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

Materials Science & Technology

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 08/5

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION MT. KENYA

KENYA, NOVEMBER 2008

Submitted by

C. Zellweger, J. Klausen, S. Henne, B. Buchmann

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

CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The fifth system and performance audit at the Global GAW station Mt. Kenya (MKN) was conducted by QA/SAC-Switzerland and WCC-Empa[1] from 2 thru 10 November 2008 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The MKN observatory is operated by the Kenya Meteorological Department (KMD) and was established in 1996.

Previous audits at Mt. Kenya GAW station were conducted in January 2000 [*Herzog, et al.*, 2000], February 2002 [*Zellweger, et al.*, 2002], February 2005 [*Zellweger, et al.*, 2005], and January 2006 [*Klausen, et al.*, 2006].

The following people contributed to the audit:

Dr Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Dr. Stephan Henne	Empa Dübendorf, QA/SAC Switzerland
Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr. Kennedy K. Thiong'o	Kenya Meteorological Department
Mr. John Aseyo	Kenya Meteorological Department

Our assessment of the Mt. Kenya observatory in general, as well as the surface ozone and carbon monoxide measurements in particular, is summarised below. The assessment criteria for the ozone inter-comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003].

This report is distributed to the GAW Country Contact (KMD, Mr. Peter M. Bundi), the station manager and operator (KMD, Mr. Kennedy K. Thiong'o and Mr. John Aseyo) and the World Meteorological Organization in Geneva. The executive summaries will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

The Global GAW station Mt. Kenya (MKN) is located at high altitude in a data-sparse region of the world and provides a unique opportunity to monitor background air as well as to conduct research in a pristine continental environment. The location is adequate for the intended purpose.

Access to the site consists of a dirt road and requires a 4WD vehicle and a 30-minute hike. During the audit, the condition of the dirt road was poor, and access to the site was extremely difficult. The recommendations made in the previous audit report remain still valid.

Recommendation 1 (, on-going)**
KMD is encouraged to highlight the importance of Mt. Kenya GAW station to the National Park Service and to ensure that the access road up to Moses Camp is improved and well maintained.

Recommendation 2 (*, immediately)**
The existing Land Rover is beyond the end of its useful lifetime. KMD should anticipate the need for a replacement vehicle in their budgetary planning process.

[1] WMO/GAW GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

Station Facilities

The station consists of two containers that provide adequate laboratory and office space, including an instrument rack and personal computers.

The containers are not air-conditioned and the diurnal temperature variation inside the laboratory can easily exceed 10 K. This is inadequate for high quality atmospheric monitoring as it can affect the measurements. An electric heating fan had previously been provided to the station; however, this proved to be unfit at such high altitude, and an alternative solution must be found.

The power supply to the station improved over the past years, but is still inadequate due to frequent failures that prohibit sustainable operation of the station to this date. The power outages in the past were usually due to faulty joints in the overland line. Typically, a minimum of 10 days were required to report the power outage (KMD), identify the fault (KPLC Nanyuki), call in jointers from Nairobi (KPLC Nanyuki), confirm the location of the fault and repair the line (KPLC Nairobi). The longest power outage experienced so far effectively extended from October 2004 to March 2005. Such periods cannot be bridged with the battery backed-up UPS system. MeteoSwiss is commended for having financed replacement batteries in 2009. As a consequence, the overall data coverage for the period February 2001 – January 2006 is less than 50 %.

Recommendation 3 (, ongoing)**
KMD is strongly encouraged to ensure a sustainable power supply to the station since this is a prerequisite for successful operation of the station.

Recommendation 4 (, immediately)**
KMD is encouraged to explore the availability in Kenya of a radiator-type heating device with thermostat. A wall-mounted air-conditioning unit should be installed to prevent excessive heating during the day .

Recommendation 5 (, 2010)**
KMD should allocate a budget for the Mt. Kenya station / Nanyuki office:
- Clothing, other equipment for operators.
- Upgrade of the office computers that are needed to work with data.
- Establish internet access in the Nanyuki office.

Recommendation 6 (, 2010)**
KMD is strongly encouraged to improve the infrastructure at the station:
- Installation of some sanitary facilities.
- Installation of bunk beds so that operators can stay over-night.
- Seek ways to improve remote data access.

Station Management and Operation

In the past, the station was usually visited weekly by officers of the Kenya Meteorological Department (KMD) who reside in nearby Nanyuki (1.5 h from the station). More recently, theses visits were less regular due to difficulties accessing the station (vehicle and road condition). The current staff consist of one meteorologists and a technician who have adequate technical expertise to operate and maintain the equipment, albeit somewhat limited scientific experience to work with the data. A twinning relationship between KMD, Mt. Kenya staff and QA/SAC Switzerland is ongoing, but communication proved to be difficult after the current audit. Collaboration with external partners is important for the future of the station. The web presence of the Mt.Kenya GAW station is currently limited to its appearance in GAWSIS and an outdated page at KMD that was set up for the stations official inauguration ceremony in 1999. In order to improve the visibility of KMD's GAW activities within Kenya and abroad, a better web coverage should be considered.

Recommendation 7 (*, on-going)**
KMD needs to intensify technical and scientific exchange with existing and new external partners, and to participate more actively in such partnerships.

Recommendation 8 (, on-going)**
KMD should further the collaboration with the University of Nairobi and UNEP. In addition, it is recommended to highlight the Kenyan GAW activities on the KMD web pages and to maintain GAWSIS.

Recommendation 9 (, on-going)**
KMD is invited to continue taking advantage of the opportunity for training offered by GAWTEC. Other possibilities for continuing education of both station scientist and technicians should also be explored by KMD.

Air Inlet System

The design of the air inlet system is adequate, and a new air blower was installed as recommended in the previous audit report.

Surface Ozone Measurements

Instrumentation. At the time of the audit the stations was equipped with one ozone analyser (TEI 49C). The instrument was initially calibrated at WCC-Empa and delivered to the station after the audit in 2006. It replaces the TEI49 (see previous audit report). The current instrumentation is adequate for its intended purpose.

Standards. No ozone standard is available at the station. A TEI 49PS is available at KMD (see previous audit report). However, this instrument is no longer suitable to calibrate the current ozone analyser of MKN.

Recommendation 10 (, 2010)**
KMD is strongly encouraged to seek funding to purchase an ozone calibrator for use at the Mt. Kenya station.

Intercomparison (Performance Audit). The inter-comparisons extended over a period of two days. Only the last five runs were considered for the final data assessment to allow long enough stabilisation time of the WCC-Empa travelling standard. The result is summarised below (1) and the following equation characterises the instrument bias:

TEI49C #58106-318: 0 – 90 ppb, good agreement

Unbiased O_3 mixing ratio (ppb) XO3 (ppb) = ([OA] - 0.20 ppb) / 0.999 (1)

The result of the inter-comparison is presented in Figure 1. This result confirmed that the initial calibration of the instrument by WCC-Empa is still valid.

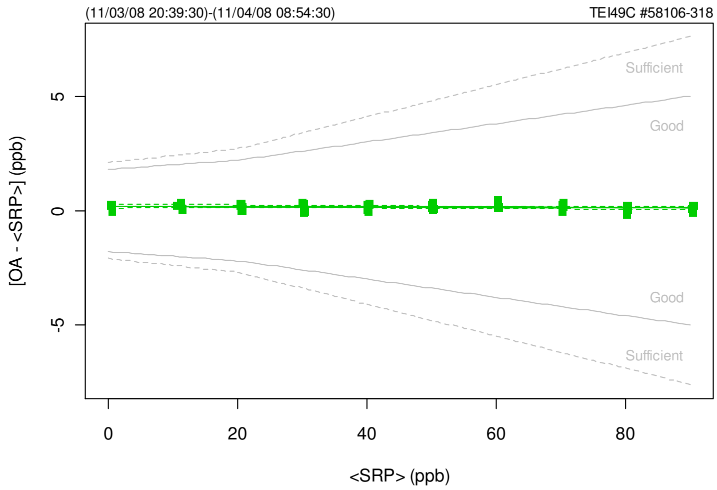

Figure 1. Bias of the Mt. Kenya ozone analyser (TEI 49C) with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [Klausen, et al., 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Carbon Monoxide Measurements

Instrumentation. A refurbished Horiba APMA 360 NDIR analyser was installed during the audit in addition to the TEI 48C-TL. The instruments are currently running in parallel, and both analysers were inter-compared during the audit. The instrumentation is adequate for the intended purpose. Parallel measurements of the two analysers are encouraged for a total period of 1 year.

