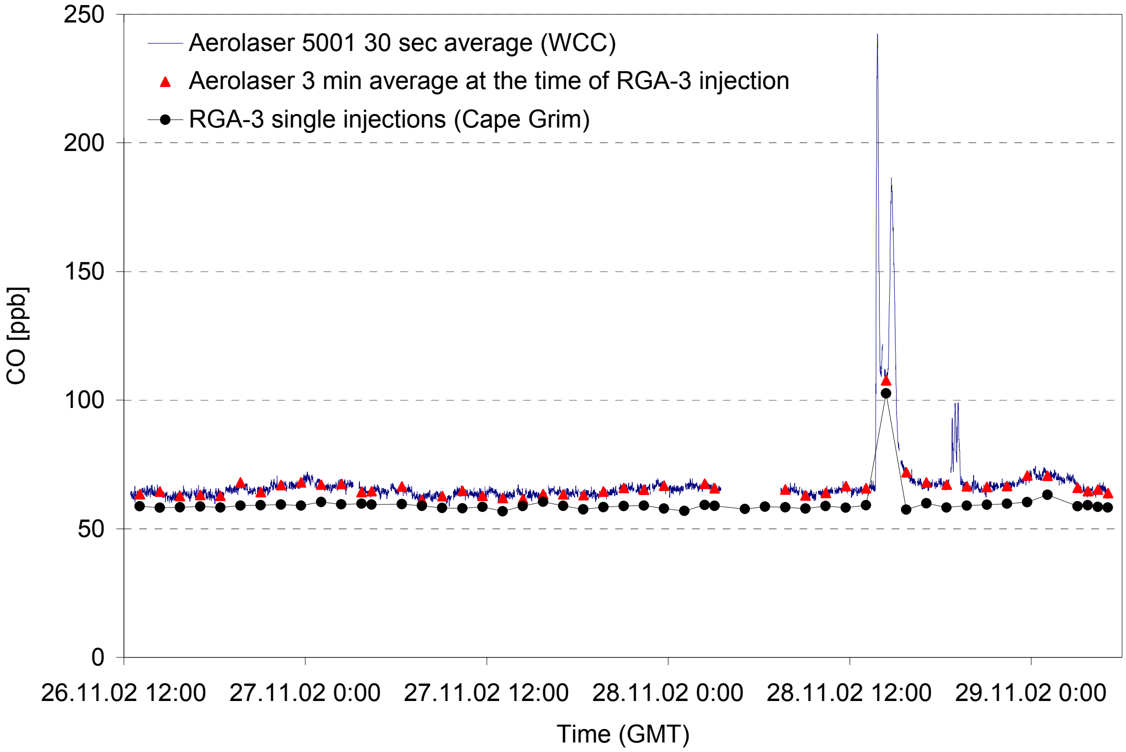

Figure 16: Ambient air measurements at Cape Grim with the Aerolaser 5001 (WCC-EMPA) and RGA-3 (station instrument). RGA-3 injections were made every 80 minutes, and corresponding 3 min averages of the AL instrument are shown.

It can be seen from Figure 16 that the CO concentration remained relatively constant throughout most of the time period. However, two episodes with higher concentrations were observed on 28. November 02. The RGA-3 instrument was only capable to detect one of these events because the second was just between two injections. Generally lower concentrations (average 9.6%) were found with the RGA-3 instrument. This is significantly lower than expected from the inter-comparison of the transfer standards (lower findings between 2.8 and 5.2%). Furthermore, no clear relationship between the two instruments was observed for low concentrations. As an example, the RGA-3 instrument detected local minimum after the first event on 28. November, but the AL instrument still measured elevated CO at this time. Because the data of the RGA-3 instrument was not available during the inter-comparison, the reason for this behaviour can not be explained at the moment.

5.4. Discussion of the Inter-comparison Results

The relative agreement between WCC-EMPA and Cape Grim based on the inter-comparison of the WCC-EMPA transfer standards was very good, with lower findings of Cape Grim between 2.8 and 5.2 % throughout the audited concentration range from 36 to 234 ppb CO. This lower finding can be explained by the recent revision of the carbon monoxide scale by CMDL. The Cape Grim measurements are referenced against the scale maintained at CSIRO and are in excellent agreement with measurements of the same air standards made at CSIRO. Differences are within ±1% over the audited concentration range. For further details see also Section 6.

5.5. 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 Cape Grim using various standards for calibrations and consistency checks is encouraged.
- During the time of the audit the instrument response function was not sufficiently characterized. The station operators were aware of the problem; however, the instrument was running for a relatively long time period without a valid calibration. Because corrections of the data can be a difficult task, WCC-EMPA recommends re-calibrating the instrument in regular intervals (e.g. every three months) or earlier when problems occur. A wide range of high quality standards is available to the station form CSIRO.
- 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.

6. Inter-comparison of CO scales at CSIRO Aspendale

In addition to the audit for carbon monoxide at Cape Grim, an inter-comparison between the carbon monoxide scales of CSIRO and WCC-EMPA was performed after the Cape Grim audit between 5. and 11. December 2002. For this reason, the WCC-EMPA transfer standards were analysed at GASLAB using the RGA-3 system of CSIRO. In addition, several primary and surveillance CO standards were analysed by WCC-EMPA using a UV-Fluorescence instrument (Aerolaser AL5001).

6.1. Description of the CO scales

6.1.1. CO scale of WCC-EMPA

The carbon monoxide scale of WCC-EMPA is based on CO standards from CMDL. WCC-EMPA has five certified CMDL CO standards, however, an internal inconsistency of these standards can not be ruled out. As a consequence, WCC-EMPA decided to assign new values to the CO standards based on one of the CMDL standards and using the Aerolaser AL5001 assuming a linear response function. The linearity of the AL5001 was tested using diluted standards. Table 11 gives an overview of the WCC-EMPA CMDL standards and WCC-EMPA assigned values.

Table 11: CMDL CO Standards at WCC-EMPA. The error represents the measured standard deviation and the ultimate determination of the primary standard.

