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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 06/1

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION MT. KENYA

KENYA, JANUARY 2006

Submitted by

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

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

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

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ASSESSMENT AND RECOMMENDATIONS

The fourth system and performance audit at the Global GAW station Mt. Kenya (MKN) and an inter-comparison of the ozone calibrator at the GAW station Nairobi (NRB) were conducted by QA/SAC Switzerland[1] and WCC-Empa[2] from 18 thru 27 January 2006 in agreement with the WMO/GAW quality assurance system [*WMO*, 2001].

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

People present during the audit included

Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland and WCC-Empa
Dr. Stephan Henne	Empa Dübendorf, QA/SAC Switzerland
Mr. John Rotich	Kenya Meteorological Department, Station manager
Mr. Josiah Kariuki	Kenya Meteorological Department, Operator
Mr. John Aseyo	Kenya Meteorological Department, Operator

Our assessment of the station Mt. Kenya in general, as well as the surface ozone and carbon monoxide measurements in particular is summarized 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 Director of the Kenya Meteorological Department, the station manager 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. They were discussed during two meetings and were all strongly supported by Deputy Director Kenya Meteorological Department Mr. Nyakwada.

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 acceptable if hard on vehicle and passengers.

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 maintained or even improved.

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

[1] WMO/GAW Quality Assurance / Science Activity Centre Switzerland, Empa Dübendorf, Switzerland

[2] 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 (for example the zero drift of the carbon monoxide NDIR analyzer) in ways that are hard to predict. 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 current power supply to the station is clearly inadequate. It is still unreliable and subject 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. As a consequence, the overall data coverage for the period February 2001 – January 2006 is less than 50 %.

The station was without power upon arrival on site. Power was eventually restored after repeated interventions at the regional office of Kenya Power and Lighting (KPLC) on the 3rd day after arrival, and remained beyond the completion of the audit.

Recommendation 3 (*, immediately)**
KMD is strongly encouraged to follow-up on their pledge to send an official letter of complaint on a very high level to KPLC to ensure a sustainable upgrade of the power line within the immediate future.

Recommendation 4 (, immediately)**
KMD is encouraged to explore the availability in Kenya of a radiator-type heating device with thermostat. To reduce excessive warming-up of the containers during daytime it should be considered to paint the containers in a light colour.

Station Management and Operation

The station is usually visited weekly by officers of the Kenya Meteorological Department (KMD) who reside in nearby Nanyuki (1.5 h from the station). The current staff consist of two 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 Mt. Kenya staff and QA/SAC Switzerland is ongoing.

Recommendation 5 (, on-going)**
KMD is invited to intensify technical and scientific exchange with existing and new external partners, and to participate more actively in such partnerships.

Recommendation 6 (, on-going)**
KMD is invited to take advantage of the opportunity for training offered by GAWTEC.

Air Inlet System

The general design of the air inlet system is adequate, but the audit revealed significant deficiencies with regards to the specifications of the air blower. The air flow through the inlet system appeared to be susceptible to the local wind speed. This is inadequate, but can be resolved by replacing the current fan with a stronger air blower of different design. Replacement costs will be covered by WMO through remaining GEF funds (‘storehouse’).

Recommendation 7 (, 2006)**
KMD is requested to ensure proper installation of the replacement blower.

Surface Ozone Measurements

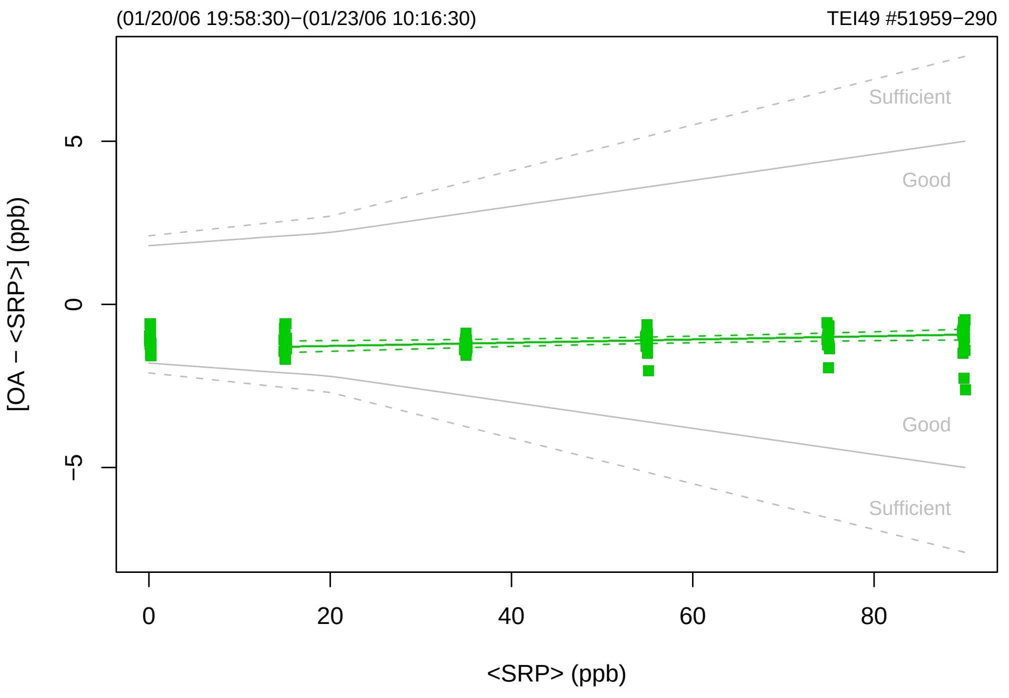
Instrumentation. In principle, the instrumentation is adequate, although it exhibits a relatively low signal-to-noise ratio in comparison to current generation instruments. Moreover, the audit demonstrated erratic behaviour of this particular ozone analyzer (a sudden, constant drop of readings that persisted for hours, but was unpredictable). The available measurement record will have to be reviewed and (re)validated in its entirety. Under these circumstances, the ozone instrument is considered inadequate and replacement urgent.

Standards. 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.

Intercomparison (Performance Audit). The inter-comparison extended over a period of nearly 78 hours, during which time 6 transitions of the instrument between its normal state and an obviously faulty state were observed. In both states, the instrument had a negative bias with respect to the SRP (see **Figure 1**), leading to the following assessment:

Instrument in normal state:	0 – 15 ppb	good agreement, analyzer non-linear	
	15 – 90 ppb	good agreement	
Unbiased O_3 mixing ratio (ppb)	X_{O3} (ppb) = ([OA] + 1.37 ppb) / 1.005		(1a)
Instrument in faulty state:	0 – 90 ppb	insufficient agreement	
Unbiased O_3 mixing ratio (ppb)	X_{O3} (ppb) = ([OA] + 9.59 ppb) / 1.005		(1b)

Here, [OA] represents surface ozone readings obtained from the Milos data logger.



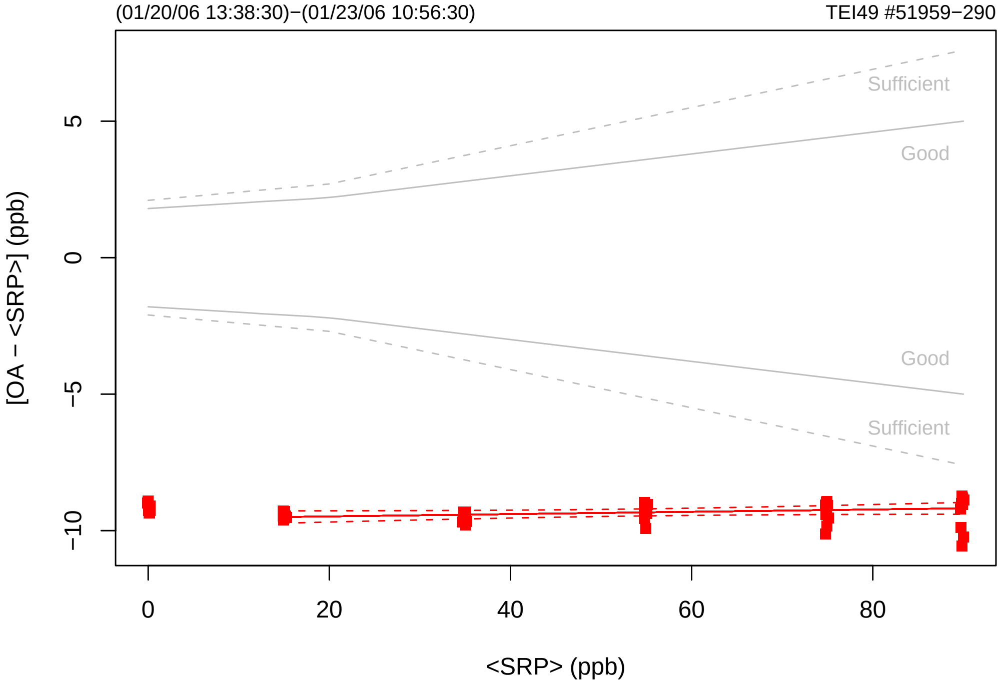


Figure 1. Bias of the Mt. Kenya ozone analyser with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are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

Recommendation 8 (*, 2006)**
The ozone analyser needs to be replaced as soon as possible. QA/SAC Switzerland has already submitted a proposal to WMO to jointly cover the costs of replacement. KMD is invited to support this move.

Recommendation 9 (, 2006)**
KMD is strongly encouraged to seek funding to purchase an ozone calibrator for use at the Mt. Kenya station. Until these resources can be found, KMD is encouraged to explore the possibility of inter-comparing the ozone analyser at Mt. Kenya station with the calibrator in Nairobi on a yearly basis.

Carbon Monoxide Measurements

Instrumentation. The instrumentation is adequate for the intended purpose, although elaborate data processing in accordance with the Standard Operating Procedure [*WMO*, in preparation-b] is necessary to achieve the required data quality. In particular, the instrument exhibits substantial zero drift, requiring very frequent calibration and correction of the raw data.

Standards. The station has been equipped with a dilution unit and 2 carbon monoxide cylinders in the high ppm range, as well as 2 carbon monoxide cylinders at the 1 ppm level, all calibrated by WCC-Empa. With this equipment, adequate calibration of the carbon monoxide measurements is possible.

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instrument with randomised carbon monoxide concentrations. During the audit, the instrument was serviced and extensively calibrated. In the absence of formal data quality objectives, the results cannot be formally assessed, however, the following characterizes the instrument bias before and after service (cf. Figure 2):

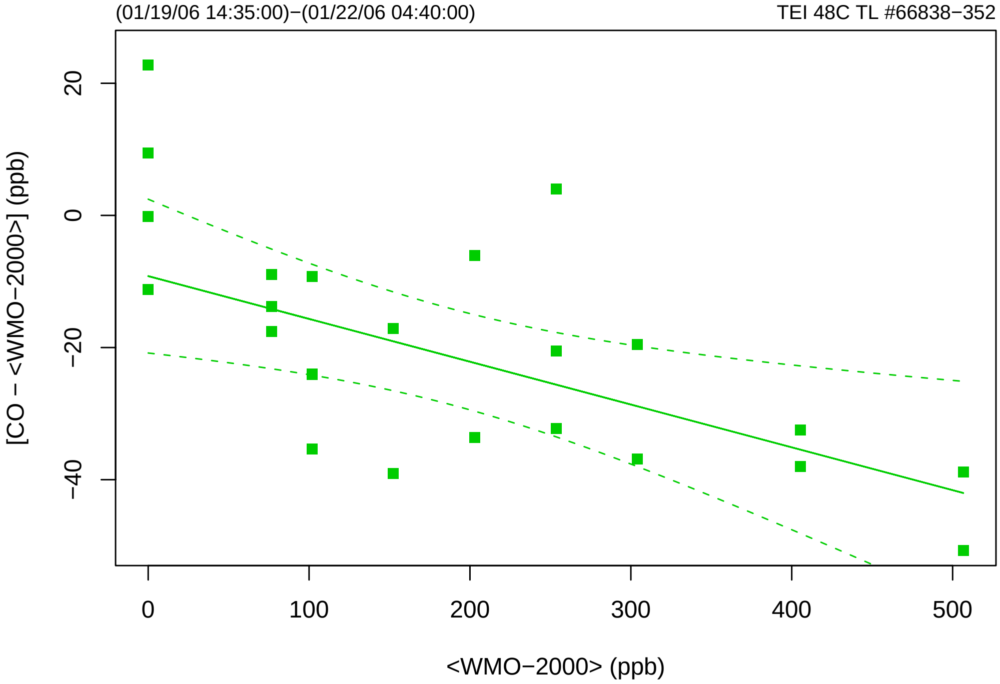
Unbiased CO mixing ratio before service (ppb):

$$\mathbf{XCO\ (ppb) = (CO + 9.5)/\ 0.93} \qquad (2a)$$

Unbiased CO mixing ratio after service (ppb):

$$\mathbf{XCO\ (ppb) = (CO + 1.35)\ /\ 0.9} \qquad (2b)$$

Here CO represents the CO analyzer readings after zero drift correction.



