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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 05/1

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION MT. KENYA

KENYA, FEBRUARY 2005

Submitted by

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

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

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	swiss calibration service		

1 EXECUTIVE SUMMARY

A system and performance audit was conducted at the Global Atmosphere Watch station Mt. Kenya from 16 to 24 February 2005 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa). The results of the third WCC-Empa audit can be summarized as follows:

1.1 System Audit of the Observatory

The Mt. Kenya global GAW station offers adequate facilities for atmospheric measurements. It is located at high altitude in a region where only few measurements are available. The location provides a unique opportunity to monitor background air as well as to conduct research in a pristine continental environment. However, power supply to the station is unreliable and long periods without power jeopardize the future of the station. Immediate action to solve this problem is crucial for the future of the GAW site Mt. Kenya.

1.2 Audit of the Ozone Measurements

The station ozone analyser was inter-compared with the travelling standard of WCC-Empa. Only a short warm-up time was possible because the station was without power at the time of the audit, and all inter-comparisons were made using a power generator. The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the ozone instrument of the station, demonstrated good agreement between the station analyser and the transfer standard. The recorded differences fulfilled the assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1).

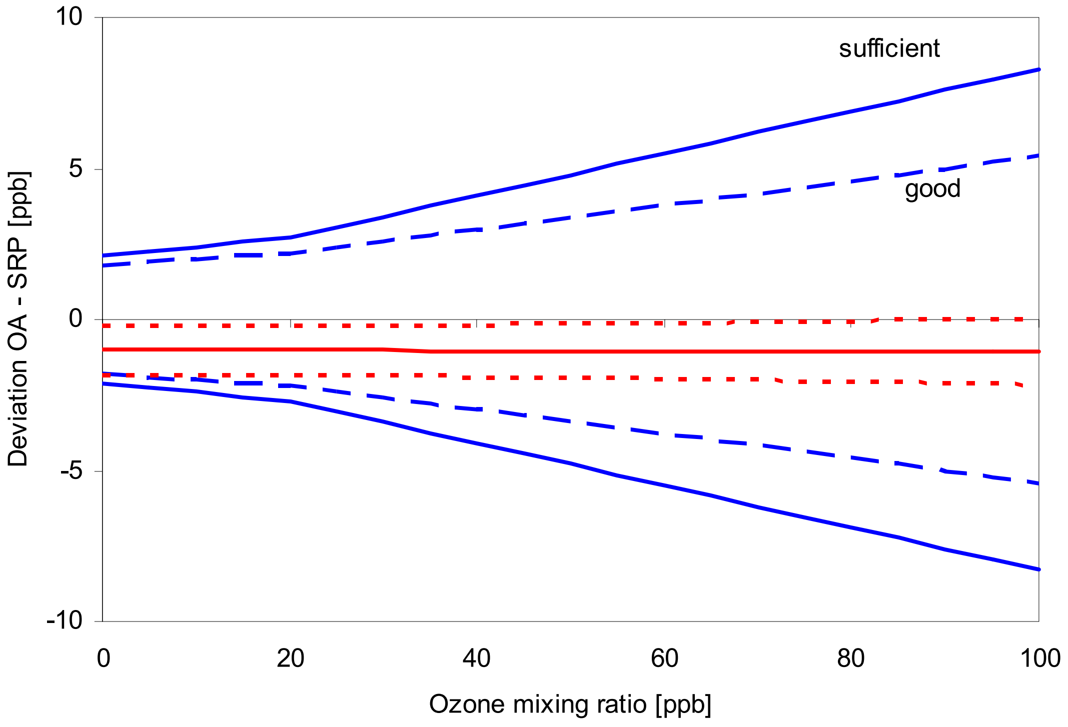

Figure 1: Inter-comparison of instrument TEI 49 #51959-290

The ozone calibrator at KMD was also compared to the WCC-Empa travelling standard and fulfilled the criteria for good agreement. The results are shown in Figure 2.

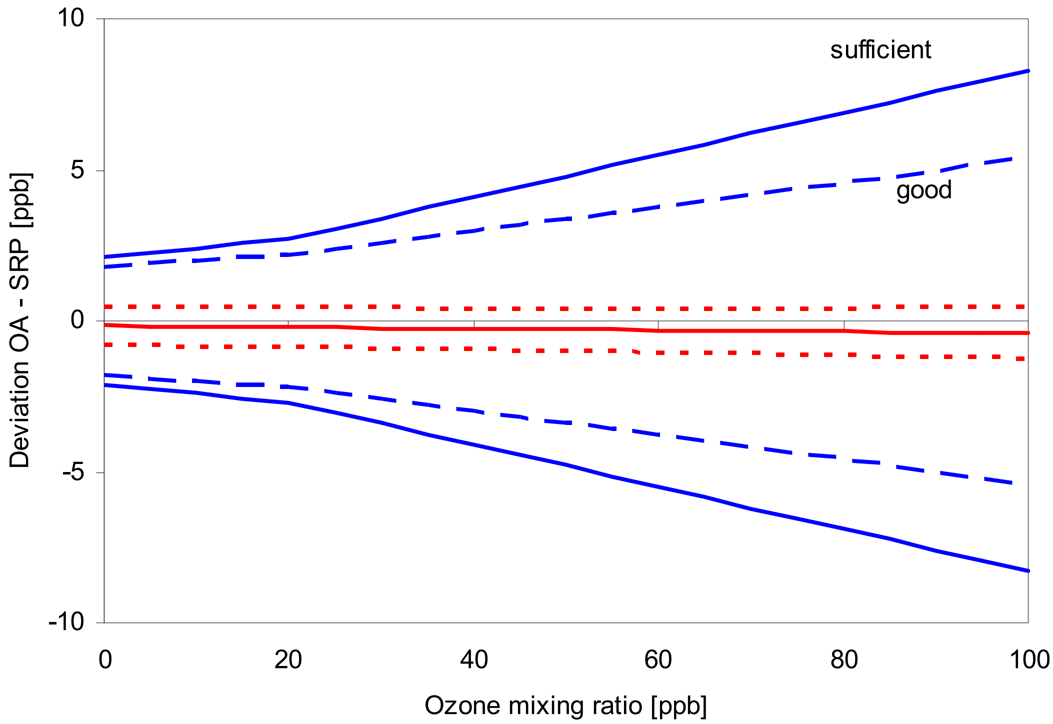

Figure 2: Inter-comparison of calibrator TEI 49PS #53677-297 (at KMD)

Due to the good results of the inter-comparison, only minor recommendations were made by WCC-Empa. However, a replacement of the ozone analysers by newer models should be considered. An executive summary of the surface ozone audit results is given in Appendix IV.

1.3 Audit of the Carbon Monoxide Measurements

Due to the fact that the station was without power at the time of the audit all inter-comparisons between WCC-Empa and the Mt. Kenya GAW station were done using a power generator. As a consequence only short warm-up times were possible.

Zero drift is the most important limiting factor for the performance of the carbon monoxide analyser. The inter-comparison results with WCC-Empa showed an acceptable agreement between the station instrument and WCC-Empa (Figure 3). A large part of the uncertainty can be attributed to imperfect zero drift correction. Furthermore, the short warm-up times resulted in larger instrument drift and noise than usual. More sophisticated tools are needed to correct for zero drift, and it should be explored if the zero drift can be reduced with instrument modifications.

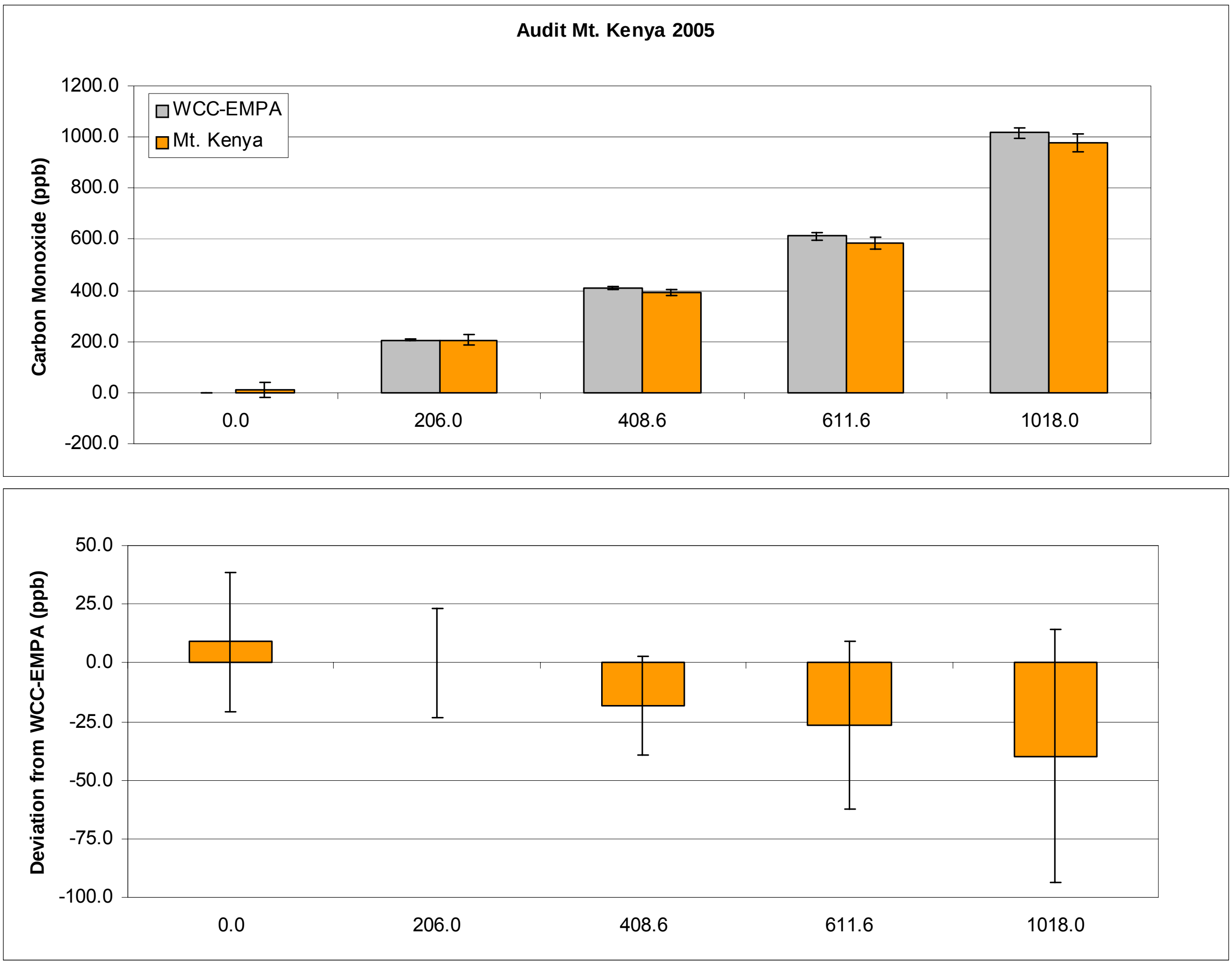

Figure 3: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the CO analyser of Mt. Kenya (orange). lower panel: deviation of the Mt. Kenya station from the conventional true value. The error bars represent the 95% confidence interval. Data are 5 minute values averaged over 30 to 150 minutes.