Standards. The station is normally equipped with at least two carbon monoxide standards. One standard has a mixing ratio of approx. 1 ppm CO in air and is used for direct calibrations of the instrument. The other standard has a mixing ratio of approx. 50 ppm CO in air and is used for automatic span checks after dilution with zero air. With this equipment, adequate calibration of the carbon monoxide measurements is possible. However, all standards have been delivered to the station by WCC-Empa, and no local supplier is available. In addition, it should be considered to replace the dilution system (MFCs) because the current units can only be manually controlled and are not integrated in the data acquisition system.

Recommendation 11 (*, 2010-2011)**
For the long term operation of the MKN station, funds are needed for the purchase of calibration gases. KMD should not rely on delivery of calibration gases by WCC-Empa.

Recommendation 12 (*, 2010-2011)
The mass flow controller of the dilution system should be replaced (recommended model: Red-y).

Intercomparison (Performance Audit). The inter-comparisons involved repeated challenges of the instruments with randomised carbon monoxide concentrations generated using a high mixing ratio CO standard, zero air and a dilution system. Zero corrected data of the analysers were used for the evaluation of the results. The following equations (2 and 3) characterises the instrument bias. The deviation to WCC-Empa is further presented in Figure 2:

HORIBA APMA360 #890617035 (Zero -8, SPAN 1.0300):

Unbiased CO mixing ratio (ppb): XCO (ppb) = ([CO] + 7.1 ppb) / 1.0151 (2)

TEI 48C-TL (Zero 4.118, SPAN 1.173):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 7.7 ppb) / 1.0119 (3)

The results show that both analysers are functioning well concerning instrument noise and linearity; however, CO readings of these instruments are associated with relatively large uncertainties due to short term instrument noise, and in the case of the TEI 48C-TL, additional temperature dependent drift.

Data Acquisition and Management

The station is equipped with a centralised NI Labview-based data acquisition system developed by QA/SAC-Switzerland that currently includes the surface ozone, CO, meteorological, black carbon and GPS measurements of MKN. No automatic data transmission is available due to a lack of internet or other means for near-real time data transfer.

Recommendation 13 (, ongoing)**
Other measurement parameters should be incorporated into the centralised data acquisition system.

Recommendation 14 (, ongoing)**
Technical means for automatic data transfer need to be explored and installed.

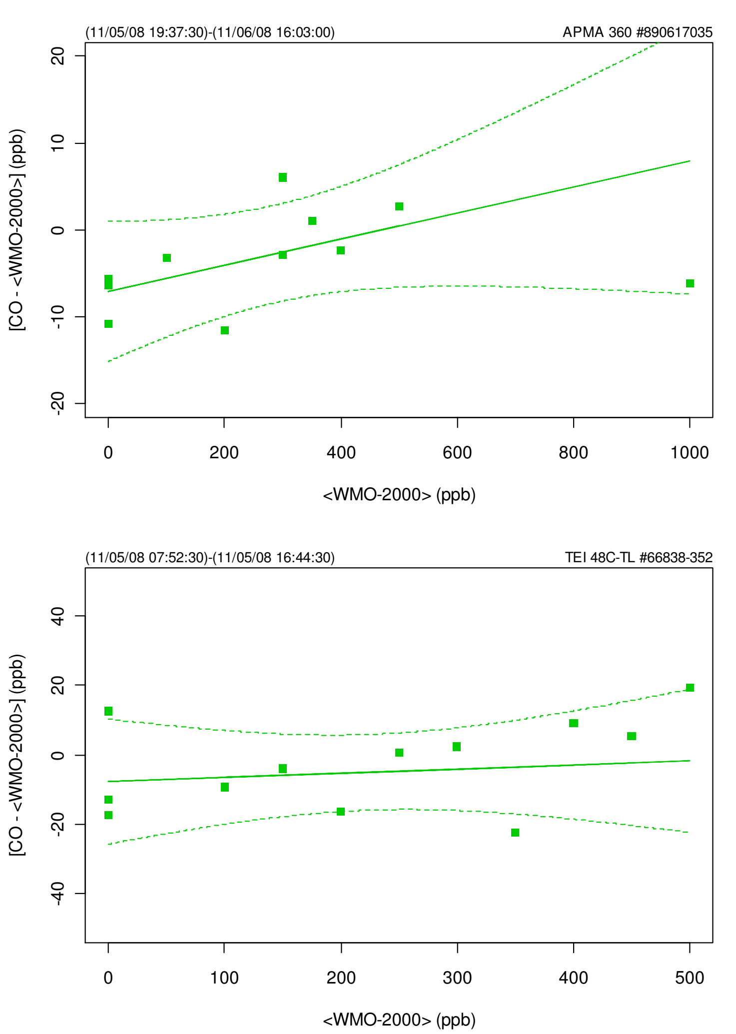

Figure 2. Bias of the Mt. Kenya carbon monoxide analyser (HORIBA APMA360) with respect to the WMO-2000 reference scale as a function of concentration. Note the different scales. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Operation and Maintenance

The station is currently irregularly visited by station operators. Visits have been on a weekly basis in the past, but became less frequent mainly because access to the site was not possible due to lack of transport. It was noticed during the audit that information available in log books and check lists was not always comprehensive and complete. In addition, communications with external partners needs to be improved.

Recommendation 15 (*, ongoing)**
Documentation is a key aspect for a successful operation of a GAW station and needs more attention by the station staff. Log files and check lists need to be carefully filled in and should be maintained and distributed electronically.

Recommendation 16 (*, ongoing)**
Communication with external partners is important for the successful operation of the station . KMD is encouraged to play a more active role in the existing twining partnerships.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently data for surface ozone (June 02 – May 06), carbon monoxide (June 02 – May 06), and the NOAA flask sampling programme (December 03 –December 08) are available at the data centre.

Recommendation 17 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year.

Conclusions

The Global GAW station Mt. Kenya comprises a still growing suite of ongoing measurements. Despite large data gaps the existing time series are a valuable contribution to the GAW programme, especially because they cover a geographical region where only sparse in-situ information about atmospheric composition is available. The continuation of existing measurements on a stable and long-term basis and the sustainable addition of new parameters are therefore strongly encouraged. All assessed measurements were of sufficiently high quality.

MeteoSwiss is gratefully acknowledged for having provided funding for replacement of the automatic weather station and a set of replacement accumulators for the UPS system.

Summary Ranking of Mt. Kenya Station

System Audit Aspect	Adequacy#	Comment
Access	(2)	Subject to road and weather conditions / vehicle availability
Facilities		
Laboratory and office space	(3)	Basic facilities only; no sanitary installations
Air Conditioning	(0)	Not available
Power supply	(1)	Frequent failures
General Management and Operation		
Organisation	(3)	Communication with external partners difficult at times
Competence of staff	(3)	Good technical expertise, scientific training needed
Air Inlet System	(4)	
Instrumentation		
Ozone	(5)	TEI 49C
Carbon monoxide	(4)	Horiba less subject to drift
Aerosol light absorption	(2)	Available, partial operation
Flask sampling	(5)	NOAA/ESRL programme
VOC canister sampling	(0)	Available, not in operation
Meteo	(5)	Automated weather station
Standards		
Ozone	(0)	Not available
Carbon monoxide	(4)	Only available through external partners
Aerosol light absorption	(0)	Not available
Data Management		
Data acquisition	(4)	Automatic data transfer needed
Data processing	(3)	Dependent on twining partners
Data submission	(4)	Data partly submitted

#0: inadequate thru 5: adequate; *refer to GAWSIS (www.empa.ch/gaw/gawsis) for a complete overview of measured parameters.