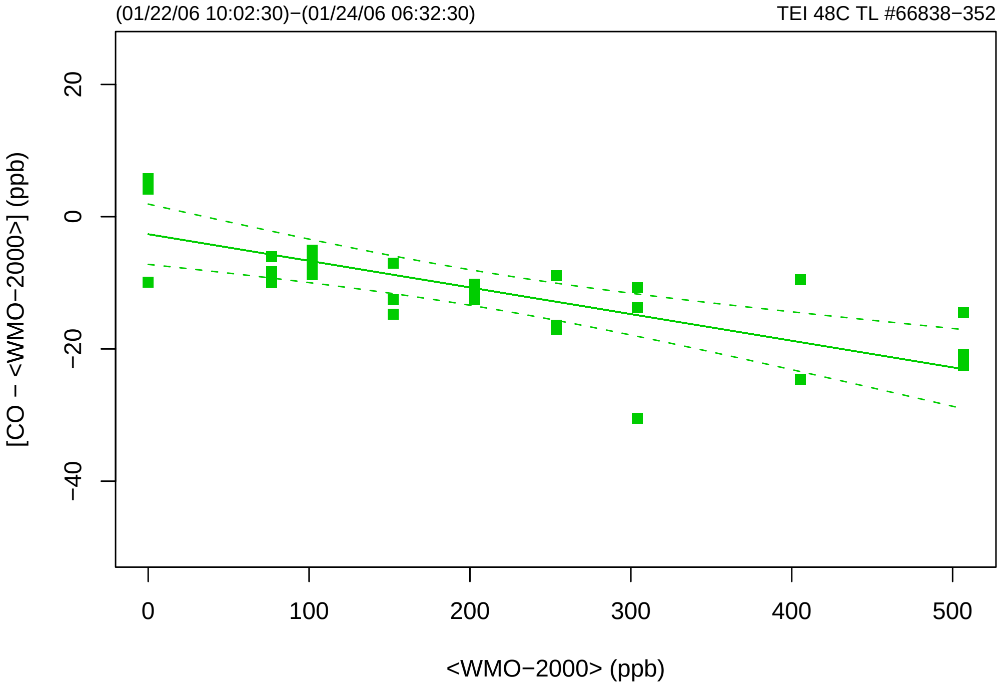


Figure 2. Bias of the Mt. Kenya carbon monoxide analyser with respect to the WMO-2000 reference scale as a function of concentration before service of the analyser. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Upper panel: Instrument before service. Lower Panel: Instrument after service.

Recommendation 10 (, on-going)**
KMD is encouraged to perform direct checks of the calibration once per month, using the 1 ppm CO standard. .

Data Acquisition and Management

Most data are acquired by a Vaisala Milos 500 data logger. This system is adequate for the intended purpose but storage capacity is limited. Furthermore, it is difficult to manage and extend, and requires a well trained operator. A mechanism for regular, automated data transfer from the Milos system to a high-volume storage medium is highly desirable to avoid the risk of data loss. Moreover, remote access to the data (e.g. using GSM-GPRS connectivity) on a daily basis is needed to bridge the periods between station visits. A GSM modem with GPRS capability has previously been provided to the station. Currently, the modem is only used to remotely check the status of the power supply.

> **Recommendation 11 (**, immediately)**
> *KMD is invited to take the necessary steps to enable GPRS connectivity through a local GSM provider and to cover the costs of operation. QA/SAC Switzerland is requested to help with the implementation of this data transfer mechanism.*

Data Submission

Neither surface ozone nor carbon monoxide data have been submitted to the responsible GAW World Data Centre (WDC) to this date. Currently, data are archived and quality-assured by QA/SAC Switzerland in collaboration with the station staff. While it was expected that data could be released to the WDC much earlier, it is planned to finalize the QA process by mid 2006 and submit data then.

> **Recommendation 12 (***, near future)**
> *QA/SAC Switzerland and KMD should collaborate in completing the QA process for the observations up to the end of 2005 and submit this data to the WDC. Later, all data should be submitted.*

Vertical Ozone Profiles, KMD Nairobi (NRB)

Instrumentation. The ozone calibrator used for calibration of the ozone sonde programme at KMD, Nairobi is adequate for that purpose, although the instrument is approaching the end of its useful lifetime.

Standards. The ozone calibrator at KMD is the only instrument available in the country, and the inter-comparison by WCC-Empa constitutes the only independent assessment at present. While this has worked in the past, it is a rather weak element in the operation and jeopardizes the success of the Nairobi ozone sounding programme.

Intercomparison (Performance Audit). The inter-comparison extended over a period of 22 hours and comprised of cycles of 6 different mixing ratios between 0 and 200 ppb. The instrument had a slight negative bias with respect to the SRP and proved to be non-linear in the low concentration range (cf. Figure 3), leading to the following assessment:

	0 – 30 ppb	good agreement, but calibrator non-linear
	30 – 200 ppb	good agreement
Unbiased O_3 mixing ratio (ppb)	X_{OC} (ppb) = ([OC] + 0.87 ppb) / 0.998	(3)

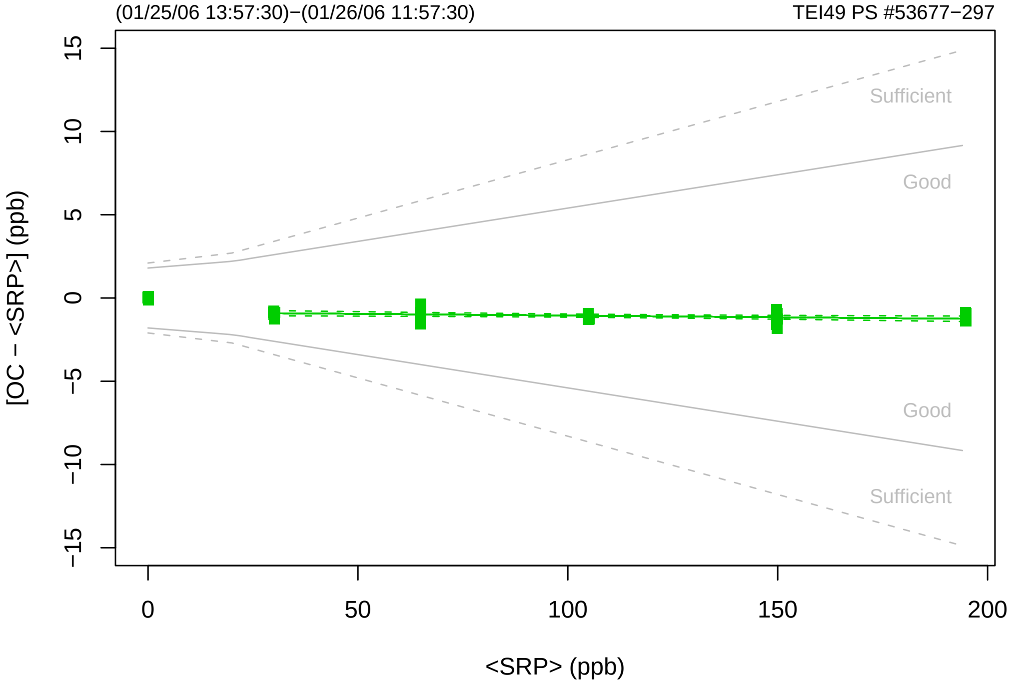


Figure 3. Bias of the Nairobi ozone calibrator with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Recommendation 13 (, 2007)**
KMD is invited to anticipate the need for a replacement of the existing calibrator in their budgetary planning process.

Conclusions

The Global GAW station Mt. Kenya is an important component of the global GAW observational network and thus far the only high-altitude monitoring station in equatorial Africa.

The weakest element in the operation and the further development of the Mt. Kenya station is the unreliable power supply operated by Kenya Power and Lighting Company (KPLC). The present situation is clearly unacceptable and a sustainable solution decisive for the future of the station.

The station has made significant progress since its establishment in the late 1990s. Nevertheless, a continued, convincing commitment on the part of Kenya Meteorological Department and an overall pro-active attitude of the Mt. Kenya staff is necessary to successfully complete the start-up phase and to secure continued support from external partners.

Summary Assessment of Mt. Kenya Station

System Audit Aspect	Adequacy[#]	Comment
Access	(3)	Subject to weather conditions and vehicle availability
Facilities		
Laboratory and office space	(3)	
Air Conditioning	(0)	Not available
Power supply	(0)	Frequent failures
General Management and Operation		
Organisation	(5)	
Competence of staff	(3)	
Air Inlet System	(2)	Residence time possibly too high
Instrumentation		
Ozone	(3)	
Carbon monoxide	(4)	
Aerosol light absorption	(0)	Available, not in operation
Flask sampling	(5)	
VOC canister sampling	(0)	Available, not in operation
Meteo	(3)	Instrumentation coming of age
Standards		
Ozone	(0)	Not available
Carbon monoxide	(4)	
Aerosol light absorption	(0)	Not available
Data Management		
Data acquisition	(4)	
Data processing	(3)	
Data submission	(0)	Data not yet submitted

[#]0: inadequate thru 5: adequate

Dübendorf, July 2006

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

APPENDIX

Global GAW Station Mt. Kenya

Site description

The Mt. Kenya GAW station, access and surroundings have been described in detail elsewhere [*Kariuki, et al.*, 2006; *Schnell, et al.*, 1978; *Zellweger, et al.*, 2005] and the station is also registered in GAWSIS (www.empa.ch/gaw/gawsis). The altitude of the site had been somewhat uncertain in the past. During this mission, the GPS receiver was serviced, and the definitive station location and altitude (0.0622°S, 37.2972°E, 3678 m a.s.l.) were confirmed.

Measurement Programme

Mt. Kenya GAW station was officially opened in December 1999 and started its operation in June 2001 with a reduced measurement programme. The status of the programme as of January 2006 is shown in Table 1:

Table 1. Measurement Programme at Mt. Kenya GAW Station

Parameter	**Current Instrument**	**Data Coverage (%)**		
		<12 months	<3 years	Overall#
In Situ Measurements				
Surface Ozone	TEI 49	46.0	53.1	55.8
Carbon Monoxide	TEI 48C-TL	40.5	46.5	45.6
Light Absorption	Aethalometer AE-21		N/A	
Flask Measurements				
Carbon Dioxide	NOAA-GMD		N/A	
Methane	NOAA-GMD		N/A	
Nitrous Oxide	NOAA-GMD		N/A	
Sulfur Hexafluoride	NOAA-GMD		N/A	
Carbon Monoxide	NOAA-GMD		N/A	
Hydrogen	NOAA-GMD		N/A	
Ancillary Measurements				
Global Radiation		46.0	53.1	55.8
Ambient Temperature		46.0	53.1	55.8
Ambient Pressure		46.0	53.0	55.8
Relative Humidity		43.9	51.1	53.9
Wind Speed		45.2	52.7	55.5
Wind Direction		45.2	52.1	54.7

since July, 2002; N/A: not available

Ozone and Carbon Monoxide Distribution at Mt. Kenya

The monthly and yearly distributions of one hourly mean values for surface ozone and carbon monoxide for the year 2005 are shown in Figure 4.

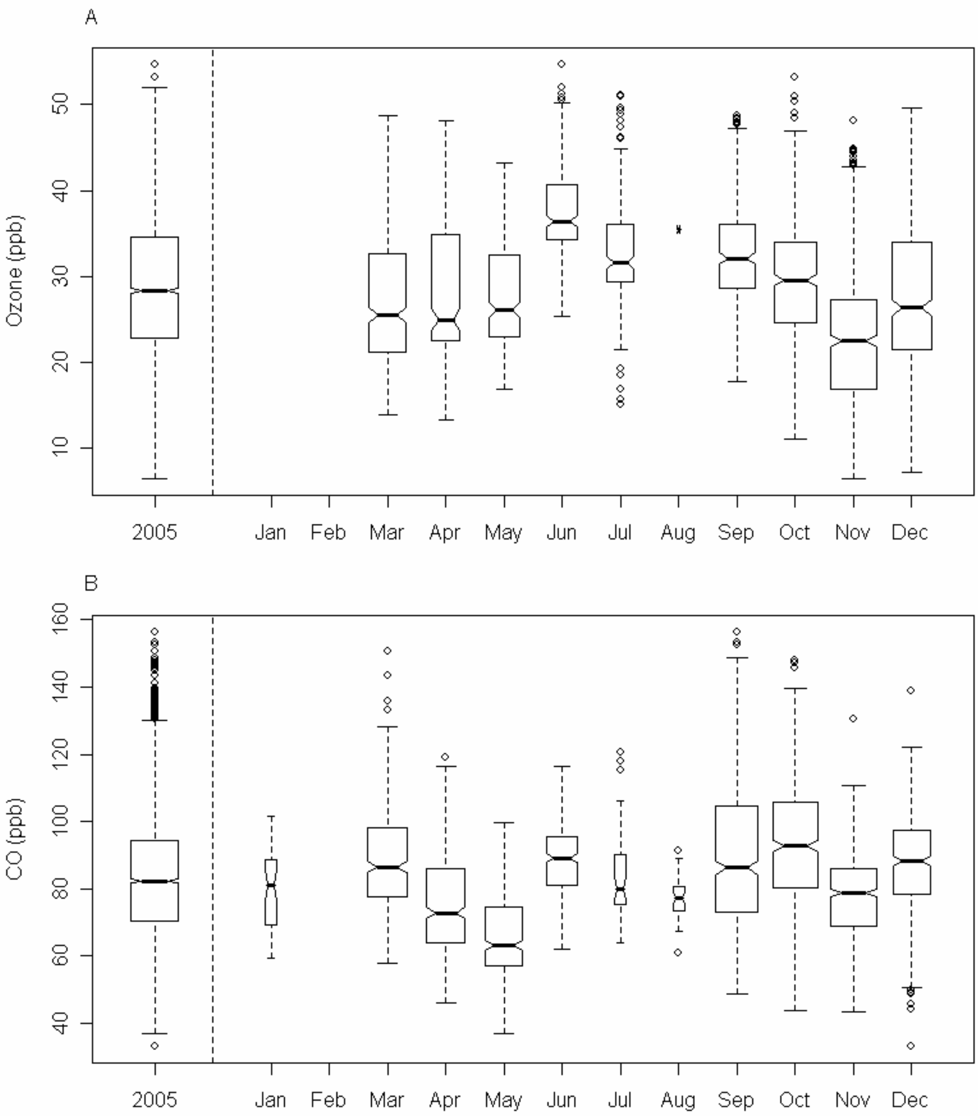


Figure 4. Yearly and Monthly Box Plots of 1-hourly aggregates for the year 2005 for (A) Surface Ozone and (B) Carbon Monoxide (zero-drift corrected). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organization 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. John Rotich (Figure 5). As of February 2006, the assignments were changed as follows: John Rotich (station manager NRB), Josiah Kariuki (station manager MKN), Evans Omeno (operator MKN).