1.4 Data Submission

Data submission to the GAW World Data Centres is one of the obligations of stations participating in the GAW programme. To date no data of the audited parameters were submitted to the World Data Centre for Greenhouse Gases (WDCGG). This is mainly because only scattered data is available which needs to be quality controlled before data submission. QA/SAC Switzerland is reviewing existing data sets in collaboration with KMD, and data submission is expected in the near future.

1.5 Conclusions and General Recommendations

The global GAW station Mt. Kenya was established under the Global Environment Facility (GEF) programme in 1999. However, the station only became operational in June 2001 with a reduced measurement programme due to the fact that no continuous power was available before that date. Since then, some parameters were measured over longer time periods until a recent power failure in October 2004. Since then power could not be restored with the exception of two very short periods in January and March 2005.

Mt. Kenya is an important station within the GAW programme, since ground based measurements of air pollutants from equatorial regions are limited. To take advantage of this, national and international co-operation for both technical and scientific staff (workshops, exchange programmes, scientific partnerships) is regarded as important. Sustainable power supply is crucial for the future of the Mt. Kenya GAW site.

The following general recommendations are made by WCC-Empa to ensure its long-term operation:

- Replacement or sustainable repair of the existing power line between the national park border and the station is of highest priority. Alternatively, the installation of self-sufficient power could be considered.
- The road between the park border and Old Moses camp was in poor condition and access to the station is difficult during the wet season. Road maintenance is important to allow regular station visits.
- Office facilities in Nanyuki are available but infrastructure needs to be improved. Access to computers and internet is not sufficient at present.
- Data should be validated and used by the station staff. At present data is mainly distributed as raw data to external partners. It is important that the station staff gets more involved in raw data validation and treatment. This is currently one of the goals of two ongoing projects between QA/SAC Switzerland and KMD.
- Collaboration with external partners, both national and international, is desirable.
- Continuing education and training of the station staff (e.g. GAWTEC) is encouraged.

Dübendorf, 15. August 2005

Empa Dübendorf, WCC-Empa

Project leader	Head of the laboratory
Dr. C. Zellweger	Dr. B. Buchmann

2 INTRODUCTION

The **Mt. Kenya Observatory** started its operation in June 2001 with a reduced measurement programme and was officially opened in December 1999 under the lead of the Kenya Meteorological Department (KMD). It is part of Kenya's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory was established within the framework of UNDP's Global Environment Facility (GEF) under a twinning partnership between KMD and the Institute for Meteorology and Climate Research (IMK-IFU), Germany. It is designated for long-term measurements of several chemical compounds and physical and meteorological parameters in the lower troposphere.

The Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa) was assigned by the WMO to operate the **GAW World Calibration Centre (WCC)** for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a coordinated quality assurance 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 GAW global stations are conducted regularly based on mutual agreement about every two to four years.

In agreement with the GAW country contact and station manger, Mr. John Rotich (KMD), a system and performance audit at the GAW global station Mt. Kenya was conducted from 16 to 24 February 2005.

The scope of the audit was the 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 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 audit report is distributed to the Director of the Kenya Meteorological Department, the station manager and the World Meteorological Organization in Geneva.

Staff involved in the audit

KMD	Mr. John Rotich	contacts, general programme, organisation
	Mr. Josiah Kariuki	technical assistance at station and KMD
	Mr. John Aseyo	technical assistance at station and KMD
	Mr. William Ayoma	technical assistance at KMD
	Mr. Joseph Mukola	technical assistance at KMD
WCC-Empa	Dr. Christoph Zellweger	lead auditor
	Mr. Stefan Bugmann	

Previous audits at the GAW station Mt. Kenya:

January 2000 and February 2002 by WCC-Empa

3 GLOBAL GAW SITE MT. KENYA

Mt. Kenya started its operation in June 2001 with a reduced measurement programme and was officially opened in December 1999. A short overview of the measurement programme at the GAW site and its status as of February 2005 is given below.

General: Station Power Supply

Power supply to the Mt. Kenya is one of the most pressing issues to be resolved. The operation of the station was delayed till June 2001 because no power was available due to problems with the power line between the national park border and the station. After repair power was restored but only disjointed data was acquired because of unreliable power supply. Since 19. October 2004 power is again interrupted with the exceptions of two short periods in January and March 2005. It is crucial for the future of the Mt. Kenya GAW station that the power supply problem can be resolved. If no further action is taken to either replace or sustainably repair the existing power line or to install self-sufficient power on site, measurements will discontinue and the status of the Mt. Kenya GAW station will have to be reconsidered.

General: Data Acquisition

A MILOS 500 data logger is installed and acquires all station data. Data is currently manually downloaded to the station computer. WCC-Empa installed a new computer at the site which is equipped with a GSM modem. This should allow remote data access with PCAnywhere. The GSM modem connection however is still not operational due to data transfer problems.

Surface Ozone

One TEI 49 ozone analyser is running at the site. In addition, a TEI 49PS calibrator is available at KMD for calibrations. Both instruments are operational when power is on.

Carbon Monoxide

A TEI 48C Trace Level analyser was installed by QA/SAC Switzerland and WCC-Empa in February 2002. The instrument has been running since then until the recent power failure in October 2004. The audit results showed that the instrument is in a good condition, however, temperature dependent zero drift remains a problem.

Meteorological Parameters

Ancillary meteorological parameters are measured and are available for periods with power.

Light Absorption (Black carbon)

The aethalometer instrument was at the site but not running. The original instrument was inspected by WCC-Empa, and the floppy disk found to be malfunctioning. The instrument was decommissioned. A newer Anderson aethalometer from NOAA/CMDL is now at the site but is still not yet hooked to the Milos data logger.

Flask Sampling (Greenhouse Gases)

The greenhouse gases flask sampling programme started in 2004, and flasks were regularly taken. Flask measurements are the only measurements that are operational during power outages.

Solar Radiation (Diffuse / Direct / Global Irradiance)

Solar radiation parameters are measured and are available for periods with power.

3.1 Site description

The Mt. Kenya station (0.033°S, 37.217°E, approx. 3697 m a.s.l., coordinates and altitude to be verified) is situated beyond Moses Camp on the northern upper slopes of Mt. Kenya in a wildlife preserve and provides measurements of the tropical mid-troposphere as well as air from the lower humid boundary layer. Access is along Sirimon Route, a distance of 21 km from the

Nanyuki-Timau tarmac. The turn-off is about 16 km from Nanyuki. A new settlement has been created in the former forest land after the turn-off. The closest town is Nanyuki with a population of approx. 30000 inhabitants. The surrounding terrain of the station is gently sloping shrub with several smaller streams nearby. The station itself is exposed in all directions on a 10 m high rock outcrop. Access to the site requires a one hour drive from Nanyuki by a 4WD vehicle up to "Old Moses" camp at 3300 m a.s.l. followed by a 30 minutes uphill walk. The national park is entered at the Sirimon Gate following a steep unpaved road, which is closed to public traffic. The road was in relatively poor condition at the time of the audit, and road maintenance is of crucial importance to keep the station accessible also during the wet season. Figure 4 shows the location of the Mt. Kenya station along with the ozone sounding stations of Nairobi and Malindi. A picture of the station is shown in Figure 5.

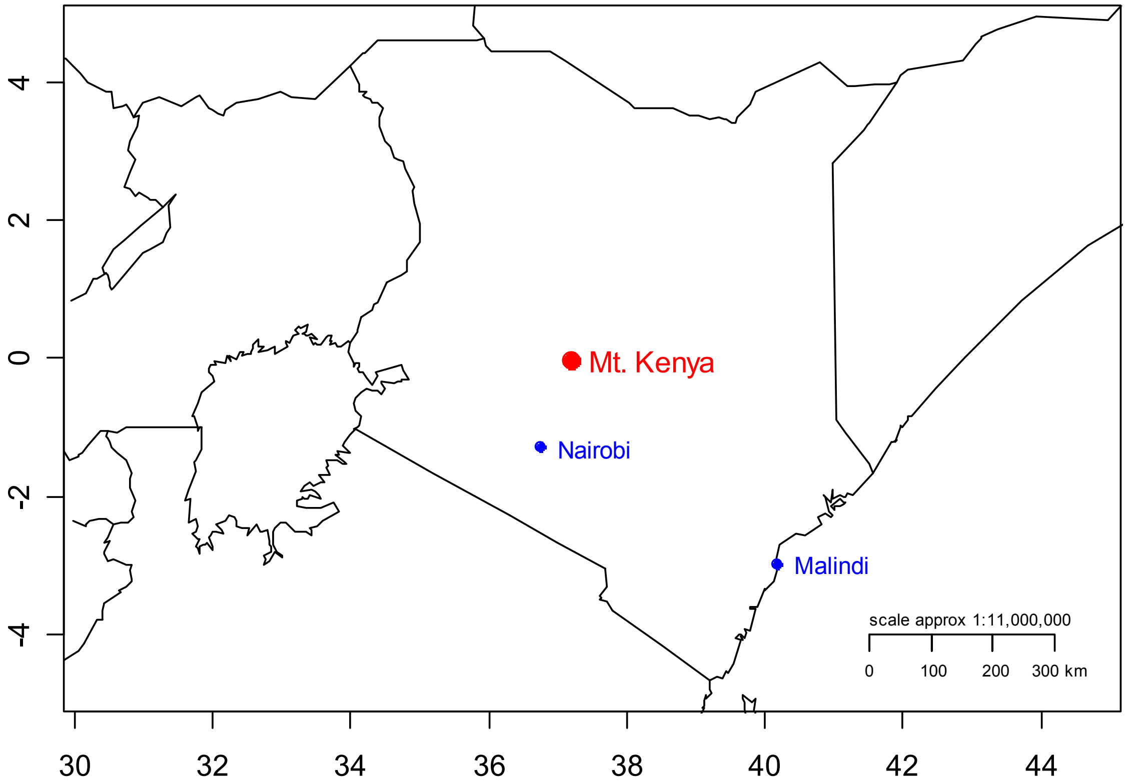

Figure 4: Location of GAW sites in Kenya

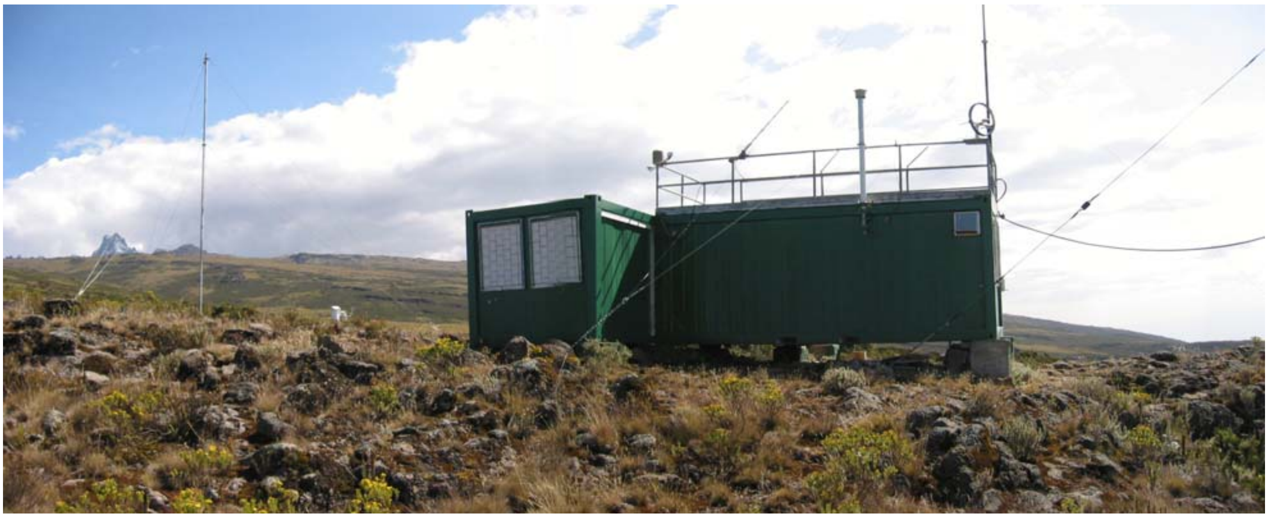

Figure 5: Mt. Kenya observatory

3.2 Ozone and carbon monoxide levels at Mt. Kenya

The frequency distributions of one hourly mean values for surface ozone and carbon monoxide are shown in Figures 6 and 7.