____

Dübendorf, January 2010

Dr. J. Klausen	Dr. S. Henne	Dr. C. Zellweger	Dr. B. Buchmann
QA/SAC Switzerland	QA/SAC Switzerland	WCC-Empa	Head of laboratory

APPENDIX

Global GAW Station Mt. Kenya

Site description

Information about the Mt. Kenya GAW station can be found in previous audit reports [*Klausen, et al.*, 2006; *Zellweger, et al.*, 2002; *Zellweger, et al.*, 2005], and the station is also registered in GAWSIS (http://gaw.empa.ch/gawsis). The climatology of the station has been described by Henne et al. [2008a], and a characterization of surface ozone and carbon monoxide was published by Henne et al. [2008b].

Measurement Programme

The Mt. Kenya observatory started its operation in 1995. A short overview of the measurement programme and its status as of October 2008 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the MKN Station

Parameter	Current Instrument	Data Coverage (%)		
		<12 m	<3 y	Overall
Aerosol				
Light absorption coefficient#	Aethalometer	0	6	6
Ozone				
Surface ozone	UV absorption (TEI 49C)	60	48	47
Greenhouse Gas				
CO_2	AIRCOA			
CO_2, CH_4, SF_6, N_2O	NOAA/ESRL flask sampling			
Reactive Gas				
CO	NDIR (HORIBA APMA360)	51	45	48
CO, H_2	NOAA/ESRL flask sampling			
Solar radiation				
Global irradiance	Pyranometer (Kipp & Zonen)	39	44	49
Diffuse irradiance	Pyranometer (Kipp & Zonen)	39	44	49
Isotopes				
CO_2 (C-13), CO_2 (O-18)	NOAA/ESRL flask sampling			
Ancillary Measurements				
Meteo (PTU, wind speed + direction)		63	52	53

#: discontinued; Missing data availability: no data coverage information was available at the time of the audit; Measurements available since 2002-05-17.

Ozone and Carbon Monoxide Distribution at Mt. Kenya

See previous audit report [*Klausen, et al.*, 2006].

Organisation and Contact Persons

The Global Atmosphere Watch Activities of Kenya Meteorological Department are organized under the Observations and Networks Section and are directed by the GAW Country Contact Mr. Peter Bundi. Currently, Mr. Kennedy K. Thiong'o is the responsible station manager, and Mr. John Aseyo is the station engineer.

Surface Ozone Measurements

Surface ozone measurements started in May 2002 at the Mt. Kenya site, and time series are available since then. It was noticed that the ozone instrument of MKN was not working properly during the audit in 2006. Consequently, the instrument was replaced by a joint project between WMO and Empa in July 2006. The original TEI49 could not be assessed due to instrument failure. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning
Unchanged since the last audit. The station is not air conditioned, and the lab temperature shows a significant diurnal variation.

Air Inlet System
The air inlet system has been described in a previous audit report [*Zellweger, et al.*, 2005]. It was recognized during the audit in 2006 that the air blower was not working, and it was replaced afterwards. Briefly, the air inlet is located 4.5 m above ground (1.7 m above the station roof) and consists of a glass manifold from which air is drawn by the instruments. The flow rate in the glass manifold is approximately 800 litres per minute since the replacement of the blower. The tubing is made of Teflon and the instrument is protected by a Teflon filter. All materials used are adequate.

Instrumentation
The original TEI49 analyser was decommissioned after an instrument failure in May 2006, and a refurbished TEI 49C instrument was installed at the site in July 2006. Instrumental details for the new ozone analyser (OA) are summarised in

Table **2**.

Standards
Unchanged since the last audit. The station does not own an ozone calibrator, and the inter-comparison of the analyser by WCC-Empa constitutes the only independent assessment at present. This is barely adequate for a Global GAW station and should be improved (cf. Recommendation 10).

Operation and Maintenance
The instrument is checked for general operation whenever the station is visited (used to be once per week). However, visits became less frequent due to difficult access to the site. The inlet filter is replaced every 2 months. Basic instrument maintenance (cleaning, replacement of consumables) is made by the station engineer.

Data Acquisition and Data Transfer
The ozone data was manually downloaded from the internal data logger after installation of the analyzer in 2006. During the current audit a centralised LabView based data acquisition system that was implemented by QA/SAC Switzerland.

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

Data Submission
Ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG). The submitted data sets currently span the period from June 2002 to May 2006.

Documentation
All information is entered in electronic log books and checklists. The information was only partly comprehensive and up-to-date. The instrument manuals are available at the site.

Inter-Comparison of the Ozone Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included inter-comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the inter-comparison of the analyser.

Setup and Connections

Table **2** details the experimental setup during the inter-comparison of the travelling standard with the station analysers and the calibrator. The data used for the evaluation was recorded by the WCC-Empa data acquisition system as indicated.

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results are valid for the calibration factors as given in

Table **2** below. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

The TEI 49C (#58106-318) instrument was installed at MKN in July 2006. The initial calibration was done against SRP#15 at the laboratory of WCC-Empa in May 2006 and confirmed to be valid during the audit in 2007. The result of the current assessment (direct comparison between TS and the analyser) is shown in Table 3.

Figure 3 shows the regression residuals of the TEI 49C ozone analyser for the inter-comparisons described above with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

Table 2. Experimental details of the ozone inter-comparison.

Travelling standard (TS)	Model, S/N	TEI 49C-PS #0421507340 (WCC-Empa)
	Settings	BKG = -0.7; COEFF = 1.019
Analyzer (OA)	Model, S/N	TEI 49C #58106-318
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = -0.3; COEFF = 1.013
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm (WCC-Empa)
Connection between instruments		Ca. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS and OA	One minute aggregates from digital output of WCC-Empa data acquisition (custom designed LabView programme)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	661 (WCC reference)
	TS	662, adjusted to 661
	OA	663, adjusted to 661

Levels (ppb)	0, 10, 20, 30, 40, 50, 60, 70, 80, 90
Duration per level (min)	15
Sequence of levels	Repeated runs of randomised fixed sequence
Runs	5 runs (2008-11-03 thru 04)

Table 3. Ten-minute aggregates (initial inter-comparison, direct TS-analyser) computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the MKN ozone analyser (OA) TEI 49C #58106-318 with the WCC-Empa travelling standard (TS).

