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 03/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION MAUNA LOA

USA, AUGUST 2003

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 ISO/IEC 17025

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Mauna Loa from 17. to 22. August 2003 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. This was the first audit by WCC-EMPA. The results of the audit can be summarized as follows:

System Audit of the Observatory

The Mauna Loa station offers excellent facilities for atmospheric research and measurement campaigns. The observatory was established in 1956 and hosts big variety of research projects in different buildings.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs of the WCC transfer standard with the new ozone instrument for the station, demonstrated good agreement between the main analyzer and the transfer standard. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1). An assessment of the old Dasibi ozone instrument could not be done directly because of an instrument failure. However, an indirect evaluation was possible via the station back-up instrument TEI 49. Parallel measurements of the old Dasibi and the back-up instruments showed relatively good agreement. Refer to Section 4.2.2 and Appendix I of the audit report for details.

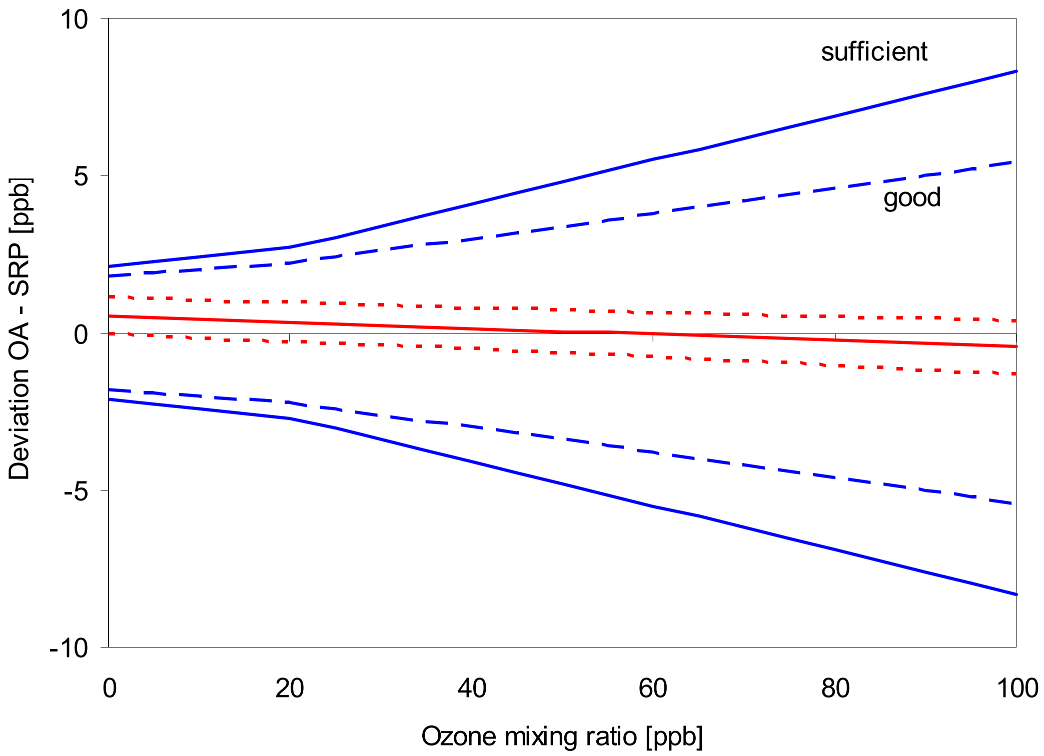


Figure 1: Deviation of the TEI 49C #66003-351 field instrument (OA) from the WCC reference (SRP#15)

Due to the good results only minor recommendations were made by WCC-EMPA concerning the ozone measurements with the new analyzer. The main recommendations include an increase of the calibration frequency at the site with a reference instrument. An executive summary of the audit results for surface ozone is given in Appendix VIII.

Audit of the Carbon Monoxide Measurement

The analysis of the WCC-EMPA transfer standards by the Mauna Loa station resulted in lower values (-2.3 to -3.4 ppb or -2.5 to -4.6%) for the concentrations between 50 and 120 ppb compared to the reference. No significant deviation was found for the transfer standard with approx. 160 ppb CO. The transfer standard with a higher concentration (234.1 ppb) resulted in a higher finding by Mauna Loa (+6.6 ppb or +2.8%) but was outside the calibrated range of the station instrument.

Transfer standards of WCC-EMPA are traceable to the CMDL scale. 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 (revised scale).

The differences observed at Mauna Loa reflect mainly the revision and uncertainty of the CO scale. The results of Mauna Loa compare well to the originally assigned numbers of the CMDL revised scale. However, WCC-EMPA assigned values still remain higher, although the revision of the scale by CMDL lowered the difference between CMDL and WCC-EMPA significantly.

Audit of the Methane Measurement

The results of the inter-comparisons between the seven WCC-EMPA transfer standards and the GC system of the Mauna Loa station showed good agreement over a concentration range of 1690 to 1900 ppb. The deviation was within ±0.25 %. No further recommendations are suggested by WCC-EMPA concerning methane measurements.

Conclusions

All measurements of the audited parameters (O_3, CO, CH_4) at Mauna Loa were performed at a high level of expertise. 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.

The absolute uncertainty of the carbon monoxide scales remains an unsolved problem and requires further investigation. The SAG reactive gases should get in the lead in this issue.

Dübendorf, 8. June 2004

EMPA Dübendorf, WCC-EMPA

Project scientist

Dr. C. Zellweger

Project manager

Dr. B. Buchmann

2. Introduction

The observatory of Mauna Loa is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters. The observatory is run by the National Oceanic and Atmospheric Administration (NOAA), under the organization of the Climate Monitoring & Diagnostics Laboratory (CMDL). Other global GAW stations operated by CMDL comprise South Pole (Antarctica), American Samoa ad Barrow (Alaska). The above **Global GAW Stations** are part of the United States contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program.

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

In agreement with the director of the CMDL Observatories, Russell C. Schnell, and the station manager, John E. Barnes, a **system and performance audit** at the Mauna Loa observatory was conducted by WCC-EMPA between 18-22 August 2003.

The scope of the audit was the whole measurement system in general and surface ozone and carbon monoxide 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 analyzers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the ozone inter-comparison have been developed by WCC-EMPA and QA/SAC Switzerland [Hofer et al., 2000; Klausen et al., 2003]. The present audit report is distributed to NOAA / CMDL and the World Meteorological Organization in Geneva.

Staff involved in the audit

Mauna Loa Observatory	Dr. John E. Barnes	contacts, general program
	Steve C. Ryan	technical assistance at the observatory
NOAA / CMDL	Samuel J. Oltmans	technical assistance at the observatory
	Dr. Paul C. Novelli	technical assistance at the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
	Dr. Brigitte Buchmann	assistant auditor

Previous audits at the GAW station Mauna Loa:

None by WCC-EMPA

3. Global GAW Site Mauna Loa, USA

3.1. Description of the Site

The Mauna Loa Observatory (MLO) (19°32'20"N 155°34'41"W) is located on the Island of Hawaii at an elevation of 3397 m on the northern flank of Mauna Loa volcano. Established in 1957, Mauna Loa Observatory has grown to become one of the premier long-term atmospheric monitoring facility on earth and is the site where the ever-increasing concentrations of global atmospheric carbon dioxide were determined. The observatory consists of 10 buildings from which up to 250 different atmospheric parameters are measured by a complement of 12 NOAA/CMDL and other agencies scientists and engineers.

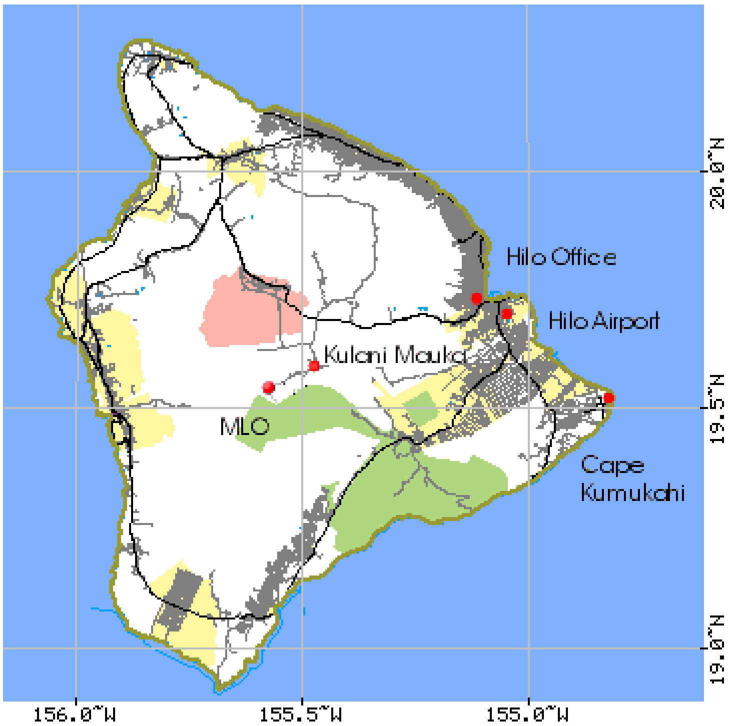


Figure 2: Map of big island with the location of the MLO observatory (from www.mlo.noaa.gov)

Ozone, Carbon Monoxide and Methane Levels at Mauna Loa

The frequency distribution of 1 hour mean values of surface ozone, carbon monoxide and methane is shown in Figures 3 to 5.

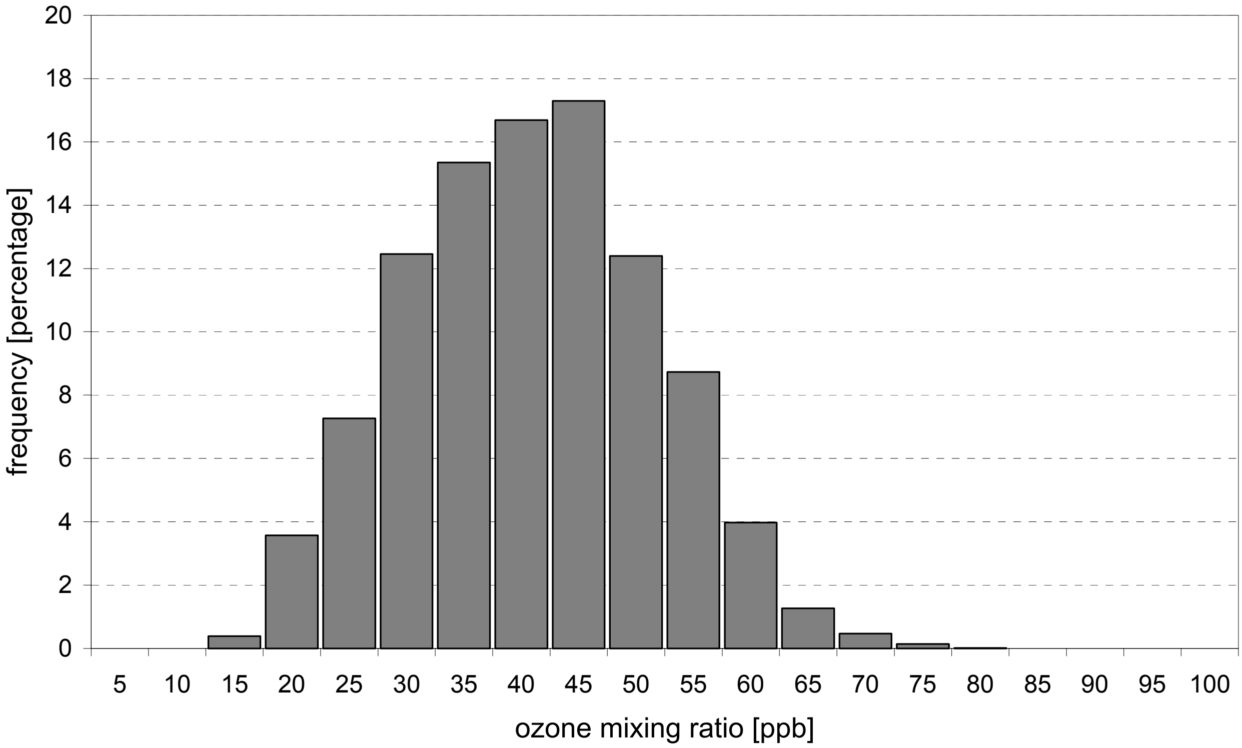


Figure 3: Frequency distribution of the 1 hour mean ozone mixing ratio (2001) at Mauna Loa. Availability of data: 97.4%.