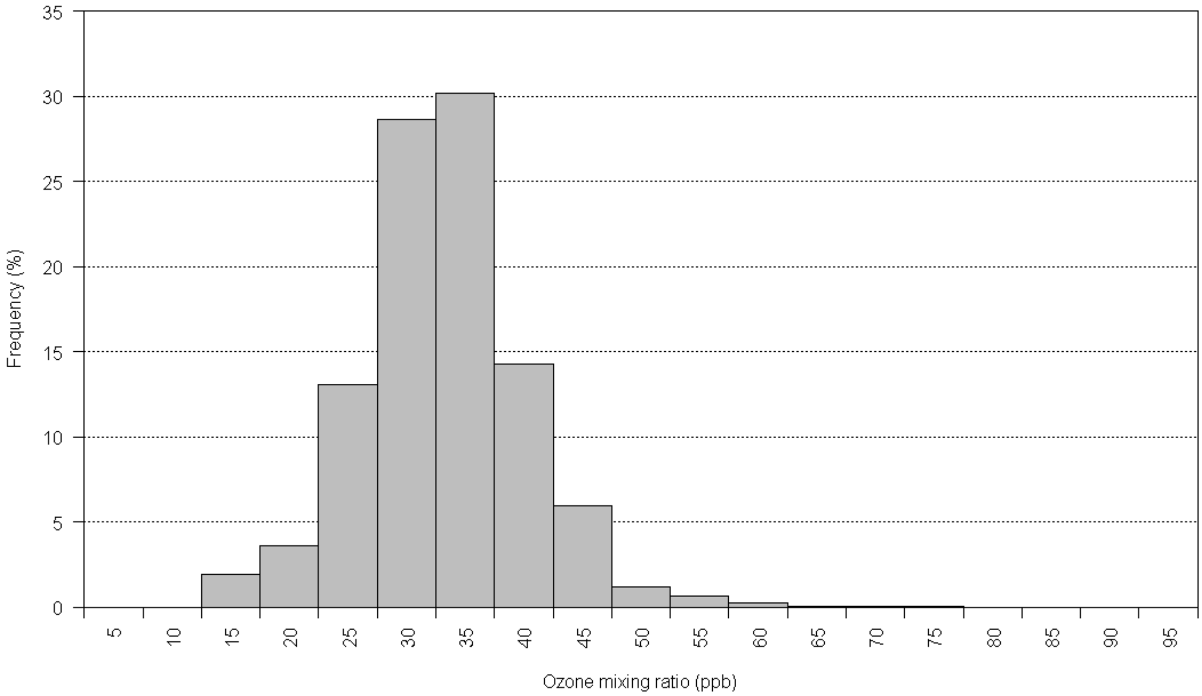

Figure 6: Frequency distribution of hourly ozone mixing ratios (ppb) at Mt. Kenya for 2004. Data availability 39.9%.

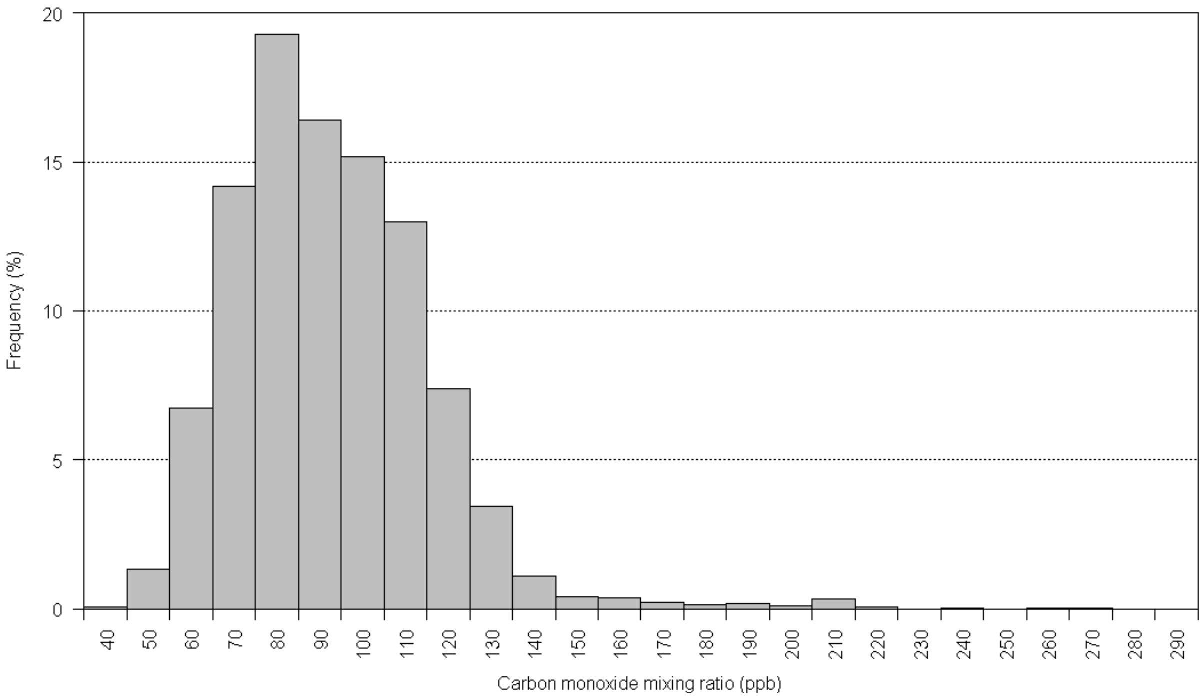

Figure 7: Frequency distribution of carbon monoxide mixing ratios (ppb) at Mt. Kenya for 2004. Data availability 43.7%.

3.3 Mt. Kenya Staff

The GAW station Mt. Kenya is usually visited three times per week (Tuesday to Thursday) by at least one station operator. The station operators are based in Nanyuki during working days and go to Nairobi occasionally on short official visits. Table 1 shows the staff responsible as of February 2005.

Table 1: Staff responsible for the GAW station Mt. Kenya (March 2005)

Name	**Position and duty**
Kenya Meteorological Department	
Dr. J. R. Mukabana	Director of KMD
Mr. J.G. Wairoto	Deputy Director of KMD
Mr. J. C. Ego	Assistant Director (Observations and Networks)
Kenya Meteorological Department GAW Team	
Mr. John Rotich	GAW country contact, station manager
Mr. Josiah Kariuki	Station operator, meteorologist
Mr. John Aseyo	Station technician
Mr. William O. Ayoma	Lead operator ozone sounding programme Nairobi
Mr. Joseph Mukola	Technician ozone sounding programme Nairobi

4 SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE

The ozone measurements at Mt. Kenya were operational since the last audit of WCC-Empa in February 2002 until the recent power failure in October 2004, and no changes were made since the last audit. The station was without power at the time of the present audit. All inter-comparisons were done using a power generator. This resulted in short warm-up times and power stability was poor.

4.1 Monitoring Set-up and Procedures

4.1.1 Air Inlet System

Sampling-location: The air inlet is mounted on top of the flat roof, approx. 1.7 m above the cabin and 4.5 m above the ground.

Sample inlet:

- Rain protection: The Inlet is protected against rain and snow by an upside-down aluminium bucket.
- Inlet-filter: Teflon inlet filter before analyser, exchanged approx. every 3 weeks depending on pollution and operation of the instrument.

Sampling-line:

- Inlet / Manifold
  - Dimensions: length = ca. 3 m, i.d. = 5 cm
  - Material: glass
- Sample line
  - Dimensions: length = ca. 1.5 m, i.d. = 4 mm

Flow rate: inlet / manifold: High volume ventilator, flow rate unknown
sample line: 2 l/min

Residence time in the sampling line: estimated to be < 10 s

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

4.1.2 Instrumentation

Ozone Analyser

The monitoring system at the global GAW station Mt. Kenya consists of an ozone analyser with an internal ozone generator, plus an external zero air unit consisting of a pump and a charcoal cartridge. The ozone instrument is installed in a 19" rack in a 6 m x 2.5 m cabin unit. The station is not air conditioned, and the lab temperature shows a significant diurnal variation. The instruments are not exposed to direct sunlight. Instrumental details for the ozone analyser are summarised in Table 2.

Table 2: Ozone instruments at Mt. Kenya

Type	TEI 49 #51959-290
Method	UV absorption at 254 nm
at Mt. Kenya	since December 1999
Range	0-1000 ppb
Analogue output	0-10 V
Settings	Span: 509; Offset: 49
Instrument specials	Internal ozone generator

Ozone Calibrator

No ozone calibrator is available at the site. An ozone calibrator model TEI 49 PS is available at KMD in Nairobi and is mainly used to check the ozone sounds. Instrumental details can be found in the Empa-WCC audit report 00/1. This instrument was also compared with the WCC-Empa transfer standard during this audit.

Operation and Maintenance

The instrument is checked for general operation when the station is visited (usually at least once per week). Checklists and a log book with all relevant instrument information were available. Furthermore, all station relevant information was noted in a station log book.

4.1.3 Data Handling

Data Acquisition and –transfer

The analogue output of the ozone analyser is connected to the MILOS 500 data acquisition system. One minute averages are stored together with meteorological data. The logger has a capacity for two weeks data storage. Data is manually downloaded to the station computer once per week.

Data Treatment

Data is regularly checked for consistency with time series plots, and data is submitted to QA/SAC Switzerland. QA/SAC is working with the station operator to transfer the responsibility of data evaluation to KMD staff.

Data Submission

Because only few data is available ozone data have not yet been submitted to the data centre for surface ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG).

4.1.4 Documentation

Station and instrument logbooks are available. All logbooks are available as hard copies and electronically. The notes are up to date and describe all important events. The instrument manual is available at the site.

4.2 Inter-comparison of the Ozone Instrument

Inter-comparisons were made using a power generator because the station was without power during the audit. This resulted in short warm-up times of 2 hours (normal: 24 h) and poor power stability. However, the results were most likely not significantly influenced because of these facts.