CMDL Standard Cylinder No.	CMDL old scale*	CMDL new scale**	WCC-EMPA scale***
CA03209	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	56.0 ± 0.8 ppb
CA02803	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	108.4 ± 1.2 ppb
CA03295	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	153.6 ± 1.6 ppb
CA02859	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	194.7 ± 1.9 ppb
CA02854	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	295.3 ± 3.1 ppb

* 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
*** Assigned value by WCC-EMPA based on the AL5001 calibrated with CA02859 new CMDL scale (194.7 ppb)

6.1.2. CO scale of CSIRO Aspendale

The carbon monoxide scale maintained at CSIRO was also based originally on the gravimetrically-derived scale of CMDL. The link was established using a single high-pressure cylinder standard with CO mole fraction of 196 ppb. This standard is one of five synthetic mixtures of CO_2, CH_4 and CO in zero air, in the range 30–196 ppb, that were calibrated against the "old" CMDL scale between 1992 and 1994. The CSIRO scale has not been adjusted to the "new" CMDL scale. Only the highest concentration standard was used to link the CSIRO and CMDL scales due to large discrepancies in the respective laboratories' determination of relative mole fraction among these standards and other high pressure cylinders exchanged since. The instrument response characteristics of the CSIRO instrument were established using a static dilution technique. Five such experiments between 1993 and 1999 showed the relative CO mole fraction among these standards to consistently differ from that indicated by the CMDL assignments, probably due to different treatment of instrument non-linearity. CSIRO use a function of the form $y = ax^2 + bx + cx^d$, where y is CO mole fraction, x is peak height counts and a, b, c, and d, are fitted parameters, in order to capture a sharp non-linearity in instrument response at low concentrations (especially below 100 ppb). Stability of the CSIRO scale and variations in instrument response are monitored with ~20 high-pressure cylinder standards, with lifetimes of 6-12+ years, spanning a CO range of 20–400 ppb. For further details see Masarie et al. (2001) and Francey et al. (2003).

6.2. WCC-EMPA Transfer Standards Measured at CSIRO

The eight transfer standards of the WCC-EMPA (concentration range 35 - 240 ppb CO, see 5.2.) were analysed at CSIRO using the RGA-3 system of the GASLAB. 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 5 and 9 times in the period from 5. to 11. December 2002. The data was acquired by the GASLAB software. This data (mean values and standard deviations) was reprocessed by CSIRO after the inter-comparison.

The CO concentrations determined by the GASLAB instrument for the eight WCC transfer standards are shown in Table 12. In addition, the results obtained from the inter-comparison at Cape Grim are shown. For each mean value the difference between the measured value and the assigned value of transfer standard is calculated in ppb and %.

Table 12: WCC-EMPA transfer standards measured at CSIRO and Cape Grim

No.	**WCC-EMPA**	**Cape Grim**			**CSIRO**		
	conc. ± 1σ (N)	conc. ± 1σ (N)	deviation from reference		conc. ± 1σ (N)	deviation from reference	
	ppb	ppb	ppb	%	ppb	ppb	%
1	36.4 ± 1.1 (130)	35.3 ± 0.2 (5)	-1.1	-2.8	34.9 ± 0.2 (5)	-1.5	-4.1
2	44.3 ± 1.1 (113)	42.8 ± 0.4 (9)	-1.5	-3.3	42.4 ± 0.8 (3)	-1.9	-4.4
3	54.7 ± 0.8 (133)	51.8 ± 0.6 (5)	-2.9	-5.2	51.7 ± 0.3 (5)	-3.0	-5.5
4	72.3 ± 0.9 (175)	68.8 ± 0.4 (5)	-3.6	-4.9	69.5 ± 0.4 (5)	-3.6	-4.9
5	81.9 ± 1.2 (137)	78.4 ± 0.7 (8)	-3.5	-4.3	78.4 ± 0.3 (7)	-3.5	-4.3
6	93.8 ± 1.0 (120)	89.8 ± 0.6 (5)	-4.0	-4.3	90.7 ± 0.8 (6)	-3.1	-3.3
7	159.6 ± 1.3 (91)	154.5 ± 0.6 (5)	-5.1	-3.2	154.7 ± 0.9 (21)	-4.9	-3.1
8	233.8 ± 1.6 (112)	225.0 ± 1.4 (6)	-8.8	-3.8	225.7 ± 0.9 (4)	-8.1	-3.5

6.3. CSIRO Standards Measured by WCC-EMPA

In addition to the transfer standards measured by CSIRO, WCC-EMPA analysed several primary and a set of surveillance standards at CSIRO using the Aerolaser AL5001 instrument. The instrument settings of the AL5001 are summarised in Table 13.

Table 13: Aerolaser AL5001 operation parameters

Instrument / serial number	Aerolaser AL5001 S/N 117
Instrument settings	Averaging time calibration: 90 s Averaging time sample: 30 s Time factor: 200 % Counter parameter: T 1000 ms, A = 1
Calibration gas	WCC-EMPA transfer standard FA30491 159.6 ± 1.3 ppb (1σ) CO in air
Calibration interval	4 minutes

The results of the measurements are summarised in Tables 14 (primary standards) and 15 (surveillance standards).

Table 14: CSIRO primary standards measured with AL5001 by WCC-EMPA

UAN No. CSIRO primary standards	**CSIRO assigned** concentration* ppb	**WCC-EMPA measured** conc. ± 1σ (N) ppb	deviation from CSIRO ppb	%
920543	23.5 ± 0.6	24.6 ± 1.1 (75)	1.1	4.6
920542	25.5 ± 0.6	26.1 ± 0.8 (57)	0.6	2.4
920546	27.1 ± 0.6	29.1 ± 0.6 (72)	2.0	7.3
920549	32.8 ± 0.7	34.5 ± 0.5 (56)	1.7	5.1
920545	36.0 ± 0.7	37.1 ± 0.7 (54)	1.1	3.1
920550	43.0 ± 0.7	44.9 ± 1.0 (64)	1.9	4.5
920544	48.6 ± 0.7	50.5 ± 0.7 (70)	1.9	3.8
920539	52.7 ± 0.8	55.8 ± 1.1 (86)	3.1	6.0
900005	64.2 ± 0.8	67.8 ± 0.8 (265)	3.6	5.6
920548	98.0 ± 1.0	101.8 ± 1.1 (73)	3.8	3.8
870001	162.7 ± 1.3	169.6 ± 1.9 (56)	6.9	4.2
920547	195.7 ± 1.5	201.8 ± 1.1 (42)	6.1	3.1
880001	201.5 ± 1.5	211.0 ± 1.4 (76)	9.5	4.7
950123	309.4 ± 2.0	319.1 ± 1.6 (246)	9.7	3.1
910346	414.0 ± 2.6	426.4 ± 1.3 (36)	12.4	3.0

* Uncertainty estimated by CSIRO based on dilution experiments as 0.5% of the CO concentration + 0.5 ppb

Table 15: CSIRO surveillance standards measured with AL5001 by WCC-EMPA

UAN No.	**CSIRO measured**	**WCC-EMPA measured**		
CSIRO surveillance standards	conc. ± 1σ (N)	conc. ± 1σ (N)	deviation from CSIRO	
	ppb	ppb	ppb	%
950554	54.7 ± 0.3 (15)	56.9 ± 0.6 (56)	2.2	4.1
961408	63.8 ± 0.6 (3)	67.0 ± 0.8 (73)	3.2	5.1
951289	114.5 ± 0.7 (7)	119.0 ± 1.4 (57)	4.5	4.0
951540	138.1 ± 1.1 (8)	143.8 ± 1.4 (57)	5.7	4.1
970009	160.7 ± 0.9 (12)	166.1 ± 1.1 (91)	5.4	3.8
950052	188.1 ± 0.7 (8)	194.2 ± 1.2 (57)	6.1	3.2
990553	294.1 ± 1.9 (12)	303.5 ± 1.4 (54)	9.4	3.2

6.4. Summary of the CO Scale Inter-comparison

The CO values assigned or measured by CSIRO were lower in comparison to the values assigned or measured by WCC-EMPA. The relation found between CSIRO and WCC-EMPA is shown in the following Figures.