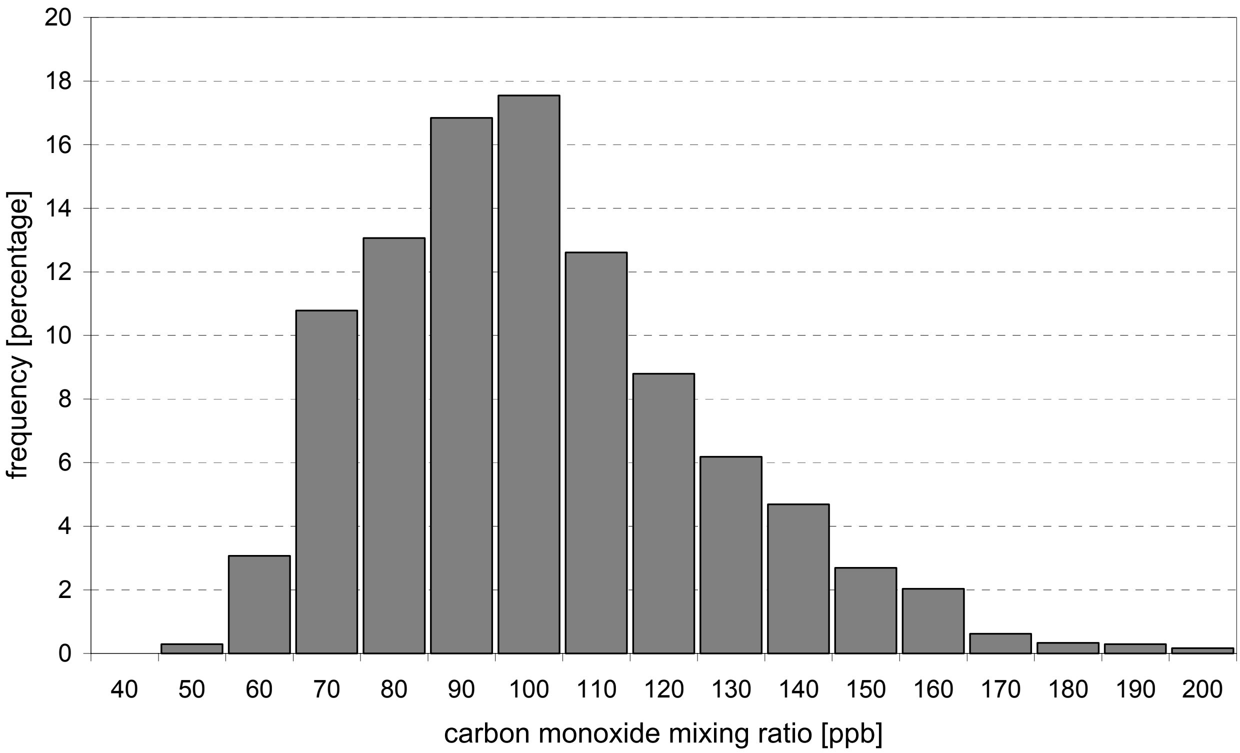


Figure 4: Frequency distribution of the 1 hour mean carbon monoxide mixing ratio (2003) at Mauna Loa.

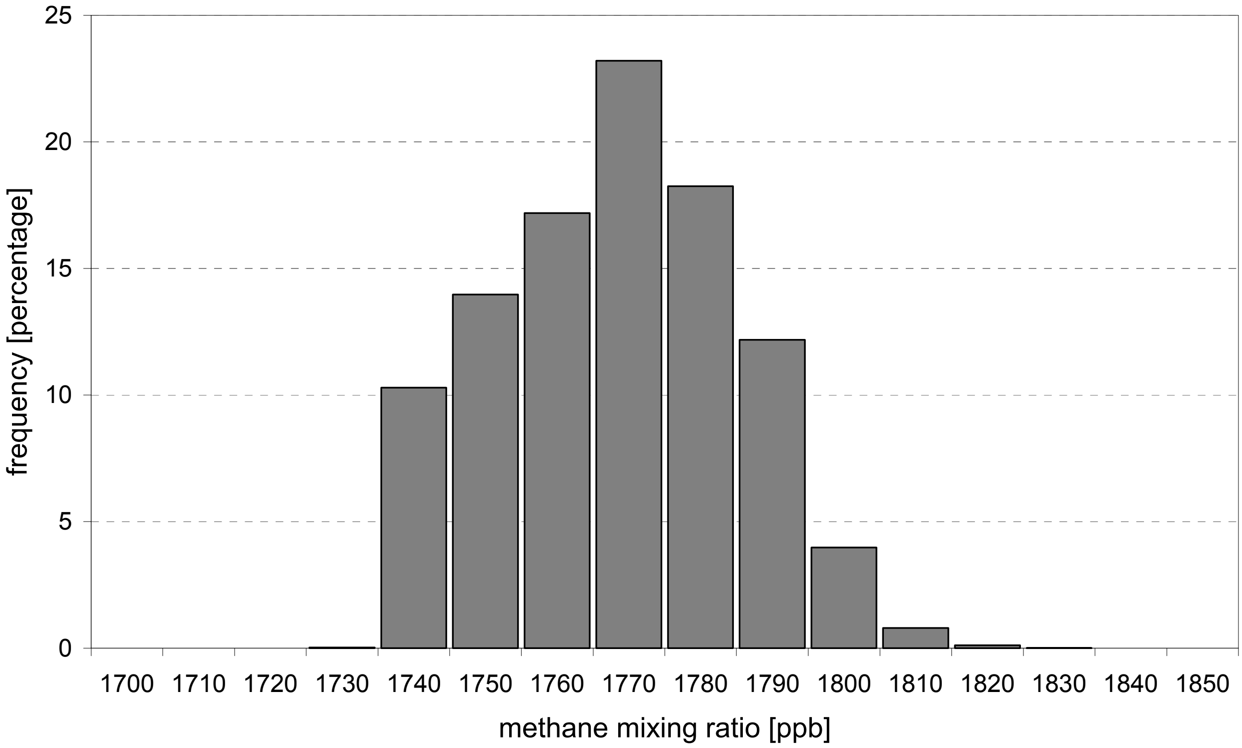


Figure 5: Frequency distribution of the 1 hour mean methane mixing ratio (2001) at Mauna Loa. Availability of data: 96.3%.

3.2. Description of the Observatory

The Mauna Loa Observatory consists of several laboratory and office buildings (Figure 6). An overview map is shown in Figure 7. Ozone measurements are carried out in the Keeling building (Figure 8), and carbon monoxide and methane are measured in the NDSC building (Figure 9). More information about station facilities and measurement program are available from the Mauna Loa web page (www.mlo.noaa.gov).

Comment

- The Mauna Loa GAW station offers spacious laboratories which meet all requirements for the measurement of atmospheric parameters. It is an established long-running observatory with a complete and diverse measurement program.

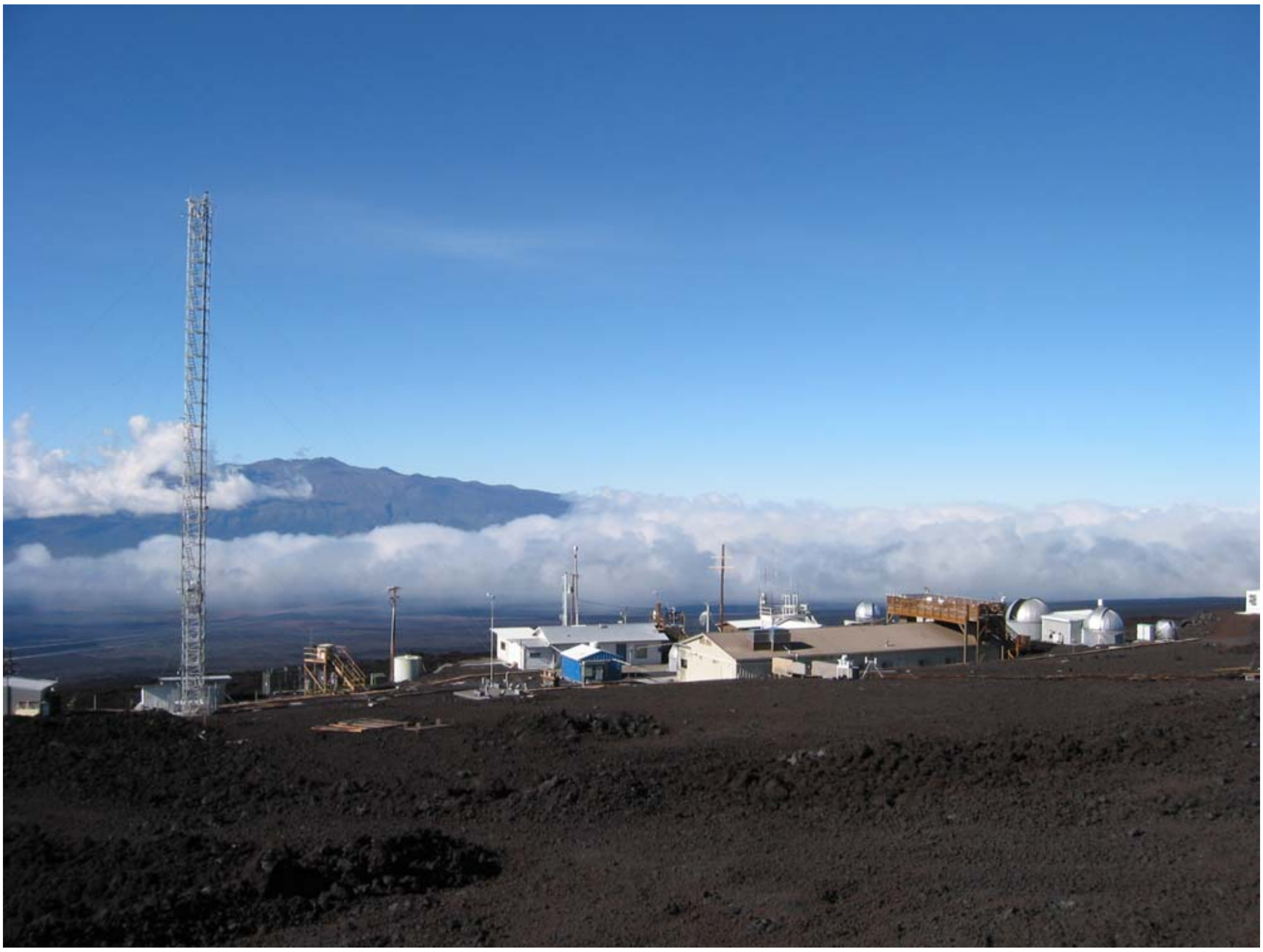


Figure 6: Mauna Loa observatory

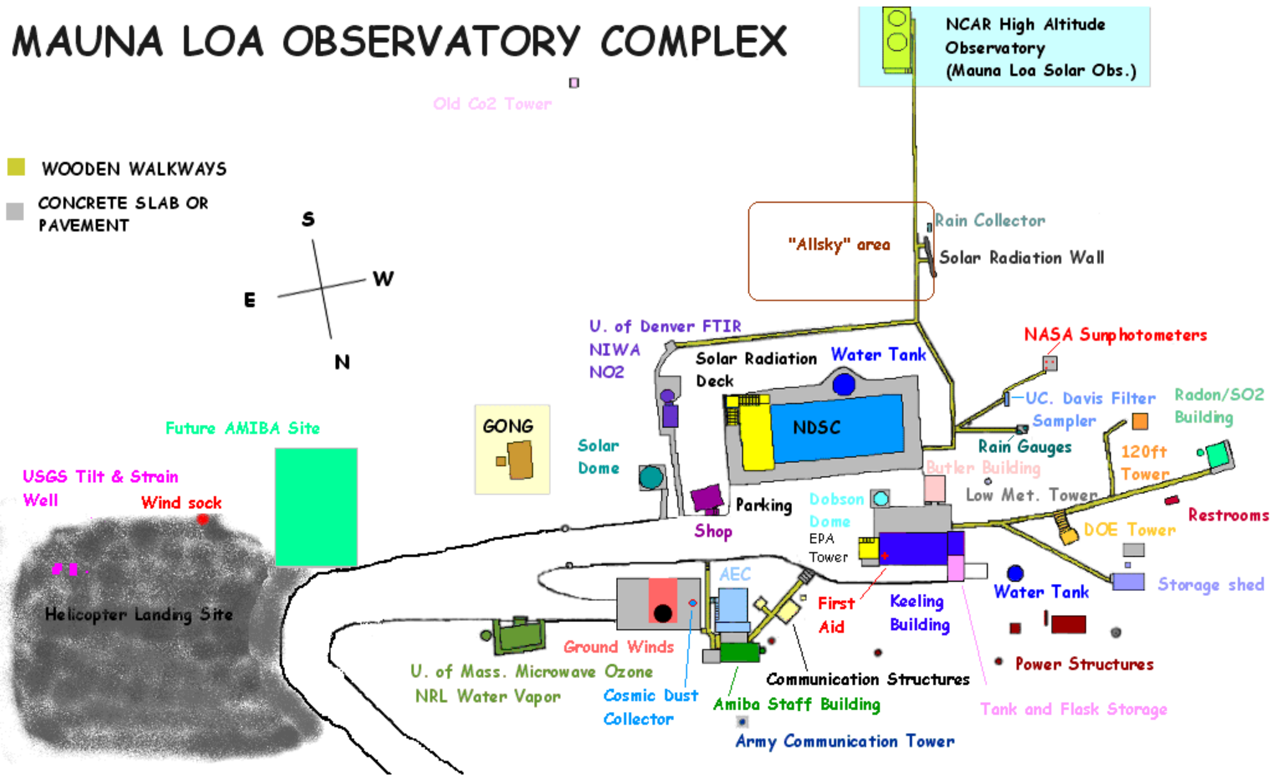


Figure 7: Map of Mauna Loa site (from www.mlo.noaa.gov)