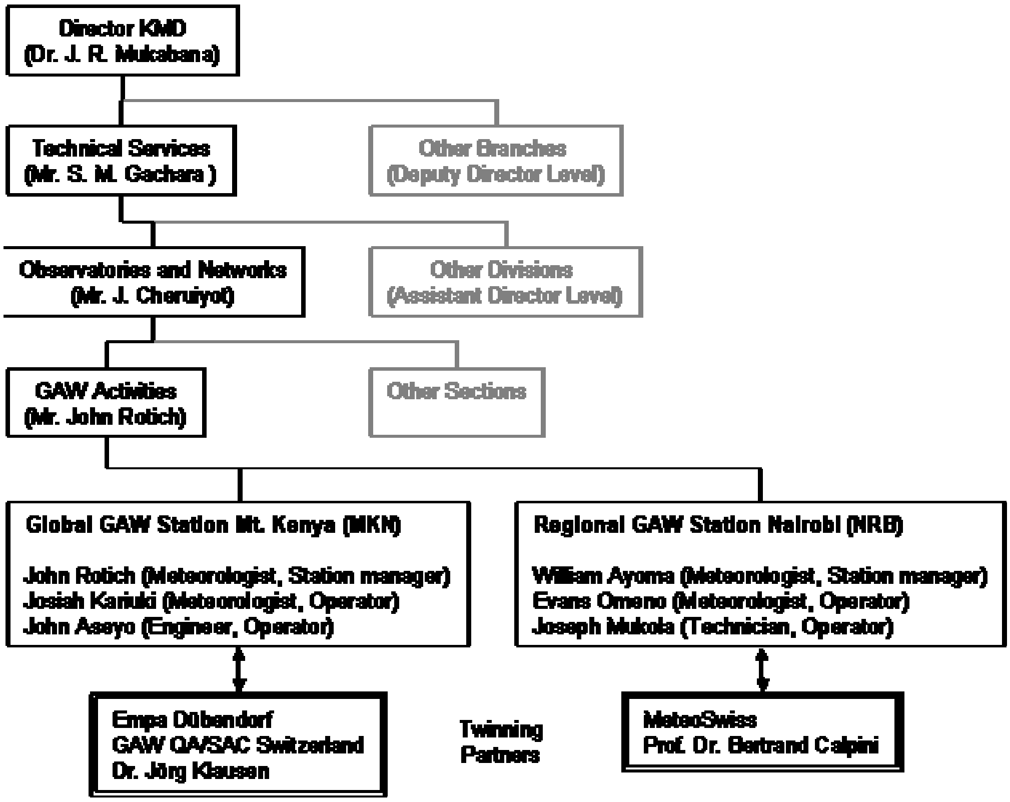


Figure 5. Organization of GAW Activities at Kenya Meteorological Department as of January 2006. Note: Only branches relevant to GAW are detailed.

Surface Ozone Measurements

No changes were made to the set-up since the last audit. The station was without power at the beginning of the present audit. Power was restored during the audit, and all inter-comparisons were done using lines power according to Standard Operating Procedures [*WMO*, 2006].

Monitoring Set-up and Procedures

Air Conditioning

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 the last audit report [*Zellweger, et al.*, 2005], and no changes were made since then. 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 tubing is made of Teflon and the instrument is protected by a Teflon filter. All materials used are adequate.

The flow through the glass manifold could not be determined; however, evidence suggests that the existing fan may be too weak to guarantee adequate residence times, at least under windy conditions and should be replaced by a stronger blower (cf. Recommendation 7).

Instrumentation

The surface ozone monitoring equipment has been described in the last audit report [*Zellweger, et al.*, 2005], and no changes were made since then. It consists of a rack-mounted TEI 49 analyser with analogue output that has been in service since December 1999. The internal ozone generator and an external zero air unit consisting of a pump and a charcoal cartridge are not in use. Instrumental details for the ozone analyser are summarised in Table 2 below.

Standards

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 9).

Operation and Maintenance

The instrument is checked for general operation whenever the station is visited (usually once per week). The inlet filter is replaced every 2 months. The ozone lamp is replaced when faulty; however, the instrument has never been serviced directly by an authorized service engineer in the past.

Data Acquisition and Data Transfer

The analogue output of the ozone analyser is connected to the central Milos 500 data logger that stores one minute averages. In its present configuration, the logger has a capacity for 12 days data storage. To date, data is manually downloaded to the station computer during station visits. A mechanism for regular, automated data transfer from the Milos system to a high-volume storage medium is highly desirable to avoid the risk of data loss. Moreover, the possibility of remote access to the data on a daily basis is needed to bridge the periods between station visits.

The most economical solution to improve data access and management involves regular, automated transfer of data from the Milos system to the station personal computer and from there to the internet. QA/SAC Switzerland has explored the possibilities available in Kenya and recommends use of GSM-GPRS as offered by Safaricom. QA/SAC Switzerland is willing to lead the technical implementation of this automatic data transfer (cf. Recommendation 11).

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

To date, no data have been submitted to the GAW World Data Centre for Surface Ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG). Currently, data are archived and quality-assured by QA/SAC Switzerland in collaboration with the station staff. While it was expected that data could be released to the WDC much earlier, it is planned to finalize the QA process by mid 2006 and submit data then (cf. Recommendation 12).

Documentation

Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. During the audit, the checklists were revised and an electronic spread-sheet solution developed. This will simplify the visualization of instrument parameters, indicate the need for maintenance early on, and facilitate information exchange with QA/SAC Switzerland. The instrument manual is available at the site.

Inter-Comparison of Ozone Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2006] and included inter-comparisons of the transfer 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 transfer standard and station analyser. The data used for the evaluation was recorded by both WCC-Empa and Mt. Kenya data acquisition systems as indicated, and no corrections were applied.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.012
Ozone analyzer (OA)	Model, S/N	TEI 49-003 #51959-290
	Principle	UV absorption
	Range	1 ppm
	Settings	ZERO = 509 ; SPAN = 49
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. 2.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS	One minute aggregates from digital output (custom designed LabView programme)
	OA	One minute aggregates from 0 – 10 V analogue output (Milos)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	659.9 (Milos)
	TS	663.5, adjusted to 659.8 (495.0 mmHg)
	OA	not checked
Levels (ppb)		0, 15, 35, 55, 75, 90
Duration per level (min)		20
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		31 runs (20 thru 23 January, 2006)

Loss During Sampling

The ozone concentration was inter-compared using two different sampling lines. Ozone concentrations sampled through the standard station manifold were compared with samples taken through a Teflon tube that was directly taking in air from the same height as the station manifold. A series of 3 inter-comparisons suggested a loss of 3.0 ppb [2.1 ppb – 3.8 ppb, α = 0.05] in ozone concentrations when sampling through the Teflon tube. This is counter-intuitive and does not alleviate our concerns about the adequacy of the current manifold fan (cf. Recommendation 7).

Results

Each ozone level was applied for 20 minutes, and the last 10 one-minute averages were aggregated (cf. Table 3). These aggregates were used in the assessment of the inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results refer to the calibration factors as given in Table 2 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values (cf Appendix for details).

Table 3. Ten-minute aggregates computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the Mt. Kenya ozone analyzer (OA) with the WCC-Empa transfer standard (TS).

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
(01/20/06 13:38:30)	1	0	0.13	-9.04	1	0.08	0.13
(01/20/06 13:58:30)	1	90	89.85	79.28	1	0.09	0.64
(01/20/06 14:18:30)	1	55	54.94	45.00	1	0.10	0.21
(01/20/06 14:38:30)	1	15	14.99	5.49	1	0.14	0.26
(01/20/06 14:58:30)	1	75	74.77	64.63	1	0.08	0.33
(01/20/06 15:18:30)	1	35	34.76	25.05	1	0.13	0.21
(01/20/06 15:38:30)	2	0	0.02	-8.92	1	0.06	0.18
(01/20/06 15:58:30)	2	90	89.74	79.83	1	0.13	0.25
(01/20/06 16:18:30)	2	55	54.79	45.22	1	0.11	0.30
(01/20/06 16:38:30)	2	15	14.96	5.32	1	0.12	0.30
(01/20/06 16:58:30)	2	75	74.94	65.10	1	0.07	0.32
(01/20/06 17:18:30)	2	35	35.06	25.24	1	0.09	0.24
(01/20/06 17:38:30)	3	0	0.10	-9.19	1	0.11	0.22
(01/20/06 17:58:30)	3	90	90.03	79.77	1	0.14	0.82
(01/20/06 18:18:30)	3	55	55.08	45.68	1	0.12	0.36
(01/20/06 18:38:30)	3	15	15.18	5.68	1	0.11	0.45
(01/20/06 18:58:30)	3	75	75.11	65.55	1	0.10	0.26
(01/20/06 19:18:30)	3	35	35.19	25.49	1	0.12	0.30
(01/20/06 19:38:30)	4	0	0.21	-8.92	1	0.09	0.27
(01/20/06 19:58:30)	4	90	90.10	87.46	0	0.12	0.55
(01/20/06 20:18:30)	4	55	55.14	53.09	0	0.08	0.62
(01/20/06 20:38:30)	4	15	15.21	13.83	0	0.11	0.28
(01/20/06 20:58:30)	4	75	75.08	73.70	0	0.10	0.27
(01/20/06 21:18:30)	4	35	35.14	33.78	0	0.12	0.17
(01/20/06 21:58:30)	5	0	0.23	-1.06	0	0.16	0.24
(01/20/06 22:18:30)	5	90	90.02	88.61	0	0.14	0.33
(01/20/06 22:38:30)	5	55	55.02	53.51	0	0.09	0.26
(01/20/06 22:58:30)	5	15	15.06	13.76	0	0.15	0.31
(01/20/06 23:18:30)	5	75	74.94	73.69	0	0.05	0.26
(01/20/06 23:38:30)	5	35	35.05	33.61	0	0.13	0.46
(01/20/06 23:59:30)	6	0	0.11	-0.88	0	0.13	0.23
(01/21/06 00:18:30)	6	90	89.97	88.93	0	0.11	0.27
(01/21/06 00:38:30)	6	55	55.01	54.08	0	0.12	0.28
(01/21/06 00:58:30)	6	15	15.02	14.07	0	0.13	0.31
(01/21/06 01:18:30)	6	75	74.94	74.16	0	0.06	0.31
(01/21/06 01:38:30)	6	35	35.01	34.10	0	0.13	0.29
(01/21/06 01:58:30)	7	0	0.22	-0.41	0	0.12	0.28
(01/21/06 02:18:30)	7	90	89.91	88.76	0	0.11	0.41
(01/21/06 02:38:30)	7	55	54.99	54.34	0	0.10	0.23
(01/21/06 02:58:30)	7	15	15.03	14.40	0	0.11	0.37
(01/21/06 03:18:30)	7	75	74.95	74.06	0	0.09	0.21
(01/21/06 03:38:30)	7	35	35.01	33.89	0	0.09	0.28
(01/21/06 03:58:30)	8	0	0.19	-0.43	0	0.10	0.18
(01/21/06 04:18:30)	8	90	89.93	89.16	0	0.07	0.19