Figure 17 shows the linear relationship between the CSIRO and WCC-EMPA analysis. CSIRO primary and CSIRO surveillance standards analysed by WCC-EMPA (AL5001) and WCC-EMPA transfer standards analysed by CSIRO (RGA-3) are shown separately. No significant difference was observed between the above experiments. The following relationship between the CSIRO and WCC-EMPA carbon monoxide scales was observed when all data are pooled:

CSIRO CO [ppb] = 0.9707 x WCC-EMPA CO [ppb] – 0.84 ppb

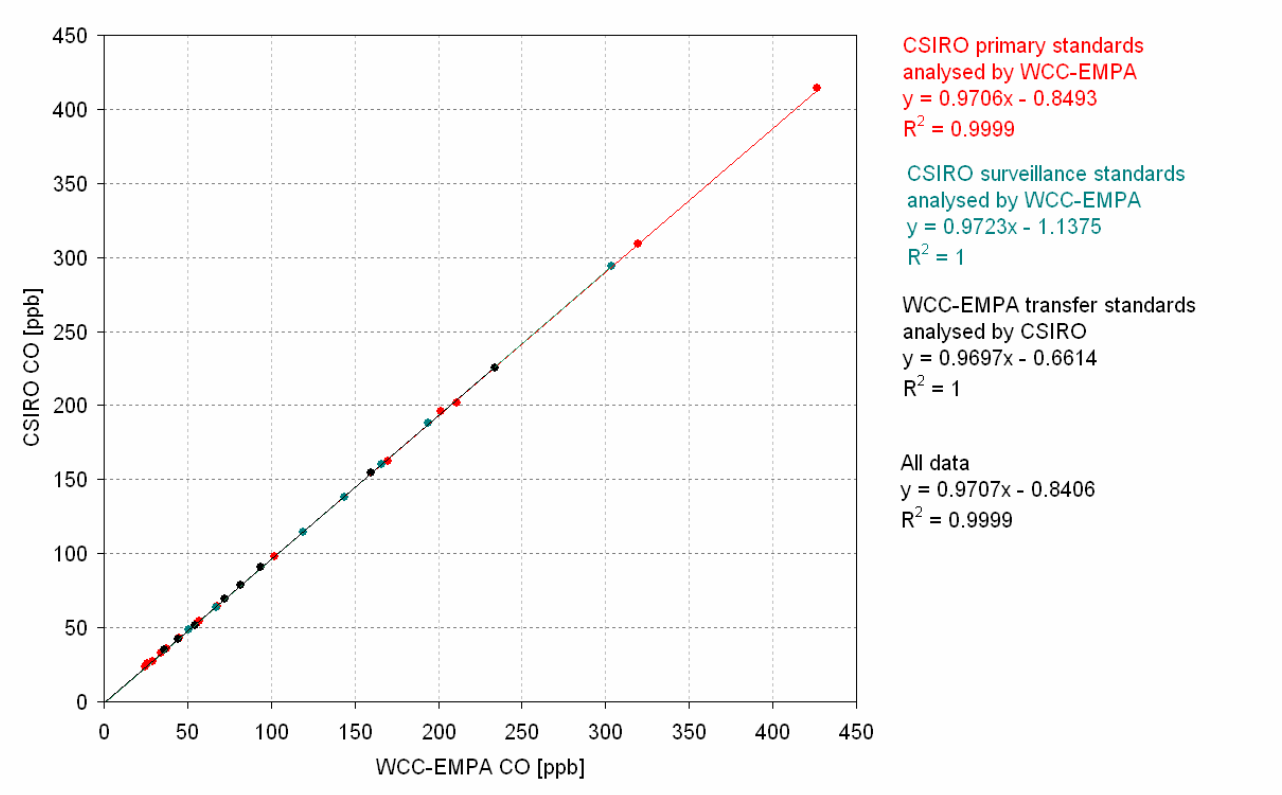

Figure 17: Relationship between CSIRO and WCC-EMPA CO scales

The residuals of the CSIRO values to the linear regression are shown in Figure 18. No significant concentration dependence was observed during the inter-comparison measurements.