Figure 8: Ozone and other measurements in the Keeling building

Figure 9: CO, CH_4 and CO_2 measurements in the NDSC building

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Mauna Loa (as of August 2003)

Name	**Position and duty**
NOAA/CMDL	
Dr Russell Schnell	Head of observatory observations group
Mr Samuel Oltmans	Head of ozone and water vapor group
Dr Paul Novelli	Carbon cycle group, responsible for CO
Dr Ed Dlugokencky	Carbon cycle group, responsible for CH_4
Mauna Loa Observatory	
Dr John Barnes	Station manager
Mr Steve Ryan	Station operator, prime contact CO, CH_4
Mr Alan Yoshinaga	Station operator, prime contact O_3,
Mr David Nardini	Station operator
Ms Leslie Pajo	Administration
Mr Robert Uchida	Station operator
Mr Darryl Kuniynki	Station operator
Mr Paul Fukumura-Sawada	Station operator

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

4.1.1. Air Inlet System

Sampling-location: 15 m above ground on top of the Keeling building.

Sample inlet:

Rain protection: The Inlet is protected against rain and snow by an up-side-down electro polished stainless steel intake.

Inlet/Manifold: 10 m sample inlet on the roof, leading to the laboratory where all instruments are connected to the main sampling line. Outer/inner diameter 50/45 mm, electro polished stainless steel. Total length ca. 12 m. Ozone instruments are connected after a total length of ca. 11 m. Flow rate 600 liter per minute.

Inlet-filter: Teflon inlet filter before analyzer, exchanged every second month

Sample line: PFTE. Length = 3 m, i.d. = 4 mm. Flow rate 1.8 liters per minute.

Residence time in the sampling line: approx. 3 s

Comment

The Teflon line was clean and free of dust. The ozone loss in the stainless steel inlet and manifold was checked by comparing with a direct PFTE sample line of a second analyzer. Ozone loss was found to be approximately 0.5% (during the last check in early 2002). No correction is applied for this loss. Materials as well as the residence time of the inlet system are adequate for trace gas measurements.

4.1.2. Instrumentation

Ozone Analyzer

A new TEI49C ozone analyzer was installed at Mauna Loa in August 03 and will replace the old TEI 49 which was the main instrument since January 03. The old TEI was the following up instrument for the Dasibi instrument being the main instrument for many years. Measurements are still performed using the two ozone analyzers running in parallel. Instrument details are summarized in Table 2. All instrumentation is installed inside the laboratory and is protected from direct sunlight. The laboratory is air-conditioned (set point 21°C), but the temperature inside the ozone rack is approx. 28°C.

Table 2: Ozone analyzers at the Mauna Loa Research Station

Type	TEI 49C #66003-351	TEI 49 #22643-206	Dasibi 1003 AH #1323[1]
Method	UV absorption	UV absorption	UV absorption
at Mauna Loa	since August 2003	since January 2002	until August 2003
Range	0-1000 ppb	0-1000 ppb	0-1000 ppb
Analog output	0-10 V	0-10 V	0-1 V
Span Coefficient	1.000	1.000	
Zero Offset	0.0	2	

[1] This instrument was the main station instrument until the time of the audit. It stopped operation during the audit, and was replaced by the TEI 49 C.

Ozone Calibrator

No ozone calibrator is available at the site. However, calibrations are performed about every 2 years with a transfer standard (TEI 49C or Dasibi 1003-AH) of NOAA/CMDL at the site. Both CMDL standards were available at the site during the audit. An inter-comparison with the WCC-EMPA reference is shown in Appendix II and III.

Operation and Maintenance

The instruments are checked on working days for general operation. These checks include inspection of flow rates and data acquisition. Weekly checks include a zero and span (~40-50 ppb) check. The weekly zero check is used for data correction. In addition, a monthly span check with three concentrations levels (25 / 40-50 / 70 ppb) is made. A full instrument calibration with a transfer standard from CMDL is performed every second year.

4.1.3. Data Handling

Data Acquisition and –transfer

A custom made data acquisition is installed at the site next to the ozone analyzers. It consists of an ADC circuit board and a PC. One-minute average concentration are stored and transferred daily to CMDL via network connection.

Data Treatment

Data processing is done at CMDL and consists of a weekly visual inspection of time series. Invalid values, i.e. data from manual calibrations, are flagged as invalid data but are not removed from the database. Based on the results of the weekly zero checks and the calibration with the CMDL transfer standard a recalculation of the acquired data is made. Refer to section 4.2.2. for the current data re-calculation.

Data Submission

Ozone data have been submitted to the recently established data center for surface ozone at JMA (World Data Center for Greenhouse Gases, WDCGG).

4.1.4. Documentation

Logbooks

Electronic station and instrument logbooks are available. The notes are up to date and describe all important events.

Standard Operation Procedures (SOPs)

A detailed SOP is available at the site. Furthermore, instrument manuals are available.

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

The WCC-EMPA audit was confined to all operational ozone instruments at the Mauna Loa station. Unfortunately, the main ozone analyzer (Dasibi) which was running at the station for several years stopped its operation due to defective parts before the audit. Considering the instrument age, the station operators decided to replace the instrument by a new TEI 49C. The link between the WCC-EMPA audit and Dasibi data can be made considering parallel measurements made between the TEI 49 and the Dasibi ozone instruments. Results from these parallel measurements are shown in Appendix I.

4.2.1. Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix IV-V) was operated in stand-by mode for warming up for 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 300 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 10 the experimental set-up during the audit. No modifications of the ozone analyzers which could influence the measurements were made for the inter-comparisons.

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

Table 3: Experimental details of the ozone inter-comparison

reference:	WCC: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49 #22643-206 TEI 49C #66003-351
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): 682.4 hPa Adjusted to ambient pressure (683.4 hPa) before the inter-comparison. TEI 49: no adjustments are possible. See comment below. TEI 49C: 684.4 hPa (no adjustment made)
concentration range	0 - 100 ppb
number of concentrations:	5 plus zero air at start and end
approx. concentration levels:	15 / 35 / 55 / 75 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 x between 19 and 21. August 2003
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

Comment: The TEI 49 used at the Mauna Loa station is an old model of the TEI 49 series. The electronics of this model does not allow to adjust to ambient pressures below 700 hPa. Therefore, pressure and temperature correction (P/T) was switched off, and pressure and temperature were compensated using data from the Dasibi instrument.

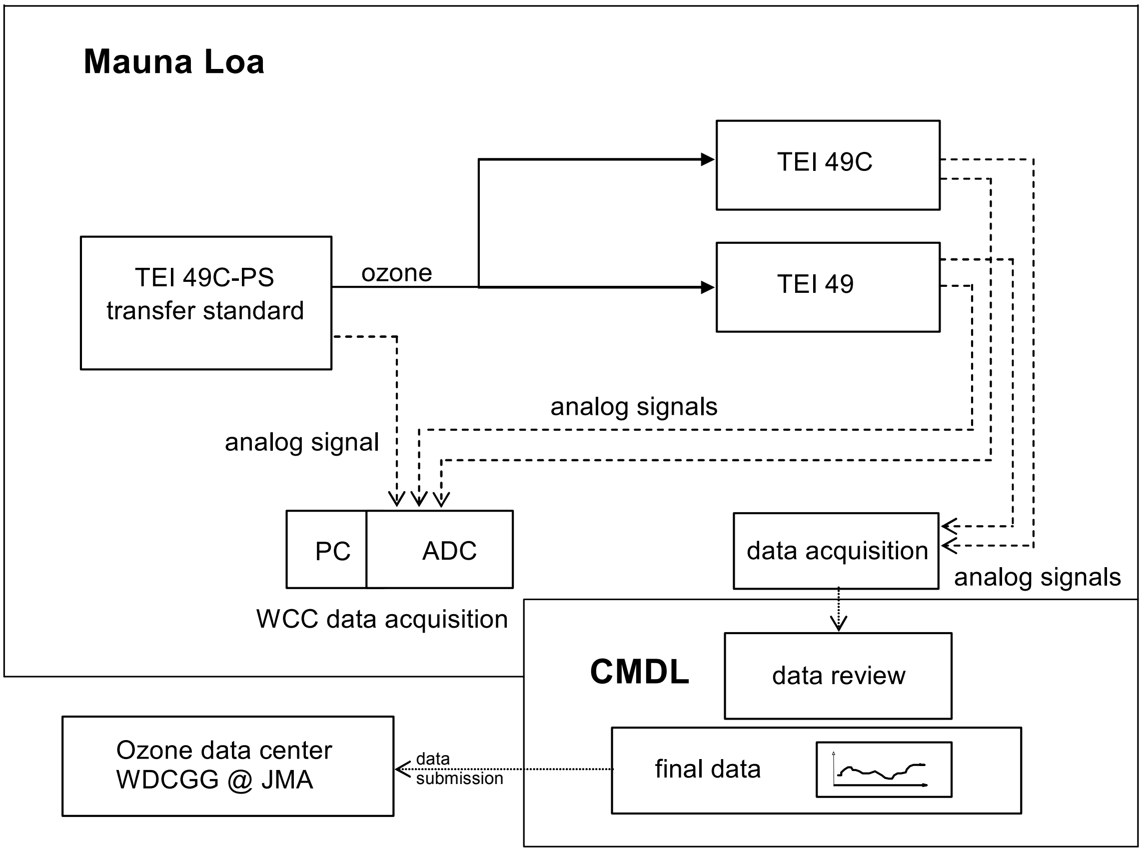


Figure 10: Experimental set up for the ozone inter-comparison

4.2.2. Results

The assessment of the inter-comparison was done according to Klausen et al. (2003).

Ozone Analyzer

The results comprise the inter-comparison between the TEI 49 #22643-206 and TEI 49C #66003-351 field instruments and the WCC transfer standard TEI 49C-PS, carried out between 19. and 21. August 2003.

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

Figures 11 to 14 show the residuals of the linear regression analysis of the field instruments compared to the EMPA transfer standard. The residuals versus the run index are shown in Figures 11 and 12 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figures 13 and 14 (concentration dependence). The result is presented for both instruments in a graph with the assessment criteria for GAW field instruments (Figures 15 and 16).

The data used for the evaluation was recorded by both EMPA and Mauna Loa data acquisition systems. This raw data was treated according to the usual station method. Corresponding to this procedure, the following corrections were applied to the raw data:

TEI 49 #22643-206

Data of this instrument were first corrected for pressure and temperature using equation (1):

O_3 [ppb] = 100*(Analog Output [V] – 0.05)*(1013/(Station pressure [hPa] -35)) * (T [K] 273.15) (1)

where 0.05 is the fixed offset and 35 hPa is the correction of the pressure drop. T is the temperature measured in the Dasibi instrument. The data from equation (1) were further re-calculated considering the last inter-comparison between the CMDL transfer standard and the relation of the transfer standard TEI49C and the NIST SRP#2 (2).