DateTime (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2008-11-03 20:39	1	0	0.41	0.71	0	0.17	0.14	0.30	NA
2008-11-03 20:54	1	30	30.18	30.53	0	0.22	0.25	0.35	1.17
2008-11-03 21:09	1	60	60.12	60.61	0	0.17	0.13	0.49	0.81
2008-11-03 21:24	1	80	80.23	80.40	0	0.24	0.30	0.17	0.21
2008-11-03 21:39	1	10	11.14	11.54	0	0.67	0.72	0.40	3.62
2008-11-03 21:54	1	50	50.03	50.31	0	0.22	0.14	0.28	0.56
2008-11-03 22:09	1	40	40.19	40.19	0	0.31	0.32	0.00	0.01
2008-11-03 22:24	1	90	90.28	90.46	0	0.15	0.16	0.19	0.21
2008-11-03 22:39	1	20	20.38	20.73	0	0.31	0.45	0.34	1.68
2008-11-03 22:54	1	70	70.16	70.30	0	0.23	0.18	0.14	0.20
2008-11-03 23:09	2	0	0.31	0.59	0	0.19	0.06	0.29	NA
2008-11-03 23:24	2	50	50.12	50.53	0	0.20	0.16	0.42	0.83
2008-11-03 23:39	2	10	11.16	11.54	0	0.61	0.81	0.38	3.37
2008-11-03 23:54	2	90	90.31	90.58	0	0.14	0.13	0.27	0.30
2008-11-04 00:09	2	80	80.23	80.50	0	0.18	0.19	0.27	0.34
2008-11-04 00:24	2	20	20.40	20.67	0	0.29	0.32	0.27	1.33
2008-11-04 00:39	2	30	29.98	30.38	0	0.23	0.08	0.41	1.36
2008-11-04 00:54	2	60	60.12	60.54	0	0.18	0.27	0.42	0.70
2008-11-04 01:09	2	40	40.18	40.39	0	0.19	0.16	0.22	0.54
2008-11-04 01:24	2	70	70.16	70.18	0	0.15	0.21	0.01	0.02
2008-11-04 01:39	3	0	0.34	0.60	0	0.14	0.10	0.26	NA
2008-11-04 01:54	3	60	60.24	60.43	0	0.19	0.26	0.20	0.33
2008-11-04 02:09	3	20	20.59	20.80	0	0.40	0.50	0.22	1.05
2008-11-04 02:24	3	10	10.45	10.68	0	0.29	0.28	0.23	2.25
2008-11-04 02:39	3	90	90.21	90.36	0	0.23	0.26	0.15	0.16
2008-11-04 02:54	3	50	50.16	50.22	0	0.24	0.23	0.06	0.13
2008-11-04 03:09	3	70	70.22	70.45	0	0.16	0.19	0.23	0.32
2008-11-04 03:24	3	40	40.05	40.13	0	0.21	0.14	0.08	0.20
2008-11-04 03:39	3	30	30.20	30.26	0	0.28	0.32	0.06	0.21
2008-11-04 03:54	3	80	80.18	80.27	0	0.18	0.18	0.09	0.12
2008-11-04 04:09	4	0	0.27	0.50	0	0.20	0.13	0.23	NA
2008-11-04 04:24	4	30	30.14	30.10	0	0.26	0.15	-0.04	-0.14
2008-11-04 04:39	4	60	60.15	60.39	0	0.23	0.23	0.24	0.40
2008-11-04 04:54	4	80	80.20	80.09	0	0.14	0.16	-0.12	-0.15
2008-11-04 05:09	4	10	11.30	11.41	0	0.62	0.83	0.11	0.99
2008-11-04 05:24	4	50	50.02	50.21	0	0.33	0.24	0.19	0.37
2008-11-04 05:39	4	40	40.01	40.33	0	0.48	0.40	0.31	0.78
2008-11-04 05:54	4	90	90.44	90.73	0	0.17	0.33	0.29	0.32
2008-11-04 06:09	4	20	20.65	20.82	0	0.53	0.54	0.17	0.85
2008-11-04 06:24	4	70	70.21	70.55	0	0.17	0.11	0.34	0.48
2008-11-04 06:39	5	0	0.46	0.46	0	0.21	0.11	0.00	NA
2008-11-04 06:54	5	50	50.25	50.37	0	0.20	0.22	0.13	0.25
2008-11-04 07:09	5	10	11.35	11.41	0	0.83	0.76	0.06	0.54
2008-11-04 07:24	5	90	90.34	90.36	0	0.17	0.24	0.02	0.02
2008-11-04 07:39	5	80	80.31	80.41	0	0.25	0.24	0.09	0.12
2008-11-04 07:54	5	20	20.55	20.59	0	0.46	0.31	0.03	0.17
2008-11-04 08:09	5	30	30.29	30.30	0	0.20	0.28	0.01	0.05
2008-11-04 08:24	5	60	60.23	60.40	0	0.17	0.19	0.16	0.27
2008-11-04 08:39	5	40	40.32	40.64	0	0.26	0.33	0.33	0.81
2008-11-04 08:54	5	70	70.32	70.75	0	0.16	0.21	0.42	0.60

#0: valid data; 1: invalid data.

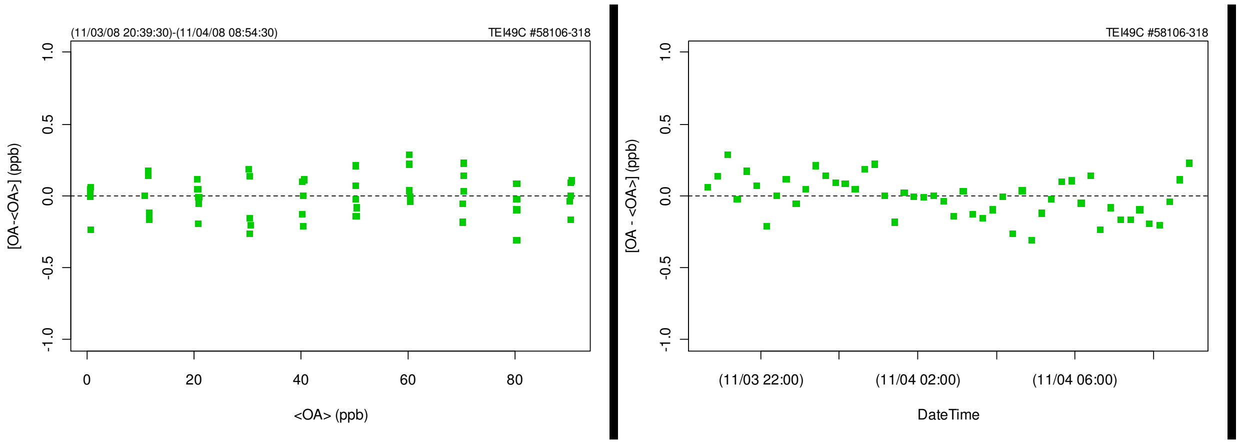

Figure 3. Regression residuals of the MKN ozone analyser (TEI 49C) as a function of concentration (left) and time (right).

Based on these inter-comparison results, unbiased ozone volume mixing ratios X_{O3} and an estimate for the remaining combined standard uncertainty u_{O3} can be computed from the one-minute data [OA] using equation (1) [*Klausen, et al.*, 2003].

TEI 49C #58106-318:

$$X_{O3} \text{ (ppb)} = ([OA] - 0.20 \text{ ppb}) / 0.999$$

$$u_{O3} \text{ (ppb)} = \text{sqrt}(0.29 \text{ ppb}^2 + 2.71\text{e-}05 * X_{O3}^2) \quad (1)$$

Conclusions

The MKN ozone analyser (TEI 49C) was found to agree very well with the WCC-Empa ozone standard. The initial calibration of the instrument made in 2006 by WCC-Empa proved to be still valid. The previous instrument (TEI 49) could not be assessed during the present audit due to instrument failure; however, sufficient inter-comparisons were available for the review and submission of the data to WDCGG (QA/SAC-Switzerland in collaboration with KMD). Nevertheless, more frequent inter-comparisons with an ozone calibrator would be very desirable for the future operation of the MKN ozone programme (cf. Recommendation 10).

Carbon Monoxide Measurements

After the audit in 2006 the TEI 48C instrument was complemented by a Horiba APMA-360 analyzer. The two instruments are running in parallel and were both inter-compared during the present audit. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

See ozone. The diurnal temperature variations influence mainly the zero-drift of the TEI 48C CO instrument. A more controlled laboratory temperature is highly desirable (cf. Recommendation 4).

Air Inlet System

The air inlet system is identical to the one for surface ozone as described above. The instruments are directly connected to the glass manifold. The tubing is made of Teflon and the instruments are protected by an inlet filter. All materials used and the residence time are adequate for CO measurements.