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
(01/21/06 04:38:30)	8	55	55.00	53.76	0	0.09	0.28
(01/21/06 04:58:30)	8	15	15.04	13.34	0	0.09	0.23
(01/21/06 05:18:30)	8	75	74.98	73.83	0	0.13	0.38
(01/21/06 05:38:30)	8	35	35.02	33.53	0	0.10	0.29
(01/21/06 06:18:30)	9	0	0.19	-0.56	0	0.08	0.29
(01/21/06 06:38:30)	9	90	89.86	89.28	0	0.09	0.25
(01/21/06 06:58:30)	9	55	54.88	53.80	0	0.10	0.24
(01/21/06 07:18:30)	9	15	14.93	13.82	0	0.13	0.27
(01/21/06 07:38:30)	9	75	74.87	73.62	0	0.09	0.22
(01/21/06 07:58:30)	9	35	34.99	33.42	0	0.13	0.42
(01/21/06 08:18:30)	10	0	0.24	-0.98	0	0.08	0.22
(01/21/06 08:38:30)	10	90	89.83	88.31	0	0.08	0.33
(01/21/06 09:18:30)	10	15	14.92	5.43	1	0.11	0.16
(01/21/06 09:38:30)	10	75	74.82	65.40	1	0.12	0.38
(01/21/06 17:36:30)	11	0	0.18	-9.06	1	0.13	0.29
(01/21/06 17:56:30)	11	75	74.93	65.98	1	0.10	0.30
(01/21/06 18:16:30)	11	35	35.07	25.74	1	0.09	0.25
(01/21/06 18:36:30)	11	55	55.00	45.88	1	0.06	0.23
(01/21/06 19:38:30)	12	0	0.16	-1.09	0	0.12	0.26
(01/21/06 19:56:30)	12	75	75.07	74.38	0	0.09	0.27
(01/21/06 20:16:30)	12	35	35.05	33.93	0	0.14	0.30
(01/21/06 20:36:30)	12	55	54.94	53.98	0	0.06	0.32
(01/21/06 20:56:30)	12	90	89.90	89.34	0	0.08	0.22
(01/21/06 21:16:30)	12	15	15.05	13.77	0	0.15	0.34
(01/21/06 21:36:30)	13	0	0.07	-1.03	0	0.17	0.31
(01/21/06 21:56:30)	13	75	74.93	74.12	0	0.08	0.34
(01/21/06 22:16:30)	13	35	34.97	33.87	0	0.09	0.25
(01/21/06 22:36:30)	13	55	54.95	54.06	0	0.10	0.20
(01/21/06 22:56:30)	13	90	89.90	89.20	0	0.11	0.22
(01/21/06 23:16:30)	13	15	15.10	13.76	0	0.14	0.23
(01/21/06 23:56:30)	14	0	0.13	-1.01	0	0.14	0.23
(01/22/06 00:16:30)	14	75	74.97	74.30	0	0.09	0.27
(01/22/06 00:36:30)	14	35	35.02	33.81	0	0.09	0.18
(01/22/06 00:56:30)	14	55	55.01	54.08	0	0.10	0.16
(01/22/06 01:16:30)	14	90	89.94	89.23	0	0.09	0.34
(01/22/06 01:36:30)	14	15	15.02	13.91	0	0.11	0.28
(01/22/06 01:56:30)	15	0	0.21	-0.86	0	0.09	0.49
(01/22/06 02:16:30)	15	75	74.92	74.17	0	0.08	0.27
(01/22/06 02:36:30)	15	35	35.04	33.86	0	0.07	0.18
(01/22/06 02:56:30)	15	55	55.04	53.54	0	0.13	0.43
(01/22/06 03:16:30)	15	90	90.03	89.55	0	0.10	0.50
(01/22/06 03:36:30)	15	15	15.18	14.12	0	0.14	0.19
(01/22/06 03:56:30)	16	0	0.17	-0.46	0	0.11	0.43
(01/22/06 04:16:30)	16	75	75.06	74.27	0	0.06	0.39
(01/22/06 04:36:30)	16	35	35.11	33.81	0	0.12	0.35
(01/22/06 04:56:30)	16	55	54.96	54.20	0	0.14	0.22
(01/22/06 05:16:30)	16	90	89.84	89.05	0	0.06	0.20
(01/22/06 05:36:30)	16	15	14.94	13.48	0	0.11	0.24
(01/22/06 06:16:30)	17	0	0.25	-1.35	0	0.10	0.78
(01/22/06 06:36:30)	17	75	74.82	73.72	0	0.13	0.15
(01/22/06 06:56:30)	17	35	34.83	33.42	0	0.09	0.23
(01/22/06 07:16:30)	17	55	54.88	53.58	0	0.16	0.31
(01/22/06 07:36:30)	17	90	89.84	88.88	0	0.09	0.25
(01/22/06 07:56:30)	17	15	14.95	5.64	1	0.10	0.20
(01/22/06 08:16:30)	18	0	-0.02	-9.04	1	0.11	0.17

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
(01/22/06 08:36:30)	18	75	74.81	65.74	1	0.06	0.21
(01/22/06 08:56:30)	18	35	34.85	25.51	1	0.15	0.27
(01/22/06 09:16:30)	18	55	54.83	45.57	1	0.14	0.33
(01/22/06 09:36:30)	18	90	89.86	80.97	1	0.07	0.24
(01/22/06 09:56:30)	18	15	14.98	5.54	1	0.11	0.22
(01/22/06 10:16:30)	19	0	0.20	-9.18	1	0.12	0.35
(01/22/06 10:36:30)	19	75	74.89	65.69	1	0.10	0.32
(01/22/06 10:56:30)	19	35	34.93	25.48	1	0.11	0.26
(01/22/06 11:16:30)	19	55	54.95	45.81	1	0.13	0.24
(01/22/06 11:36:30)	19	90	89.89	81.08	1	0.07	0.30
(01/22/06 11:56:30)	19	15	15.09	5.77	1	0.12	0.26
(01/22/06 12:36:30)	20	0	0.15	-9.03	1	0.16	0.14
(01/22/06 12:56:30)	20	75	74.89	65.90	1	0.07	0.29
(01/22/06 13:16:30)	20	35	34.95	25.51	1	0.10	0.27
(01/22/06 13:36:30)	20	55	54.80	45.50	1	0.11	0.18
(01/22/06 13:56:30)	20	90	89.80	80.79	1	0.11	0.28
(01/22/06 14:16:30)	20	15	14.94	5.48	1	0.12	0.20
(01/22/06 14:36:30)	21	0	0.12	-9.18	1	0.22	0.19
(01/22/06 14:56:30)	21	75	74.82	65.54	1	0.17	0.28
(01/22/06 15:16:30)	21	35	34.84	25.23	1	0.09	0.30
(01/22/06 15:36:30)	21	55	54.81	45.82	1	0.12	0.33
(01/22/06 15:56:30)	21	90	89.70	80.48	1	0.11	0.33
(01/22/06 16:16:30)	21	15	14.90	5.55	1	0.14	0.21
(01/22/06 16:36:30)	22	0	0.13	-9.25	1	0.15	0.25
(01/22/06 16:54:30)	22	75	74.85	65.72	1	0.09	0.17
(01/22/06 17:16:30)	22	35	34.94	25.38	1	0.11	0.31
(01/22/06 17:36:30)	22	55	54.94	45.55	1	0.10	0.25
(01/22/06 17:56:30)	22	90	89.93	80.88	1	0.16	0.34
(01/22/06 18:16:30)	22	15	15.12	5.70	1	0.10	0.21
(01/22/06 18:57:30)	23	0	0.13	-9.16	1	0.22	0.13
(01/22/06 19:16:30)	23	75	75.01	65.91	1	0.09	0.28
(01/22/06 19:36:30)	23	35	35.09	25.75	1	0.12	0.24
(01/22/06 19:56:30)	23	55	55.12	46.06	1	0.09	0.16
(01/22/06 20:16:30)	23	90	90.10	81.21	1	0.05	0.30
(01/22/06 20:36:30)	23	15	15.30	5.75	1	0.10	0.23
(01/22/06 20:56:30)	24	0	0.24	-9.05	1	0.13	0.25
(01/22/06 21:36:30)	24	35	35.10	33.74	0	0.08	0.20
(01/22/06 21:56:30)	24	55	55.05	53.81	0	0.08	0.17
(01/22/06 22:16:30)	24	90	89.95	87.68	0	0.11	0.55
(01/22/06 22:36:30)	24	15	15.15	13.82	0	0.13	0.25
(01/22/06 22:56:30)	25	0	0.10	-1.04	0	0.09	0.17
(01/22/06 23:16:30)	25	75	75.04	73.75	0	0.11	0.41
(01/22/06 23:36:30)	25	35	35.11	33.79	0	0.09	0.17
(01/23/06 00:16:30)	25	90	90.01	89.33	0	0.10	0.34
(01/23/06 00:36:30)	25	15	15.15	14.54	0	0.11	0.35
(01/23/06 01:16:30)	26	0	0.15	-1.06	0	0.13	0.20
(01/23/06 01:36:30)	26	75	75.01	73.05	0	0.06	0.36
(01/23/06 01:56:30)	26	35	35.04	33.75	0	0.12	0.32
(01/23/06 02:16:30)	26	55	55.03	54.11	0	0.11	0.35
(01/23/06 02:36:30)	26	90	89.96	88.99	0	0.08	0.48
(01/23/06 02:56:30)	26	15	15.11	13.75	0	0.13	0.31
(01/23/06 03:16:30)	27	0	0.20	-1.36	0	0.14	0.30
(01/23/06 03:36:30)	27	75	74.95	73.84	0	0.13	0.41
(01/23/06 03:56:30)	27	35	34.98	33.39	0	0.11	0.36
(01/23/06 04:16:30)	27	55	55.02	53.60	0	0.10	0.31

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
(01/23/06 04:36:30)	27	90	89.92	88.69	0	0.06	0.28
(01/23/06 04:56:30)	27	15	15.07	13.37	0	0.15	0.28
(01/23/06 05:16:30)	28	0	0.19	-1.33	0	0.17	0.30
(01/23/06 05:36:30)	28	75	74.88	73.71	0	0.12	0.34
(01/23/06 05:56:30)	28	35	34.96	33.86	0	0.13	0.56
(01/23/06 06:16:30)	28	55	54.89	53.86	0	0.09	0.24
(01/23/06 06:36:30)	28	90	89.85	88.97	0	0.07	0.34
(01/23/06 06:56:30)	28	15	15.00	14.24	0	0.13	0.31
(01/23/06 07:36:30)	29	0	0.12	-0.88	0	0.10	0.20
(01/23/06 07:56:30)	29	75	74.84	74.26	0	0.09	0.28
(01/23/06 08:16:30)	29	35	34.87	33.62	0	0.10	0.17
(01/23/06 08:36:30)	29	55	54.83	53.82	0	0.14	0.23
(01/23/06 08:56:30)	29	90	89.78	88.92	0	0.08	0.27
(01/23/06 09:36:30)	30	0	0.12	-0.91	0	0.09	0.20
(01/23/06 09:56:30)	30	75	74.86	73.84	0	0.07	0.26
(01/23/06 10:16:30)	30	35	34.90	33.71	0	0.15	0.19
(01/23/06 10:56:30)	30	90	89.85	81.10	1	0.11	0.29

[#]0: normal instrument state; 1: faulty 'offset' instrument state

Figure 6 shows the time series over the course of 30 runs of the bias of the OA. The values for the OA were grouped and colour-coded depending on whether the bias of the OA exceeded 5 ppb. It is obvious that the instrument switched between two different states at random and without a well-defined periodicity. The transition from one to the other state took place within 1 – 2 minutes (not shown). Aggregates that were composed of one-minute data from both instrument states were discarded. The reason for this disturbing behaviour could not be identified during the visit at the site.