SRP#2 = 0.27 + 1.021 * (TEI49C#75573-380) (2)

This resulted in a final ozone concentration of

O_3 final [ppb] = 0.92 + 0.9623 *(TEI 49 #22643-206) (3)

TEI 49C #66003-351

The instrument readings of the new TEI49C analyzer were also corrected using the last inter-comparison with the CMDL transfer standard and were further corrected considering the relationship between the transfer standard and SRP#2 (2). This was done just before the audit. The equation used for the re-calculation for the new instrument was

O_3 final [pbb] = 0.14 + 1.013 *(TEI 49C#66003-351) (4)

Table 4: Inter-comparison of the ozone field instrument TEI 49 #22643-206

	TEI 49C-PS WCC-EMPA		**TEI 49 #22643-206 Mauna Loa**			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.27	0.13	-1.31	0.36	-1.04	
2	14.82	0.14	13.50	0.56	-1.32	-8.89
3	54.81	0.08	53.25	0.31	-1.56	-2.84
4	34.87	0.08	33.31	0.16	-1.56	-4.49
5	89.83	0.07	88.32	0.33	-1.52	-1.69
6	74.84	0.07	73.42	0.34	-1.42	-1.90
7	-0.30	0.13	-1.38	0.41	-1.08	
8	-0.29	0.13	-1.36	0.57	-1.07	
9	54.84	0.08	53.06	0.36	-1.79	-3.25
10	89.83	0.07	88.45	0.31	-1.38	-1.53
11	34.92	0.11	33.34	0.21	-1.58	-4.54
12	74.84	0.09	73.39	0.52	-1.45	-1.93
13	14.94	0.11	13.94	0.40	-1.00	-6.70
14	-0.35	0.14	-1.28	0.54	-0.93	
15	-0.25	0.09	-1.45	0.51	-1.20	
16	14.86	0.12	13.32	0.43	-1.54	-10.40
17	89.78	0.09	88.33	0.45	-1.45	-1.62
18	34.96	0.11	33.47	0.35	-1.49	-4.26
19	74.84	0.05	73.45	0.47	-1.39	-1.86
20	54.88	0.09	53.28	0.60	-1.60	-2.92
21	-0.23	0.11	-1.16	0.57	-0.92	

Table 5: Inter-comparison of the ozone field instrument TEI 49C #66003-351

run index	TEI 49C-PS WCC-EMPA conc.	sd	TEI 49C #66003-351 Mauna Loa conc.	sd	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.19	0.11	0.40	0.15	0.58	
2	14.90	0.19	15.62	0.18	0.72	4.82
3	54.92	0.10	54.93	0.28	0.01	0.02
4	34.96	0.05	35.18	0.21	0.22	0.64
5	89.84	0.11	89.27	0.30	-0.56	-0.63
6	74.94	0.14	74.56	0.29	-0.38	-0.51
7	-0.24	0.10	0.12	0.28	0.36	
8	-0.18	0.16	0.07	0.19	0.25	
9	54.94	0.16	54.60	0.22	-0.34	-0.62
10	89.87	0.08	89.42	0.36	-0.45	-0.50
11	34.92	0.16	35.00	0.20	0.08	0.22
12	74.86	0.15	74.55	0.21	-0.31	-0.41
13	14.95	0.14	15.26	0.15	0.30	2.04
14	-0.26	0.10	0.27	0.17	0.52	
15	-0.27	0.11	0.31	0.09	0.58	
16	14.96	0.09	15.31	0.15	0.35	2.35
17	89.79	0.13	89.40	0.36	-0.39	-0.43
18	35.02	0.09	35.21	0.22	0.18	0.53
19	74.88	0.18	74.91	0.20	0.03	0.05
20	54.98	0.08	55.08	0.11	0.11	0.19
21	-0.14	0.10	0.32	0.20	0.46	

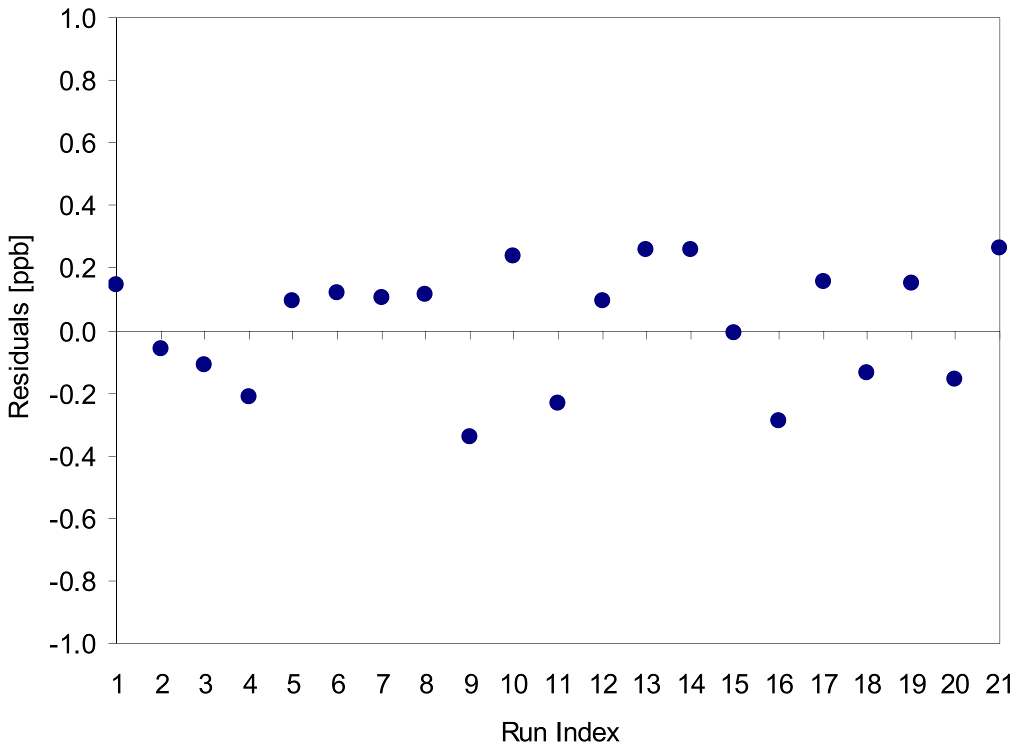


Figure 11: Residuals to the linear regression function (TEI 49 #22643-206) vs. the run index (time dependence)

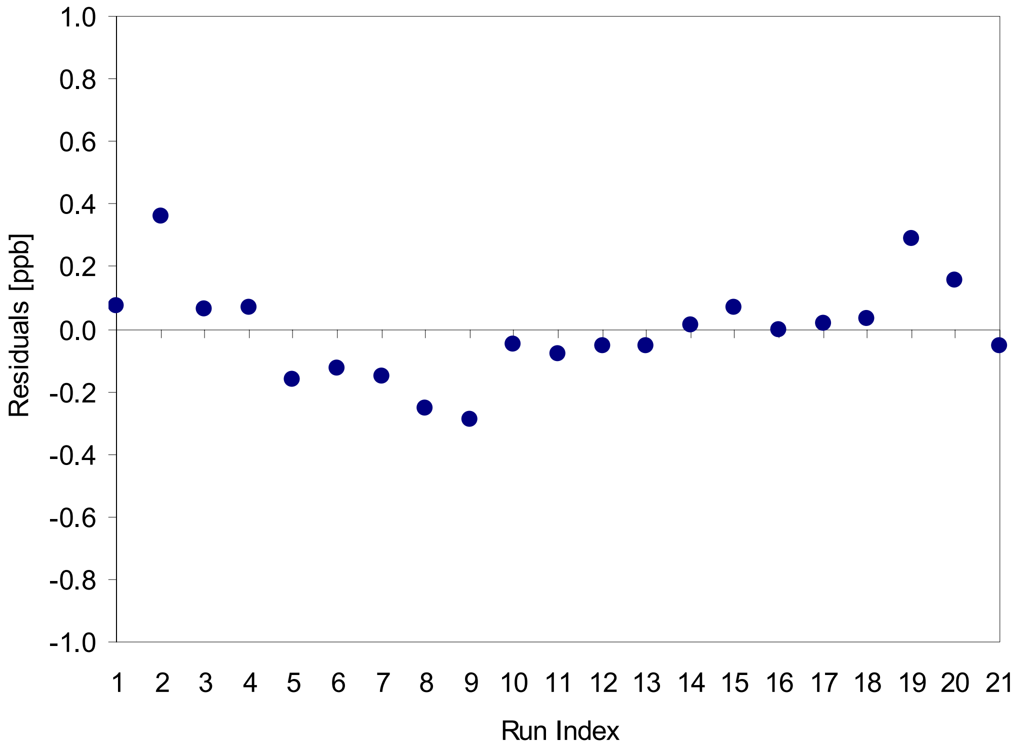


Figure 12: Residuals to the linear regression function (TEI 49C #66003-351) vs. the run index (time dependence)

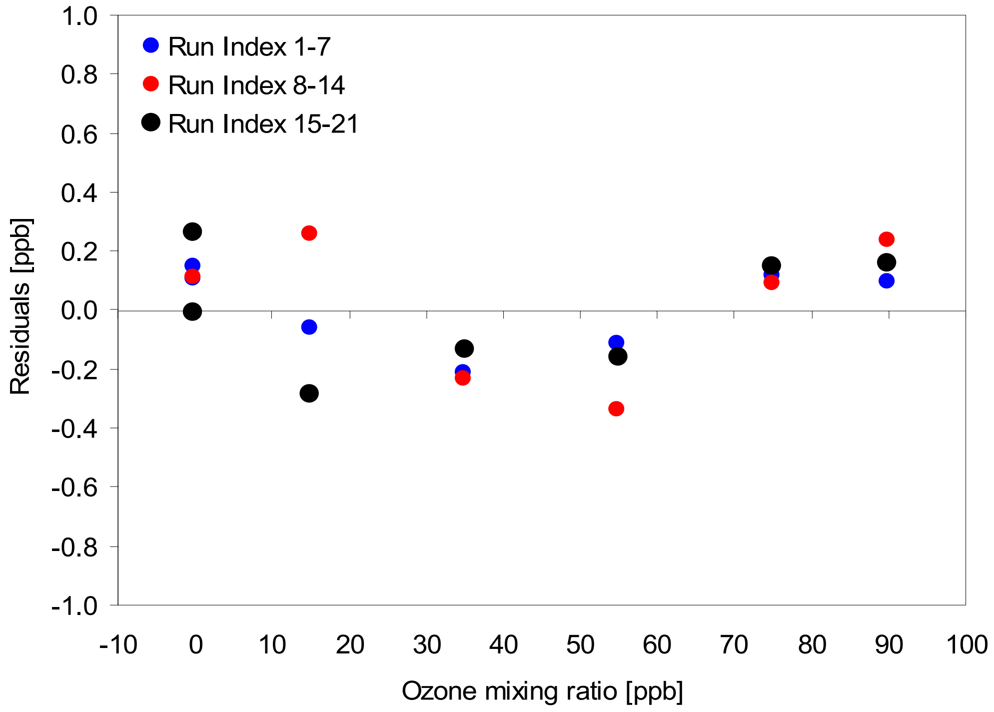


Figure 13: Residuals to the linear regression function (TEI 49 #22643-206) vs. the concentration of the WCC transfer standard (concentration dependence)

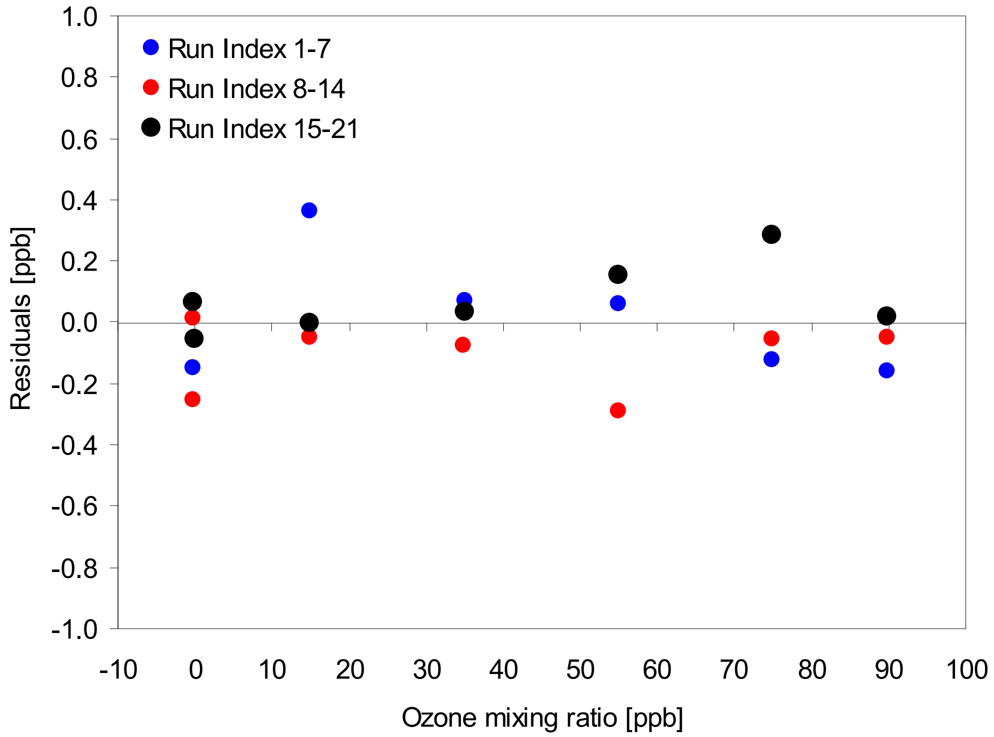


Figure 14: Residuals to the linear regression function (TEI 49C #66003-351) vs. the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49 #22643-206:

$$\text{Unbiased } O_3 = (\text{TEI 49} + 1.13) / 0.9953$$

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

TEI 49 = O_3 mixing ratio in ppb, determined with TEI49 #22643-206

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

$$u_C \approx \{(0.73 \text{ ppb})^2 + (0.00692 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 15 shows the deviation of the TEI 49 #22643-206 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