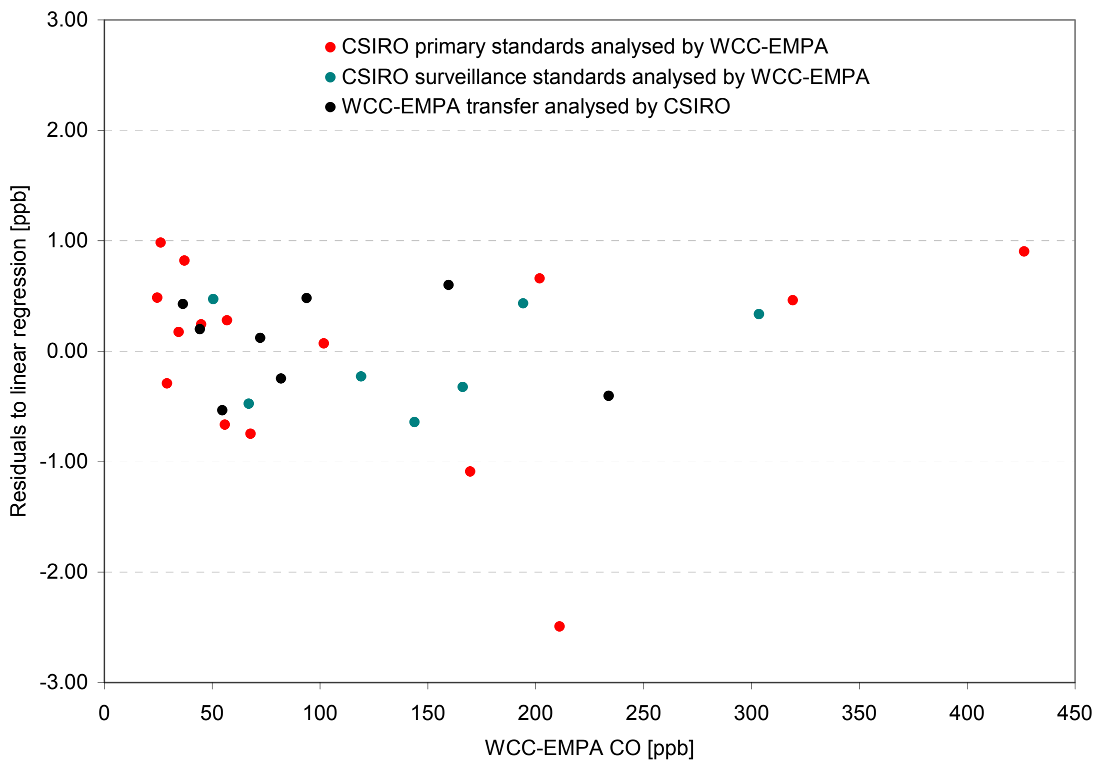

Figure 18: Residuals to the linear regression (all data)

The CSIRO primary standard UAN 880001 (201.5 ± 1.5 ppb) analysed by WCC-EMPA (211.0 ± 1.4 ppb) is potentially an outlier. However, it was not removed from the data set.

6.5. Conclusions

The CO scale inter-comparison showed a strong linear relationship between WCC-EMPA and CSIRO. CSIRO readings are lower compared to WCC-EMPA. The difference is in the order of the recent revision of the CO scale by CMDL. Both WCC-EMPA and CSIRO used a CMDL standard of approximately 200 pbb CO to define their scales by means of dilution experiments. The results of this inter-comparison will provide significant input for the recently established SAG for reactive gases and is a step towards re-solving the issue of inconsistency and uncertainty in the carbon monoxide scales.

7. System-and Performance Audit for Methane

Methane measurements became operational at Cape Grim in August 1993. The yearly average CH_4 concentration measured at Cape Grim increased from approx. 1695 ppb to over 1730 ppb since then. Since such a long time series is available from Cape Grim, the continuation of these measurements at Cape Grim is of great importance.

7.1. Monitoring Set-up and Procedures

7.1.1. 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.

7.1.2. Analytical System

Gas chromatograph

A CARLE 100A gas chromatograph with an FID detector is used for ambient methane measurements at Cape Grim. Instrument details are summarised in Table 16.

Table 16: Gas chromatograph for methane at the Cape Grim station

Instrument	CARLE 100A, S/N 40647
at Cape Grim since	August 1993
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	a few 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 working standard is injected alternating with ambient air every 20 minutes. The current cylinder (UAN 994812) was assigned with a CH_4 concentration of 1827.59 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.

Maintenance includes regular instrument checks, including checks of flows, temperature, pressures and general operation of the system. Measures are taken when necessary.

7.1.3. 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 CSIRO, 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. 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.

7.1.4. 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.

7.2. Inter-Comparison of in-situ Methane Measurements

7.2.1. 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 eight transfer standards of the WCC (approx. concentration range 1690 - 1950 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 (CA04462, CA04580) at EMPA before and after the audit (see Appendix V). 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 26. to 29. November 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 17.

Table 17: 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. 1690 – 1950 ppb
injections per concentration:	5 to 12

7.2.2. Results of the Methane Inter-comparison

The results of the inter-comparison between the CARLE 100A field instrument and the eight WCC transfer standards are shown in Table 18. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 19 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 Cape Grim. The data from the CARLE 100A field instrument were reprocessed during the audit and are based on the comparison with the working standard.

Table 18: Methane inter-comparison measurements at Cape Grim

No.	WCC standard	Cape Grim analysis (CARLE 100A GC-FID, Peak Height)				
	conc. ± 1σ (N)	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1692.3 ± 3.0 ppb (17)	1691.8	1.0	8	-0.5	0.0
2	1694.1 ± 3.1 ppb (20)	1693.4	1.1	9	-0.7	0.0
3	1720.1 ± 3.2 ppb (18)	1719.1	0.9	5	-1.0	-0.1
4	1773.8 ± 3.0 ppb (19)	1774.7	1.1	5	0.9	0.1
5	1796.3 ± 2.5 ppb (19)	1798.7	1.2	6	2.6	0.1
6	1816.8 ± 4.1 ppb (19)	1817.5	0.9	5	0.7	0.0
7	1820.3 ± 4.1 ppb (19)	1820.6	1.0	6	0.3	0.0
8	1945.8 ± 3.0 ppb (20)	1944.1	1.3	5	-1.7	-0.1