Instrumentation

In addition to the TEI 48C described in the previous audit reports, a Horiba APMA-360 analyser was installed during the present audit by QA/SAC-Switzerland. The instrument was initially calibrated by WCC-Empa before shipment to Kenya. A Permapure Nafion dryer in split flow mode is used for sample air drying. Instrumental details are listed in

Table **5**. The TEI 48C instrument was still available at the site and both analysers are currently running in parallel.

Standards and Calibration
The station has been provided with calibration gases by WCC-Empa.

Table **4** gives details of the cylinders currently available at the station. Two types of calibration standards are available: Low levels (approx. 1 ppm) for direct calibrations of the instrument, and higher levels (15 to 50 ppm) for automatic span checks using the dilution system.

Table 4. Carbon monoxide standards available at the MKN station

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Sauerstoffwerk Lenzburg, SL3845H, Direct use	1060±21 ppb, CO 99.997% in synthetic air 99.9995%	2001	WCC-Empa	Feb 2002	continued
Sauerstoffwerk Lenzburg, SL6395E, Dilution unit	15000±300 ppb, CO 99.997% in synthetic air 99.9995%	2001	WCC-Empa	Feb 2002	Oct 2004
Sauerstoffwerk Lenzburg, SL16887e, Dilution unit	51100±1000 ppb, CO 99.997% in synthetic air 99.9995%	Jan 2005	WCC-Empa	Feb 2005	Jun 2006
Sauerstoffwerk Lenzburg, SL68810, Direct use	1007±8 ppb, CO 99.997% in synthetic air 99.9995%	Dec 2005	WCC-Empa		
Sauerstoffwerk Lenzburg, SL68820, Dilution unit	20120±200 ppb (α=0.05), 99.997% in synthetic air 99.9995%	Dec 2005	WCC-Empa	Jun 2006	Jul 2008
Scott Marin, 080304_CA06112	51021±510 ppb, CO in natural air	Mar 2008	WCC-Empa	Jul 2008	continued
Scott Marin, 080304_CA04549	1288±13 ppb, CO in natural air	Mar 2008	WCC-Empa		
Scott Marin, 080808_CA08202	59772±598 ppb, CO in natural air	Aug 2008	WCC-Empa		
Scott Marin, 080808_CA08210	859.5±8.6 ppb, CO in natural air	Aug 2008	WCC-Empa		

** WMO-2000 carbon monoxide scale*

Operation and Maintenance

Both CO systems are running fully automated. Zero and span checks using the dilution system are made every two hours. The system is checked for general operation during station visits. A weekly check list should be filled in. The purpose of the check list is to record parameters that are not available through the data acquisition (calibration factors, further instrument parameters, pressures of the calibration gases etc.). The inlet filter is changed every two weeks. However, these tasks are not always performed due to irregular station visits. The IR source has been changed in the past and the correlation filter wheel of the TEI 48C has been cleaned once; however, the instrument has never been serviced directly by a TEI representative in the past.

Data Acquisition and Data Transfer

Until the current audit the serial interface of the TEI 48C was connected to the Milos system (since 2006, see [*Klausen, et al.*, 2006]). The Milos system has a capacity for 12 days data storage and is manually downloaded to the station computer during station visits.

During the present audit, the MILOS data logger was retired and data from the TEI48C instrument are now only recorded by its internal data logger. The APMA360 was connected to a custom-made NI Labview-based data acquisition system, implemented by QA/SAC Switzerland. One minute averages are automatically transferred to a data base along with ancillary instrument parameter.

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. Stable zero/span-readings are used for zero/span-correction using `loess` regression [*R Development Core Team*, 2009]. Span values from the automatic span checks are used for quality control purposes and have also been used for the correction of a span drift. Data validation and flagging is still dependent on collaboration with QA/SAC-Switzerland. Responsibility for data validation should however be transferred to the station staff.

Data Submission

Carbon monoxide data have been submitted to the World Data Centre for CO at JMA (WDCGG). The submitted data sets currently span the period from June 2002 to May 2006.

Documentation

All information is entered in electronic log books and checklists. The information was only partly comprehensive and up-to-date. The instrument manuals are available at the site.

Inter-Comparison of Carbon Monoxide Analysers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 10 below.

Setup and Connections

Table **5** shows details of the experimental setup during the inter-comparison of transfer standard and station analyser. The data used for the evaluation was recorded by the MKN data acquisition systems as indicated, and corrected for zero drift according to the usual data treatment procedure.

Table 5. Experimental details of the carbon monoxide inter-comparison.

<table>
<tr><td colspan="2">Travelling standard (TS)</td><td>One cylinder (SMI, 080808-CA08202 59.77±0.60 ppm CO in natural air) and a zero-air generator (silica gel - inlet filter 5 μm - metal bellow pump - Sofnocat - outlet filter 5 μm) custom-built by WCC-Empa, in combination with a dilution system (Breitfuss, MGM)</td></tr>
<tr><td colspan="2">Levels (ppb)</td><td><table>
<tr><th>Level</th><th>Reference</th><th>St.Uncertainty</th></tr>
<tr><td>1</td><td>0.0</td><td>1.0</td></tr>
<tr><td>2</td><td>50.1</td><td>1.0</td></tr>
<tr><td>3</td><td>100.1</td><td>1.0</td></tr>
<tr><td>4</td><td>150.1</td><td>1.5</td></tr>
<tr><td>5</td><td>200.2</td><td>2.0</td></tr>
<tr><td>6</td><td>250.3</td><td>2.5</td></tr>
<tr><td>7</td><td>300.3</td><td>3.0</td></tr>
<tr><td>8</td><td>350.3</td><td>3.5</td></tr>
<tr><td>9</td><td>400.4</td><td>4.0</td></tr>
<tr><td>10</td><td>500.5</td><td>5.0</td></tr>
<tr><td>11</td><td>1000.8</td><td>10.0</td></tr>
</table></td></tr>
<tr><td rowspan="5">Field instrument (new)</td><td>Model, S/N</td><td>Horiba APMA-360 #890617035</td></tr>
<tr><td>Principle</td><td>NDIR, Cross Flow Modulation</td></tr>
<tr><td>Modification</td><td>Nafion drier PERMAPURE PD-50T-12MSS
split flow mode using critical orifice and external pump</td></tr>
<tr><td>Range</td><td>10 ppm</td></tr>
<tr><td>Settings</td><td>Zero -8, Span 1.0300</td></tr>
<tr><td rowspan="5">Field instrument (since 2001)</td><td>Model, S/N</td><td>TEI 48C Trace Level #66838-352</td></tr>
<tr><td>Principle</td><td>NDIR, Gas Filter Correlation Technique</td></tr>
<tr><td>Modification</td><td>Nafion drier PERMAPURE PD-50-24''
reflux mode using critical orifice and pump of instrument</td></tr>
<tr><td>Range</td><td>1 ppm</td></tr>
<tr><td>Settings</td><td>BKG = 4.118; CO COEFF = 1.173; Initial S/R = 1.14302</td></tr>
<tr><td colspan="2">Connection of TS to field analysers</td><td>Sample inlet with inlet filter</td></tr>
<tr><td colspan="2">Data Acquisition</td><td>1-min aggregates (TEI48C), 3-min aggregates (Horiba APMA-360)</td></tr>
<tr><td colspan="2">Duration per level (min)</td><td>Dependent on level, inclusive of interspersed automatic zero and span checks</td></tr>
<tr><td colspan="2">Sequence of levels</td><td>Repeated runs of randomised fixed sequence</td></tr>
<tr><td colspan="2">Runs</td><td>1 run; TEI 48C: 2008-11-05, Horiba 2008-11-05/06</td></tr>
</table>

Results – Horiba APMA-360

Different carbon monoxide levels were generated with the WCC-Empa dilution system and applied to the analyser. The experiment yielded between 6 and 136 useable 3-min averages per level and run, depending on the duration of the level. These 3-min averages were corrected for zero-drift (using loess regression) and further aggregated by level before use in the assessment (cf. Table 6). No span correction was applied to the data for the evaluation of the result.