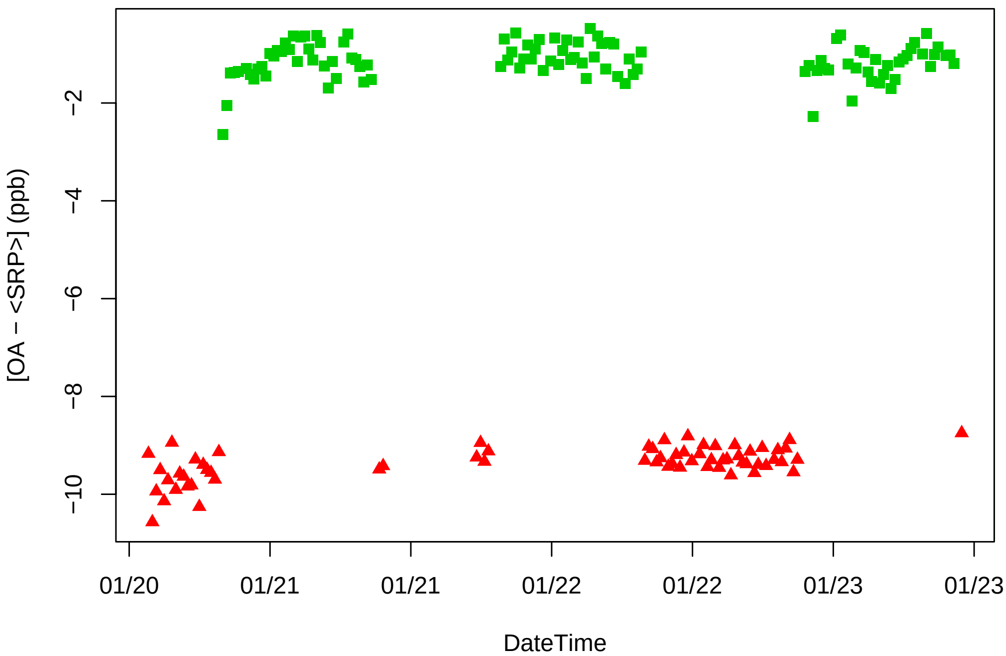
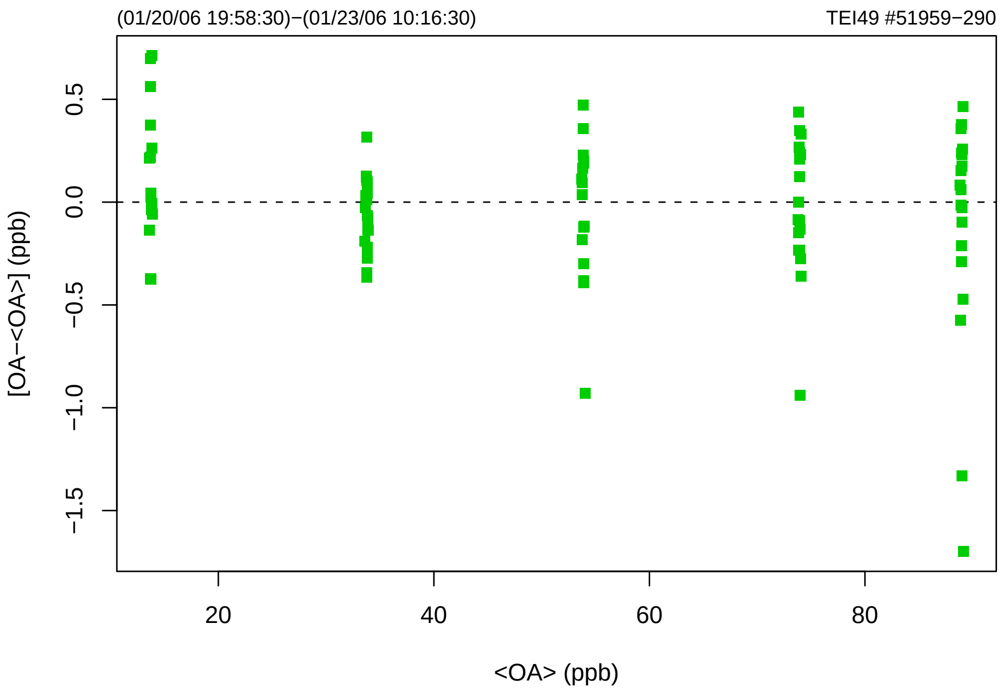


Figure 6. Time series of the bias of the Mt. Kenya ozone analyser with respect to the SRP. Each point represents the average of the last 10 one-minute values at a given level. Data are colour-coded to indicate the two apparent states of the instrument.

Figure 7 shows the regression residuals of the OA with respect to the SRP as a function of ozone concentration for the range 15 – 90 ppb. The instrument appears to be non-linear somewhere below 15 ppb (see **Figure 1**) and readings at such low mixing ratios have to be analyzed carefully.



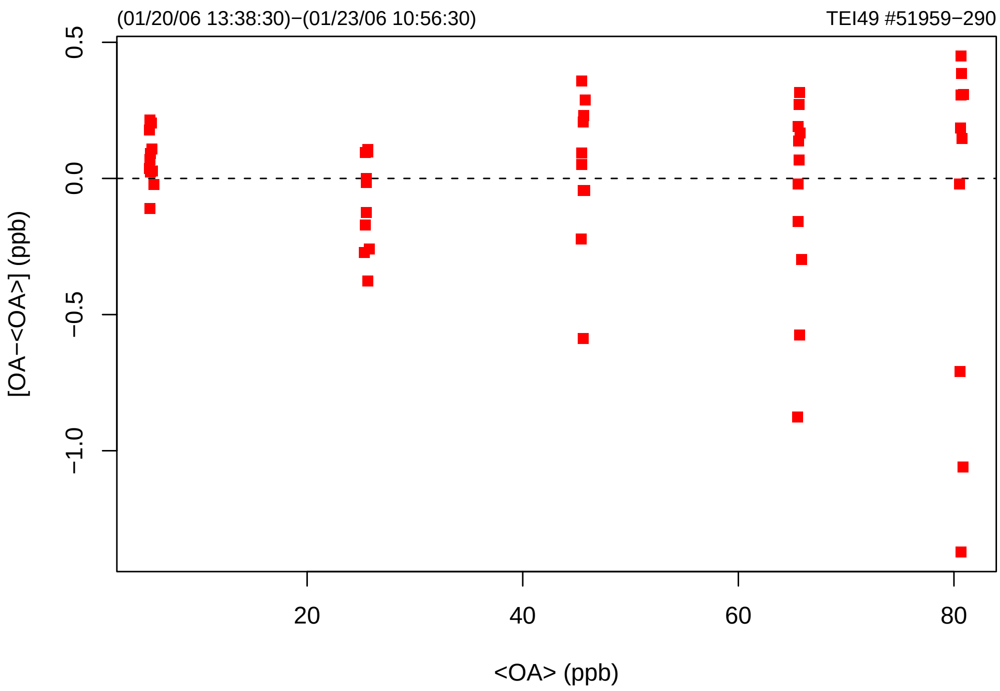


Figure 7. Regression residuals of the Mt. Kenya ozone analyser as a function of concentration. Upper panel: Instrument in regular state. Lower panel: Instrument in 'offset' state.

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 Milos one-minute data [OA] using equation (1) [*Klausen, et al.*, 2003], For the instrument in its normal state:

$$X_{O3}\ \text{(ppb)} = ([OA] + 1.37\ \text{ppb}) / 1.005$$

$$u_{O3}\ \text{(ppb)} = \text{sqrt}(0.40\ \text{ppb}^2 + 2.58\text{e-}05 * X_{O3}^2) \quad (1a)$$

For the instrument in its faulty ‚offset' state:

$$X_{O3}\ \text{(ppb)} = ([OA] + 9.59\ \text{ppb}) / 1.005$$

$$u_{O3}\ \text{(ppb)} = \text{sqrt}(0.40\ \text{ppb}^2 + 2.63\text{e-}05 * X_{O3}^2) \quad (1b)$$

Changes Made to Instrument

No changes were made to the instruments, all settings remained. The Teflon tubing connecting the instrument to the manifold was replaced on 21 January (16:00 UTC) without any effect on the instrument readings.

Conclusions

The findings of this audit have serious implications for the quality of the Mt. Kenya ozone data. There is no indication in the monitoring data itself whether the instrument was in its normal or in the faulty 'offset' state during data collection. The entire data set must be critically reviewed to identify the times of the transitions. Fortunately, the offset during the faulty instrument state is remarkably constant. Periods of data that is unambiguously identified as being 'faulty' can be corrected by simply adding a constant term. Nevertheless, the situation is totally unsatisfying, and the only apparent solution a replacement of the ozone analyser without undue delay (cf. Recommendation 8). In addition, more frequent inter-comparisons with an ozone calibrator would be very desirable (cf. Recommendation 9).

Carbon Monoxide Measurements

No changes were made to the set-up since the last audit. The station was without power at the beginning of the present audit. Power was restored during the audit, and all inter-comparisons were done using lines power according to Standard Operating Procedures [*WMO*, in preparation-b].

Monitoring Set-up and Procedures

Air Conditioning

The station is not air conditioned, and the lab temperature shows a significant diurnal variation. Considering that this is likely the most important driver for the substantial zero-drift of the 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 and the same observations concerning the flow through the manifold apply (cf. Recommendation 7).

Instrumentation

The carbon monoxide monitoring equipment has been described in the last audit report [*Zellweger, et al.*, 2005], and no changes were made since then. It consists of a rack-mounted TEI 48C-TL NDIR analyser with digital and analogue outputs that has been in service since February 2002. Instrumental details are listed in

Table 6 below.

Standards

The station is equipped with 2 cylinders in the 1000 ppb range for direct span checks of the instrument and a dilution system based on higher concentration standards and mass flow controllers for automatic or also manual span checks. Table 4 gives details of all cylinders at the station since the last audit. The internal zero air (Sofnocat™ cartridge) was compared to the air produced by the resident external zero-air generator (MKN) and the zero-air generator brought to the site during the audit (WCC; both consisting of silica gel - inlet filter 5 μm - metal bellow pump - Sofnocat - outlet filter 5 μm; custom-built by WCC-Empa). While the internal zero air is automatically applied to the instrument every 120' for 20', both external zero air generators were inter-compared during the inter-comparison runs and also directly by switching from one to the other. The first inter-comparison run was performed with the MKN external zero air generator, while all other inter-comparisons were performed with the WCC model. The results of the inter-comparison runs are included in Table 7. The additional direct inter-comparison yielded values of -0.03 ppb for the WCC zero-air unit and -6.4, -12.4 ppb for the MKN zero air unit. Considering the zero drift of the instrument during this period, the overall differences of the WCC and MKN zero air units amount to 0.2 – 2.5 ppb, which is well within the instruments uncertainty. Therefore, it can be concluded that all zero air units produced similar carbon monoxide free air.

Table 4. History of carbon monoxide standards available at Mt. Kenya GAW 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	continues
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	Continues
Sauerstoffwerk Lenzburg, SL68810, Direct use	1007±8 ppb, CO 99.997% in synthetic air 99.9995%	Dec 2005	WCC-Empa	Jan 2006	Continues
Sauerstoffwerk Lenzburg, SL68820, Dilution unit	20120±200 ppb (α=0.05), 99.997% in synthetic air 99.9995%	Dec 2005	WCC-Empa	Jan 2006	Continues

The mass flow controllers were inter-compared on 20 January, 2006 with a DryCal DC-2 Primary Flow Meter (Bios International Corporation) that was itself calibrated against molbloc reference flow meters (DH Instruments). The results are shown in Table 5. With these numbers, the dilution factor for the span gas employed for automatic span checks is computed as f = 0.00961 ±

0.00047 (α = 0.05). Applying the reference gas SL16887e with a concentration of 51.1 ± 1 (ppm) (α = 0.05) to the dilution unit a span gas concentration of 491 ± 26 (ppb) (α = 0.05) is obtained.

Table 5. Inter-comparison of mass-flow controllers at Mt. Kenya GAW station. All flows are expressed at standard conditions (0°C, 1013 mbar)

Model, S/N	Bronkhorst HI-TEC S/N 413212.A 100 ml/min				
Control Unit, S/N	Bronkhorst M1206113A			**Setting**	10.0 %
Date of previous calibration		**Calibration by**	WCC-Empa	**Reference**	Molbloc
Date of last calibration	2006-01-20	**Calibration by**	WCC-Empa	**Reference**	Molbloc
Flows (slpm)	0.01021, 0.01025, 0.01021, 0.01017, 0.01021 0.01025, 0.01021, 0.01021, 0.01021, 0.01021 (n = 10)				
Mean flow (slpm)	**0.010218**		**Standard Deviation (slpm)**		0.000253

Model, S/N	Bronkhorst HI-TEC S/N 413212.B 5000 ml/min				
Control Unit, S/N	Bronkhorst M1206113A			**Setting**	20.0 %
Date of previous calibration		**Calibration by**	WCC-Empa	**Reference**	Molbloc
Date of last calibration	2006-01-20	**Calibration by**	WCC-Empa	**Reference**	Molbloc
Flows (slpm)	1.053, 1.053, 1.053, 1.053, 1.053 1.050, 1.053, 1.053, 1.053, 1.053 (n = 10)				
Mean flow (slpm)	**1.0527**		**Standard Deviation (slpm)**		0.0009

Operation and Maintenance

The instrument is checked for general operation whenever the station is visited (usually once per week). The inlet filter is replaced at least every 2 weeks. The IR source has been changed in the past and the correlation filter wheel has been cleaned once; however, the instrument has never been serviced directly by a TEI representative in the past.

Data Acquisition and Data Transfer

The analogue output of the carbon monoxide analyser was connected to the central Milos 500 data logger that stores one minute averages. The analogue output of the instrument is limited to ca. -100 mV and readings below ca. -100 ppb were not correctly logged. Due to the substantial zero drift of the instrument, readings below this level occurred, resulting in data gaps in the Milos record. The instrument also has an internal data logger that was used to store 5-minute averages including auxiliary instrument parameters. These readings were always reported, regardless of the zero-offset of the instrument. As part of this audit, the serial interface of the instrument was connected to the Milos system, and zero drift of the instrument should henceforth have no consequence for data coverage.

In its present configuration, the logger has a capacity for 12 days data storage. To date, data is manually downloaded to the station computer during station visits. A mechanism for regular, automated data transfer from the Milos system to a high-volume storage medium is highly desirable to avoid the risk of data loss. Moreover, the possibility of remote access to the data on a daily basis is needed to bridge the periods between station visits.

The most economical solution to improve data access and management involves regular, automated transfer of data from the Milos system to the station personal computer and from there to the internet. QA/SAC Switzerland has explored the possibilities available in Kenya and recommends use of GSM-GPRS as offered by Safaricom. QA/SAC Switzerland is willing to lead the technical implementation of this automatic data transfer (cf. Recommendation 11).