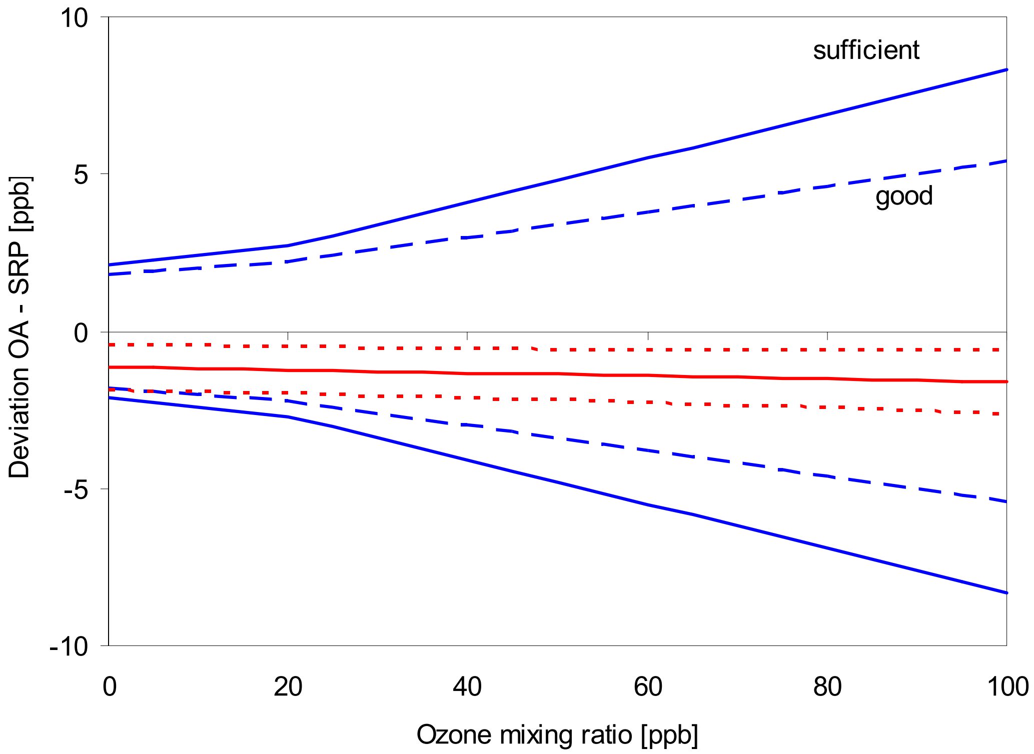


Figure 15: Inter-comparison of instrument TEI 49 #22643-206

TEI 49C #66003-351:

$$\text{Unbiased } O_3 = (\text{TEI 49C} - 0.56) / 0.9899$$

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

TEI 49C = O_3 mixing ratio in ppb, determined with TEI49C #66003-351

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

$$u_C \approx \{(0.61 \text{ ppb})^2 + (0.00609 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 16 shows the deviation of the TEI 49C #66003-351 from SRP#15 with the assessment criteria for "good" and "sufficient" agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

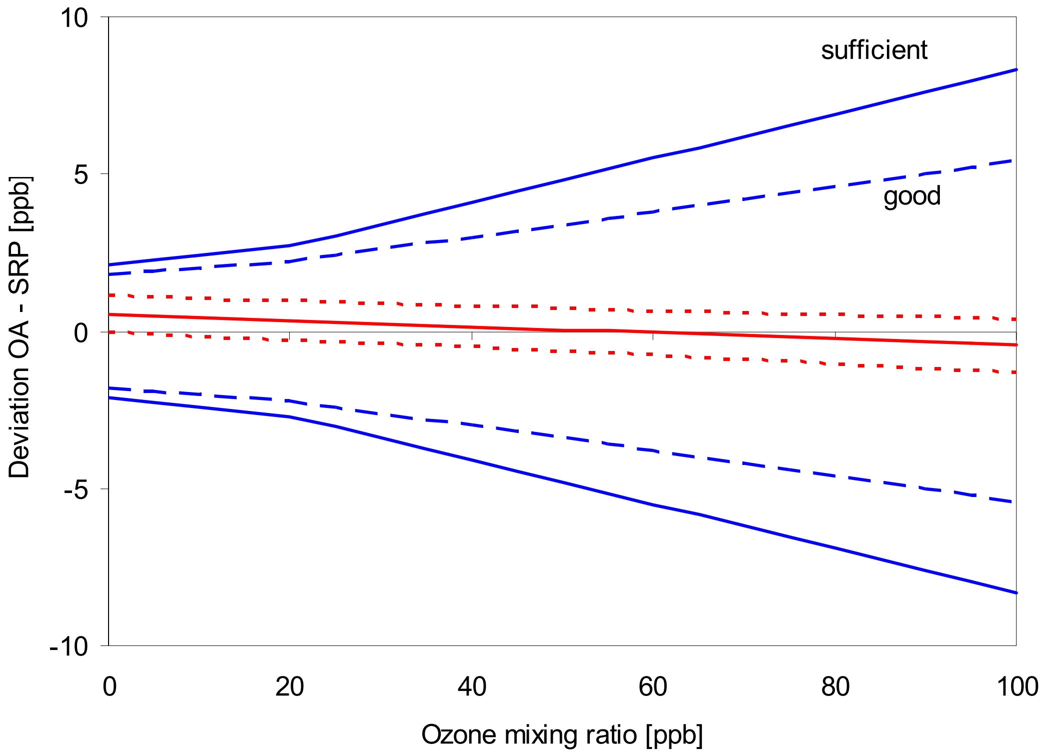


Figure 16: Inter-comparison of instrument TEI 49C #66003-351

Comment

The ozone concentrations observed at Mauna Loa (2001) ranged between 21 and 56 ppb (5- and 95-percentile of 60 min mean values). Both ozone analyzers of Mauna Loa fulfill the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone. However, a significant bias in the intercept (TEI49) and the slope (TEI49C) was observed.

4.3. Recommendation for the Ozone Measurements

The TEI 49C ozone instrument at Mauna Loa fulfils the assessment criteria as "good" over the tested range of 0 to 100 ppb. In addition, a TEI 49 is running as a backup instrument. Due to the good results, only minor recommendations are be made by WCC-EMPA, as summarized below:

- The TEI49 ozone analyzer is an old model which is not capable to measure low ambient pressures for the pressure correction. As a consequence, the P/T correction is switched off, and pressure and temperature are corrected manually from the raw data reading. The instrument pressure is not measured and estimated from ambient pressure assuming a constant pressure drop of 35 hPa in the instrument. Internal temperature was also not recorded in the instrument itself; instead, the internal temperature of the Dasibi instrument was used for the correction. It is strongly recommended to use the TEI49 as a backup instrument only.
- The main ozone instrument Dasibi 1003 AH was replaced during the audit by a TEI 49C. Unfortunately no overlap between main instruments was possible due to a complete instrument failure of the Dasibi before the audit. Replacement of instruments should be planned well in advance and should take place before major instrument problems occur. A replacement of the backup analyzer TEI 49 is also strongly recommended because of instrument age and capabilities.
- Calibrations (with a reference instrument) are performed only every two years. It is recommended to perform calibrations at least in yearly intervals.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Mauna Loa 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 Mauna Loa station.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO

Sampling-location: top of the 40 m tower

Inlet description:

Inlet (40m):	ca 50 m long Dekabon tube (outer diameter ⅓ inch) - pump and overflow (3 l/min)
Sample line:	1/16'' stainless steel. Length approx. 5 m. Flow rate ca. 20-50 ml/min to stream selection valve.
Driying:	Cold trap – 70°C

Residence time in the sampling line: approx. 30 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 analyzer. Instrumental details are listed in Table 6.

Table 6: Carbon monoxide gas chromatograph at Mauna Loa

instrument	Trace Analytical Inc.
model, S/N	RGA-3 S/N 031589-007
at Mauna Loa	since May 1992
configuration	two columns system
method	GC / HgO Reduction Detector
loop	3 ml
columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
carrier gas	Ultra pure N_2 Grade 99.9999%, flow rate 25 ml/min
operating temperatures	Detector: 277 °C, Column: 116 °C
analog output	1 V
calibration interval	3 times per hour with three reference standards
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 7 shows the CMDL gas standards available at Mauna Loa. The standards refer to the revised CO scale. The life time of a station standard is approximately one year, followed by a re-calibration at CMDL.

Table 7: Station CO cylinders

Gas cylinder	Description	Conc. [ppb]
CA01783	CMDL certified CO standard	71.0
CA14503	CMDL certified CO standard	98.3
CA04505	CMDL certified CO standard	142.7

Operation and Maintenance

Analysis: Injections are made every 5 minutes. The sequence is ambient air injection followed by injections of the 3 station reference standards.

Daily checks on working days (Monday to Friday) of tank pressures, temperatures, flow rates, and retention times are made. The cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

5.1.3. Data Handling

Data Acquisition and –transfer

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

Data Treatment

In a first step, the station operator plots the data and examines the chromatograms. Comments and notes are made in electronic log files. The final data evaluation is done at CMDL and includes again plausibility checks and the application of the appropriate calibration factors. The whole data is re-calculated using the calibration results of the station standards against the CMDL primary scale. One hourly and daily averages are calculated for the final data set.

Data Submission

For scientific reasons data have been submitted to different groups. 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 instrument manual and a SOP 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 Analyzer

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 analyzers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CO audits.

The seven transfer standards of WCC-EMPA (concentration range approx. 50-240 ppb CO) were stored in the same room as the CO measurement system to equilibrate over night. The transfer standards were calibrated against the (revised) CMDL scale at EMPA before and after the audit (Appendix VI). 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 analyzed between 4 and 13 times in the period from 20. to 22. August 2003. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the station operator after the audit. The experimental details are summarized in Table 8.

Table 8: Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA-3 S/N 031589-007
reference:	WCC-EMPA transfer standards
data acquisition system:	Station data acquisition
approx. concentration levels:	50 to 240 ppb
injections per concentration:	4 to 13

5.2.2. Results

The CO concentrations determined by the RGA-3 field instrument for the seven WCC transfer standards are shown in Table 9. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 17 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (reference). 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 Mauna Loa. The data of the RGA-3 field instrument were processed after the audit by the Paul Novelli and are based on calibration of the instrument against the reference standards available at the site.

Table 9: Carbon monoxide inter-comparison measurements at Mauna Loa

No.	**WCC standard**	**Mauna Loa analysis (RGA-5, Peak Area)**				
	conc. ± 1σ (N)	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	53.2 ± 0.7 (152)	50.9	0.4	11	-2.3	-4.6
2	72.4 ± 0.9 (114)	69.7	0.3	6	-2.6	-3.7
3	82.9 ± 0.8 (132)	79.4	0.5	13	-3.4	-4.2
4	95.5 ± 1.0 (133)	92.7	0.2	6	-2.8	-2.9
5	117.5 ± 1.2 (126)	114.6	0.2	10	-2.9	-2.5
6	160.2 ± 1.0 (114)	159.9	0.5	7	-0.3	-0.2
7	234.1 ± 1.3 (147)	240.7[1]	1.1	4	6.6	2.8

[1] This standard was outside the calibrated range of the station instrument.