Table 6. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the MKN HORIBA APMA360 CO analyser (AL) with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	AL (ppb)	uAL(ppb)	No. 3' av.	AL-TS(ppb)	AL-TS(%)
(11/05/08 19:37:30)	200.2	2.0	188.6	9.8	14	-11.6	-5.8
(11/06/08 00:28:41)	400.4	4.0	398.0	10.1	136	-2.4	-0.6
(11/06/08 08:27:11)	300.2	3.0	297.3	8.7	17	-2.9	-1.0
(11/06/08 09:24:00)	0.0	1.0	-6.4	8.6	7	-6.4	NA
(11/06/08 10:32:40)	350.3	3.5	351.4	5.3	9	1.1	0.3
(11/06/08 12:25:30)	1000.8	10.0	994.7	15.2	14	-6.1	-0.6
(11/06/08 13:24:30)	0.0	1.0	-5.7	10.0	6	-5.7	NA
(11/06/08 13:55:10)	300.3	3.0	306.4	11.8	18	6.0	2.0
(11/06/08 14:33:00)	500.5	5.0	503.2	14.5	12	2.7	0.5
(11/06/08 15:31:09)	100.1	1.0	96.9	7.0	13	-3.2	-3.2
(11/06/08 16:03:00)	0.0	1.0	-10.9	9.0	12	-10.9	NA

Figure 4 shows the regression residuals of the analyser over the course of the inter-comparison runs. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of a concentration dependence (right panel) in the residuals indicates linearity of the instrument.

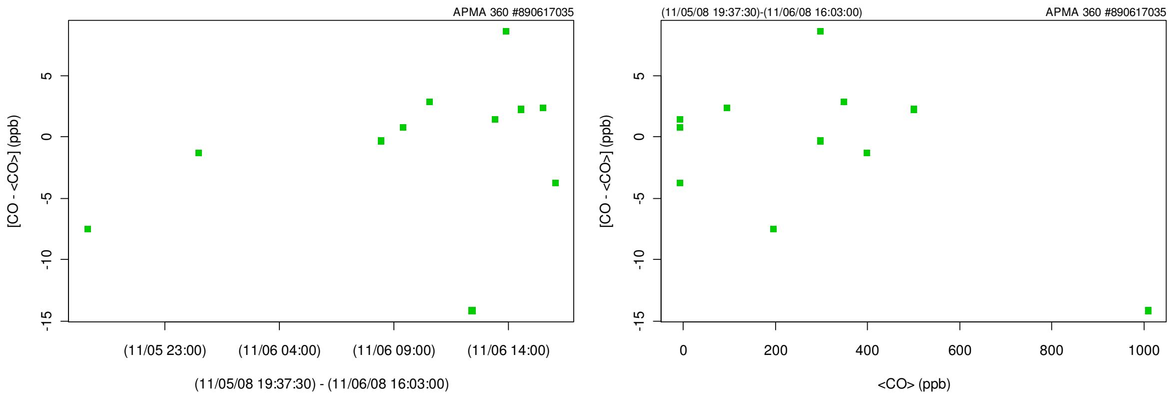

Figure 4. Regression residuals of the Horiba APMA-360 carbon monoxide analyser based on the initial inter-comparison with the dilution unit. Points represent averages of valid 3-min values. Left panel: time dependence; Right panel: concentration dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} of 5 min averages can be computed from the zero corrected five-minute data CO that was taken initially of the analyser using equation (2).

$$\mathbf{X_{CO}\ (ppb) = ([CO] + 7.1\ ppb) / 1.0151}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(41.3\ ppb^2 + 1.36e\text{-}04 * X_{CO}^2)} \qquad \textbf{(2)}$$

Results – TEI 48C-TL

Different carbon monoxide levels were generated with the WCC-Empa dilution system and applied to the analyser. The experiment yielded between 8 and 44 useable 1-min averages per level and run, depending on the duration of the level. These 1-min averages were corrected for zero-drift (using loess regression) and further aggregated by level before use in the assessment (cf. Table 6). No span correction was applied to the data for the evaluation of the result.

Table 7. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the MKN TEI 48C-TL CO analyser (AL) with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	AL (ppb)	uAL(ppb)	No. 1' av.	AL-TS(ppb)	AL-TS(%)
(11/05/08 07:52:30)	0.0	1.0	-17.4	12.9	38	-17.4	NA
(11/05/08 08:35:30)	200.1	2.0	183.7	9.7	44	-16.4	-8.2
(11/05/08 09:37:30)	400.3	4.0	409.6	10.1	8	9.3	2.3
(11/05/08 10:04:38)	100.1	1.0	90.8	6.4	41	-9.2	-9.2
(11/05/08 10:44:00)	150.1	1.5	146.2	13.1	33	-3.9	-2.6
(11/05/08 11:45:00)	250.2	2.5	251.0	10.9	23	0.8	0.3
(11/05/08 12:20:30)	450.4	4.5	455.9	8.7	44	5.5	1.2
(11/05/08 12:52:00)	300.3	3.0	302.7	5.0	17	2.4	0.8
(11/05/08 13:53:00)	0.0	1.0	-12.9	12.0	39	-12.9	NA
(11/05/08 14:35:30)	350.3	3.5	327.9	7.6	44	-22.4	-6.4
(11/05/08 15:38:00)	500.5	5.0	519.7	14.0	9	19.2	3.8
(11/05/08 16:05:00)	1000.9	10.0	1057.2	13.8	43	56.3	5.6
(11/05/08 16:44:30)	0.0	1.0	12.6	10.1	32	12.6	NA
(11/05/08 07:52:30)	0.0	1.0	-17.4	12.9	38	-17.4	NA

Figure 4 shows the regression residuals of the analyser over the course of the inter-comparison runs. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of a concentration dependence (right panel) in the residuals indicates linearity of the instrument.

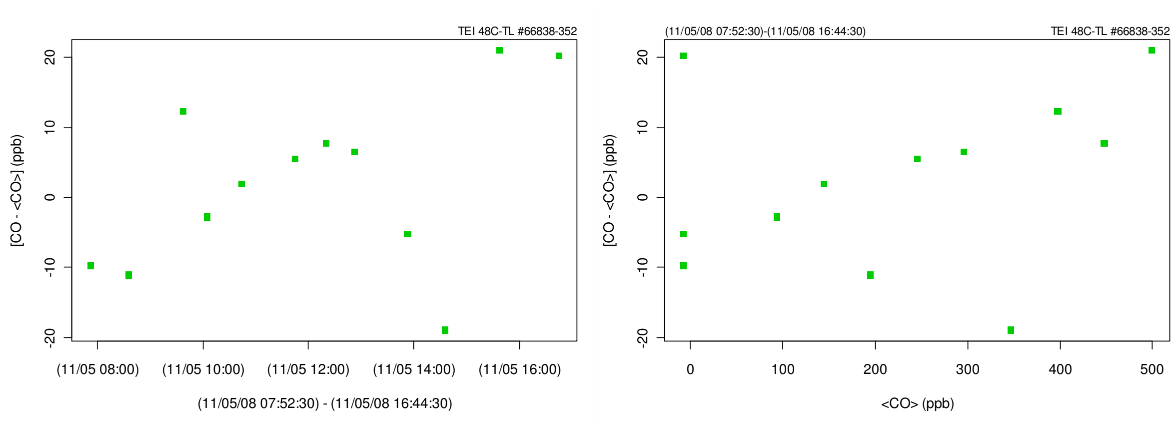

Figure 5. Regression residuals of the TEI 48C-TL carbon monoxide analyser based on the initial inter-comparison with the dilution unit. Points represent averages of valid 1-min values. Left panel: time dependence; Right panel: concentration dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mixing ratios X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} of 5 min averages can be computed from the zero corrected five-minute data CO that was taken initially of the analyser using equation (3).

$$\mathbf{X_{CO}\ (ppb) = ([CO] + 7.7\ ppb) / 1.0119}$$
$$\mathbf{u_{CO}\ (ppb) = sqrt(151.1\ ppb^2 + 3.00e\text{-}05 * X_{CO}^2)} \quad \mathbf{(3)}$$

The estimate of the remaining standard uncertainty u_{CO} based on instrument noise, a linear concentration dependent contribution of 0.5% and an uncertainty of the zero correction of 3 ppb.