4.2.1 Experimental Procedure

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode to warm up for approximately 2 hours. During this stabilisation time the transfer standard, the station analyser and the PFA tubing between the instruments were conditioned with 400 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instrument and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 8 the experimental set-up during the audit. No modifications of the ozone analysers which could influence the measurements were made for the inter-comparisons.

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

Table 3: Experimental details of the ozone inter-comparison

reference	Empa: TEI 49C-PS #56891-310 transfer standard
field instrument	TEI 49 #51959-290
ozone source	WCC: TEI 49C-PS, internal generator
zero air supply	Empa: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm
data acquisition systems	16-channel ADC circuit board with acquisition software (Hunter & Caprez)
pressure transducer readings	Ambient Pressure: 660.8 hPa TEI 49C-PS (WCC): 665.2 hPa, adjusted to 661.2 hPa TEI 49 #51959-290: 661.2 hPa, not adjusted
concentration range	0 - 100 ppb
number of concentrations	5 + 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 runs on 19. February 2005
connection between instruments	about 1.5 meter of 1/4" PFA tubing

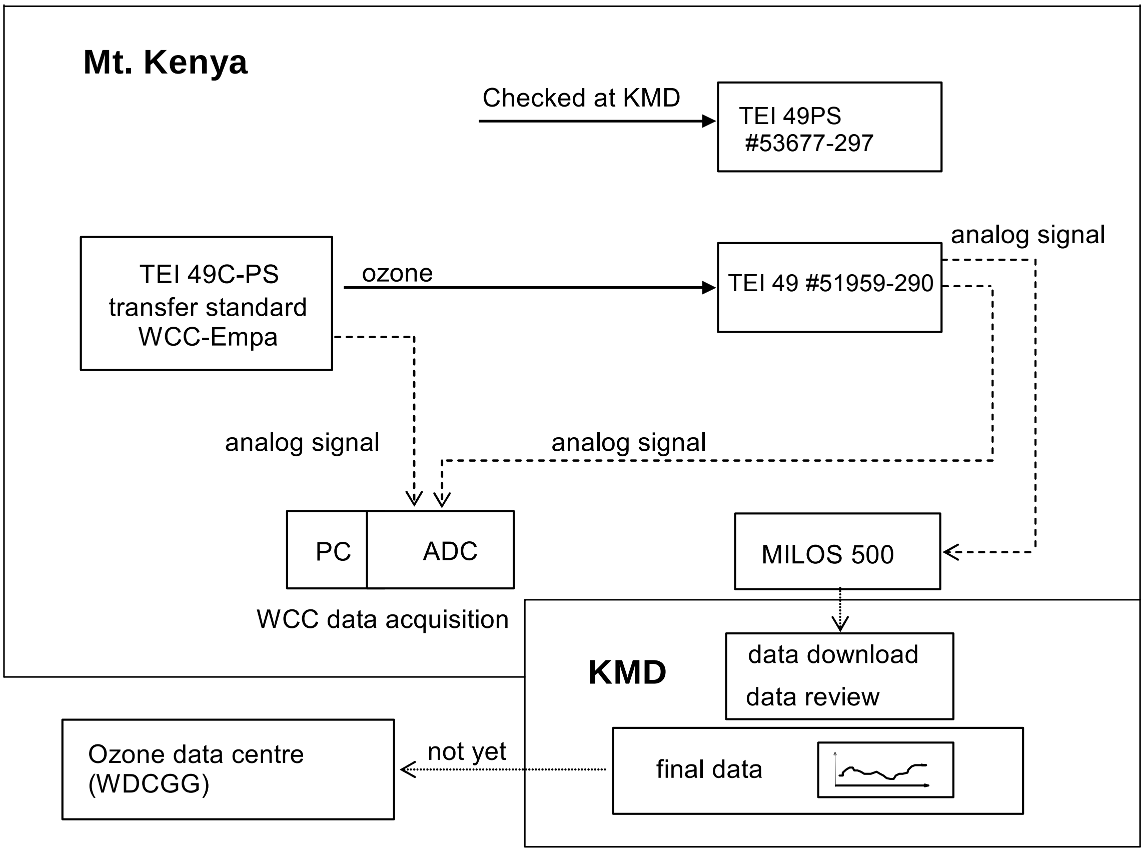

Figure 8: Experimental set up for the ozone inter-comparison

4.2.2 Results

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

Ozone Analyser

The results comprise the inter-comparison between the TEI 49 #51959-290 field instrument and the WCC transfer standard TEI 49C-PS, carried out on 19 February 2005.

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

Figures 9 and 10 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 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 WCC-Empa and Mt. Kenya data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 4: Inter-comparison of the ozone field instrument TEI 49 #51959-290

run index	**WCC TEI 49C-PS** conc.	s_d	**TEI 49 #51959-290** conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.33	0.11	-0.67	0.63	-1.00	
2	74.87	0.30	73.23	0.68	-1.64	-2.20
3	34.67	0.18	33.45	0.61	-1.22	-3.52
4	14.92	0.08	13.58	0.40	-1.35	-9.03
5	54.71	0.05	53.51	0.25	-1.20	-2.19
6	89.50	0.07	88.07	0.74	-1.43	-1.60
7	0.42	0.10	-0.67	0.47	-1.09	
8	0.43	0.11	-0.59	0.52	-1.02	
9	74.52	0.13	73.42	0.54	-1.10	-1.48
10	14.90	0.09	13.73	0.26	-1.17	-7.87
11	89.95	0.13	88.81	0.70	-1.14	-1.27
12	34.76	0.16	33.83	0.35	-0.93	-2.69
13	54.52	0.11	53.44	0.62	-1.08	-1.99
14	0.41	0.18	-0.16	0.64	-0.56	
15	0.43	0.19	-0.50	0.44	-0.92	
16	89.47	0.12	88.57	0.66	-0.90	-1.01
17	74.11	0.12	72.79	0.37	-1.33	-1.79
18	53.97	0.06	52.78	0.51	-1.19	-2.21
19	34.73	0.14	33.61	0.18	-1.12	-3.23
20	13.85	0.21	13.15	0.52	-0.70	-5.02
21	0.43	0.32	-0.37	1.42	-0.79	

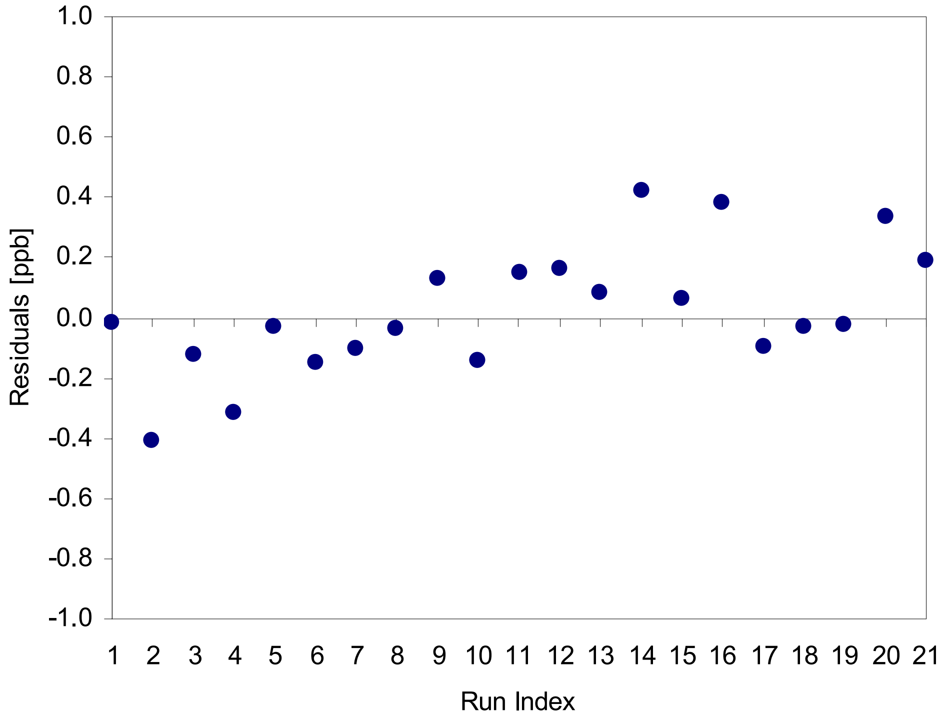

Figure 9: Residuals to the linear regression function (TEI 49 #51959-290) vs. the run index (time dependence)

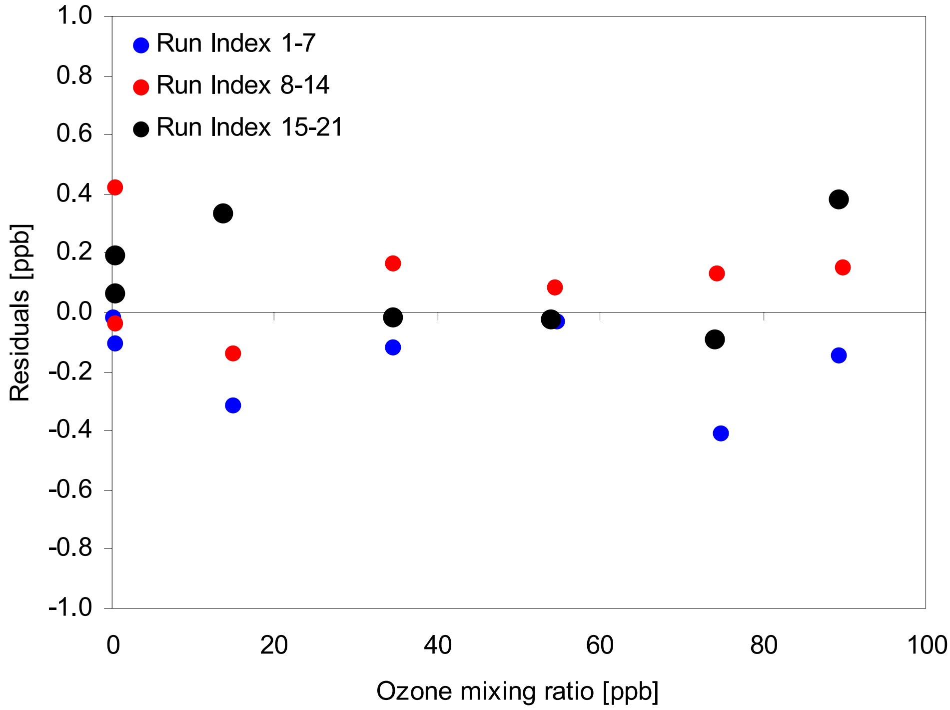

Figure 10: Residuals to the linear regression function (TEI 49 #51959-290) vs. the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49 #51959-290:

$$\text{Unbiased } O_3 = (\text{TEI 49} + 1.01) / 0.9994$$

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

TEI 49 = O_3 mixing ratio in ppb, determined with TEI 49 #51959-290

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

$$u_C \approx \{(0.81 \text{ ppb})^2 + (0.00733 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 11 shows the deviation of the TEI 49 #51959-290 from SRP#15 with the assessment criteria for "good" and "sufficient" agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