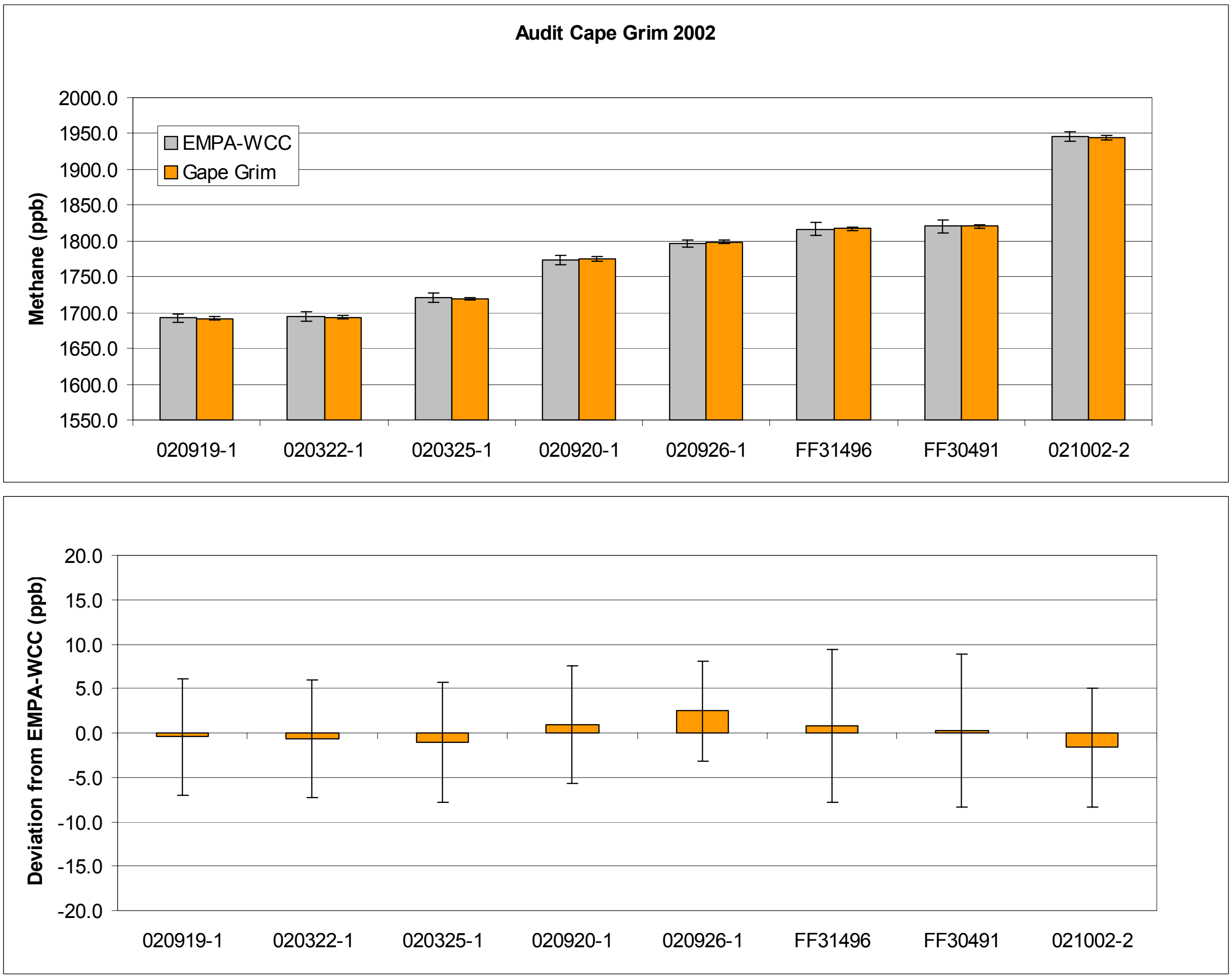

Figure 19: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix V) measured with the GC system of Cape Grim (orange).
lower panel: deviation of Cape Grim from the conventional true value.
The error bars represent the 95% confidence interval.

Comment

The CH_4 concentrations of the WCC-EMPA transfer standards as obtained with the Cape Grim field instrument agrees very well with the conventional true value in the concentration range between 1690 and 1950 ppb methane. The deviation from the transfer standards is less than 0.1 %. Thus, the Cape Grim methane measurements can be considered to be fully traced to the GAW reference standards.

7.3. 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.

8. Conclusions

The global GAW station Cape Grim is a well-established site within the GAW programme, and long time series of high quality are available 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. Only minor recommendations are made concerning these parameters.

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

As a first step towards re-solving this issue, the CO scale of CSIRO was inter-compared with WCC-EMPA after the Cape Grim audit. A strong linear relationship between WCC-EMPA and CSIRO was observed, with a difference is in the order of the recent revision of the CO scale by CMDL. The results of the inter-comparison will provide significant input for the recently established SAG for reactive gases and is a step towards re-solving the issue of inconsistency and uncertainty in the carbon monoxide scales.

9. References

Francey, R.J., L.P. Steele, D.A. Spencer, R.L. Langenfelds, R.M. Law, P.B. Krummel, P.J. Fraser, D.M. Etheridge, N. Derek, S.A. Coram, L.N. Cooper, C.E. Allison, L. Porter and S. Baly, The CSIRO (Australia) measurement of greenhouse gases in the global atmosphere, *report of the 11th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques*, Tokyo, Japan, September 2001, S.Toru and S. Kazuto (editors), World Meteorological Organization Global Atmosphere Watch, 97-111, 2003.

Masarie, K.A., R.L. Langenfelds, C.E. Allison, T.J. Conway, E.J. Dlugokencky, R.J. Francey, P.C. Novelli, L.P. Steele, P.P. Tans, B. Vaughn and J.W.C. White, NOAA/CSIRO Flask Air Intercomparison Experiment: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories, *J. Geophys. Res.*, 106, 20445-20464, 2001.

Appendix

I Inter-comparison Results for the Back-up Ozone Analyser ML9810

The results comprise the inter-comparison between the Monitor Labs 9810 instrument field instrument and the WCC transfer standard TEI 49C-PS, carried out on 28. November 2002. This instrument is operated as a backup instrument, and data are not submitted.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Table 19. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 20 and 21 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 20 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 21 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 22).

Table 19: Inter-comparison of the ML9810 field instrument

	TEI 49C-PS		**ML9810 #327B-125**			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.34	0.08	0.15	0.29	-0.2	
2	19.94	0.09	18.52	1.17	-1.4	-7.1%
3	9.99	0.08	9.04	0.59	-1.0	-9.6%
4	89.98	0.07	88.29	0.98	-1.7	-1.9%
5	30.04	0.08	28.98	0.62	-1.1	-3.5%
6	50.06	0.12	48.19	0.89	-1.9	-3.7%
7	0.30	0.14	0.42	0.53	0.1	
8	0.31	0.10	0.14	0.19	-0.2	
9	30.04	0.09	28.79	0.60	-1.3	-4.2%
10	90.00	0.08	87.99	1.16	-2.0	-2.2%
11	50.06	0.07	48.60	1.01	-1.5	-2.9%
12	20.09	0.11	18.86	0.72	-1.2	-6.1%
13	10.08	0.13	9.10	0.78	-1.0	-9.7%
14	0.27	0.12	0.07	0.13	-0.2	
15	0.28	0.09	0.18	0.30	-0.1	
16	10.05	0.17	9.12	0.59	-0.9	-9.2%
17	90.01	0.06	88.34	1.42	-1.7	-1.9%
18	30.03	0.27	29.03	0.54	-1.0	-3.3%
19	20.09	0.09	18.93	0.44	-1.2	-5.8%
20	50.05	0.11	48.77	0.62	-1.3	-2.6%
21	0.33	0.15	0.28	0.22	0.0	