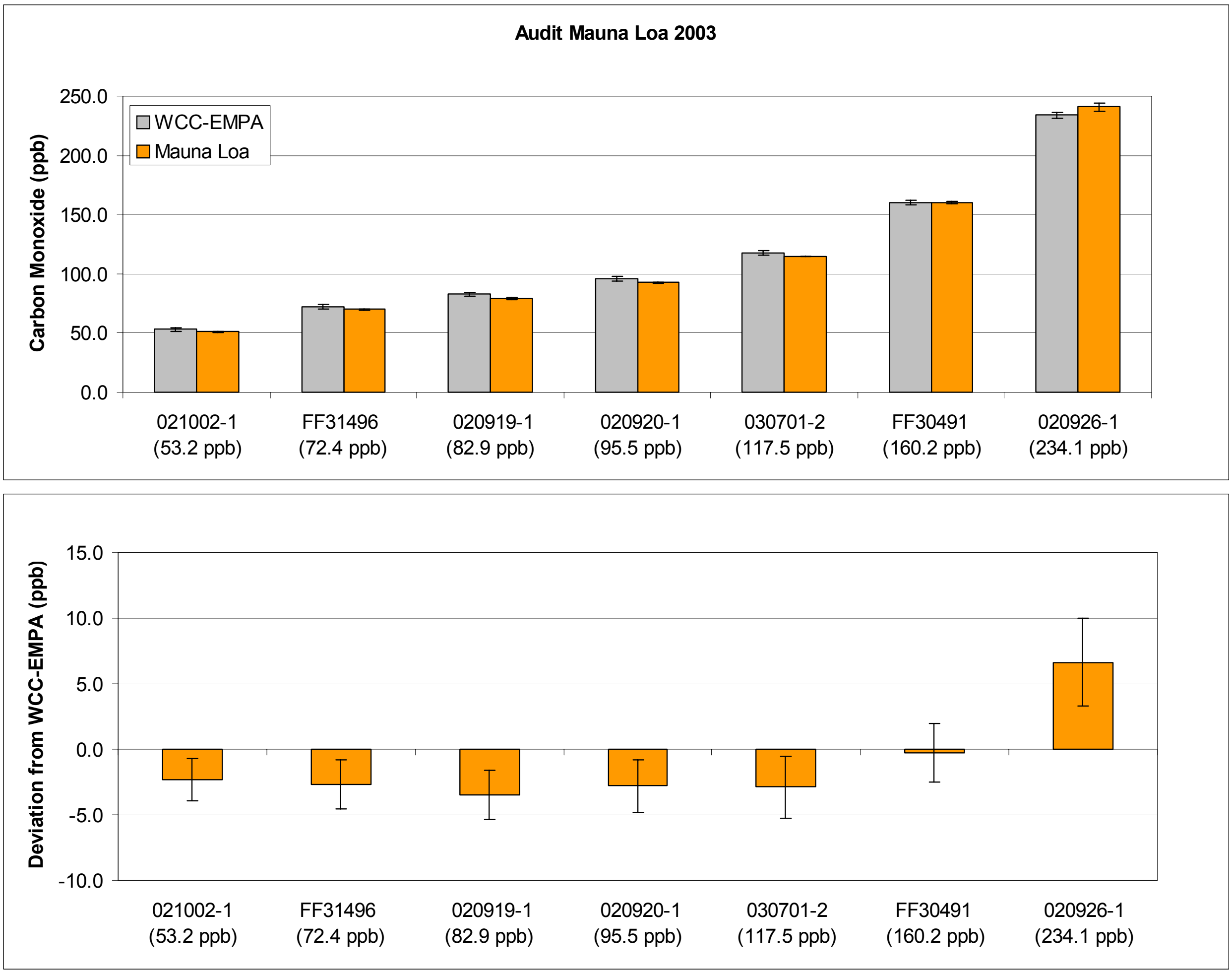


Figure 17: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mauna Loa (orange).
lower panel: deviation of the Mauna Loa station from the reference.
The error bars represent the 95% confidence interval.

5.3. Discussion of the Inter-comparison Results

The analysis of the WCC-EMPA transfer standards by the Mauna Loa station resulted in lower values (-2.3 to -3.4 ppb or -2.5 to -4.6%) for the concentrations between 50 and 120 ppb compared to the reference. No significant deviation was found for the transfer standard with approx. 160 ppb CO. The transfer standard with a higher concentration (234.1 ppb) resulted in a higher finding by Mauna Loa (+6.6 ppb or +2.8%) but was outside the calibrated range of the station instrument.

Transfer standards of WCC-EMPA are traceable to the CMDL scale (see Appendix VI). 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. The instrument linearity and zero was checked for the calibrations of the WCC-EMPA transfer standards. 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 (revised scale).

The differences observed at Mauna Loa reflect mainly the revision and uncertainty of the CO scale. The results of Mauna Loa compare well to the originally assigned numbers of the CMDL revised scale. However, WCC-EMPA assigned values still remain higher, although the revision of the scale by CMDL lowered the difference between CMDL and WCC-EMPA significantly.

5.4. Recommendation for Carbon Monoxide Measurements

The major problem for CO measurements is still the uncertainty of the CO scale. This issue needs to be addressed in the recently established SAG Reactive Gases.

Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended as soon as issue of the uncertainty of the CO scale is resolved.

6. System-and Performance Audit for Methane

Methane measurements became operational at Mauna Loa in April 1987. The yearly average CH_4 concentration measured at Mauna Loa increased from approx. 1680 ppb to over 1760 ppb since then. Since such a long time series is available from Mauna Loa, the continuation of these measurements at Mauna Loa 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 HP 6890 gas chromatograph with an FID detector is used for ambient methane measurements at Mauna Loa. Instrument details are summarised in Table 10.

Table 10: Gas chromatograph for methane at the Mauna Loa station

Instrument	HP 6890, S/N US00001275
at Mauna Loa since	November 1995
method	GC / FID Detector
sample loop	12 ml
columns	Silica gel pre-column, molecular sieve 5Å analytical column
carrier gas	N_2 99.999%
operating temperatures	Column: 80°C, Detector: 150°C
calibration interval	station standard every 15 min
instrument specials	30 seconds before injection, the flow through the loop is stopped to equilibrate pressure.

Gas Standards

One CMDL certified standard (at present #64032, 1739.1 ppb CH4) is available for the calibration of the instrument. The standard is returned to CMDL for re-calibration before the end of its lifetime. No additional CH_4 standards are available at the site.

Operation and Maintenance

Analysis: Injections are made every 7.5 minutes, alternating between station standard and ambient air.

Daily checks on working days (Monday to Friday) of tank pressures, temperatures, flow rates, and retention times are made. The cold trap is exchanged when necessary. Further action is taken when something unusual is observed.

6.1.3. Data Handling

Data Acquisition and –transfer

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

Data Treatment

In a first step, the station operator plots the data and examines the chromatograms. Comments and notes are made in electronic log files. The final data evaluation is done at CMDL and includes again plausibility checks and the application of the appropriate calibration factors. In addition, the raw data files are examined using a rule-based expert system (developed in-house) that flags large variations in peak responses in standards, peak width, retention time, and other parameters. The whole data is re-calculated using the calibration results of the station standards against the CMDL primary scale. One hourly and daily averages are calculated for the final data set.

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 and a SOP 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 seven transfer standards of the WCC (approx. concentration range 1690 - 1900 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate over night. The transfer standards were calibrated against CMDL laboratory standards (CA05316,CA04462, CA04580) at EMPA before and after the audit (see Appendix VII). 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 8 to 30 times and analysed between 20. to 22. August 2003. 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 after the audit by CMDL. The experimental details are summarised in Table 11.

Table 11: Experimental details of the methane inter-comparison

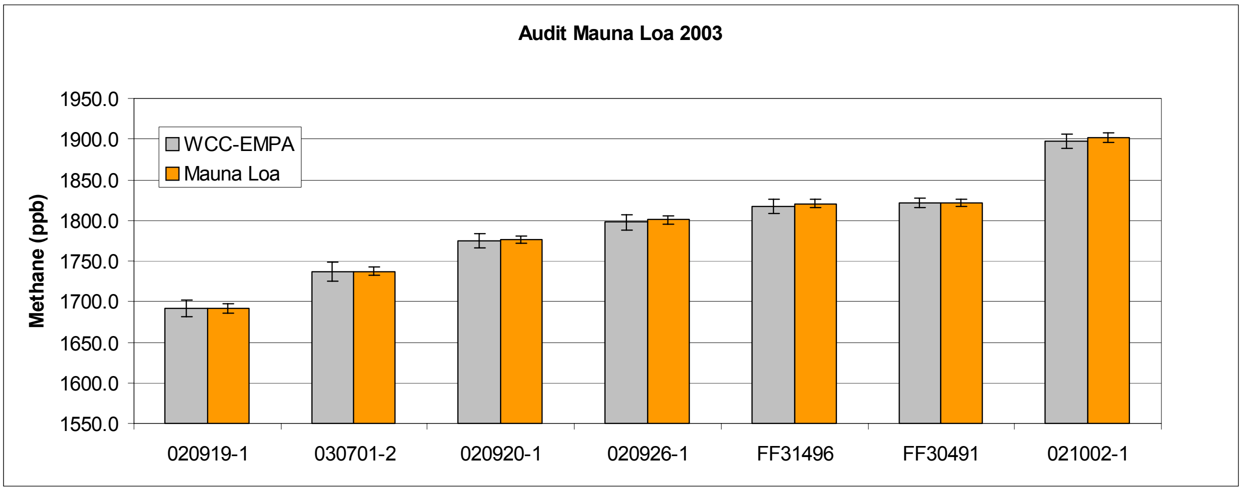
field instrument:	HP 6890, S/N US00001275
reference:	7 WCC-EMPA transfer standards
data acquisition system:	Station GC control software
approx. concentration levels:	concentration range approx. 1690 – 1900 ppb
injections per concentration:	8 to 30

6.2.2. Results of the Methane Inter-comparison

The results of the inter-comparison between the HP 6890 field instrument and the seven WCC transfer standards are shown in Table 12. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 18 shows the absolute differences (ppb) between the measurements of the HP 6890 GC and the WCC transfer standards (TS) (reference). The transfer standards were analysed before and after the audit. The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at Mauna Loa. The data from the HP 6890 field instrument were reprocessed after the audit and are based on the comparison with the station standard.

Table 12: Methane inter-comparison measurements at Mauna Loa

No.	WCC standard conc. ± 1σ (N) ppb	Mauna Loa analysis (HP 6890 GC-FID, Peak Height) conc. ppb	sd ppb	No. of injections	deviation from reference ppb	%
1	1692.0 ± 4.9 ppb (20)	1692.0	2.8	14	0.0	0.00
2	1736.9 ± 5.4 ppb (18)	1737.3	2.2	8	0.4	0.03
3	1774.4 ± 4.3 ppb (19)	1775.9	2.1	30	1.5	0.09
4	1797.8 ± 4.7 ppb (20)	1800.5	2.3	29	2.7	0.15
5	1817.4 ± 4.8 ppb (19)	1820.5	2.2	13	3.1	0.17
6	1821.5 ± 4.9 ppb (18)	1821.7	2.4	28	0.2	0.01
7	1897.1 ± 5.6 ppb (15)	1901.6	2.6	13	4.5	0.24



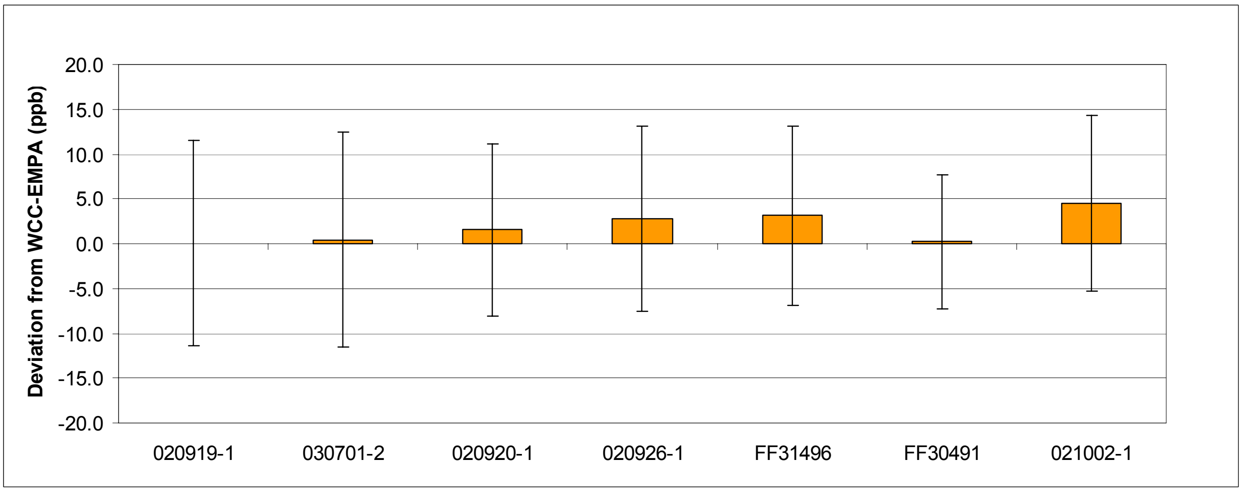


Figure 18: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix VII) measured with the GC system of Mauna Loa (orange).
lower panel: deviation of Mauna Loa from the reference.
The error bars represent the 95% confidence interval.