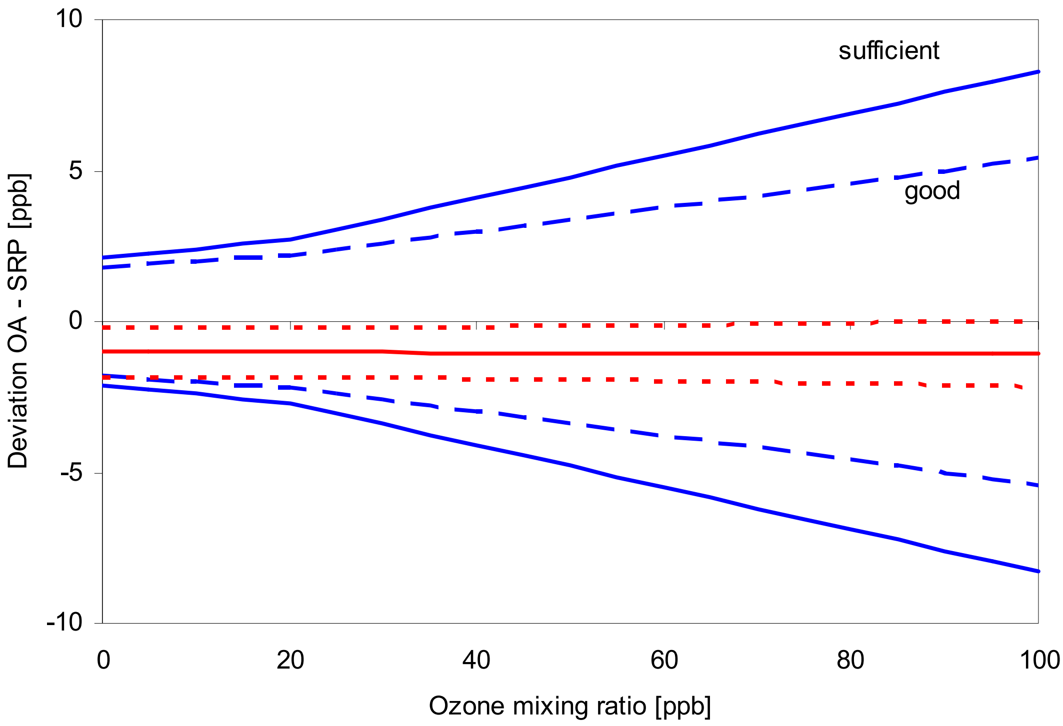

Figure 11: Inter-comparison of instrument TEI 49 #51959-290

Ozone Calibrator

The inter-comparison of the ozone calibrator TEI 49PS was done at KMD. The results comprise the inter-comparison between the TEI 49PS #53677-297 field calibrator and the WCC transfer standard TEI 49C-PS, carried out on 16 February 2005. Experimental details are described in Table 5.

Table 5: Experimental details of the ozone inter-comparison (calibrator at KMD)

reference	Empa: TEI 49C-PS #56891-310 transfer standard
field instrument	TEI 49PS #53677-297
ozone source	WCC: TEI 49C-PS, internal generator
zero air supply	Empa: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition systems	16-channel ADC circuit board with acquisition software (Hunter & Caprez)
pressure transducer readings	Ambient Pressure: 822.3 hPa TEI 49C-PS (WCC): 822.9 hPa, adjusted to 822.3hPa TEI 49 #51959-290: 822.32 hPa, not adjusted
concentration range	0 - 100 ppb
number of concentrations	5 + 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 runs on 15. February 2005
connection between instruments	about 1.5 meter of 1/4" PFA tubing

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 6. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

Figures 12 and 13 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 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 the WCC-Empa data acquisition system.

Table 6: Inter-comparison of the ozone field calibrator TEI 49PS #53677-297

run index	WCC TEI 49C-PS		TEI 49PS #53677-297			
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.34	0.07	0.24	0.30	-0.10	
2	49.66	0.13	49.39	0.26	-0.28	-0.56
3	149.83	0.06	148.61	0.23	-1.22	-0.82
4	239.81	0.06	238.91	0.52	-0.90	-0.37
5	99.79	0.08	99.15	0.18	-0.64	-0.64
6	199.84	0.06	199.02	0.23	-0.81	-0.41
7	0.27	0.12	0.47	0.34	0.20	
8	0.25	0.11	0.24	0.33	-0.02	
9	239.79	0.07	238.60	0.35	-1.19	-0.50
10	199.81	0.09	198.72	0.27	-1.08	-0.54
11	49.85	0.08	49.31	0.19	-0.53	-1.07
12	99.83	0.13	98.96	0.26	-0.87	-0.87
13	149.85	0.13	148.97	0.36	-0.88	-0.59
14	0.32	0.09	0.25	0.30	-0.07	
15	0.25	0.11	0.15	0.15	-0.09	
16	99.83	0.08	99.15	0.07	-0.68	-0.68
17	149.86	0.06	148.61	0.26	-1.25	-0.83
18	239.88	0.08	238.68	0.19	-1.21	-0.50
19	49.87	0.04	48.99	0.18	-0.88	-1.76
20	199.85	0.06	198.76	0.27	-1.09	-0.54
21	0.29	0.10	0.20	0.20	-0.10	

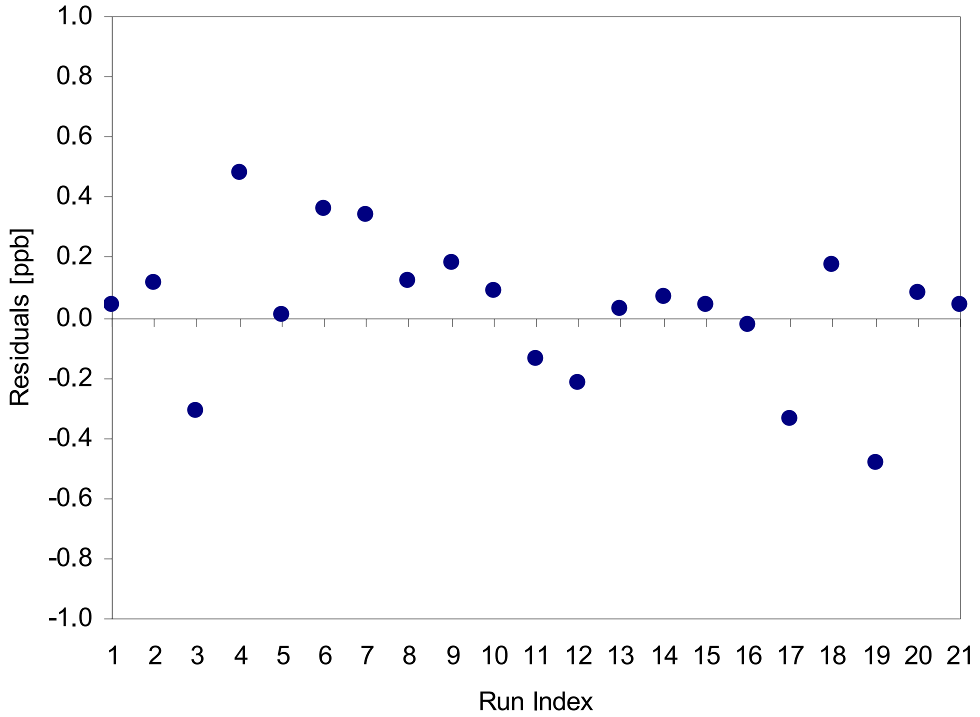

Figure 12: Residuals to the linear regression function (TEI 49PS #53677-297) vs. the run index (time dependence)

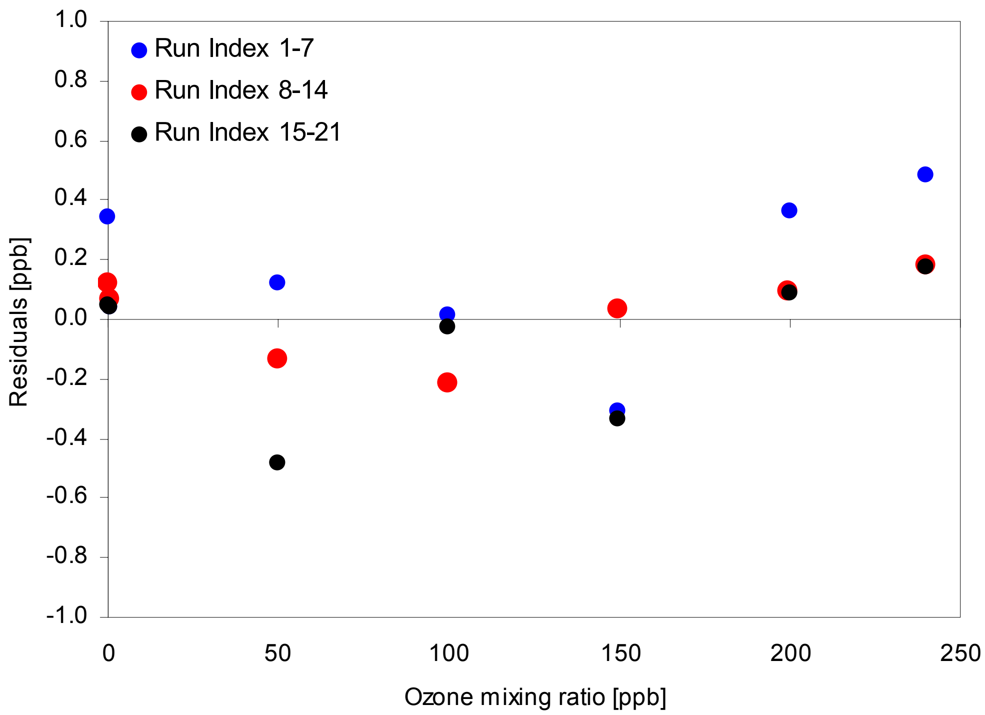

Figure 13: Residuals to the linear regression function (TEI 49PS #53677-297) vs. the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49PS #53677-297:

$$\text{Unbiased } O_3 = (\text{TEI 49PS} + 0.16) / 0.9976$$

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

TEI 49PS = O_3 mixing ratio in ppb, determined with TEI 49PS #53677-297

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

$$u_C \approx \{(0.65 \text{ ppb})^2 + (0.00550 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 19 shows the deviation of the TEI 49PS #53677-297 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