Data Treatment

Data is visually inspected and flagged. Both Milos one-minute data (based on analogue output) and 5-minute data from the internal data logger were used in the past [*Kariuki, et al.*, 2006]. In future, the primary data source will be Milos one-minute data obtained directly from the internal data logger. Stable zero/span-readings are used for zero/span-correction using `lowess` regression [*R Development Core Team*, 2004]. Zero corrected data are span-corrected and further aggregated to hourly values. Appropriate uncertainty estimates are provided for each data point. 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

To date, no data have been submitted to the GAW World Data Centre for Surface Ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG). Currently, data are archived and quality-assured by QA/SAC Switzerland in collaboration with the station staff. While it was expected that data could be released to the WDC much earlier, it is planned to finalize the QA process by mid 2006 and submit data then (cf. Recommendation 12).

Documentation

Checklists, an instrument log book, as well as a station log book were available, sufficiently comprehensive and up-to-date. Electronic checklists also exist. During the audit, the checklists were revised to encourage more frequent and more regular manual checks of the instrument calibration (cf. Recommendation 10). The instrument manual is available at the site.

Inter-Comparison of Carbon Monoxide Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation-b] 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-GMD are given in Table 12 in the Appendix. After a first set of comparison runs the field instrument was serviced, resulting in different settings of the instrument and different calibration functions.

Setup and Connections

Table 6 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 both WCC-Empa and Mt. Kenya data acquisition systems as indicated, and no corrections were applied.

Table 6. Experimental details of the carbon monoxide inter-comparison.

Travelling standard (TS)		One cylinder (Sauerstoffwerk Lenzburg, SL68820, 20120±200 ppm in synthetic 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) One cylinder (Sauerstoffwerk Lenzburg, SL68810, 1007±8 ppb in synthetic air) for direct inter-comparison;
Field instrument	Model, S/N	TEI 48C Trace Level #66838-352
	Principle	NDIR, Gas Filter Correlation Technique
	Modification	Nafion drier PERMAPURE PD-50-24'' reflux mode using critical orifice and pump of instrument
	Range	1 ppm
	Settings	Before Service: BKG = 11.466; CO COEFF = 1.132; Initial S/R = 1.158794 After Service: BKG = 0.037; CO COEFF = 1.173; Initial S/R = 1.14302
Connection of TS to field instrument		Sample inlet
Data Acquisition		5-minute aggregates from instrument internal data logger (TEI C Series communications software version 2.2.0)
Levels (ppb)		Level / Reference / St.Uncertainty 1 / 0.00 / 0.05 2 / 76.65 / 0.37 3 / 101.9 / 0.49 4 / 152.4 / 0.73 5 / 202.8 / 0.97 6 / 253.7 / 1.2 7 / 304.1 / 1.5 8 / 405.3 / 1.9 9 / 506.7 / 2.4
Duration per level (min)		90, inclusive of interspersed automatic zero (20') and span (10') checks every second hour
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		7 runs (20 thru 23 January, 2006)

Results

Each carbon monoxide level was effectively applied for 60 – 90 minutes, depending on the occurrence of the 20' automatic zero and 10' automatic span every 120', which resulted in a maximum of 16 useable 5' averages per level and run. These were corrected for zero-drift (using loess regression) and further aggregated by level before use in the assessment (cf. Table 7).

Table 7. CO aggregates (mean and standard uncertainty of mean) computed from 5' averages for each level during the inter-comparison of the Mt. Kenya CO analyzer (CA) with the WCC-Empa transfer standard (TS).

Date Time (UTC)	TS (ppb)	sdTS (ppb)	CO (ppb)	sdCO(ppb)	No. 5' av.
Before Service					
(01/19/06 14:35:00)	0.00	0.051	22.79	2.188	11
(01/19/06 16:20:00)	101.88	0.489	77.81	1.357	17
(01/19/06 18:05:00)	76.65	0.369	59.07	1.133	11
(01/19/06 19:15:55)	253.69	1.216	233.15	1.615	11
(01/19/06 20:32:30)	304.14	1.448	284.63	1.443	12
(01/19/06 22:20:00)	152.37	0.731	135.28	1.321	17
(01/20/06 00:02:30)	202.83	0.972	169.22	1.619	10
(01/20/06 01:11:30)	506.67	2.428	467.86	2.326	10
(01/20/06 02:32:30)	405.27	1.943	372.80	1.589	12
(01/20/06 04:17:30)	0.00[3]	0.051	-11.20	0.901	16
(01/20/06 06:20:00)	101.88	0.489	77.89	2.483	17
(01/21/06 10:54:30)	0.00	0.051	9.42	3.554	10
(01/21/06 12:27:30)	101.88	0.489	92.64	3.526	14
(01/21/06 14:12:30)	76.65	0.369	62.90	2.534	14
(01/21/06 15:45:30)	253.69	1.216	221.42	3.496	10
(01/21/06 16:54:30)	304.14	1.458	267.30	3.504	10
(01/21/06 18:12:30)	152.37	0.731	113.33	2.239	8
(01/21/06 20:12:30)	202.83	0.972	196.77	1.958	14
(01/21/06 21:45:30)	506.67	2.428	455.94	2.281	10
(01/21/06 22:46:00)	405.27	1.943	367.27	1.578	10
(01/22/06 00:25:00)	0.00	0.051	-0.14	2.996	15
(01/22/06 02:10:00)	101.88	0.489	66.52	2.098	13
(01/22/06 03:37:00)	76.65	0.369	67.68	3.181	10
(01/22/06 04:40:00)	253.69	1.216	257.67	2.818	9
After Service					
(01/22/06 10:02:30)	101.88	0.489	94.36	1.059	10
(01/22/06 11:11:30)	76.65	0.369	66.64	3.870	10
(01/22/06 12:32:30)	253.69	1.216	236.69	1.846	12
(01/22/06 14:17:30)	304.14	1.458	273.62	2.355	16
(01/22/06 16:02:30)	152.37	0.731	137.65	1.431	10
(01/22/06 17:06:40)	202.83	0.972	190.27	1.141	9
(01/22/06 18:32:30)	506.67	2.428	492.16	2.118	12
(01/22/06 20:17:30)	405.27	1.943	380.68	1.295	16
(01/22/06 22:00:00)	0.00	0.051	-9.88	1.717	9
(01/22/06 23:07:44)	101.88	0.489	93.07	1.445	11
(01/23/06 00:32:30)	76.65	0.369	68.36	2.388	12
(01/23/06 02:15:00)	253.69	1.216	237.28	1.148	15
(01/23/06 03:54:00)	304.14	1.458	290.38	2.043	10
(01/23/06 05:03:00)	152.37	0.731	139.82	1.095	10
(01/23/06 06:30:00)	202.83	0.972	191.10	1.717	13

[3] MKN zero-air generator

Date Time (UTC)	TS (ppb)	sdTS (ppb)	CO (ppb)	sdCO(ppb)	No. 5’ av.
(01/23/06 08:15:00)	506.67	2.428	485.80	1.390	15
(01/23/06 14:20:00)	0.00	0.051	4.17	0.921	17
(01/23/06 16:05:00)	101.89	0.489	96.82	0.888	11
(01/23/06 17:15:33)	76.65	0.369	70.60	1.649	9
(01/23/06 18:32:30)	253.69	1.216	244.76	1.485	12
(01/23/06 20:17:30)	304.14	1.458	293.40	1.435	16
(01/23/06 22:02:30)	152.37	0.731	145.30	1.643	10
(01/23/06 23:11:30)	202.83	0.972	192.62	2.335	10
(01/24/06 00:32:30)	506.67	2.428	484.21	1.034	12
(01/24/06 02:17:30)	405.27	1.943	395.71	1.383	16
(01/24/06 04:02:30)	0.00	0.051	5.74	1.415	10
(01/24/06 05:07:44)	101.88	0.489	95.45	1.834	11
(01/24/06 06:32:30)	76.65	0.369	67.24	1.819	12

Figure 8 shows the regression residuals of the analyzer over the course of the first 3 runs, before service of the instrument. The absence of a temporal trend (upper panel) indicates stable instrument conditions, even though the data are noisy. The absence of a concentration dependence (lower panel) in the residuals indicates linearity of the instrument.

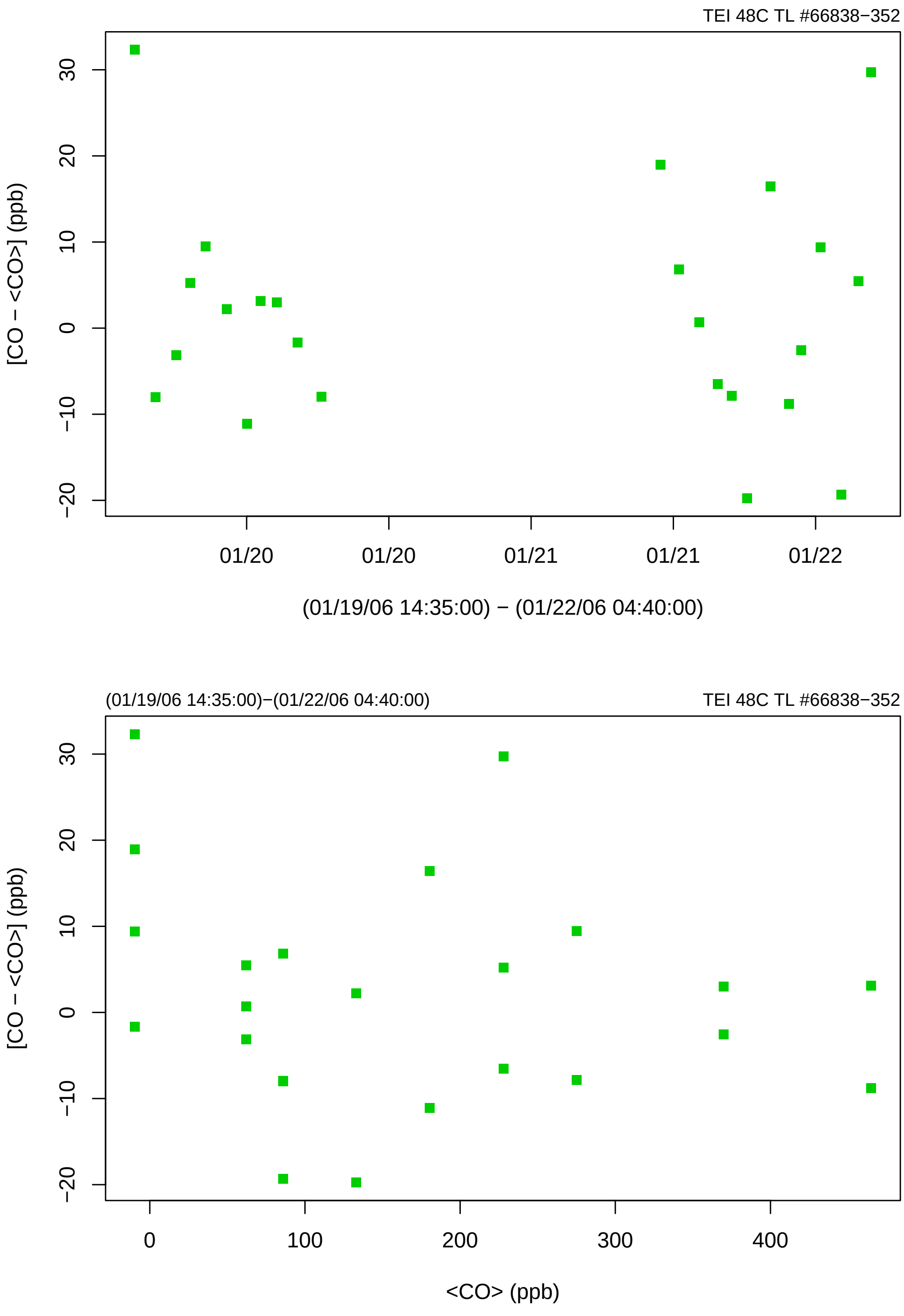


Figure 8. Regression residuals of the Mt. Kenya carbon monoxide analyser before service of the instrument. Points represent averages of valid 5'-aggregates. Upper panel: time dependence; Lower panel: Concentration dependence.

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 **before the service** of the analyser using equation

$$X_{CO}\ (ppb) = (CO + 9.5)/\ 0.936$$

$$u_{CO}\ (ppb) = =sqrt(209\ ppb^2 + 4.06e\text{-}05 * X_{CO}^2) \quad (2a)$$

Figure 9 shows the regression residuals of the analyzer after service of the instrument. The absence of a temporal trend (upper panel) indicates stable instrument conditions, even though the data are noisy. The absence of a concentration dependence (lower panel) indicates linearity of the instrument.