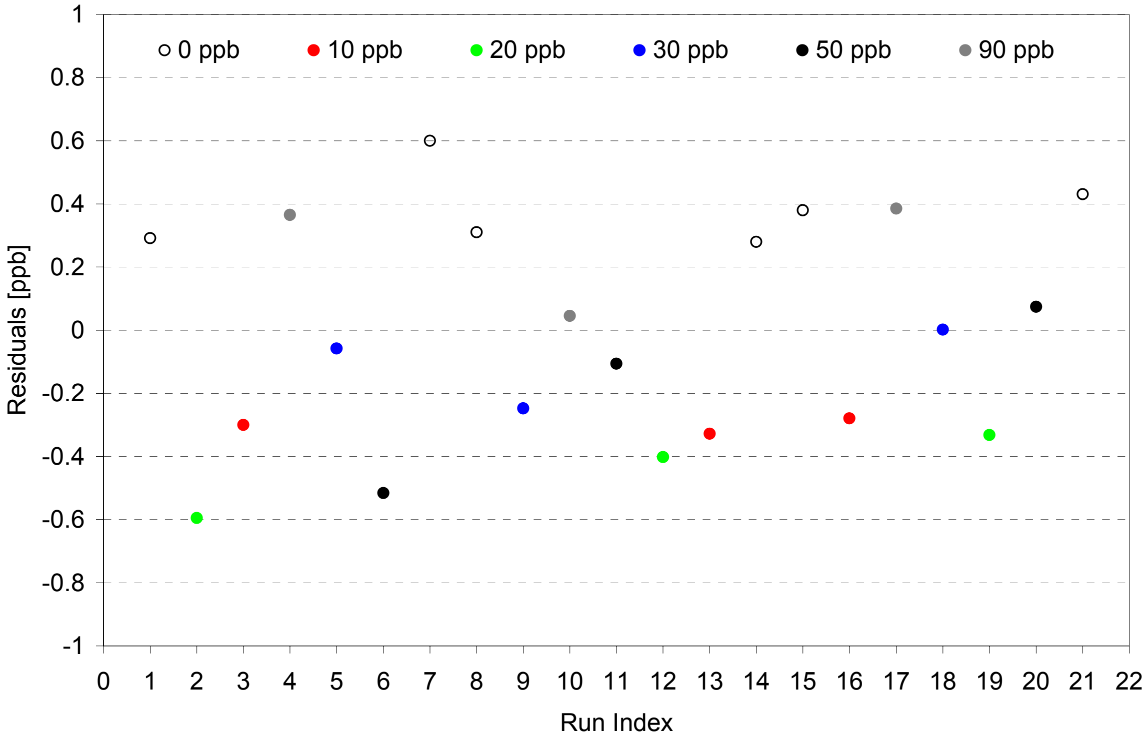

Figure 20: Residuals to the linear regression function (ML9810 #327B-125) vs the run index (time dependence)

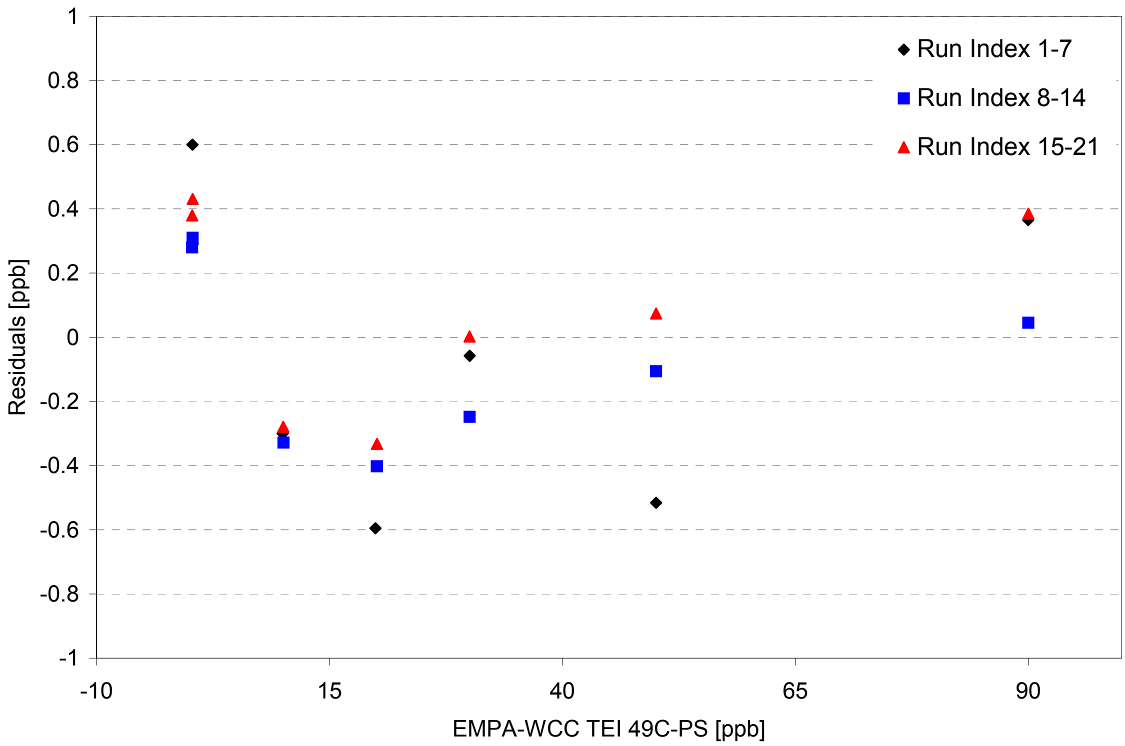

Figure 21: Residuals to the linear regression function (ML9810 #327B-125) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI ML9810 #327B-125 field instrument with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 10-100 ppb ozone) is:

ML9810 #327B-125:

ML9810 #327B-125 = 0.982 x TEI 49C-PS - 0.47 ppb

ML9810 #327B-125 = O3 mixing ratio in ppb, determined with ML9810 #327B-125

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

Standard deviation of:	- slope s_m	0.003	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.11	(f = 19)
	- residuals in ppb	0.25	(n = 21)