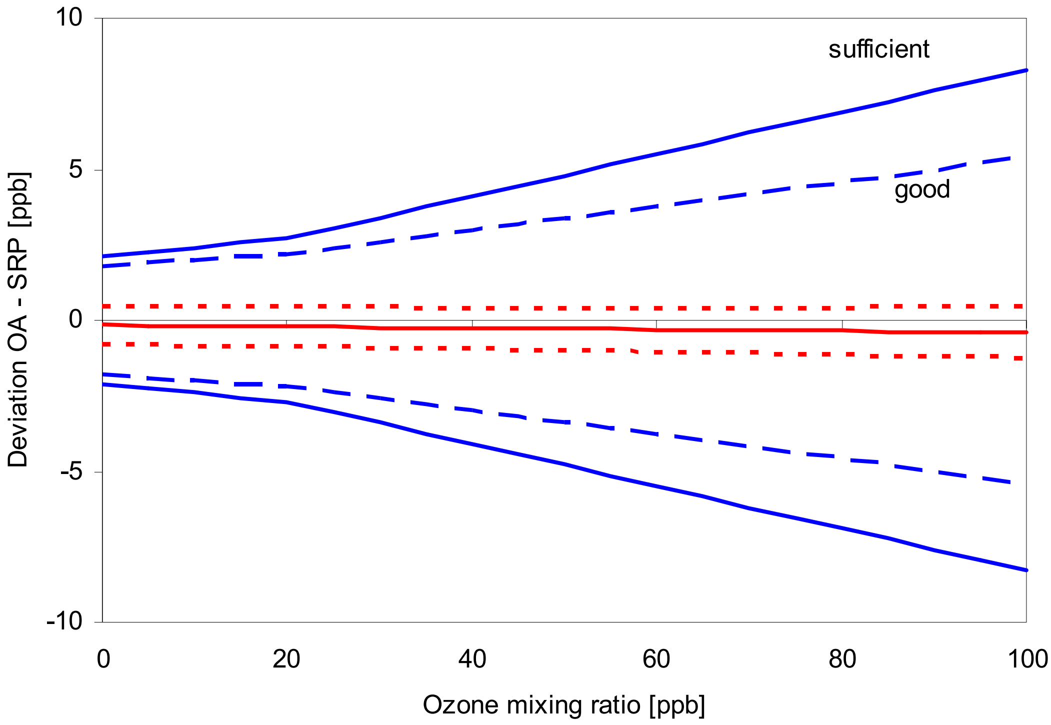

Figure 14: Inter-comparison of instrument TEI 49PS #53677-297

Comment

The ozone concentrations observed at Mt. Kenya ranged approximately between 10 and 75 ppb (60 min mean values of 2004). The main ozone analyser and the station calibrator of Mt. Kenya fulfil the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3 Recommendation for Surface Ozone Measurements

The most pressing issue concerning the whole measurement programme at Mt. Kenya is a continuous and stable power supply (see general recommendations in Section 1). The UPS was installed by the station operators as recommended by the WCC-Empa Report 02/1. However, only power outages of less than 6 hour can be bridged by the UPS.

The following recommendations are suggested by WCC-Empa for surface ozone measurements at Mt. Kenya:

- The use of electronic log books and check lists is encouraged.
- The TEI 49 is still running but it is approaching the end of its useful lifetime. It should be considered to replace the ozone analyser by a newer model, e.g. a TEI 49C. Instrument noise and accuracy of the new models is better compared to the TEI 49, and digital data can be acquired.
- It is recommended to have a station ozone calibrator available at the site. If this is not feasible yearly inter-comparisons of the ozone analyser with the calibrator at KMD are encouraged.
- Submission of the surface ozone data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly recommended after the existing data is quality controlled. Data submission is one of the obligations of a GAW station.

5 SYSTEM AND PERFORMANCE AUDIT FOR CARBON MONOXIDE

Carbon monoxide measurements started Mt. Kenya in 2002 and were initiated and installed by WCC-Empa and QA/SAC Switzerland with WMO funding. Continuous carbon monoxide time series are available since then; however, large data gaps exist due to discontinuous power supply to the station. The monitoring set-up was since then only slightly modified and is in detail described in WCC-Empa Report 02/1. The most relevant modification is the implementation of automated span checks.

5.1 Monitoring Set-up and Procedures

5.1.1 Air Inlet System

Sampling-location:

The same air inlet system (inlet, manifold) as for the ozone measurements is used. The instrument is connected to the manifold with approx. 1.5 m Teflon tubing, and the residence time is estimated to be less than 10 s.

5.1.2 Instrumentation

A TEI48C NDIR monitor was installed at Mt. Kenya in 2002 by WCC-Empa and QA/SAC Switzerland. The instrument was modified with a Nafion dryer. More details about instrument set-up and modifications can be found in WCC-Empa report 02/1. Instrumental details are listed in Table 7.

Table 7: Carbon monoxide gas chromatograph at Mt. Kenya

Instrument type and S/N	TEI 48C Trace Level #66838-352
Analytical method	NDIR, Gas Filter Correlation Technique
Modification	Nafion drier PERMAPURE PD-50-24'' reflux mode using critical orifice and pump of instrument
At Mt. Kenya	since February 2002, installed by WCC-Empa
Range	0-1000 ppb
Calibration settings	CO COEFF: 1.110; BKG: 8.200 ppm
Analogue output	0-10 V (not used)
Serial output	RS 232

5.1.3 Calibration Equipment

The calibration equipment used for zero / span checks and calibrations is listed in Table 8.

Table 8: CO calibration equipment at Mt. Kenya

Standard gas for direct calibrations	1060 ppb CO ± 2%, 3845H (CO 99.997% in synth. air 99.9995%) traced back to NIST at WCC-Empa in 2001
Standard gas for span checks (dilution)	15000 ppb CO ± 2%, 6395E (CO 99.997% in synth. air 99.9995%) traced back to NIST at WCC-Empa in 2001
Zero air unit (for dilution)	Custom built by WCC-Empa Inlet Filter – Pump – Rubin Gel – Sofnocat 423 – Outlet Filter
Dilution unit	MFC Bronkhorst HI-TEC S/N 413212.A 0 – 100 ml/min MFC Bronkhorst HI-TEC S/N 413212.B 0 – 5000 ml/min Bronkhorst Control Unit S/N M1206113A

A schematic overview of the instrumental set-up is shown in Figure 15. The original instrument set-up was modified before the audit by introducing an automatic activation of span checks with the dilution unit. Currently, a zero check is automatically performed starting every odd hour for 20 minutes, followed by span for 10 minutes. The mass flow controllers are set to obtain a span level of approximately 506 ppb CO (zero air 1.0 l/min, CO 51.1 ppm 10 ml/min).

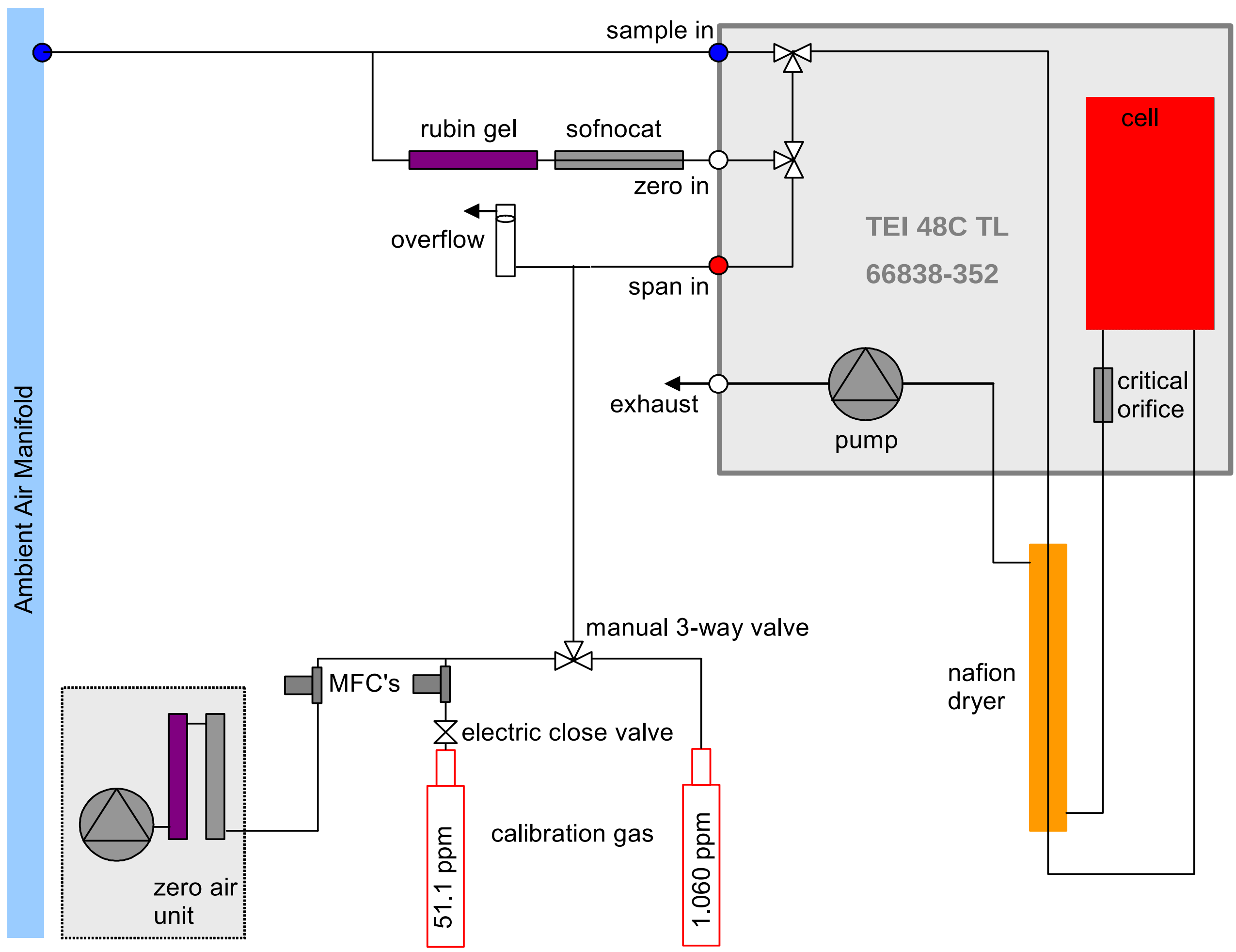

Figure 15: Instrument set-up (carbon monoxide) at Mt. Kenya

Operation and Maintenance

Analysis: The system is alternating between sample and a zero/span check (20 min zero, 10 min span) every odd hour.

Weekly checks: A checklist is filled in once per week. All information accessible through the instrument diagnostics menu is recorded along with calibration factors, instrument time and calibration standard pressures.

Inlet filters are changed every two weeks or earlier when necessary. Further maintenance is done on a case by case basis.

5.1.4 Data Handling

Data Acquisition and –transfer

The TEI 48C is connected to the MILOS 500 data logger. The analogue output (0-1 V, corresponding to 0-1000 ppb CO) of the instrument is recorded by the MILOS and one minute averages are stored. In addition, data of the TEI internal data logger is downloaded at least weekly with the C series communication software (version 2.2.0) from Thermo Environmental Instruments. This data consist of 5 and 15 minute average values with ancillary instrument information.

Data Treatment

The first five minute average value after a switch of the zero/span valve is discarded. The remaining five minute average values are used for further data evaluation. Zero values are used to correct for instrument zero drift using a lowess fit. Zero corrected five minute means are further averaged to 30 min values. Span values from the automatic span checks will be used for quality control purposes, but will not be used for data correction.

Data evaluation is challenging due to the fact that the instrument shows a significant (temperature dependent) zero drift. An additional project was submitted to START/PACOM by KMD in collaboration with Empa. One of the goals is to enable the KMD staff to meet international standards with respect to data management and data analysis. This project is currently ongoing.

Data Submission

Data have not yet been submitted to the GAW data centre for greenhouse gases (WDCGG).