Changes made to the instrument after the audit
None.

Conclusions
Both CO analysers of MKN are working well within the limitations of the NDIR technique. The installation of the Horiba APMA-360 significantly improved the situation concerning zero drift and instrument uncertainty. WCC-Empa recommends using the data of the Horiba system for submission to WDCGG. Nevertheless, CO data of Horiba instrument is associated with a relatively high uncertainty, and valid data should be aggregated to hourly values before further scientific use.

WCC-Empa Travelling Standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the Standard Reference Photometer before and after use during the field audit. Details of these inter-comparisons at the Empa calibration laboratory are summarised in Table 8, the inter-comparison data is given in Table 9.

Table 8. Experimental details of the inter-comparison of travelling standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Travelling standard (TS)	Model, S/N	TEI 49C-PS #0421507340 (WCC-Empa)
	Settings	BKG = -0.7; COEFF = 1.019
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (2008-10-02) 3 runs after return of TS (2008-12-12)

Table 9. Five-minute aggregates computed from 10 valid 30-second values for the inter-comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard (TS).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2008-10-02	1	0	-0.39	0.37	-0.04	0.16
2008-10-02	1	90	92.63	0.33	92.60	0.20
2008-10-02	1	60	62.47	0.23	62.42	0.18
2008-10-02	1	140	142.87	0.25	142.99	0.18
2008-10-02	1	190	194.20	0.40	194.31	0.23
2008-10-02	1	30	32.87	0.30	32.62	0.18
2008-10-02	1	0	-0.04	0.33	0.00	0.24
2008-10-02	2	0	0.10	0.46	0.04	0.13
2008-10-02	2	140	142.74	0.14	142.89	0.13
2008-10-02	2	30	32.68	0.31	32.83	0.16
2008-10-02	2	90	92.77	0.23	92.62	0.22
2008-10-02	2	190	193.73	0.26	193.82	0.20
2008-10-02	2	60	62.57	0.21	62.66	0.19
2008-10-02	2	0	0.03	0.33	-0.23	0.27
2008-10-02	3	0	0.26	0.27	0.10	0.16
2008-10-02	3	60	62.54	0.35	62.60	0.19
2008-10-02	3	140	142.94	0.16	142.84	0.14
2008-10-02	3	90	92.76	0.30	92.79	0.11
2008-10-02	3	190	194.16	0.36	194.25	0.40
2008-10-02	3	30	32.74	0.17	32.86	0.16
2008-10-02	3	0	0.08	0.26	-0.20	0.09
2008-12-12	4	0	0.10	0.39	0.01	0.08
2008-12-12	4	30	32.55	0.42	32.40	0.13
2008-12-12	4	140	139.92	0.18	139.73	0.09
2008-12-12	4	190	188.67	0.27	188.23	0.19
2008-12-12	4	60	61.63	0.31	61.54	0.16
2008-12-12	4	90	90.78	0.26	90.86	0.13
2008-12-12	4	0	0.01	0.28	-0.05	0.08
2008-12-12	5	0	-0.05	0.25	-0.08	0.15
2008-12-12	5	60	61.67	0.22	61.65	0.22
2008-12-12	5	140	139.94	0.29	139.72	0.15
2008-12-12	5	30	32.53	0.38	32.55	0.23
2008-12-12	5	190	188.65	0.23	188.30	0.23
2008-12-12	5	90	91.27	0.21	91.12	0.14
2008-12-12	5	0	0.09	0.28	0.02	0.20
2008-12-12	6	0	0.02	0.20	-0.07	0.14
2008-12-12	6	90	91.23	0.20	91.05	0.17
2008-12-12	6	60	61.90	0.11	61.65	0.20
2008-12-12	6	140	139.97	0.29	139.73	0.16
2008-12-12	6	190	188.73	0.17	188.35	0.19
2008-12-12	6	30	32.44	0.30	32.36	0.24
2008-12-12	6	0	-0.07	0.22	-0.08	0.24

[#]The level is only indicative.

The travelling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 6). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (equation 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [*Klausen, et al.*, 2003]).

X_{TS} (ppb) = ([TS] + 0.04 ppb) / 0.9996

u_{TS} (ppb) = sqrt((0.43 ppb)^2 + (0.0034 * X)^2) (3)

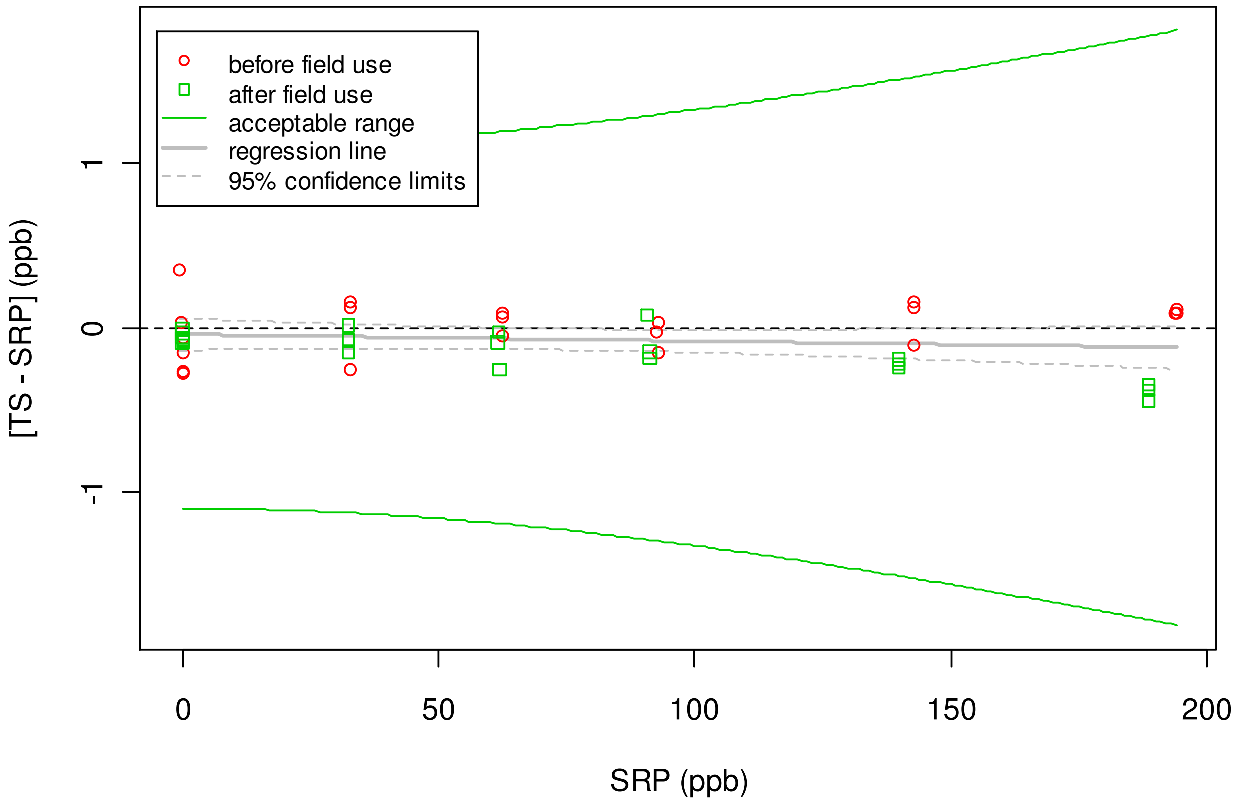

Figure 6. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly inter-compared with the CCL by way of travelling standards. The scale was transferred to the travelling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. The inter-comparison was made using a CO cylinder that was shipped to MKN in 2008, and the dilution system was calibrated against the WCC-Empa flow reference before and after the audit. Details are given in Table 10.