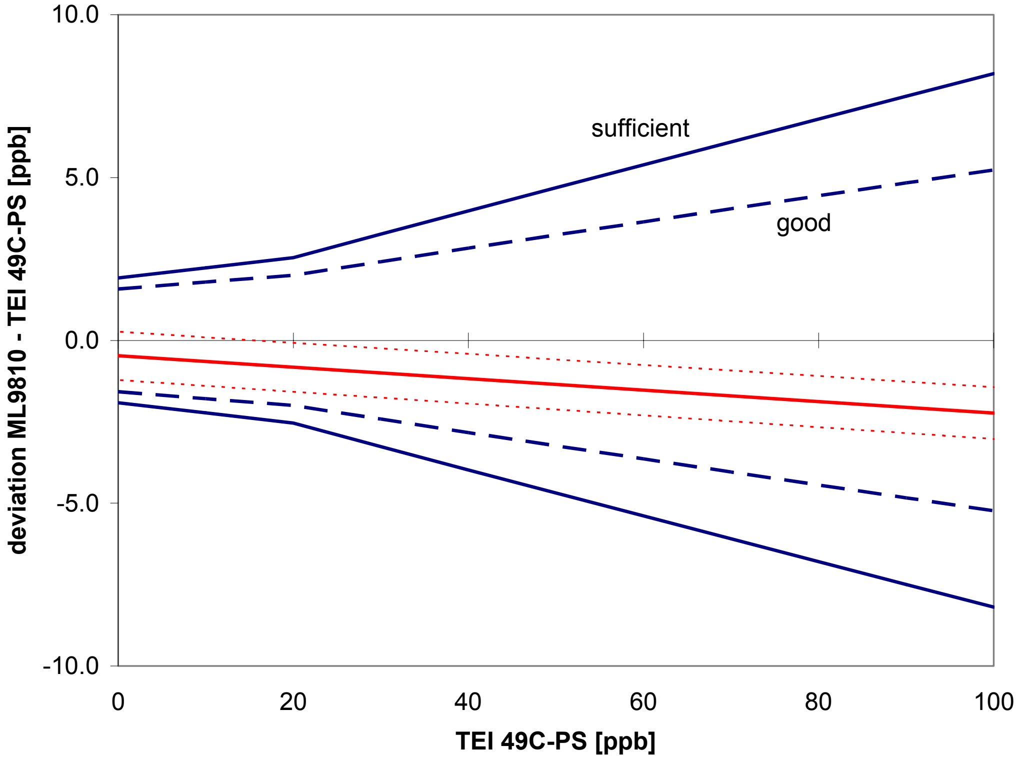

Figure 22: Inter-comparison of instrument ML9810 #327B-125

II 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 23. 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.

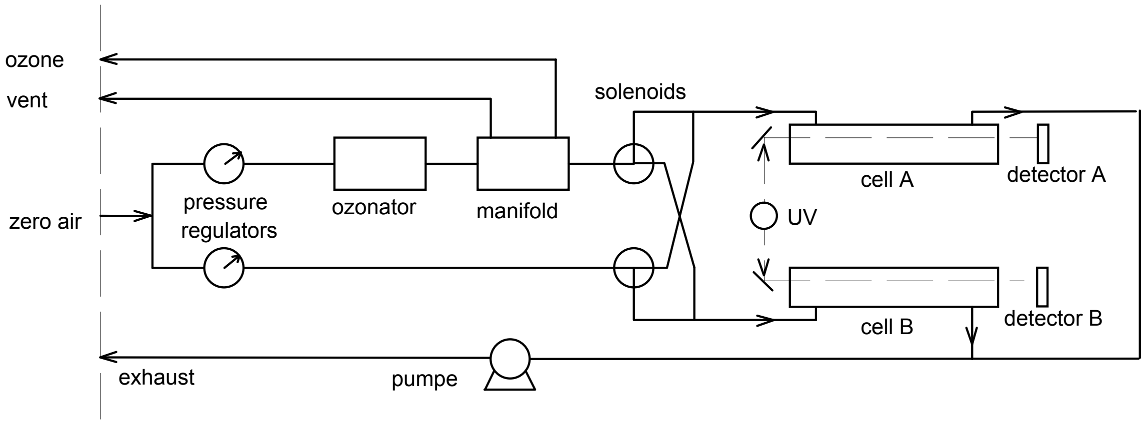

Figure 23: Flow schematic of TEI 49C-PS

III 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 20 and Figure 24.

Table 20: 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

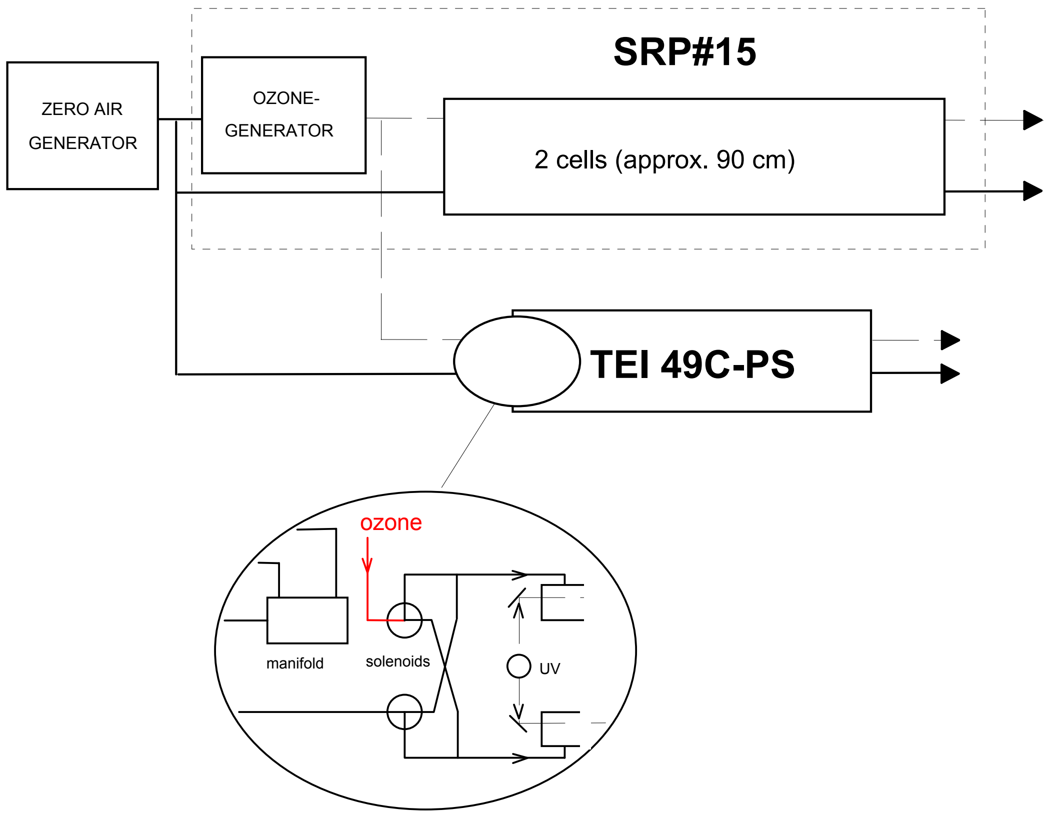

Figure 24: Instruments set up SRP -TEI 49C-PS

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 25 and 26 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.