5.1.5 Documentation

Logbooks / SOPs

A logbook is available for the carbon monoxide instrument. The notes are up-to-date and describe all important events. The instrument manual and instrument check lists are available at the site.

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

5.2.1 Experimental Procedure

WCC-Empa provided different CO concentrations using a high concentration CO standard and a dilution unit. Details and traceability to CMDL are described in Appendix III. Each concentration was measured by the station instrument between 30 and 150 minutes. A zero check was made every two hours for 30 minutes. Data was corrected for zero drift with a linear interpolation between two bracketing zero checks. Thirty second averages were acquired which were further averaged to 5 minute values. The final result thus comprises an average of 6 to 30 zero drift corrected values. The experimental details are summarized in Table 9.

Table 9 Experimental details of the carbon monoxide inter-comparison

field instrument:	TEI 48C Trace Level #66838-352
reference:	WCC-Empa dilution unit
data acquisition system:	16-channel ADC circuit board with acquisition software (Hunter & Caprez)
approx. concentration levels:	0 to 1000 ppb

5.2.2 Results

The CO concentrations determined by the main station instrument TEI 48C-TL #66838-352 for six different concentrations provided by the WCC-Empa dilution system are shown in Table 10. For each value the difference between the tested instrument and the dilution unit is calculated in ppb and %. Figure 16 shows the absolute differences (ppb) between the measurements of the TEI 48C-TL #66838-352 and WCC-Empa (reference). The WCC-Empa dilution system was calibrated before and after the audit against a flow reference and tested with an Aerolaser AL5001 CO instrument (before audit only) which was calibrated with a CMDL certified standard (CMDL CA02854, 295.5 pbb). The error bars represent the combined 95% confidence interval for the calibration of the dilution system against the CMDL standard and of the 5 minutes average values at Mt. Kenya.

Table 10: Carbon monoxide inter-comparison measurements at Mt. Kenya

No.	**WCC-Empa**	**Mt. Kenya analysis (TEI 48C-TL #66838-352)**				
	conc. ± uncertainty*	conc.	s_d	No. of 5 min	deviation from reference	
	ppb	ppb	ppb	values	ppb	%
1	0.0 ± 2.0	9.0	12.0	6	9.0	N/A
2	206.1 ± 4.1	205.9	10.2	18	-0.2	-0.1
3	409.0 ± 8.2	390.1	6.0	20	-18.9	-4.6
4	612.2 ± 12.2	585.0	10.7	11	-27.2	-4.4
5	1018.1 ± 20.4	978.2	16.9	30	-39.9	-3.9

* Uncertainties were estimated to be ± 2 ppb (conc. ≤ 100 ppb) or 2 % (conc. > 100 ppb)

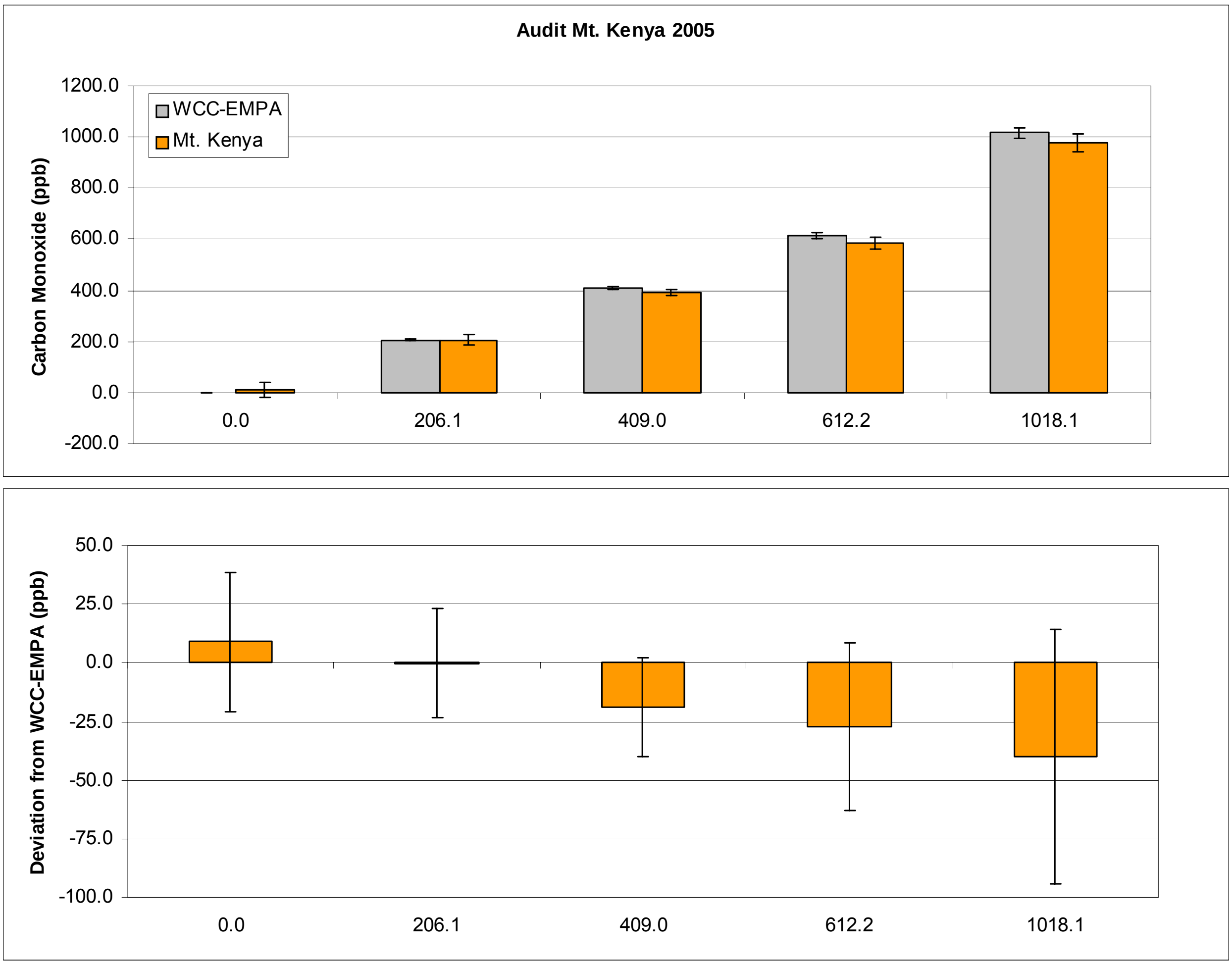

Figure 16: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the CO analyser of Mt. Kenya (orange). lower panel: deviation of the Mt. Kenya station from the conventional true value. The error bars represent the 95% confidence interval. Data are 5 minute values averaged over 30 to 150 minutes.

5.3 Discussion of the Inter-comparison Results

The inter-comparison between WCC-Empa and Mt. Kenya station showed relatively large deviations from the reference value with high uncertainties. The reason for this is discussed below:

a) Instrument drift

The TEI 48C shows a significant zero drift. The drift seems to be correlated with the laboratory temperature. Furthermore the instrument shows a large drift after it is switched on. The warm-up time during the audit was not sufficient because the station was without power at the time of the audit, and all inter-comparisons were made with the analyser running only for a few hours. This affected the measurements and made zero drift correction difficult.

b) Instrument noise

Instrument noise is also limiting the precision of NDIR instruments. Series of 10 or more one minute averages of zero or span measurements show usually a standard deviation of up to 10 ppb. This instrument noise is however typical for NDIR instruments and the TEI 48C of Mt. Kenya does not show higher noise compared to other NDIR analysers.

5.4 Recommendation for Carbon Monoxide Measurements

Zero drift of the TEI 48C was identified to be the most limiting factor for accurate CO measurements with the current instrument set-up.

The following recommendations address the issue of the zero drift and zero correction of time series:

- Data evaluation should be done using sophisticated statistical tools to account for zero drift. Development of this tool is ongoing in the frame of the START/PACOM project. In a first step raw data is flagged, and the following flags should be used:
  - Flag 0: Measuring ambient (valid raw ambient CO data)
  - Flag 1: Zero check (valid raw zero data)
  - Flag 2: Span check (valid raw span data)
  - Flag 3: Transient data (invalid data after zero/span valve switch)
  - Flag 4: Invalid data of unknown quality

  This raw data should further be assessed using e.g. lowess fit for the correction of the zero drift. In order to get good fits, time series need to be as complete as possible.
- The instrument set-up uses currently the internal zero and span valves for automatic zero and span checks (every odd hour). The valves are controlled by the TEI 48C analyser. Two hours is the shortest possible period if the valves are controlled by the instrument. This interval should be sufficient if the laboratory temperature is not fluctuating more than a few degrees per day and no fast temperature changes occur. However, more frequent zero checks (e.g. alternating between ambient and zero every 10 minutes) would improve data quality. This can only be done if the valves are controlled via RS-232 by an external device (e.g. an external data acquisition with instrument control functions).
- It should be explored if the instrument can be modified to obtain a more stable temperature of the IR source and optical bench.
- The laboratory is not air-conditioned. A constant laboratory temperature would minimize the zero drift due to temperature changes. It should be explored if the lab could be temperature controlled without high energy consumption. For example it should be considered to paint the lab building light-coloured.

The following recommendations are made by WCC-Empa to further improve the quality and availability of carbon monoxide measurements at Mt. Kenya:

- Electronic log books and check lists should be used instead of paper copies.
- Direct checks of the calibration settings of the instrument should be made every three months using the 1 ppm CO standard. This was not done or not documented and communicated in the past.
- Raw data should be backed up, e.g. on CD.
- Submission of CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is encouraged after data have been quality controlled.

6 REFERENCES

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

Klausen, J., C. Zellweger, B. Buchmann, and P. Hofer, Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, Journal of Geophysical Research-Atmospheres, 108 (D19), 4622, doi:10.1029/2003JD003710, 2003.

Novelli, P.C., K.A. Masarie, P.M. Lang, B.D. Hall, R.C. Myers, and J.W. Elkins, Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, Journal of Geophysical Research-Atmospheres, 108 (D15), 4464, doi:10.1029/2002JD003031, 2003.

Press, W.H., T. S.A., Vetterling, W.T., and B.P. Flannery, Numerical Recipes in C: The Art of Scientific Computing, 994 pp., Cambridge University Press, Cambridge, U.K., 1995.

APPENDIX

I. Empa Transfer Standard TEI 49C-PS

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

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 17. 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.