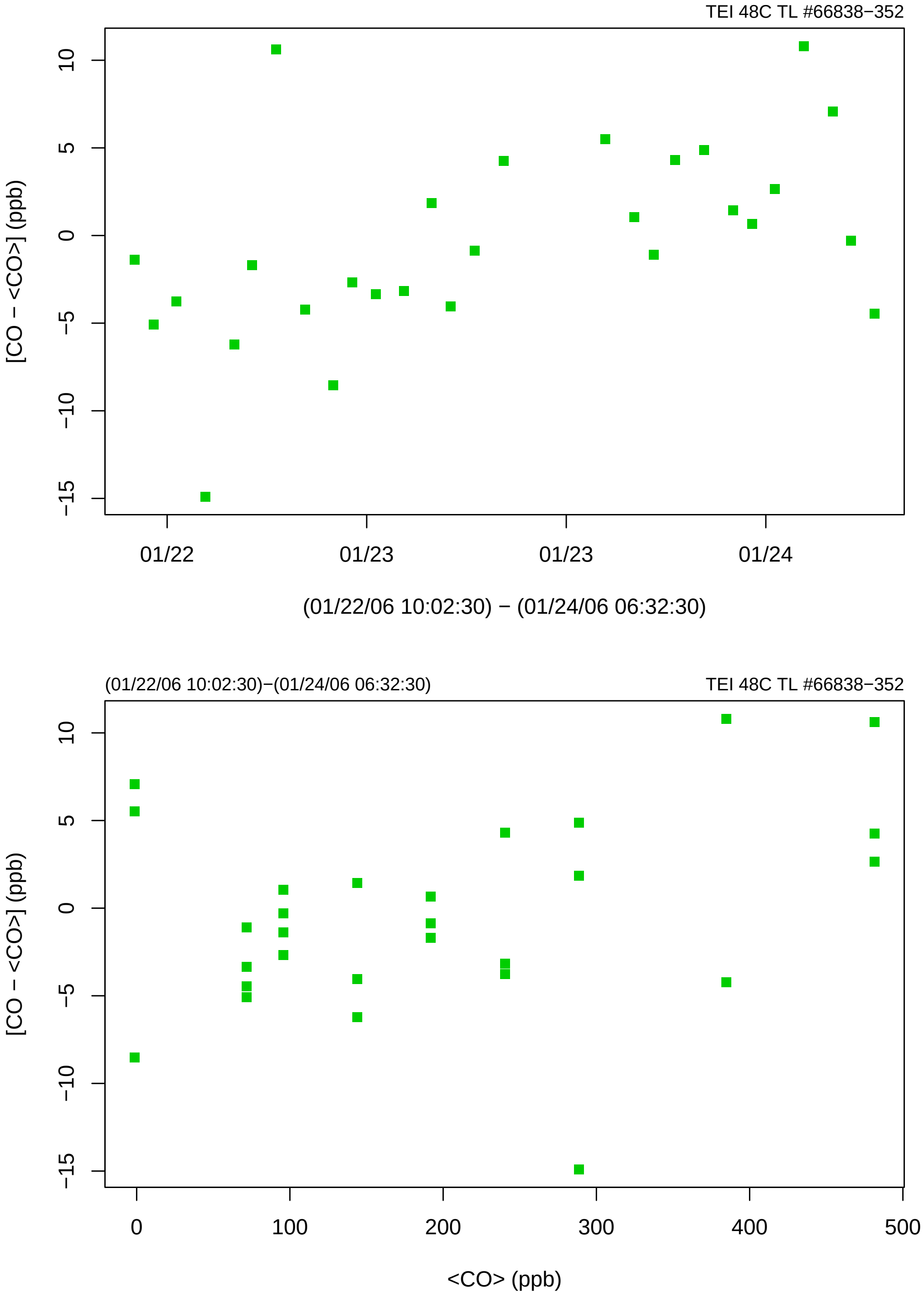


Figure 9. Regression residuals of the Mt. Kenya carbon monoxide analyser as a function of concentration after service and calibration of the instrument. Points represent averages of valid 5'-aggregates. Upper panel: Time dependence; Lower panel: Concentration dependence

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 minute averages can be computed from the zero corrected five-minute data CO that was taken **after the service** of the analyser:

$$\mathbf{X_{CO}\ (ppb) = (CO + 1.35) / 0.953}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(45\ ppb^2 + 3.40e\text{-}05 * X_{CO}^2)} \qquad (2b)$$

Discussion

The inter-comparison between WCC-Empa and Mt. Kenya station showed relatively large deviations from the reference value and relatively large uncertainties. The bias and the remaining uncertainty were reduced after service and calibration of the instrument.

The combined uncertainty of the instrument is composed of various elements, namely

a) Instrument drift: The TEI 48C shows a significant zero drift even after warm-up that appears to be correlated with the laboratory temperature; and an intolerable drift during warm-up (e.g., after power failures). All raw data has to be zero corrected before further use.

b) Instrument noise: The uncertainty of 5' averages due to noise was estimated to be $u_{TEI48C,noise}$ = 6.6 ppb (σ=2.6, n=52) at zero and different span levels. This is within the limits of the manufacturer's specification.

c) Linearity: The uncertainty of 5' averages due to non-linearity was estimated as the standard deviation of the regression residuals of the inter-comparison, minus the noise component, resulting in $u_{TEI48C,linearity}$ = 2.9 ppb.

d) Instrument drift: The instrument specification $u_{TEI48C,drift.span}$ = 0.005 * CO was used, while assuming that the uncertainty due to zero drift is taken care of by the zero correction.

The contribution of the MKN TEI48C instrument to the combined standard uncertainty of the mixing ratios determined (i.e. ignoring uncertainties in the calibration) is then estimated as

$$\mathbf{u_{TEI48C} = sqrt(u^2_{TEI48C,noise} + u^2_{TEI48C,linearity} + u^2_{TEI48C,drift.span}) = sqrt(7.2^2 + 0.005^2 * X_{CO}^2)} \qquad (4)$$

which is within the range of the manufacturer's specification.

Changes made to the instrument

After a first set of inter-comparison runs, the TEI48C was serviced. This included cleaning of the correlation filter wheel and setting the S/R ratio. See

Table 6 for changes in instrument parameters after the service. In addition, the Nafion drier was exchanged (old model: PD-50T-24PP, SN 289-0601-14; new model: PD-50T-24MPP, SN: 298-1105-10). No change in the instrument readings (under zero and span conditions) could be observed after the replacement.

Conclusions

The TEI 48C was found to operate well within the limits of the instrument specifications. It is important to consider the uncertainties of the estimated CO concentration in any further analysis of the data. The analyser showed a large bias before the audit and data obtained prior to this audit should be corrected. After service and calibration of the instrument, this bias was reduced but should still be corrected.

Vertical ozone profiles, KMD Nairobi (NRB)

Vertical ozone profiles are obtained weekly using balloon soundings. As an additional service to the Kenya GAW activities, the ozone calibrator based at KMD Headquarters in Nairobi was also inter-compared. This instrument is used to check the ozone sondes prior to launch.

Inter-Comparison of Ozone Calibrator

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

Setup and Connections

The internal ozone-generator of the ozone calibrator at KMD was disconnected so that the analyser unit of the instrument could be operated independently. Table 8 details the experimental setup during the inter-comparison of transfer standard and station analyser. The data used for the evaluation was recorded as indicated, and no corrections were applied.

Table 8. Experimental details of the ozone inter-comparison.

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.012
Ozone calibrator (OC)	Model, S/N	TEI 49PS #53677-297
	Settings	Gain = 6 ; Ozone = 000
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 meter of 1/4" PFA tubing between TS manifold and inlet filter of OC
Data acquisition	TS	One minute aggregates from digital output (custom designed LabView programme)
	OC	One minute aggregates of 0 – 1 V analogue output (Onset HOBO U12-013 data logger)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	819.8 (KMD pressure sensor)
	TS	821.0, not adjusted
	OC	821.0, not adjusted
Levels (ppb)		0, 15, 35, 55, 75, 90, 140, 195
Duration per level (min)		20
Sequence of Levels		Repeated runs of randomised fixed sequence
Runs		31 runs (25 thru 26 January, 2006)

Results

Each ozone level was applied for 20 minutes, and the last 10 one-minute averages were aggregated (cf. Table A1). These aggregates were used in the assessment of the inter-comparison as described elsewhere [*Klausen, et al.*, 2003]. All results refer to the calibration factors as given in Table 2 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

Figure 10 shows the regression residuals of the calibrator in the analyzer configuration (OA) both as a function of time and concentration. No temporal trend is evident in the data, indicating stable instrument conditions. It was apparent that the instrument exhibits slight non-linear behaviour in the low concentration range (cf. Figure 3). Therefore, the zero point was excluded for the regression analysis. Care should be taken if the instrument is used at mixing ratios below about 30 ppb.

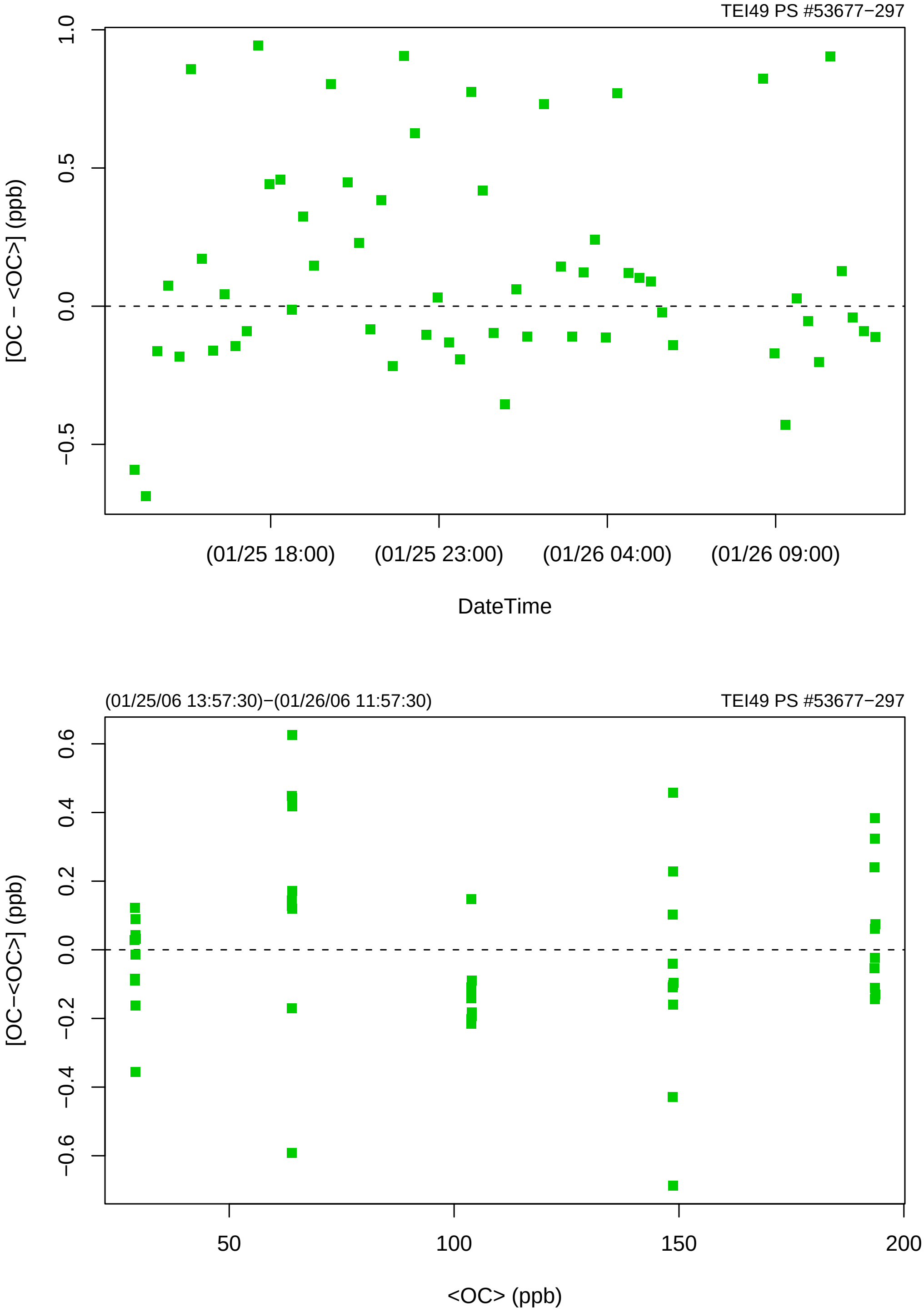


Figure 10. Regression residuals of the Nairobi ozone calibrator. Each point represents the average of the last 10 one-minute values at a given level. Upper panel: Time dependence; Lower panel: Concentration dependence

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

$$\mathbf{X_{OC}\ (ppb) = ([OC] + 0.87\ ppb) / 0.998}$$

$$\mathbf{u_{OC}\ (ppb) = (0.42\ ppb^2 + 2.61e\text{-}05\ X_{OC}^2)^{0.5}} \qquad (3)$$

Changes Made to Instrument

Changes made to the instruments were restricted to the disconnection and reconnection of tubing necessary to isolate the analyzer unit of the calibrator. All changes were reversed after completion of the inter-comparison, and all settings remained.

Conclusions

The ozone calibrator fully meets the assessment criteria and is perfectly adequate for its intended use. The bias of about -0.88 ppb can be corrected, but is well within the expanded uncertainty (and the display resolution) of the instrument. Because the instrument is fairly old and approaching the end of its useful life-time, we recommend to plan ahead and foresee the necessity of replacement within the next 3 years (cf. Recommendation 13).