Comment

The CH_4 inter-comparison between WCC-EMPA and Mauna Loa agreed very well with the reference in the concentration range between 1690 and 1900 ppb methane. The deviation from the transfer standards is less than 0.3 %.

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 Mauna Loa is a well-established site within the GAW program, and long time series of high quality exist for many 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 (new instrument) and methane. Only minor recommendations are made concerning these parameters.

However, the data quality of ozone measurements until the date of the audit could not be fully assessed due to a failure of the main station instrument. Replacement in time of old instrumentation is regarded of importance to ensure consistent time series of known and sufficient data quality.

The results of the carbon monoxide inter-comparison confirmed recent findings of informal inter-comparisons between CMDL and WCC-EMPA. The analysis of the WCC-EMPA transfer standards by the Mauna Loa station resulted in lower values for the concentrations between 50 and 120 ppb compared to the reference. No significant deviation was found for the transfer standard with approx. 160 ppb CO.

The differences observed at Mauna Loa reflect mainly the uncertainty of the CO scale. The results of Mauna Loa compare well to the originally assigned numbers of the CMDL revised scale. However, WCC-EMPA assigned values still remain higher, although the revision of the scale by CMDL lowered the difference between CMDL and WCC-EMPA significantly. The SAG reactive gases should get in the lead to solve this issue.

8. References

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Appendix

I Parallel measurements of the Dasibi 1003 AH and the TEI 49

The main station instrument Dasibi 1003 AH (until August 2003) could not be inter-compared by WCC-EMPA due to an instrument failure just before the audit. However, parallel measurements were performed over a one year period (Jan 02 – Jan 03) with the backup instrument TEI 49. One hourly averages of the TEI 49 vs. Dasibi 1003 AH are shown in Figure 20.

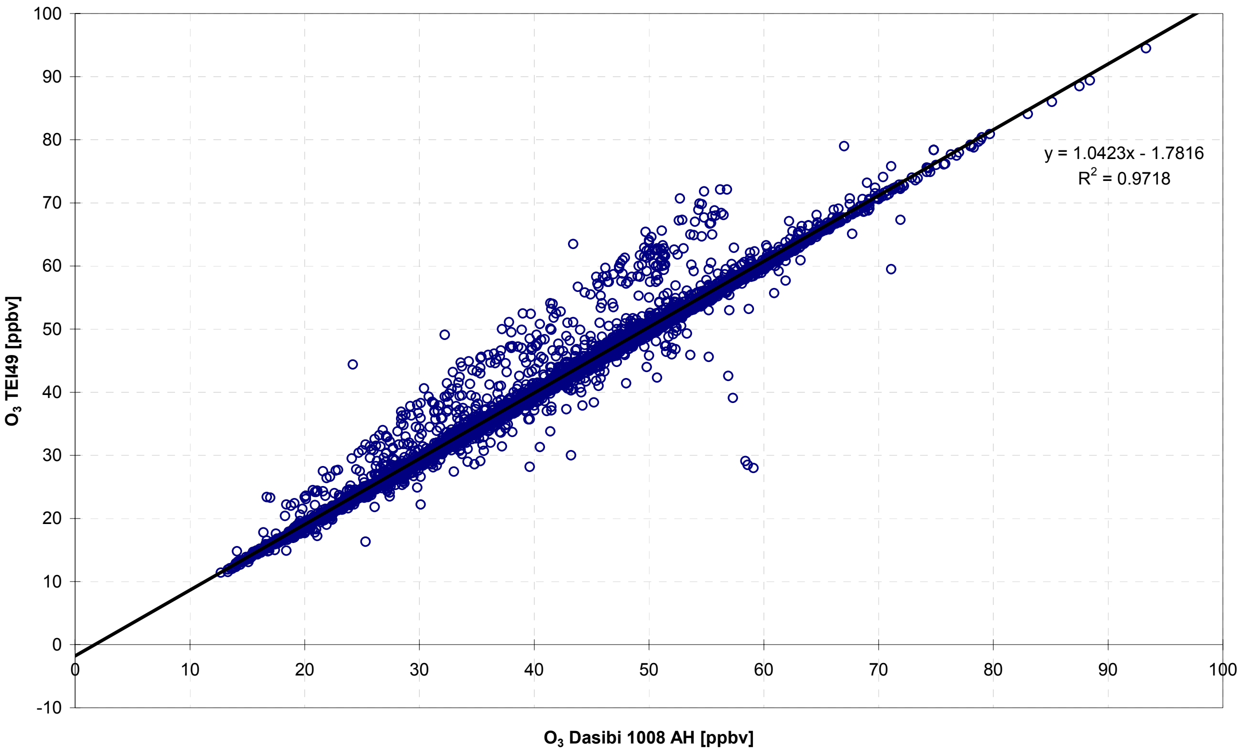

Figure 20: Relationship between the Dasibi 1003 AH and the TEI 49 ozone instruments at Mauna Loa based on one hour average values between January 02 and January 03.

The observed relation between the Dasibi and the TEI instruments translates into an unbiased ozone (SRP#15) ozone concentration for the Dasibi instrument of

$$\text{Unbiased } O_3 = (\text{Dasibi} - 0.65) / 0.9551$$

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

Dasibi = O_3 mixing ratio in ppb, determined with Dasibi 1003 AH #1323

However, due to the large variation of the inter-comparison results between the TEI and the Dasibi instruments, and due to imperfect compensation of temperature and pressure of the TEI instrument, WCC-EMPA suggests to consider the Dasibi 1003 AH and the TEI 49 data to be of unknown quality.

II CMDL Transfer Standard Dasibi 1003 AH

The CMDL transfer standard Dasibi 1003-AH #5275 was also inter-compared with WCC-EMPA during the audit. The comparison was made as described in section 4.2.2. The results are summarized below:

Dasibi 1003-AH #5275:

$$\text{Unbiased } O_3 = (\text{Dasibi 1003-AH} - 0.56) / 0.9917$$

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

Dasibi 1003-AH = O_3 mixing ratio in ppb, determined with Dasibi 1003-AH #5275

The remaining standard uncertainty after compensation of the calibration bias is

$$u_C \approx \{(0.78 \text{ ppb})^2 + (0.00494 \times C)^2\}^{½}$$

where u_c is the ozone concentration in ppb

Figure 21 shows the deviation of the Dasibi 1003-AH #5275 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

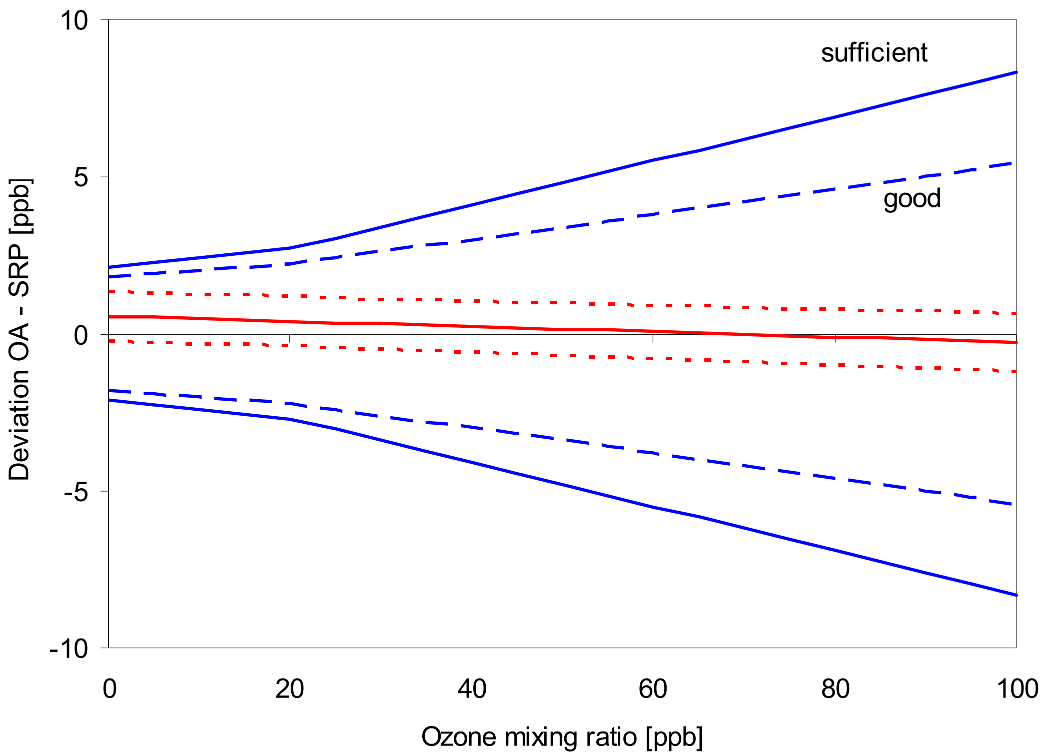

Figure 21: Inter-comparison of instrument Dasibi 1003-AH #5275

III CMDL Transfer Standard TEI 49C

The CMDL transfer standard TEI 49C #75573-380 was also inter-compared with WCC-EMPA during the audit. The comparison was made as described in section 4.2.2. The equation used for the re-calculation of the data was O_3 final [pbb] = 0.27 + 1.016 *(TEI 49C#75573-380) based on the last inter-comparison between CMDL and NIST. The results are summarized below:

TEI 49C #75573-380:

$$\text{Unbiased } O_3 = (\text{TEI 49C} – 0.55) / 0.9887$$

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

TEI 49C = O_3 mixing ratio in ppb, determined with TEI 49C #75573-380

The remaining standard uncertainty after compensation of the calibration bias is

$$u_C \approx \{(0.59 \text{ ppb})^2 + (0.00605 \text{ x } C)^2\}^{½}$$

where u_c is the ozone concentration in ppb

Figure 22 shows the deviation of the TEI 49C #75573-380 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

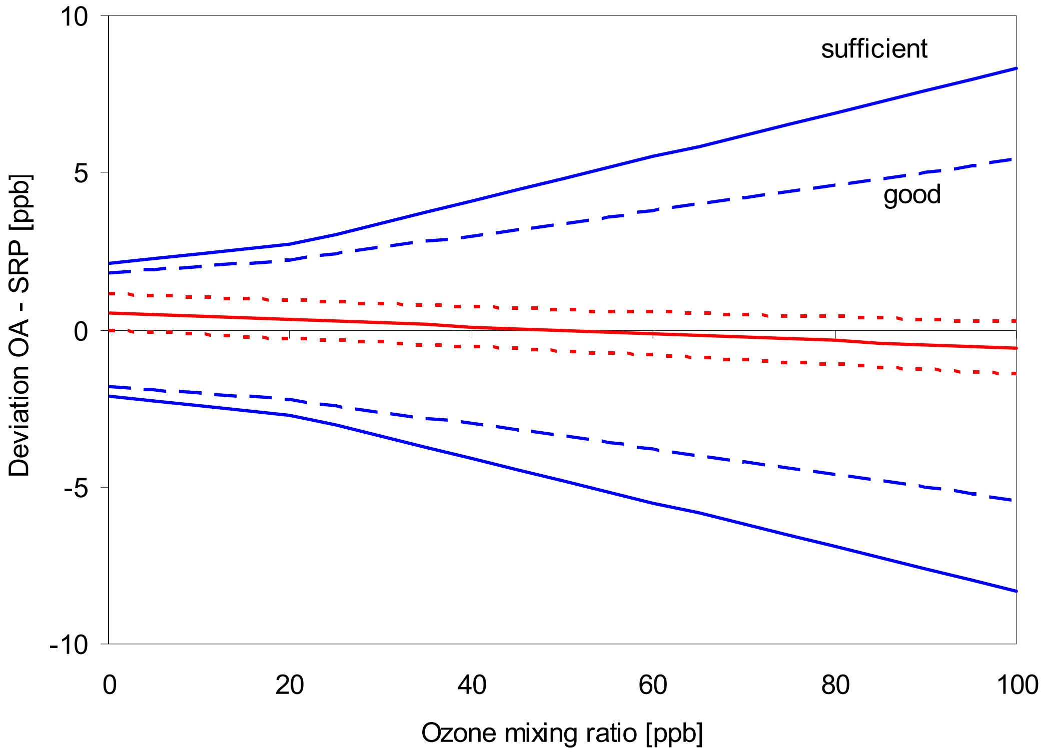

Figure 22: Inter-comparison of instrument TEI 49C #75573-380

IV 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.