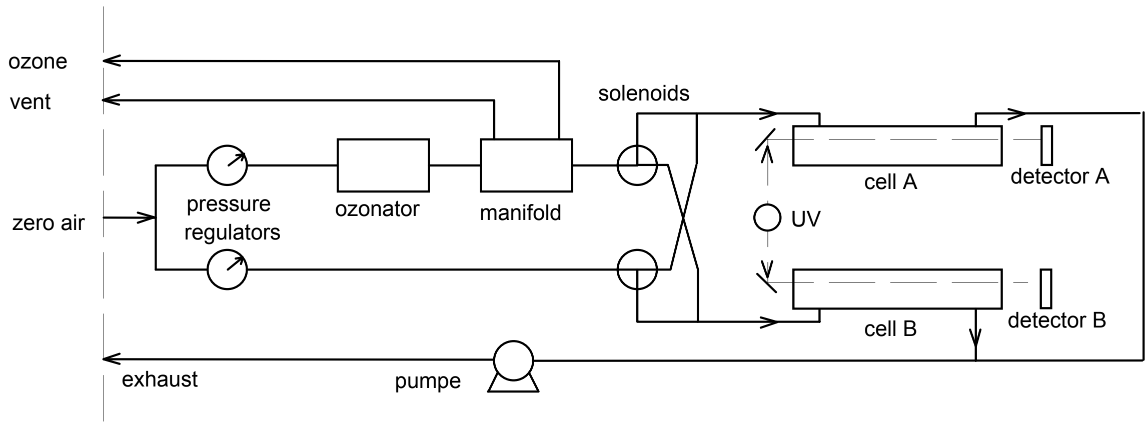

Figure 17: Flow schematic of TEI 49C-PS

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

To exclude errors that might result from transportation of the transfer standard, the TEI 49C PS #56891-310 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 11 and Figure 18.

Table 11: Inter-comparison procedure SRP - TEI 49C-PS

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

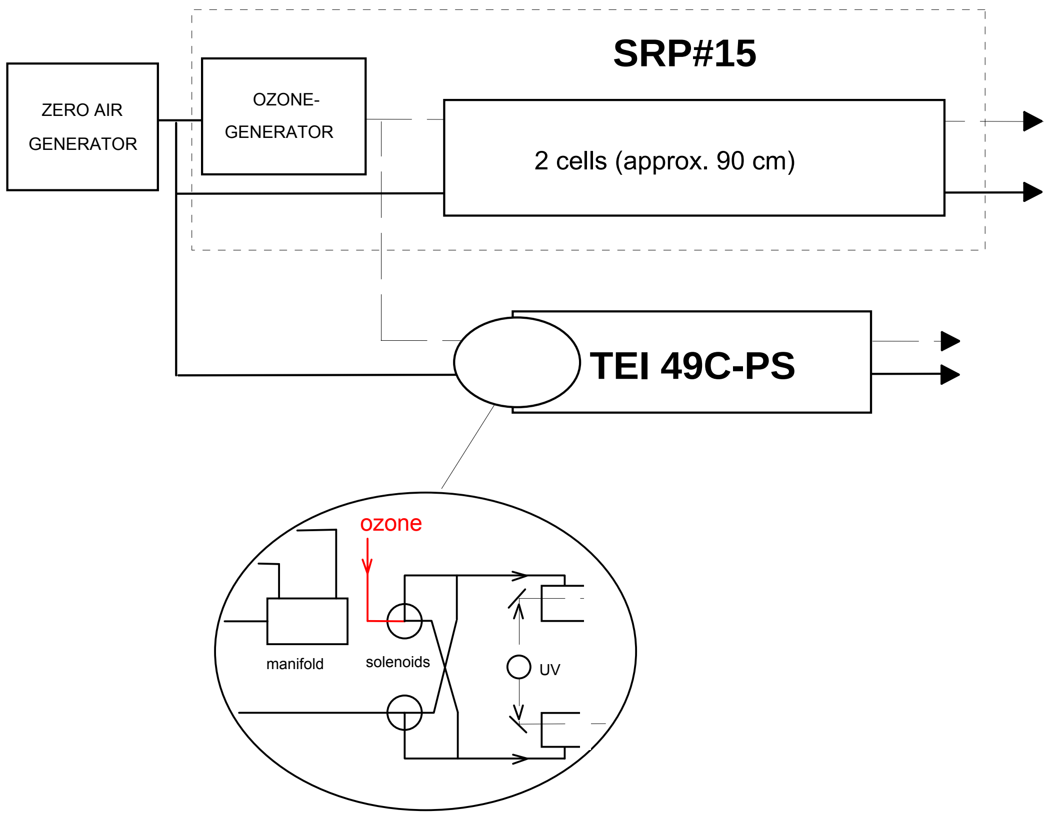

Figure 18: Instruments set up SRP -TEI 49C-PS

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 19 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 #56891-310 = 1.0028 x SRP#15 - 0.03 ppb

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

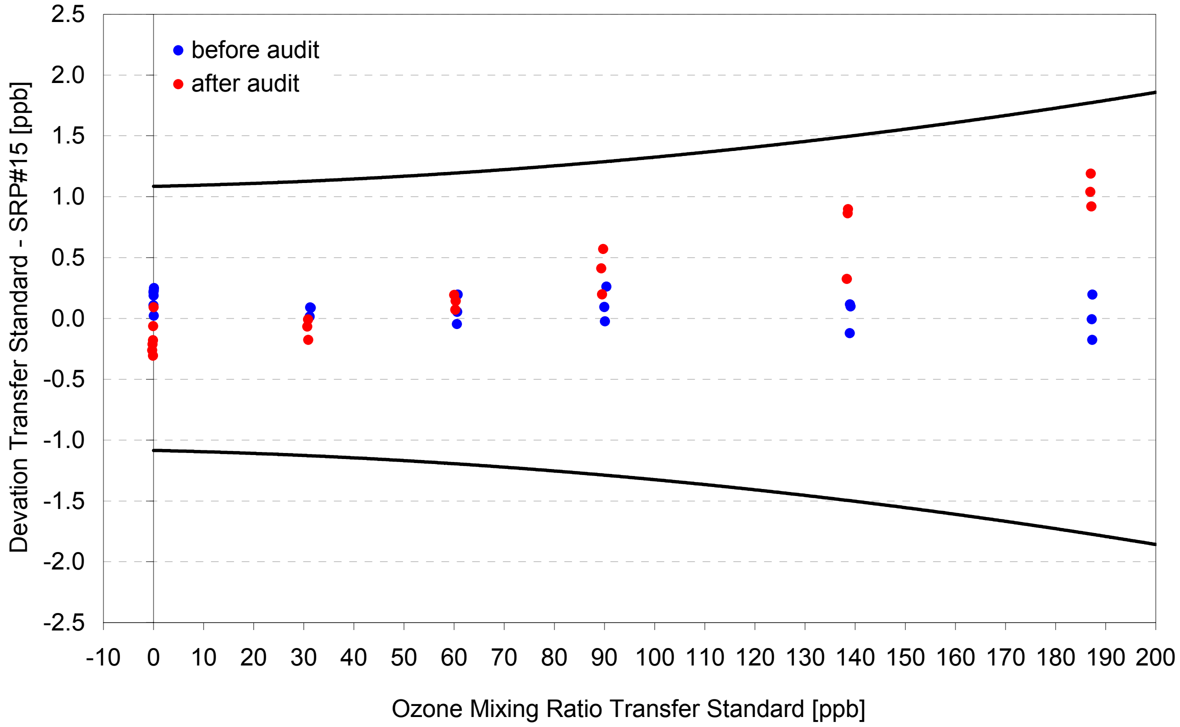

Figure 19: Deviation of the WCC-Empa transfer standard from SRP#15 before and after the audit

III. WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW programme. The standards used at WCC-Empa are listed in Table 12:

The CO scale of the CMDL was recently revised (Novelli et al., 2003). WCC-Empa refers to the revised scale (WMO 2000).

A MGM dilution unit (Breitfuss, Serial # 2262/91/1) was used to generate different CO concentrations. This dilution unit was calibrated against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851) before the audit. Zero air was generated using a zero air generator (Ambient Air – Rubingel – Sofnocat – Filter – Pump – Purafil – Sofnocat – Filter). This zero air system was tested and completely removed CO from ambient levels of > 1 ppm at 3.5 litres per minute. A CO standard (Sauerstoffwerk Lenzburg) in synthetic air was used for the dilution system. This standard was calibrated against CMDL revised scale CA02854 with the Aerolaser AL5001, resulting in a concentration of 50.117 ppm CO. In addition, the whole dilution system was checked by measuring the resulting concentrations with the AL5001. The results (flows, expected and measured CO concentrations) are listed in Table 13. The expected CO concentration from the dilution was assigned to be the conventional true value.

Table 12: 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 revised scale**	WCC-Empa assigned***	Cylinder
CMDL Laboratory Standard	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	56.3 ± 1.0 ppb	CA03209
CMDL Laboratory Standard	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	108.6 ± 1.1 ppb	CA02803
CMDL Laboratory Standard		129.8 ± 1.3 ppb	131.7 ± 1.3 ppb	CA05373
CMDL Laboratory Standard	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	153.9 ± 1.5 ppb	CA03295
CMDL Laboratory Standard	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	295.5 ± 3.0 ppb	CA02854

* Certificates from 5.8.97 (97.6, 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; Certificate from 15.4.04 (129.8 ppb)
** WCC-Empa assigned valued based on calibrations with CA02859 and CA02854

Table 13: MGM dilution system

Mass Flow Controller Setpoint [ml/min]		Mass Flow Controller Actual value before audit [ml/min]		Expected CO concentration before audit [ppb]	Measured CO concentration before audit [ppb ± 1σ]	Mass Flow Controller Actual value after audit [ml/min]		Expected CO concentration after audit [ppb]	Average expected CO concentration [ppb]
MFC1	MFC2	MFC1	MFC2			MFC1	MFC2		
2000.0	0.0	1991.3	0.0	0.0	0.3 ± 0.7	1990.8	0.0	0.0	0.0
1992.0	8.0	1983.1	8.2	206.0	205.3 ± 0.8	1987.2	8.2	206.2	206.1
1984.0	16.0	1974.7	16.2	408.6	408.5 ± 1.2	1978.6	16.3	409.3	409.0
1976.0	24.0	1966.4	24.3	611.6	611.6 ± 2.0	1969.6	24.4	612.9	612.2
1960.0	40.0	1949.1	40.4	1018.0	1016.3 ± 3.5	1957.4	40.6	1018.2	1018.1

IV. Ozone Audit Executive Summary

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

Ozone Audit Executive Summary

0.1	Station Name:	Mt. Kenya
0.2	GAW ID:	MKN
0.3	Coordinates/Elevation:	0.033°S, 37.217°E (ca. 3697 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1 Date of Audit: February 16 - 20, 2005

1.2 Auditors: Dr. C. Zellweger and S. Bugmann

1.2.1 Station staff involved in audit:
J. Rotich, J. Kariuki, J. Aseyo, W. Ayoma, J. Mukola

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: 56891-310
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0028±0.0010) × [SRP] - (0.03±0.09)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49 S/N 51959-290
1.6.2	Coefficients prior to audit	OFFSET: 49 SPAN: 509
1.6.3	Coefficients during and after audit	OFFSET: 49 SPAN: 509
1.6.4	Range of calibration: 0 – 100 ppb	
1.6.5	Calibration before audit (ppb):	[OA] = (0.9966±0.0052) × [TS] - (0.98±0.24)
1.6.6	Calibration after audit (ppb):	same as 1.6.5.
1.6.7	Unbiased ozone concentration (ppb):	C = ([OA] + 1.0092) / 0.9994
1.6.8	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{(0.81\text{ ppb})^2 + (0.0073 \times C)^2\}^{1/2}$

1.7 Comments: Inter-comparison was done using a power generator. Only a short warm-up time was possible.

1.8 Reference: Empa-WCC Report 05/1