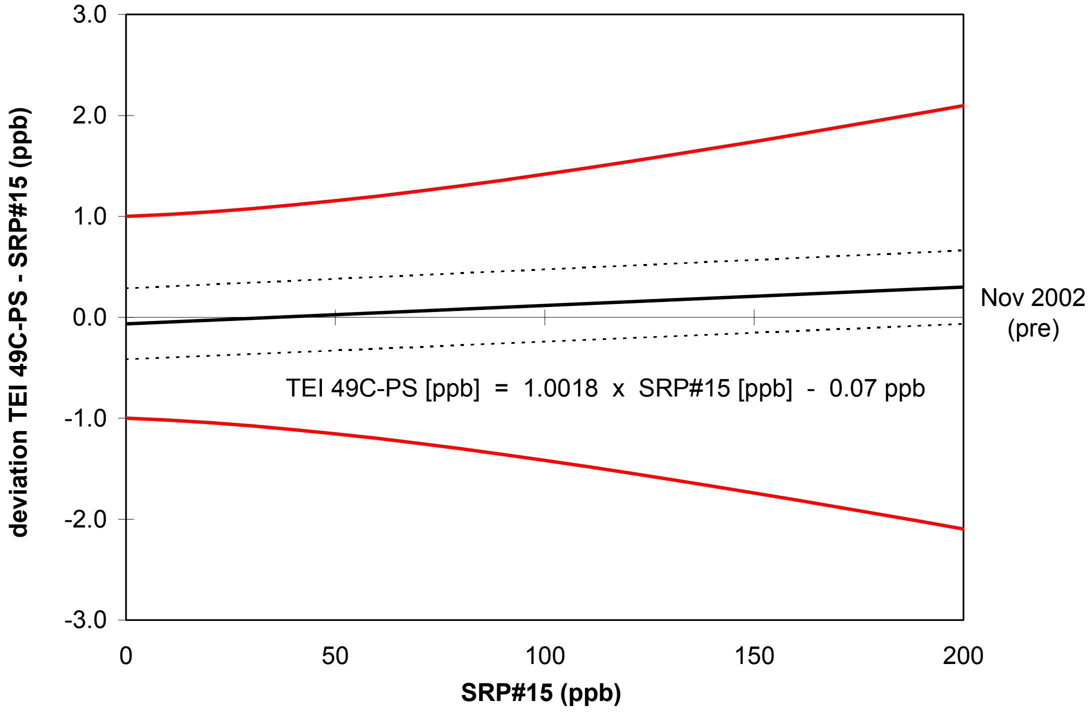

Figure 25: Transfer standard before audit

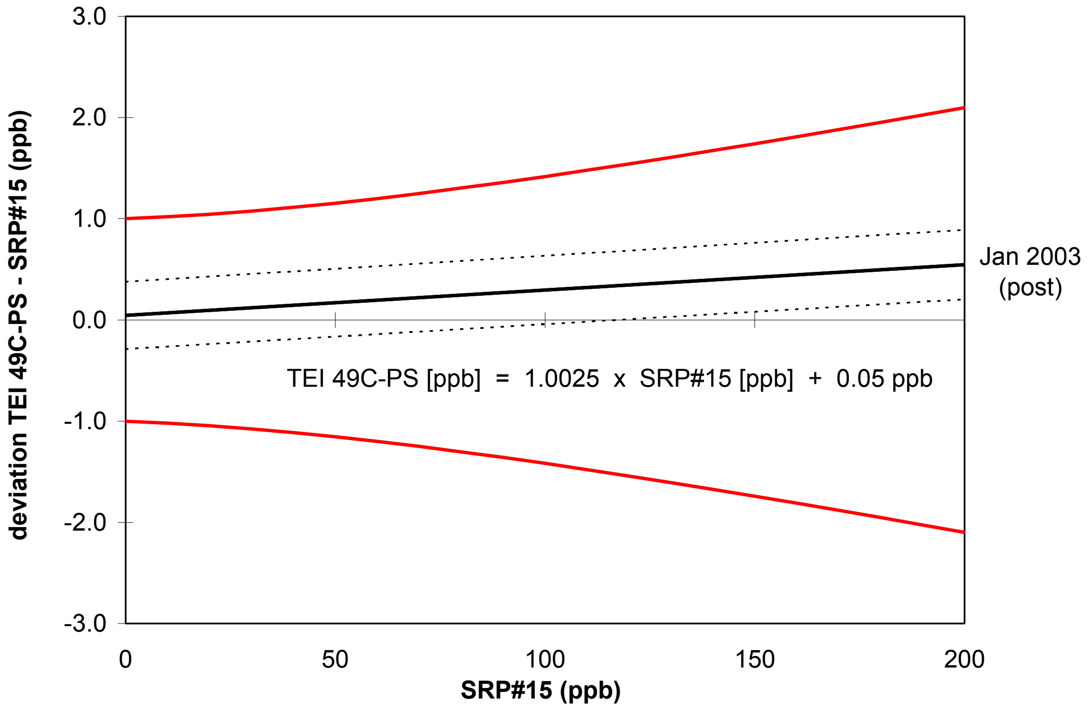

Figure 26: Transfer standard after audit

IV 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 21:

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 22.

Table 21: 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 22: CO transfer standards of the WCC (average of calibrations from September 02 and January 03). 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 (2 l cylinder)	35.9 ± 0.8 ppb	36.8 ± 1.1 ppb	021002-2
WCC Transfer Standard (2 l cylinder)	44.3 ± 1.1 ppb	44.3 ± 1.0 ppb	020322-1
WCC Transfer Standard (2 l cylinder)	54.4 ± 0.6 ppb	55.0 ± 0.9 ppb	020325-1
WCC Transfer Standard (6 l cylinder)	72.3 ± 0.8 ppb	72.3 ± 1.1 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	81.6 ± 0.8 ppb	82.2 ± 1.4 ppb	020919-1
WCC Transfer Standard (2 l cylinder)	93.4 ± 0.7 ppb	94.2 ± 1.1 ppb	020920-1
WCC Transfer Standard (6 l cylinder)	158.8 ± 0.9 ppb	160.3 ± 0.8 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	233.5 ± 0.8 ppb	234.1 ± 2.1 ppb	020926-1

V 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 23. The WCC-EMPA transfer standards (Table 24) are traced back to the CMDL standards shown below.

Table 23: 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 24: WCC CH_4 transfer standards (average of calibrations from September 02 and January 03). 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 (2 l cylinder)	1691.3 ± 4.3 ppb	1693.2 ± 1.7 ppb	020919-1
WCC Transfer Standard (2 l cylinder)	1692.1 ± 3.0 ppb	1696.0 ± 3.1 ppb	020322-1
WCC Transfer Standard (2 l cylinder)	1718.5 ± 4.4 ppb	1721.7 ± 1.9 ppb	020325-1
WCC Transfer Standard (2 l cylinder)	1774.1 ± 3.6 ppb	1773.5 ± 2.4 ppb	020920-1
WCC Transfer Standard (2 l cylinder)	1798.0 ± 2.9 ppb	1794.5 ± 2.0 ppb	020926-1
WCC Transfer Standard (6 l cylinder)	1819.0 ± 4.4 ppb	1814.5 ± 3.8 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	1819.9 ± 5.6 ppb	1820.7 ± 2.5 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	1947.1 ± 3.2 ppb	1944.4 ± 2.7 ppb	021002-2