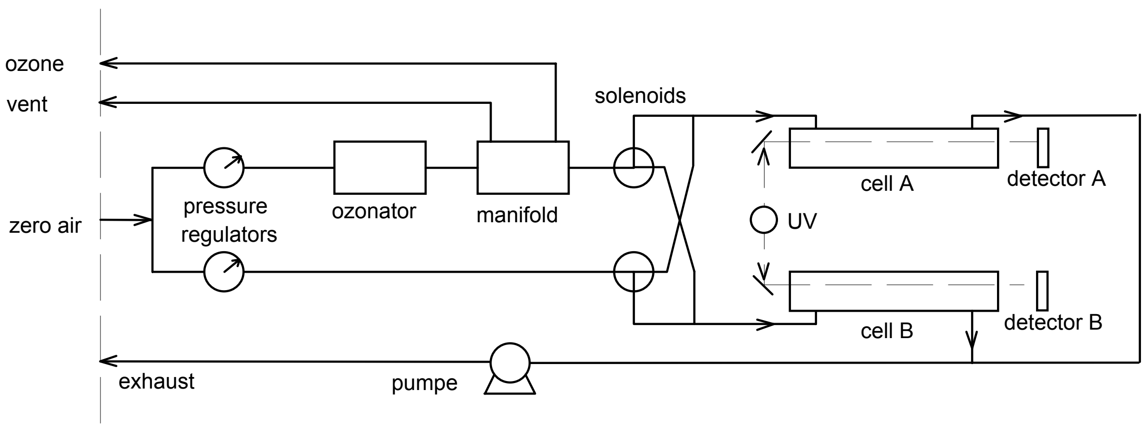

Figure 23: Flow schematic of TEI 49C-PS

V Stability of the Transfer Standard TEI 49C-PS

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

The procedure and instrumental details of this inter-comparison at the EMPA calibration laboratory are summarized in Table 13 and Figure 24.

Table 13: Inter-comparison procedure SRP - TEI 49C-PS

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

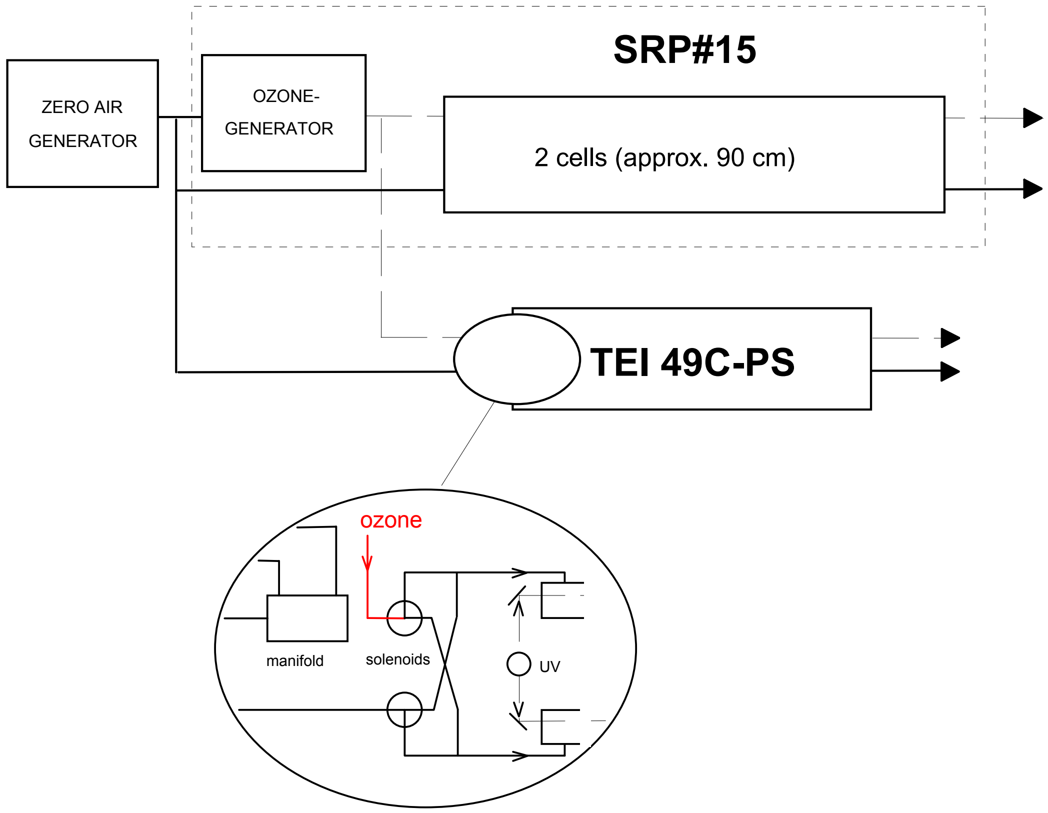

Figure 24: Instruments set up SRP -TEI 49C-PS

The transfer standard fulfilled the criteria given in Klausen et al. (2003), which means that neither intercept nor slope were different from 0 and 1,respectively, on the 95% confidence level.
Figure 25 shows the deviation of the transfer standard from SRP#15 before and after the audit. The maximum allowed deviation is also shown in this figure. The regression statistics between the WCC-EMPA transfer standard and SRP#15 were calculated using the procedure `fitexy` given in Press et al. (1995). The following relationship was found for the pooled data of the inter-comparisons before and after the audit:

TEI 49C-PS #54509-300 = 0.9999 x SRP#15 + 0.29 ppb

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

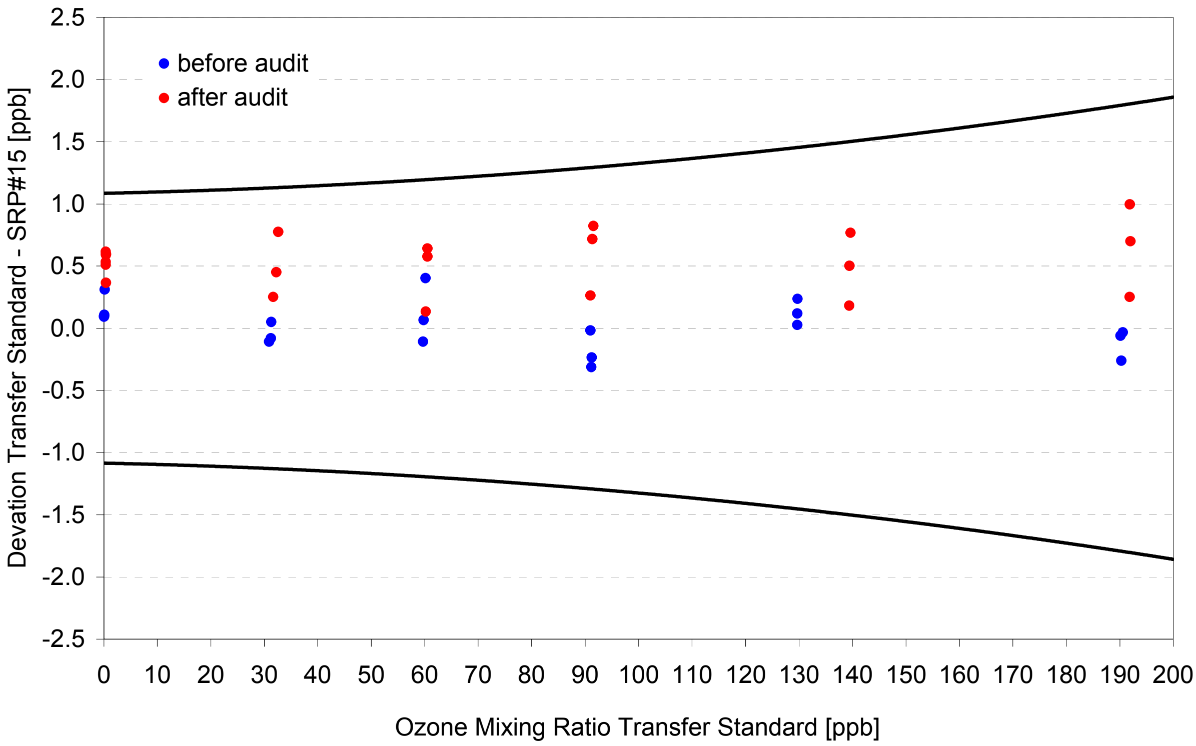

Figure 25: Deviation of the WCC-EMPA transfer standard from SRP#15 before and after the audit

VI WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at the WCC are listed in Table 14:

The CO scale of the CMDL was recently revised (Novelli et al., 2003). WCC-EMPA refers to the **new** scale. The WCC-EMPA transfer standards used during the audit are listed in Table 15.

Table 14: 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 15: CO transfer standards of the WCC (average of calibrations from July 03 and September 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)	53.3 ± 0.7 ppb	53.1 ± 0.7 ppb	021002-1
WCC Transfer Standard (6 l cylinder)	72.4 ± 0.8 ppb	72.3 ± 1.1 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	82.9 ± 0.7 ppb	82.8 ± 0.9 ppb	020919-1
WCC Transfer Standard (2 l cylinder)	95.0 ± 0.8 ppb	96.0 ± 0.9 ppb	020920-1
WCC Transfer Standard (2 l cylinder)	117.2 ± 1.2 ppb	117.8 ± 1.2 ppb	030701-2
WCC Transfer Standard (6 l cylinder)	160.1 ± 0.8 ppb	160.2 ± 1.1 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	234.0 ± 1.1 ppb	234.1 ± 1.3 ppb	020926-1

VII 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 16. The WCC-EMPA transfer standards (Table 17) are traced back to the CMDL standards shown below.

Table 16: 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)	1691.6 ± 0.30 ppb	CA05316
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 (CA04462 and CA04580) and 1.04.2003 (CA05316)

Table 17: 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)	1688.9 ± 4.7 ppb	1695.0 ± 2.9 ppb	020919-1
WCC Transfer Standard (2 l cylinder)	1733.0 ± 3.4 ppb	1740.7 ± 3.9 ppb	030701-2
WCC Transfer Standard (2 l cylinder)	1773.2 ± 3.5 ppb	1775.5 ± 4.8 ppb	020920-1
WCC Transfer Standard (2 l cylinder)	1795.5 ± 3.3 ppb	1800.0 ± 4.8 ppb	020926-1
WCC Transfer Standard (6 l cylinder)	1818.2 ± 3.0 ppb	1816.5 ± 5.8 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	1820.2 ± 2.2 ppb	1822.8 ± 2.8 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	1895.1 ± 4.3 ppb	1898.5 ± 3.3 ppb	021002-1

VIII System and Performance Audits Executive Summary

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Swiss Federal Laboratories for Materials Testing and Research (EMPA)
EMPA Dübendorf, CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

System and Performance Audits Executive Summary

0.1	Station Name:	Mauna Loa
0.2	GAW ID:	
0.3	Coordinates/Elevation:	19°32'20"N 155°34'41"W (3397 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1 Date of Audit: 18.08.2003 –22.08.2003

1.2 Auditors: Dr. C. Zellweger and Dr. B. Buchmann

1.3 Station staff involved in audit:
Dr. John E. Barnes
Steve C. Ryan
Samuel J. Oltmans
Dr Paul C. Novelli

1.4 Ozone Reference [SRP]: NIST SRP#15

1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS S/N: 54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0000±0.0010) × [SRP] + (0.05±0.13)

1.6	Ozone Analyzer [OA]	
1.6.1	Model:	TEI49C S/N: 66003-351
1.6.2	Coefficients prior to audit	ZERO: 0.0 SPAN: 1.000
1.6.3	Coefficients during and after audit	ZERO: 0.0 SPAN: 1.000
1.6.4	Range of calibration: 0 – 100 ppb	
1.6.5	Calibration after audit (ppb):	[OA] = (0.9898±0.0032) × [TS] + (-0.51±0.15)
1.6.6	Unbiased ozone concentration (ppb):	C = ([OA] – 0.5570)/0.9899
1.6.7	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.61 \text{ ppb})^2 + (0.0061 \times C)^2\}^{1/2}$

1.7 Comments:
The audited instrument was installed at the station during the audit. No direct quality assessment of the "old" station instrument Dasibi 1003-AH was possible because of instrument malfunction. The Dasibi instrument is no longer in use.

1.8 Reference: EMPA-WCC Report 03/3