WCC-Empa Transfer Standards

Ozone

The WCC-Empa transfer 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 summarized in Table 9, the inter-comparison data is given in Table 10.

Table 9. Experimental details of the inter-comparison of transfer standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.012
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (CO catalyst, 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 (13 December, 2006) 3 runs after return of TS (15 February, 2006)

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

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2005-12-13	1	0	0.22	0.36	-0.16	0.06
2005-12-13	1	140	140.13	0.37	139.53	0.10
2005-12-13	1	90	89.89	0.27	89.63	0.18
2005-12-13	1	30	30.12	0.26	30.20	0.12
2005-12-13	1	190	188.67	0.20	188.55	0.08
2005-12-13	1	60	60.29	0.16	60.14	0.12
2005-12-13	1	0	-0.09	0.26	-0.14	0.06
2005-12-13	2	0	0.05	0.25	-0.01	0.04
2005-12-13	2	90	89.52	0.37	89.58	0.10
2005-12-13	2	190	188.53	0.39	188.41	0.14
2005-12-13	2	60	59.98	0.34	60.18	0.07
2005-12-13	2	140	139.42	0.36	139.23	0.12
2005-12-13	2	30	30.40	0.32	30.37	0.09
2005-12-13	2	0	-0.10	0.21	-0.13	0.07
2005-12-13	3	0	-0.08	0.28	-0.13	0.06
2005-12-13	3	30	30.22	0.26	30.00	0.09
2005-12-13	3	190	188.68	0.21	188.31	0.09
2005-12-13	3	90	89.61	0.26	89.69	0.08
2005-12-13	3	140	139.30	0.33	139.21	0.11
2005-12-13	3	60	60.17	0.21	60.22	0.05
2005-12-13	4	0	-0.05	0.29	-0.01	0.08
2006-02-15	4	0	-0.15	0.34	-0.03	0.08
2006-02-15	4	140	135.39	0.15	135.1	0.15
2006-02-15	4	90	86.84	0.31	86.74	0.05
2006-02-15	4	30	29.12	0.26	28.88	0.07
2006-02-15	4	190	183.62	0.25	183.6	0.17
2006-02-15	4	60	58.13	0.19	58.32	0.07
2006-02-15	4	0	0.02	0.34	0	0.09
2006-02-15	5	0	0.14	0.34	-0.08	0.09
2006-02-15	5	90	86.86	0.21	86.9	0.08
2006-02-15	5	190	183.91	0.44	184.35	0.21
2006-02-15	5	60	58.49	0.3	58.57	0.11
2006-02-15	5	140	135.86	0.29	135.98	0.08
2006-02-15	5	30	29.33	0.26	29.42	0.11
2006-02-15	5	0	0.2	0.24	-0.06	0.09
2006-02-15	6	0	0.02	0.42	0.03	0.08
2006-02-15	6	30	29.27	0.37	29.33	0.08
2006-02-15	6	190	183.93	0.41	184.2	0.13
2006-02-15	6	90	87.18	0.31	87.67	0.1
2006-02-15	6	140	136.02	0.26	136.32	0.13
2006-02-15	6	60	58.43	0.29	58.73	0.11
2006-02-15	6	0	-0.12	0.27	-0.03	0.09

#The level is only indicative.

The transfer standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 11). 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]).

$$\mathbf{X_{TS}\ (ppb) = ([TS] + 0.03\ ppb) / 1.0002}$$

$$\mathbf{u_{TS}\ (ppb) = sqrt((0.43\ ppb)^2 + (0.0034 * X)^2)} \quad (4)$$

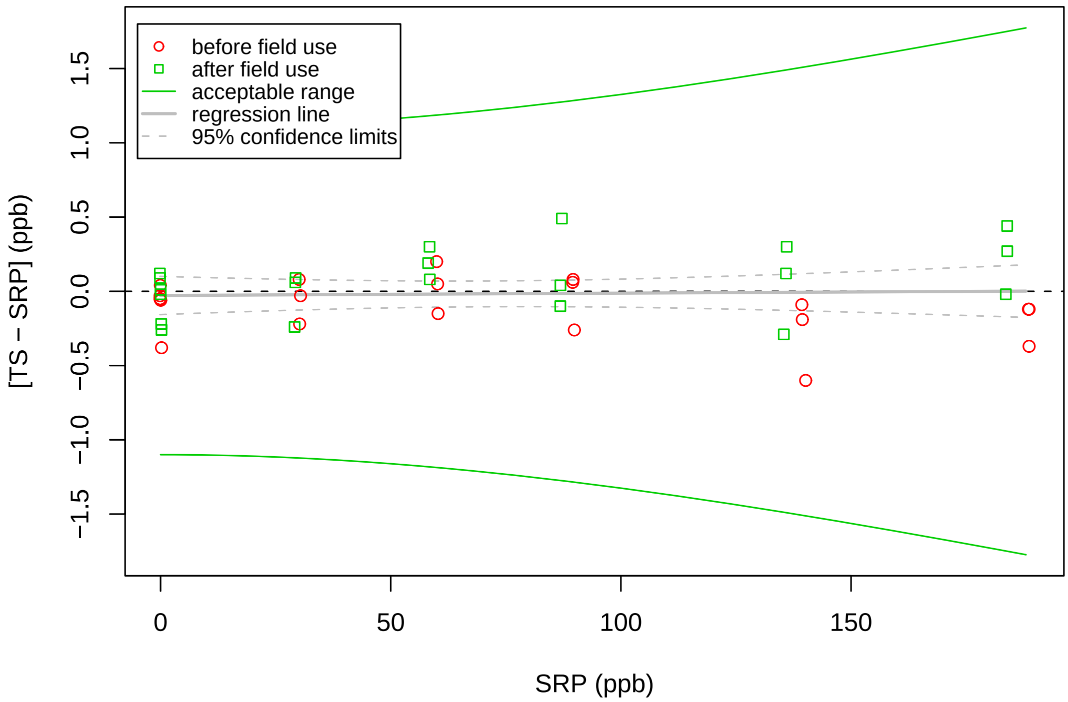


Figure 11. Deviations between transfer standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 AL5001 vacuum-fluorescence analyzer (Aerolaser), an instrument with high precision and proven linearity. Details are given in Table 11 and Table 12.

Table 11. 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 is 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 – Rubingel drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder	Sauerstoffwerk Lenzburg, SL68820, 20120±200 (α=0.05). Cylinder remained at the station.
(3) Dilution unit	Breitfuss MGM #2262/91/1. The levels used were calibrated before and after the field inter-comparison against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851).
Connection between instruments	Ca. 2.5 meter 1/4" PFA tubing
Data acquisition	Aerolaser 1-min averages
Levels (ppb)	0, 75, 100, 150, 200, 250, 300, 400, 500
Duration per level (min)	Three 4-minute averages alternating with calibrations
Sequence of Levels	Repeated runs of randomised sequence
Runs	3 runs before shipment of TS (13 December, 2006) 3 runs after return of TS (15 February, 2006)

Table 12. Calibration of Breitfuss dilution system and carbon monoxide mixing ratios.

Date	Mass Flow Controller MFC 1 (mL min^{-1})		Mass Flow Controller MFC 2 (mL min^{-1})		Carbon Monoxide Mixing Ratio (ppb)	
	Setpoint	Measured#	Setpoint	Measured	Expected	Measured#
2005-12-13	2000.0	1992.2±0.3	0.000	-0.023±0.416	0.0	-0.1±0.5
2005-12-13	1990.1	1984.2±0.3	9.940	10.085±0.007	101.7	101.7±0.8
2005-12-13	1992.5	1986.1±0.3	7.455	7.596±0.006	76.7	76.1±0.8
2005-12-13	1975.1	1968.4±0.3	24.851	25.091±0.007	253.2	252.2±1.4
2005-12-13	1970.2	1963.1±0.3	29.821	30.088±0.009	303.7	304.0±1.4
2005-12-13	1985.1	1977.6±0.3	14.911	15.071±0.008	152.2	152.0±0.8
2005-12-13	1980.1	1972.6±0.3	19.881	20.082±0.007	202.8	201.9±1.3
2005-12-13	1950.3	1942.1±0.3	49.702	50.080±0.006	505.8	505.5±1.6
2005-12-13	1960.2	1951.8±0.3	39.761	40.062±0.008	404.7	405.2±2.2
2006-02-21	2000.0	1993.6±0.2	0.000	0.182±0.002	0.0	NA
2006-02-21	1990.1	1984.3±0.3	9.940	10.083±0.002	101.7	NA
2006-02-21	1992.5	1987.9±0.2	7.455	7.592±0.002	76.5	NA
2006-02-21	1975.1	1970.0±0.2	24.851	25.156±0.002	253.7	NA
2006-02-21	1970.2	1965.1±0.3	29.821	30.188±0.002	304.4	NA
2006-02-21	1985.1	1979.5±0.2	14.911	15.100±0.002	152.3	NA
2006-02-21	1980.1	1974.3±0.2	19.881	20.134±0.002	203.1	NA
2006-02-21	1950.3	1943.8±0.2	49.702	50.264±0.002	507.2	NA
2006-02-21	1960.2	1953.9±0.2	39.761	40.206±0.002	405.7	NA

#Average±sd (n =10); NA: data not available because cylinder was not shipped back to WCC-Empa

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:	20 – 23 January, 2006
1.2	Auditors:	Dr. J. Klausen, Dr. S. Henne
1.2.1	Station staff involved in audit:	J. Rotich, J. Kariuki, J. 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 #54509-300
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0002±0.0010) × [SRP] - (0.03±0.08)
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49 # 51959-290
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	OFFSET: 49 SPAN: 509
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.005±0.001) × [SRP] - (1.36±0.06)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] + 1.3632) / 1.00455
1.5.6	Standard uncertainty of 5' aggregates after compensation of calibration bias (ppb) at start of audit:	$u_X \approx (0.40\ \text{ppb}^2 + 0.00003 \times X^2)^{1/2}$
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 of 5' aggregates after compensation of calibration bias (ppb) after audit:	unchanged
1.6	Comments:	Instrument enters faulty condition with a constant offset of -9.6 ppb at random and should be replaced as soon as possible. Assessment valid for mixing ratios > 15 ppb.
1.7	Reference:	WCC-Empa Report 06/1

[OA]: Instrument readings; [SRP]: SRP readings; X: volume 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:	20 – 23 January, 2006
1.2	Auditors:	Dr. J. Klausen, Dr. S. Henne
1.2.1	Station staff involved in audit:	J. Rotich, J. Kariuki, J. Aseyo
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	SL68820, 20120±200 (ppb) (α=0.05)
1.4.2	Zero Air:	Ambient Air, Sofnocat, Purafil, filter (WCC-Empa)
1.4.3	Dilution unit:	Breitfuss MGM #2262/91
1.4.4	Range of calibration:	0 – 500 ppb
1.5	CO analyzer [CA]	
1.5.1	Model:	TEI 48C TL # 66838-352
1.5.2	Range of calibration:	0 – 500 ppb
1.5.3	Coefficients at start of audit	BKG: 11.466 CO COEF: 1.132
1.5.4	Calibration at start of audit (ppb):	CO = (0.936±0.003) $\times$ X - (9.5±0.6)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 9.5) / 0.936
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (205\ ppb^2 + 4.06e\text{-}05 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	BKG: 0.037 CO COEF: 1.173
1.5.8	Calibration after audit (ppb):	CO = (0.953±0.002) $\times$ X - (1.3±0.5)
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	X = (CO + 1.3) / 0.953
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	$u_X \approx (45\ ppb^2 + 3.40e\text{-}05 \times X^2)^{1/2}$
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 06/1

[CO]: Zero-corrected instrument readings; X: volume mixing ratios on the WMO-2000 CO scale.

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 (NRB)

0.1	Station Name:	Dagoretti Corner, Nairobi
0.2	GAW ID:	NRB
0.3	Coordinates/Elevation:	1.300°S 36.750°E (1798 m a.s.l.)
Parameter:		Surface Ozone (Calibrator)

1.1	Date of Audit:	25 – 26 January, 2006
1.2	Auditors:	Dr. J. Klausen, Dr. S. Henne
1.2.1	Station staff involved in audit:	J. Rotich, J. Kariuki, J. 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 #54509-300
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0002±0.0010) × [SRP] - (0.03±0.08)
1.5	Ozone Calibrator [OC]	
1.5.1	Model:	TEI 49 PS # 53677-297
1.5.2	Range of calibration:	0 – 190 ppb
1.5.3	Coefficients at start of audit	not applicable
1.5.4	Calibration at start of audit (ppb):	[OC] = (0.998±0.001) × [SRP] - (0.87±0.09)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OC] + 0.87) / 0.998
1.5.6	Standard uncertainty of 5' aggregates after compensation of calibration bias (ppb) at start of audit:	$u_X \approx (0.42\ ppb^2 + 0.00003 \times X^2)^{1/2}$
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 5' aggregates after compensation of calibration bias (ppb) at start of audit:	unchanged
1.6	Comments:	Assessment valid for mixing ratios > 30 ppb.
1.7	Reference:	WCC-Empa Report 06/1

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

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