Table 10. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the travelling standard (TS) used during the field inter-comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale was based on two specific cylinders, CA02859 (194.7±1.9 ppb) CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Travelling standard (TS)		zero air (1) and a high concentration carbon monoxide cylinder (2), in combination with a dilution unit (3)
(1) Zero air supply		Ambient air – Silicagel PS drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		SMI, 080808-CA08202 59.77±0.60 ppm CO in natural air (α=0.05). The cylinder was calibrated against the WCC-Empa reference scale and shipped to MKN (2008-09-25) and remained at the site.
(3) Dilution unit		2 Redy MFCs: Redy1: GSC B5SA BB23 (5 l/min) #121705 Redy2: GSC A3SA BB21 (100 ml/min) #121792 The MFCs were calibrated against the Empa flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851) before and after the audit. Redy1 = 0.9999±0.0008 * Reference Redy2 = 1.0009±0.0005 * Reference
Connection between instruments		Ca. 2.5 meter 1/4" PFA tubing
Sequence of Levels		Repeated runs of randomised sequence
Calibrations of MFCs		1 run before shipment of TS (2008-09-23) 1 run after return of TS (2009-02-12)

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland

mailto:gaw@empa.ch

Ozone Audit Executive Summary (MKN)

0.1	Station Name:	Mt. Kenya
0.2	GAW ID:	MKN
0.3	Coordinates/Elevation:	0.033°S, 37.217°E (ca. 3678 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	2008-11-03 thru 11
1.2	Auditor:	Dr. J. Klausen, Dr. S. Henne
1.2.1	Station staff involved in audit:	Mr. Kennedy K. Thiong'o, Mr. John Aseyo
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #0421507340
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(0.9996±0.0009) × [SRP] - (0.0.4±0.14)
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49C #58106-318
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG-0.3 ppb, SPAN 1.013
1.5.4	Calibration at start of audit (ppb):	[OA] = (0.999±0.001) × [SRP] + (0.20±0.09)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] – 0.20) / 0.999
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.30\ \text{ppb}^2 + 2.71\text{e-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	-main station instrument since July 2006
1.7	Reference:	WCC-Empa Report 08/5

[OA]: Instrument readings; [SRP]: SRP readings; X: mixing ratios on SRP scale

GAW World Calibration Centre for Carbon Monoxide
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland

mailto:gaw@empa.ch

Carbon Monoxide Audit Executive Summary (MKN)

0.1	Station Name:	Mt. Kenya
0.2	GAW ID:	MKN
0.3	Coordinates/Elevation:	0.033°S, 37.217°E (ca. 3678 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2008-11-03 thru 11
1.2	Auditor:	Dr. J. Klausen, Dr. S. Henne
1.2.1	Station staff involved in audit:	Mr. Kennedy K. Thiong'o, Mr. John Aseyo
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	CA08202 59.77±0.60 ppm CO (α=0.05)
1.4.2	Zero Air:	Ambient Air, Sofnocat, Purafil, filter (WCC-Empa)
1.4.3	Dilution unit:	WCC-Empa Dilution unit with Redy MFCs
1.4.4	Range of calibration:	0 – 1000 ppb
1.5	CO analyzer [CA]	
1.5.1	Model:	HORIBA APMA360 #890617035
1.5.2	Range of calibration:	0 – 1000 ppb
1.5.3	Coefficients at start of audit	Zero -8, Span 1.0300
1.5.4	Calibration at start of audit (ppb):	CO = (1.015±0.006) $\times$ X - (7.1±1.6)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 7.1) / 1.015
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (41.3\ ppb^2 + 1.14e\text{-}04 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.6	Comments:	Main station analyser since November 2008
1.7	Reference:	WCC-Empa Report 08/5

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 CO scale.

GAW World Calibration Centre for Carbon Monoxide
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland

mailto:gaw@empa.ch

Carbon Monoxide Audit Executive Summary (MKN)

0.1	Station Name:	Mt. Kenya
0.2	GAW ID:	MKN
0.3	Coordinates/Elevation:	0.033°S, 37.217°E (ca. 3678 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2008-11-03 thru 11
1.2	Auditor:	Dr. J. Klausen, Dr. S. Henne
1.2.1	Station staff involved in audit:	Mr. Kennedy K. Thiong'o, Mr. John Aseyo
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	CA08202 59.77±0.60 ppm CO (α=0.05)
1.4.2	Zero Air:	Ambient Air, Sofnocat, Purafil, filter (WCC-Empa)
1.4.3	Dilution unit:	WCC-Empa Dilution unit with Redy MFCs
1.4.4	Range of calibration:	0 – 1000 ppb
1.5	CO analyzer [CA]	
1.5.1	Model:	TEI 48C Trace Level #66838-352
1.5.2	Range of calibration:	0 – 1000 ppb
1.5.3	Coefficients at start of audit	BKG 4.118, Span 1.173
1.5.4	Calibration at start of audit (ppb):	CO = (1.024±0.006) × X - (8.9±1.0)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 7.7) / 1.0119
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (151.1\ \text{ppb}^2 + 3.00\text{e-}05 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 08/5

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 CO scale.

REFERENCES

Henne, S., et al. (2008a), Mount Kenya Global Atmosphere Watch Station (MKN): Installation and Meteorological Characterization, *Journal of Applied Meteorology and Climatology*, *47*, 2946-2962.

Henne, S., et al. (2008b), Representativeness and climatology of carbon monoxide and ozone at the global GAW station Mt. Kenya in equatorial Africa, *Atmos. Chem. Phys.*, *8*, 3119-3139.

Herzog, A., et al. (2000), System Audit of Surface Ozone Measurements at GAW Global Mountain Station Mt. Kenya, Including Ozone Sounding, Nairobi, January 2000, WCC-Empa Report 00/01, 25 pp, Dübendorf, Switzerland.

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

Klausen, J., et al. (2006), System and Performance Audit of Surface Ozone and Carbon Monoxide at the Global GAW Station Mt. Kenya, January 2006, Empa-WCC Report 06/1, 39 pp, Dübendorf, Switzerland.

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

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

R Development Core Team (2009), R: A Language and Environment for Statistical Computing, edited, Vienna, Austria.

WMO (2007a), Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland.

WMO (2007b), WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, GAW Report No. 172, World Meteorological Organization, Geneva, Switzerland.

WMO (in preparation), Standard Operating Procedure (SOP) for Performance Audits of Surface Ozone Measurements at WMO/GAW Sites, Draft Version 1.0, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland.

Zellweger, C., et al. (2002), System and Performance Audit of Surface Ozone, Global GAW Station Mt. Kenya, February 2000, Empa-WCC Report 02/1, 39 pp, Dübendorf, Switzerland.

Zellweger, C., et al. (2005), System and Performance Audit of Surface Ozone and Carbon Monoxide at the Global GAW Station Mt. Kenya, February 2005, WCC-Empa Report 05/1, 39 pp, Dübendorf, Switzerland.

LIST OF ABBREVIATIONS

a.s.l	above sea level
CCL	Central Calibration Laboratory
DAQ	Data Acquisition System
GAWSIS	GAW Station Information System
KMD	Kenya Meteorological Department
KPLC	Kenya Power & Lighting Company
MFC	Mass Flow Controller
MKN	Mt. Kenya GAW station
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyzer
QA/SAC	Quality Assurance/Science Activity Centre
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Traveling Standard
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation