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World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Materials Science & Technology

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SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE AND CARBON MONOXIDE AT THE GLOBAL GAW STATION MT. KENYA KENYA, JUNE 2010

Submitted by
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ASSESSMENT AND RECOMMENDATIONS

The sixth system and performance audit at the Global GAW station Mt. Kenya (MKN) was conducted by QA/SAC-Switzerland and WCC-Empa[1] from 15 thru 25 June 2010 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The MKN observatory was established in 1996 and is operated by the Kenya Meteorological Department (KMD).

In addition to the audit, a Picarro G1301 instrument was installed at the station for continuous observations of carbon dioxide and methane. This project was funded by MeteoSwiss.

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], January 2006 [*Klausen, et al.*, 2006], and November 2008 [*Zellweger, et al.*, 2008].

The following people contributed to the mission:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Dr. Charles Mutai	Kenya Meteorological Department
Mr. Kennedy K. Thiong'o	Kenya Meteorological Department
Mr. Constance C. Okuku	Kenya Meteorological Department
Mr. John Aseyo	Kenya Meteorological Department
Mr. Charles Kioko	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 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. Kennedy K. Thiong'o), the station manager and operator, and the World Meteorological Organization in Geneva. The report will be made available on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date. Some of the recommendations were already made after previous audits; these are repeated in the current report for issues that have not yet been resolved.

Station Location and Access

The Global GAW station Mt. Kenya is located at high altitude in equatorial Africa. This location provides a unique opportunity to monitor background air as well as to conduct research in a data-sparse region of the world. 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. The road improved slightly since the last audit in 2008; the improvements following substantial efforts made in 2009 have basically been eradicated by the rains in the following rainy season. Access to the site remains difficult and the road requires regular maintenance. KMD is commended for bringing the operations at Mt. Kenya GAW station to the attention of other agencies in the country. 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 Kenya Wildlife Service (KWS), the Kenya Power and Lightning Company (KPLC) and other involved partners.
Recommendation 2 (, ongoing)**
KMD must ensure that the access to the site is possible year round. A dedicated and well maintained Land Rover is needed, and costs for maintenance and replacement should be anticipated in the 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 small but 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 radiator has been provided to the station during the audit.

The power supply to the station improved until 2009, but a bushfire caused severe damage to the power line in March 2009. As a consequence, power became extremely unreliable since November 2009. The current situation is inadequate due to frequent failures that prohibit sustainable operation of the station. In addition, the UPS unit was damaged by a power surge. As a consequence, the data coverage decreased to less than 20 % since November 2009.

It was noticed during the audit that the whole instrument rack was under power of approximately 100 V; however, the reason could not be identified. This is a security issue, and the electrical installation of the station needs to be checked.

The facilities at the station are complemented by an office in Nanyuki. However, the facilities are not adequate; the available computer is no longer capable for data analysis, and viruses were abundant due to lack of internet access and outdated virus definitions of the anti-virus software.

Recommendation 3 (*, immediately)**
KMD, together with KPLC and KWS, must ensure a sustainable power supply to the station since this is a prerequisite for successful operation of the station. The options include replacement of the current cable by vertically spread, PVC coated cables or an underground power line, as well as local power production (wind or solar).

Recommendation 4 (*, immediately)**
The UPS unit needs to be repaired and serviced. Since the batteries have a limited lifetime, replacement should be anticipated in the budgetary planning process. Furthermore, the whole electrical installation of the stations needs a careful check, since leakage caused the instrument rack to be energised by 100 V. In addition, the fuse box needs to be redesigned to account for the additional instrumentation and the high start-up current after a power failure.

Recommendation 5 (*, immediately)**
Internet access is needed both at the station and the Nanyuki office. The bills of the Safaricom modem in use at MKN must be settled in time.

Recommendation 6 (*, 2010-11)**
KMD needs to allocate a budget for the Mt. Kenya station / Nanyuki office:
- Clothing, other equipment for operators.
- New office computers that are needed to work with data.

Recommendation 7 (, 2010-11)**
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.
- Construct housing for the generator to reduce noise.
- Clean out the station (decommissioned instruments and other unused items).

Station Management and Operation

In the beginning of continuous operations the station was usually visited weekly by officers of the Kenya Meteorological Department (KMD) who reside in nearby Nanyuki (2 h from the station). For several year during the recent past these visits were less regular due to prolonged power outages. The staff consists of one meteorologist and a technician. As of 1st July 2010, both positions were assigned with new personnel. It is regarded of highest importance that the technical expertise to operate and maintain the equipment is transferred to the new staff. Furthermore, more scientific experience is needed to work with the data. A twinning relationship between KMD, Mt. Kenya staff and QA/SAC Switzerland is ongoing, but communication remains difficult. Collaboration with external partners is important for the future of the station, and the recently established co-operation between KMD and the University of Nairobi (UoN) should be intensified. The web presence of the Mt. Kenya GAW station is currently still limited. In order to improve the visibility of KMD's GAW activities within Kenya and abroad, a better web coverage should be considered.

Recommendation 8 (*, 2010-11)**
Technical expertise must be transferred to the new station manager and technician. It is of highest priority that the knowledge of the former technician will still be available; KMD is encouraged to facilitate this process.

Recommendation 9 (*, on-going)**
KMD still needs to intensify technical and scientific exchange with existing and new external partners, and to participate more actively in such partnerships.

Recommendation 10 (, on-going)**
KMD successfully established collaboration with the University of Nairobi. Such activities are important for the station and should be continued. KMD could explore if internships of UoN students based at Nanyuki/MKN are feasible. In addition, it is recommended to highlight the Kenyan GAW activities on the KMD web pages and to maintain GAWSIS.

Recommendation 11 (*, on-going)**
KMD is invited to continue taking advantage of the opportunity for training offered by GAWTEC. Especially, the participation of the new station technician is of highest importance. 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 for the measurements performed, although no additional ports are available at the main manifold. The greenhouse gas measurements are using their own dedicated inlets on the meteo mast, as well as one port of the manifold.

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. The current instrumentation is adequate for its intended purpose. During the audit, the instrument fuse blew as a result of a power surge. The fuse could be replaced, but a stock of spare fuses as well as protection by the UPS is elemental for successful operation of the instrument.

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 12 (*, 2011-13)
KMD is encouraged to seek funding to purchase an ozone calibrator for use at the Mt. Kenya station.

Comparison (Performance Audit). The comparisons extended over a several hours. 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] - 0.29 ppb) / 0.999 (1)

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

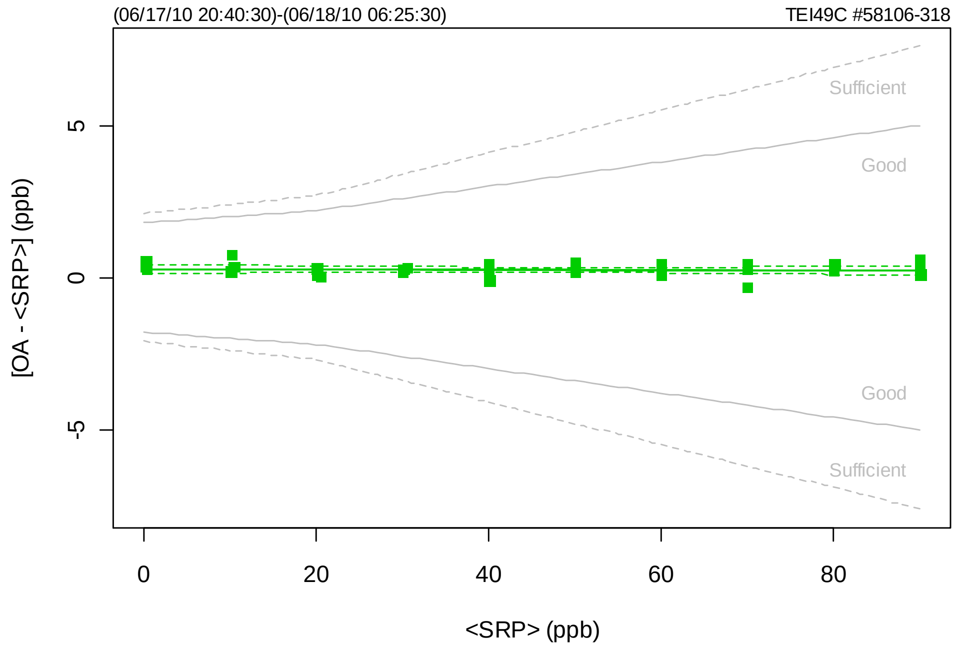


Figure 1. Bias of the Mt. Kenya ozone analyser (TEI 49C) with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 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 WCC-Empa audit in 2008 in addition to the TEI 48C-TL [*Zellweger, et al.*, 2008]. The instruments have been running in parallel for a few months; however, the internal battery of the TEI 48C-TL was empty at the time of the audit. The instrument therefore lost the internal time, and the data could not be compared. Both analysers were compared during the audit. The new instrumentation is adequate for the intended purpose; however, this instrument showed periods with low readings during the audit. A possible reason could be the instable power supply from the generator in combination with short warm-up times. If the problem persists with the instrument connected to the main power supply, the reason for this behaviour must be identified.

Recommendation 13 (*, 2010-11)**
Data of the Horiba instrument need to be carefully controlled once the main power re-established at the site; if periods with negative readings occur, the instrument needs to be serviced.

Recommendation 14 (*, 2010-11)
The TEI 48C analyser should be decommissioned and used at a polluted site, e.g. in Nairobi.

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.

Recommendation 15 (*, 2010-11)**
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. This is especially becoming important with the recent addition of more parameters (CH_4 and CO_2), for which the same recommendation also apply.

Comparison (Performance Audit). The 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] + 6.8 ppb) / 0.9779 (2)

TEI 48C-TL #66838-352 (Zero 4.107, SPAN 1.173):

Unbiased CO mixing ratio (ppb): XCO (ppb) = ([CO] + 8.2 ppb) / 1.0630 (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. The current comparison was done with only very short warm-up time due to limited availability of power.

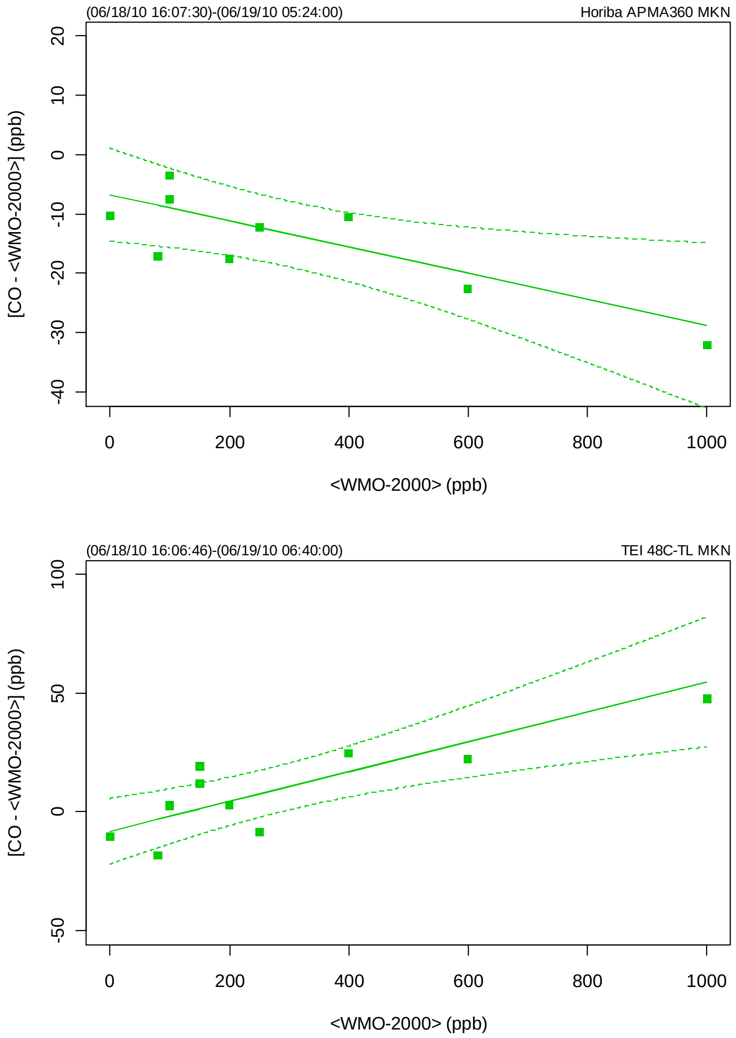


Figure 2. Bias of the Mt. Kenya carbon monoxide analysers (Horiba APMA360, upper panel, and TEI 48C-TL, lower panel) with respect to the WMO-2000 reference scale as a function of mole fraction. Note the different scales. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Data Acquisition and Management

The station is equipped with a centralised LabView-based data acquisition system developed by QA/SAC-Switzerland that is currently designed to acquire surface ozone, CO, meteorological parameters, black carbon and GPS data of MKN. Automatic data transmission using GSM connectivity was set up during the audit. Data are automatically transferred to an FTP server at Empa, and transfer to KMD is planned as soon as the infrastructure at KMD becomes available. Towards the end of the audit, the automatic data transfer was discontinued because the GSM connection had been cut by the provider as a result of unsettled accounts.

Recommendation 16 (, 2010-11)**
KMD should open an FTP account located on KMD servers for direct data transmission to KMD (accomplished in July 2010). QA/SAC-Switzerland should establish direct data transfer to KMD servers.
The internet access at MKN needs urgently to be re-established (cf. recommendation 5).

Documentation and Maintenance

The station is currently irregularly visited by station operators. For a successful operation of the station, regular visits at least once per week are necessary. It was noticed during the audit that the information available in log books and check lists was not always comprehensive and complete. In addition, communications with external partners on station related issues needs to be improved.

Recommendation 17 (*, ongoing)**
Documentation is a key aspect for a successful operation of a GAW station and needs more attention by the station staff. SOPs are needed for all instruments as well as for the data acquisition, the UPS and power supply, and the generator. Log files and check lists need to be carefully filled in and should be maintained and distributed electronically.

Recommendation 18 (*, 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 twinning 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 19 (, 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. Submission of recent CO and ozone data is strongly encouraged.

Expansion of the MKN measurement programme with CH_4 and CO_2 Measurements

QA/SAC-Switzerland and WCC-Empa installed a Picarro G1301 system for the continuous measurements of CH_4 and CO_2 at MKN. Due to limited power availability, the system could not be extensively tested at the station. Details of the instrument set-up are given in Appendix I. The instrumentation is state of the art for the intended purpose; however, issues related to the Nafion drier need further measurements for final conclusions; it might be advisable to bypass the drier and to apply a correction for water vapour. This is not of highest priority because accurate measurements are possible with the current set-up.

Conclusions

The Global GAW station Mt. Kenya comprises a still growing suite of ongoing measurements. All assessed parameters were of sufficiently high quality. With the addition of continuous CO_2 and CH_4 measurements during the current audit, information about climate relevant gases as well as other parameters will now be available from a geographical region where only sparse in-situ information about atmospheric composition exists. However, the lack of a stable power supply jeopardises the operation of the MKN station. This issues needs to be solved immediately to ensure continuous support of external partners.

The findings of the audit were discussed with the Director of KMD, Dr. Joseph Mukabana; the minutes of the meeting are attached to this report in Appendix II.

Summary Ranking of Mt. Kenya Station

System Audit Aspect	Adequacy#	Comment
Access	(2)	Subject to road and weather conditions
Facilities		
Laboratory and office space	(2)	Basic facilities only; no sanitary installations
Internet access	(3)	Available through GSM modem, currently out of service
Air Conditioning	(0)	Not available
Power supply	(0)	No sustainable power supply
General Management and Operation		
Organisation	(3)	Communication with external partners difficult at times
Competence of staff	(2)	Technical and scientific training of new staff needed
Air Inlet System	(4)	Adequate system
Instrumentation		
Ozone	(5)	TEI 49C
Carbon monoxide	(3)	NDIR instrument
Carbon dioxide / methane	(5)	Picarro G1301
Aerosol light absorption	(2)	Available, partial operation
Flask sampling	(5)	NOAA/ESRL programme
Meteo	(5)	Automated weather station
Standards		
Ozone	(0)	Not available
CO, CH_4 and CO_2	(3)	Only available through external partners
Data Management		
Data acquisition	(3)	Robust internet access needed
Data processing	(3)	Support of twining partners
Data submission	(3)	Data partly submitted, large delays

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

Dübendorf, December 2010

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

APPENDIX I

Global GAW Station Mt. Kenya

Site description

Information about the Mt. Kenya GAW station can be found in previous audit reports [*Herzog, et al.*, 2000; *Klausen, et al.*, 2006; *Zellweger, et al.*, 2002; *Zellweger, et al.*, 2005; 2008], 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. An overview of the measurement programme and its status as of July 2010 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			
Ozone				
Surface ozone	UV absorption (TEI 49C)			
Greenhouse Gas				
CO_2	AIRCOA			
CO_2 and CH_4	Picarro G1301	NA	NA	NA
CO_2, CH_4, SF_6, N_2O	NOAA/ESRL flask sampling			
Reactive Gas				
CO	NDIR (HORIBA APMA360)			
CO, H_2	NOAA/ESRL flask sampling			
Solar radiation				
Global irradiance	Pyranometer (Kipp & Zonen)			
Diffuse irradiance	Pyranometer (Kipp & Zonen)			
Isotopes				
CO_2 (C-13), CO_2 (O-18)	NOAA/ESRL flask sampling			
Meteo				
PTU, wind speed + direction				

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

Ozone, Carbon Monoxide, Carbon Dioxide and Methane Distribution at Mt. Kenya

The monthly and yearly distributions for surface ozone, carbon monoxide, methane and carbon dioxide oxide are shown in Figure 3.

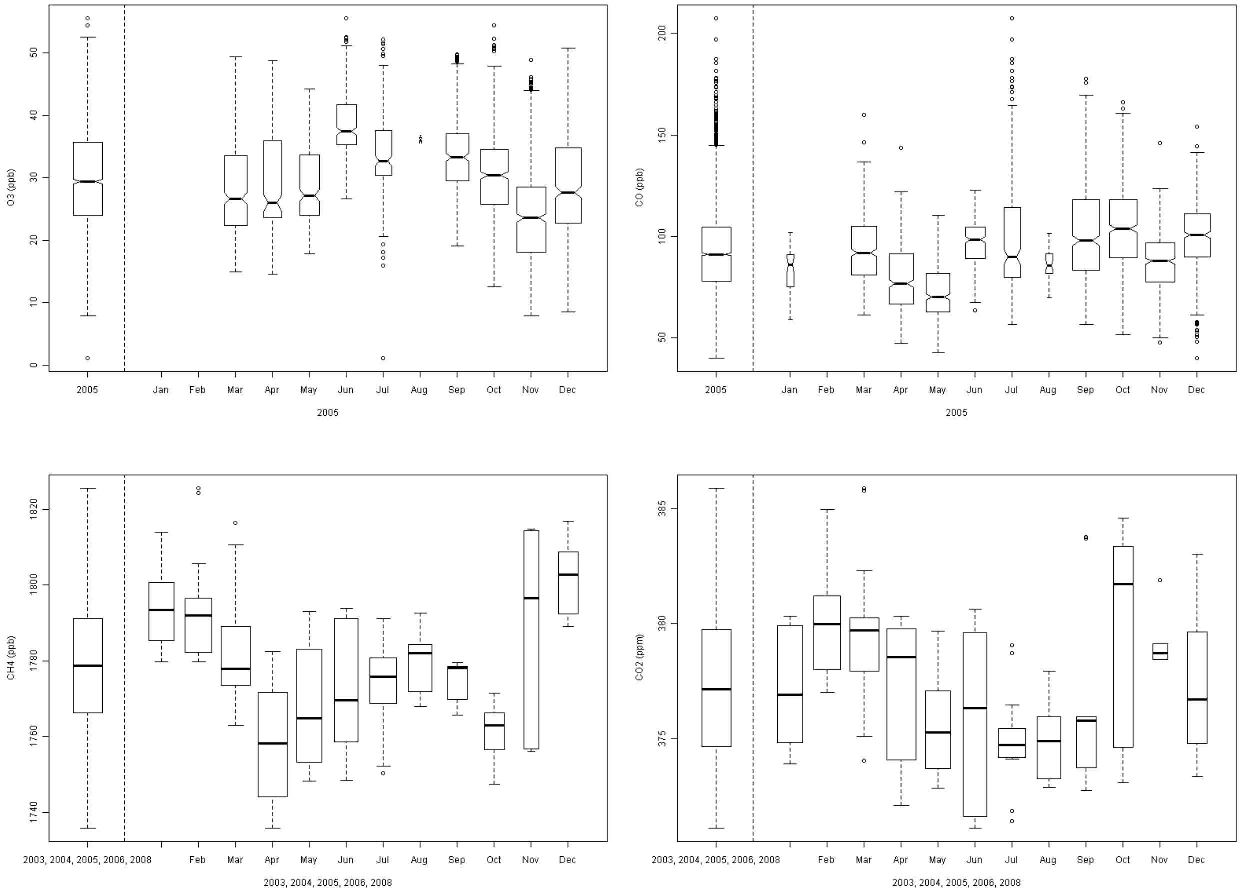


Figure 3. Yearly and monthly box plots for surface ozone, carbon monoxide (both for 2005), methane and carbon dioxide (both for 2003-2008, NOAA flask data). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

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 Dr. Charles Mutai. At the time of the audit, Mr. Kennedy K. Thiong'o was the responsible station manager, and Mr. John Aseyo was the station engineer. As of 1st July 2010, Mr. Constance Okuku was appointed as the station manager, and Charles Kioko as the station technician. An organisational chart for the GAW relevant parts of KMD as of 1st July 2010 is shown in Figure 4.

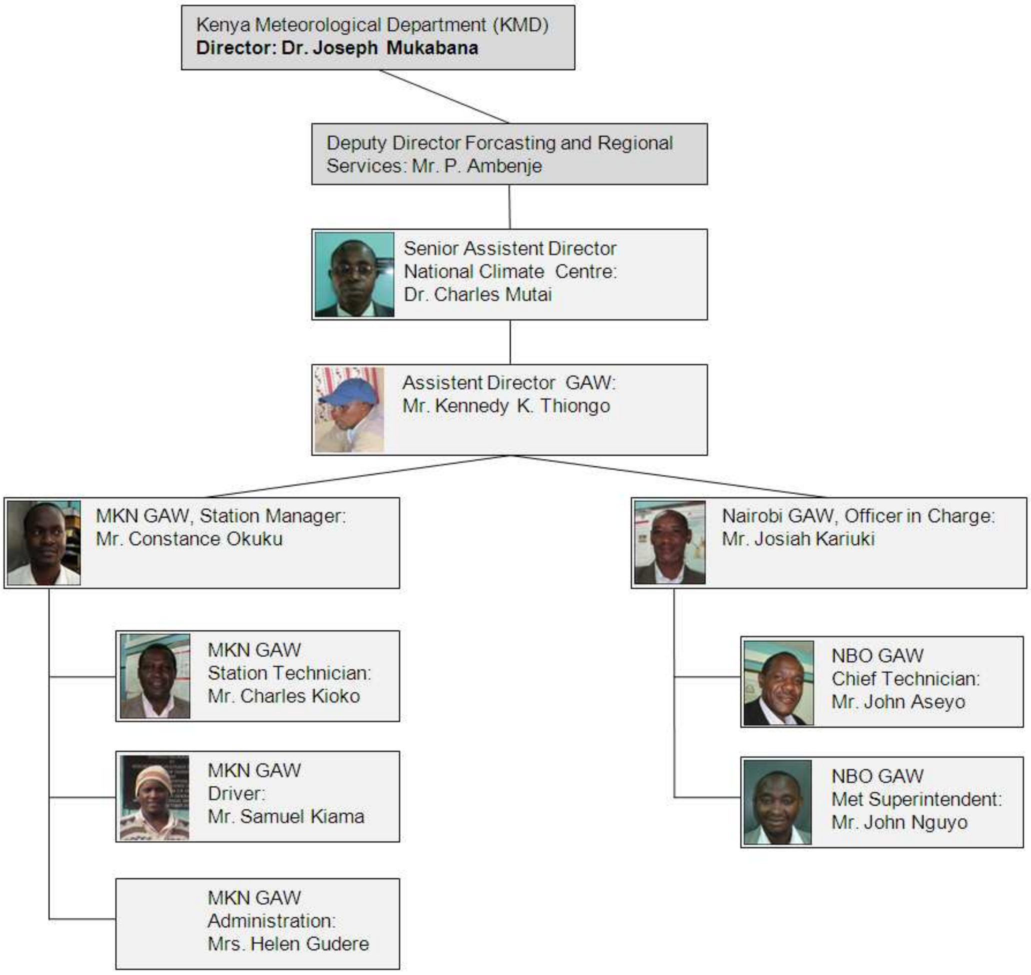


Figure 4. Organisational chart of the KMD GAW activities of as of 1st July 2010.

Surface Ozone Measurements

Surface ozone measurements started in May 2002 at MKN, and time series are available since then. All 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 is located 4.5 m above ground (1.7 m above the station roof) and has been described in the previous audit reports. The flow rate in the glass manifold is approximately 800 l/min since the replacement of the blower in 2008. The total length of the manifold is approx. 3 m. Air is drawn from the manifold by the ozone instrument. The tubing is made of Teflon (1.5 m, inner diameter 4 mm, flow rate 1 l/min), and the instrument is protected by a Teflon filter. The residence time is estimated to be less than 5 seconds. The air inlet is adequate for analyzing ozone concerning materials and residence time.

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 ozone analyser (OA) are summarised in Table 2.

Standards

Unchanged since the last audit. The station does not own an ozone calibrator, and the comparison of the analyser by WCC-Empa constitutes the only independent assessment at present. This is not adequate for a Global GAW station and should be improved (cf. Recommendation 12).

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 and limited power availability. 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

During the current audit a new version of the centralised LabView based data acquisition system was installed by QA/SAC Switzerland. One minute ozone data and all available instrument parameters are automatically stored in a Microsoft Access data base. Increments of the data base are automatically transferred to a FTP server at Empa; direct transfer to KMD is planned. However, the direct data transfer requires permanent internet connection (cf. Recommendation 5).

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.

Comparison of the Ozone Analyzer

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

Setup and Connections

Table 2 details the experimental setup during the 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 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 2008. The result of the current assessment (direct comparison between TS and the analyser) is shown in Table 3.

Figure 5 shows the regression residuals of the TEI 49C ozone analyser for the 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 comparison.

Travelling standard (TS)	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
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 comparison (hPa)	Ambient	659.3 (WCC reference)
	TS	662.1, adjusted to 659.0
	OA	658.5, no adjustments were made
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		4 runs (2010-06-17 thru 18)

Table 3. Ten-minute aggregates (initial comparison, direct TS-analyser) computed from the last 10 of a total of 15 one-minute values for the 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 (%)
2010-06-17 20:45	1	0	0.17	0.82	0	0.25	0.06	0.65	NA
2010-06-17 21:00	1	30	30.45	30.85	0	1.38	0.46	0.41	1.33
2010-06-17 21:15	1	90	89.98	90.49	0	0.13	0.07	0.51	0.56
2010-06-17 21:30	1	80	79.99	80.43	0	0.17	0.23	0.43	0.54
2010-06-17 21:45	1	60	60.02	60.55	0	0.19	0.15	0.53	0.88
2010-06-17 22:00	1	20	20.01	20.38	0	0.16	0.09	0.37	1.87
2010-06-17 22:15	1	40	39.97	40.30	0	0.13	0.12	0.33	0.82
2010-06-17 22:30	1	70	70.01	70.54	0	0.15	0.13	0.53	0.76
2010-06-17 22:45	1	10	10.04	10.87	0	0.24	0.10	0.83	8.28
2010-06-17 23:00	1	50	50.00	50.33	0	0.16	0.12	0.33	0.66
2010-06-17 23:15	2	0	0.19	0.68	0	0.27	0.06	0.49	NA
2010-06-17 23:30	2	20	20.03	20.39	0	0.25	0.07	0.36	1.80
2010-06-17 23:45	2	80	80.06	80.57	0	0.17	0.11	0.51	0.64
2010-06-18 00:00	2	90	89.99	90.65	0	0.18	0.23	0.66	0.73
2010-06-18 00:15	2	40	40.01	40.41	0	0.18	0.10	0.40	1.00
2010-06-18 00:30	2	60	59.99	60.13	0	0.07	0.11	0.13	0.22
2010-06-18 00:45	2	10	10.33	10.78	0	0.45	0.16	0.45	4.32
2010-06-18 01:00	2	70	69.97	70.47	0	0.12	0.11	0.50	0.71
2010-06-18 01:15	2	30	30.01	30.35	0	0.28	0.10	0.34	1.14
2010-06-18 01:30	2	50	49.98	50.57	0	0.15	0.09	0.59	1.18
2010-06-18 01:45	3	0	0.17	0.59	0	0.30	0.08	0.42	NA
2010-06-18 02:00	3	30	29.99	30.33	0	0.17	0.11	0.33	1.11
2010-06-18 02:15	3	50	50.00	50.44	0	0.10	0.15	0.44	0.88
2010-06-18 02:30	3	10	10.00	10.26	0	0.39	0.10	0.26	2.60
2010-06-18 02:45	3	90	90.02	90.59	0	0.18	0.16	0.57	0.63
2010-06-18 03:00	3	60	59.97	60.17	0	0.14	0.11	0.20	0.33
2010-06-18 03:15	3	20	19.97	20.11	0	0.19	0.10	0.15	0.74
2010-06-18 03:30	3	80	80.01	80.54	0	0.17	0.14	0.53	0.66
2010-06-18 03:45	3	70	70.00	70.36	0	0.22	0.16	0.36	0.52
2010-06-18 04:00	3	40	39.98	40.50	0	0.31	0.15	0.52	1.29
2010-06-18 04:15	4	0	0.30	0.63	0	0.21	0.05	0.33	NA
2010-06-18 04:30	4	30	29.96	30.22	0	0.27	0.16	0.26	0.87
2010-06-18 04:45	4	90	90.05	90.23	0	0.06	0.08	0.18	0.20
2010-06-18 05:00	4	80	79.97	80.25	0	0.15	0.07	0.29	0.36
2010-06-18 05:15	4	60	59.94	60.13	0	0.10	0.14	0.19	0.31
2010-06-18 05:30	4	20	20.37	20.46	0	0.71	0.27	0.09	0.43
2010-06-18 05:45	4	40	40.02	40.00	0	0.21	0.10	-0.02	-0.05
2010-06-18 06:00	4	70	70.00	69.77	0	0.17	0.12	-0.24	-0.34
2010-06-18 06:15	4	10	9.97	10.24	0	0.30	0.04	0.27	2.74
2010-06-18 06:30	4	50	49.99	50.24	0	0.17	0.13	0.25	0.49

[#]0: valid data; 1: invalid data.

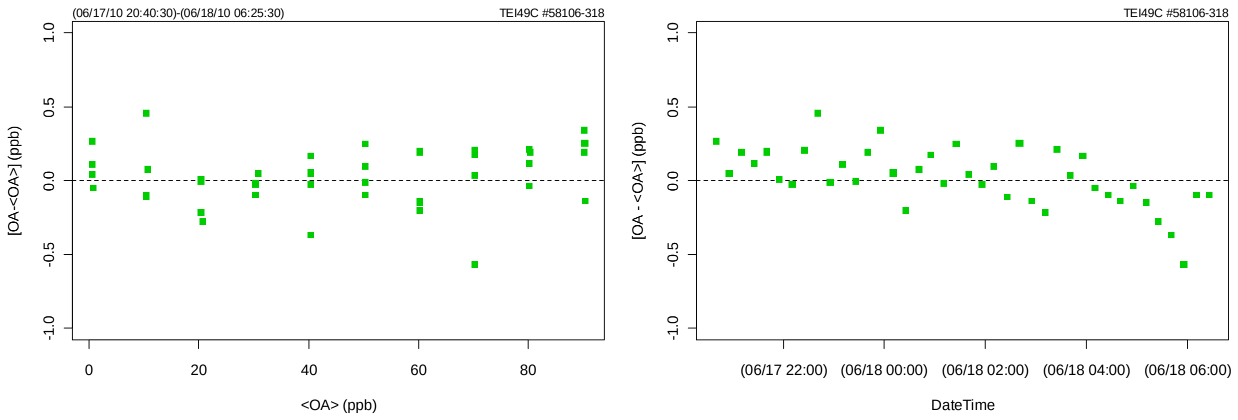


Figure 5. Regression residuals of the MKN ozone analyser (TEI 49C) as a function of concentration (left) and time (right).

Based on these 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:

$$X_{O3} \text{ (ppb)} = ([OA] - 0.29 \text{ ppb}) / 0.999$$

$$u_{O3} \text{ (ppb)} = \text{sqrt}(0.32 \text{ ppb}^2 + 2.70\text{e-}05 * X_{O3}^2) \qquad (1)$$

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. However, more frequent comparisons with an ozone calibrator would be very desirable for the future operation of the MKN ozone programme (cf. Recommendation 12).

Carbon Monoxide Measurements

Carbon monoxide measurements started in 2002 at MKN. The original TEI 48C instrument was complemented by a Horiba APMA-360 analyzer in 2008. The two instruments were running in parallel for a few months since then, and were both compared during the present audit. All comparisons were done according to Standard Operating Procedures [*WMO*, 2007a]. The TEI 48C instrument was decommissioned after the present audit and should be used at a more polluted site.

Monitoring Set-up and Procedures

Air Conditioning

See ozone. The diurnal temperature variations affected mainly the zero-drift of the TEI 48C CO instrument. The current instrument should be more stable; nevertheless, a more controlled laboratory temperature is highly desirable.

Air Inlet System

The air inlet system is identical to the one for surface ozone as described above. The Horiba instrument is directly connected to the glass manifold. Eaton (Dekabon) and stainless steel tubing is used, and the instruments are protected by an inlet filter. All materials as well as the residence time are adequate for CO measurements.

Instrumentation

The Horiba APMA-360 analyser was installed during the audit in 2008 by QA/SAC-Switzerland [*Zellweger, et al.*, 2008], and was initially calibrated by WCC-Empa. 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 but was not used for CO measurements. It was decommissioned after the current audit.

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.

Operation and Maintenance

The Horiba APMA-360 CO system is running fully automated. Zero and span checks using the dilution system are made every three 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.

Data Acquisition and Data Transfer

The station is equipped with a centralised Labview-based data acquisition system developed by QA/SAC-Switzerland that currently acquires the surface ozone, CO, meteorological parameters, black carbon and GPS measurements of MKN. Automatic data transmission was set up during the audit using a GSM modem; currently, data are automatically transferred to an FTP server at Empa; however, transfer to KMD is planned as soon as the infrastructure at KMD becomes available. Towards the end of the audit, the automatic data transfer was discontinued because the GSM invoice has not been timely settled by KMD.

Data Treatment

QA/SAC-Switzerland developed a software tool (GAW Data Analysis and Data Integration - DANDI) that allows station data managers to concisely organise their monitored data and report it to the world data centres (WDC). The package uses rationale databases to store data in an individual database. The package incorporates the concepts of raw data import, data flagging/reviewing, data corrections, data aggregation, and uncertainty reporting. DANDI was programmed using the freely available R environment [*R Development Core Team*, 2009]. Until now, 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.

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	Jun 2010
Sauerstoffwerk Lenzburg, SL6395E, Dilution unit	15000±300 ppb, CO 99.997% in synthetic air 99.9995%	2001	WCC-Empa	Feb 2002	Oct 2004
SL, SL16887e, Dilution unit	51100±1000 ppb, CO 99.997% in synthetic air 99.9995%	Jan 2005	WCC-Empa	Feb 2005	Jun 2006
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, Dilution unit	51021±510 ppb, CO in natural air	Mar 2008	WCC-Empa	Jul 2008	continued
Scott Marin, 080304_CA04549, Direct use	1288±13 ppb, CO in natural air	Mar 2008	WCC-Empa	Jun 2010	continued
Scott Marin, 080808_CA08202, Dilution unit	59772±598 ppb, CO in natural air	Aug 2008	WCC-Empa	Stock	
Scott Marin, 080808_CA08210, Direct use	859.5±8.6 ppb, CO in natural air	Aug 2008	WCC-Empa	Stock	

** WMO-2000 carbon monoxide scale*

Documentation

All information is entered in electronic log books and checklists. The information was only partly comprehensive and up-to-date. The instrument manuals as well as a documentation of the DANDI package are available at the site.

Comparison of Carbon Monoxide Analysers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included comparisons of the travelling standards at Empa before and after the 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 13 below.

Setup and Connections

Table 5 shows details of the experimental setup during the 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 comparison.

<table>
<tr><td colspan="2">Travelling standard (TS)</td><td>One cylinder (Scott Marrin, 080304_CA06112 51.02 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 (Red-y MFCs)</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</td><td>1.0</td></tr>
<tr><td>2</td><td>80</td><td>1.0</td></tr>
<tr><td>3</td><td>100</td><td>1.0</td></tr>
<tr><td>4</td><td>150</td><td>1.5</td></tr>
<tr><td>5</td><td>200</td><td>2.0</td></tr>
<tr><td>6</td><td>250</td><td>2.5</td></tr>
<tr><td>7</td><td>400</td><td>4.0</td></tr>
<tr><td>8</td><td>600</td><td>6.0</td></tr>
<tr><td>9</td><td>1000</td><td>10.0</td></tr>
</table></td></tr>
<tr><td rowspan="5">Field instrument (since 2008)</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 (2001-2010)</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 = 4.107; 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; 2010-06-18/19</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 2 and 15 useable 5-min averages per level and run, depending on the duration of the level. The raw data was corrected for zero-drift using loess regression and further aggregated to 5-min averages 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 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. 5' av.	AL-TS(ppb)	AL-TS(%)
(06/18/10 16:07:30)	0	0	-10.3	11.0	14	-10.3	NA
(06/18/10 16:49:30)	100	1	92.4	0.9	2	-7.6	-7.6
(06/18/10 20:46:30)	80	0.8	62.8	6.9	6	-17.2	-21.5
(06/18/10 22:07:30)	200	2	182.4	7.7	14	-17.6	-8.8
(06/18/10 23:24:00)	250	2.5	237.7	7.3	15	-12.3	-4.9
(06/19/10 01:07:30)	600	6	577.3	8.3	14	-22.7	-3.8
(06/19/10 02:23:00)	400	4	389.5	6.5	15	-10.5	-2.6
(06/19/10 04:06:30)	1000	10	967.8	9.2	14	-32.2	-3.2
(06/19/10 05:24:00)	100	1	96.4	7.9	15	-3.6	-3.6

Figure 6 shows the regression residuals of the analyser over the course of the 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.

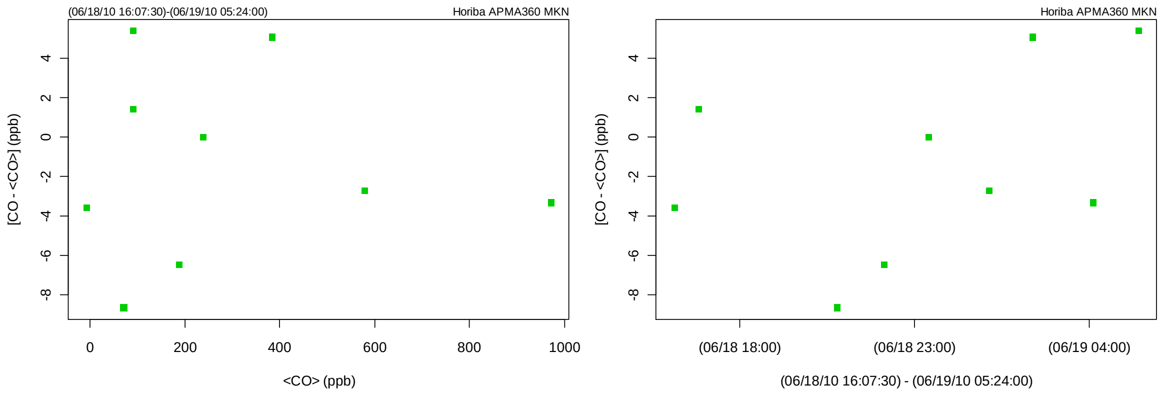


Figure 6. Regression residuals of the Horiba APMA-360 carbon monoxide analyser based on the initial comparison with the dilution unit. Points represent averages of valid 3-min values. Left panel: concentration dependence; Right panel: time dependence.

Based on these 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).

$$X_{CO} \text{ (ppb)} = ([CO] + 6.8 \text{ ppb}) / 0.9779$$

$$u_{CO} \text{ (ppb)} = \text{sqrt}(62.5 \text{ ppb}^2 + 7.94\text{e-}05 * X_{CO}^2) \qquad (2)$$

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 9 and 15 useable 5-min averages per level and run, depending on the duration of the level. The 1-min raw data was corrected for zero-drift using loess regression and further aggregated to 5-min averages 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 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(%)
(06/18/10 16:06:46)	0	0	-10.4	9.7	13	-10.4	NA
(06/18/10 17:36:15)	100	1	103.0	7.8	12	3.0	3.0
(06/18/10 18:53:45)	150	1.5	161.7	11.8	12	11.7	7.8
(06/18/10 20:18:30)	80	0.8	61.7	8.2	14	-18.3	-22.9
(06/18/10 22:04:30)	200	2	202.9	8.1	14	2.9	1.5
(06/18/10 23:36:15)	250	2.5	241.5	4.0	12	-8.5	-3.4
(06/19/10 00:54:11)	600	6	622.1	6.7	11	22.1	3.7
(06/19/10 02:25:00)	400	4	424.5	7.5	15	24.5	6.1
(06/19/10 04:05:00)	1000	10	1047.6	7.5	15	47.6	4.8
(06/19/10 05:36:15)	100	1	102.2	11.4	12	2.2	2.2
(06/19/10 06:40:00)	150	1.5	169.2	5.3	9	19.2	12.8

Figure 6 shows the regression residuals of the analyser over the course of the 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.

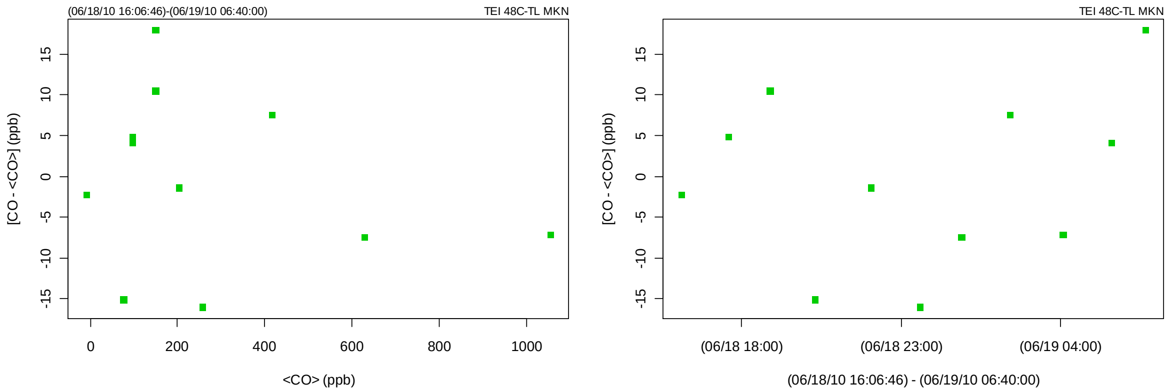


Figure 7. Regression residuals of the TEI 48C-TL carbon monoxide analyser based on the initial comparison with the dilution unit. Points represent averages of valid 5-min values. Left panel: concentration dependence; Right panel: time dependence.

Based on these 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).

$$X_{CO} \text{ (ppb)} = ([CO] + 8.2 \text{ ppb}) / 1.0630$$

$$u_{CO} \text{ (ppb)} = \text{sqrt}(109.6 \text{ ppb}^2 + 6.53e\text{-}05 * X_{CO}^2) \qquad (3)$$

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

The set-up of the Horiba system was slightly modified during the audit. The new instrumental set-up is shown in Figure 8. The manual valve is used to select between automatic operation and manual span checks using the 1 ppm cylinder. The TEI 48C-TL instrument was decommissioned after the audit.

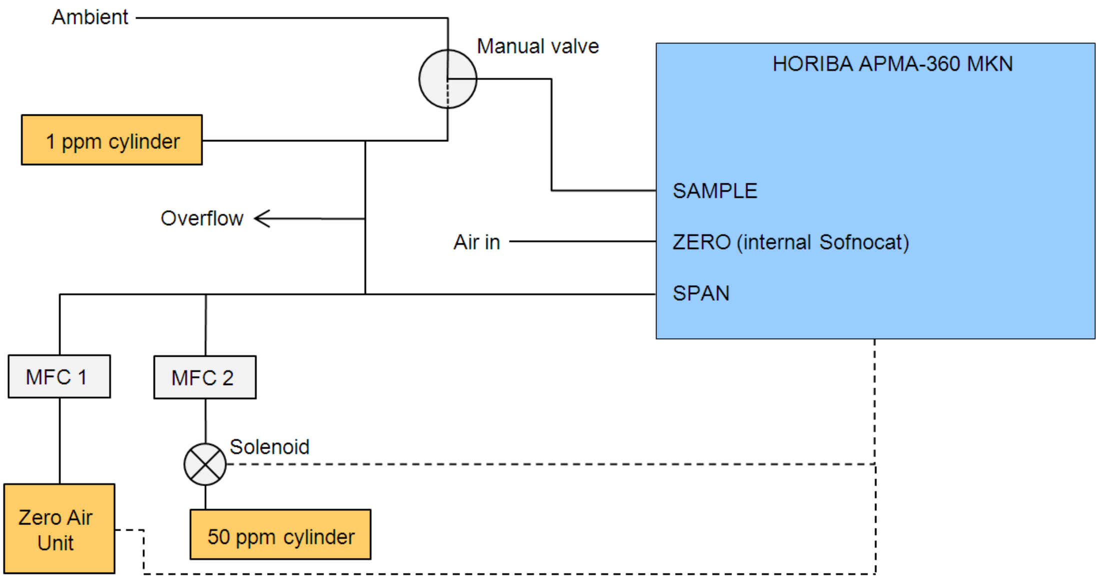


Figure 8. Set-up of the Horiba APMA-360 CO analyser at MKN.

Conclusions

The Horiba CO analyser of MKN is working well within the limitations of the NDIR technique; however, the instrument drifted to negative values for periods up to two hours during the audit. The reason for this behaviour could not be identified. Once power will be re-established, this issue has to be followed up. 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.

Carbon Dioxide and Methane Measurements

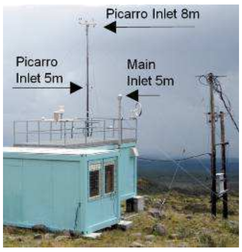
A Picarro G1301 analyser for the continuous measurement of carbon dioxide and methane was installed during the current audit. A valve box was designed by QA/SAC-Switzerland; the documentation of the box is shown in Appendix 3.

Monitoring Set-up and Procedures

Air Conditioning

The instrument is installed in the same rack as the other analysers. No air conditioning is available, which is less critical for this type of instrument. Nevertheless, a more controlled laboratory temperature is highly desirable.

Air Inlet System



The valve box has three sample ports. Port 1 is connected to the manifold of the main inlet by approx. 1.5 m ¼ inch Dekabon tubing. Ports 2 and 3 have dedicated ¼ inch Dekabon inlet lines to the meteo mast on the 5 m (Port 2) and 8 m (Port 3) levels. The air flow through the Dekabon tubing is approx. 2.5 lpm, which corresponds to residence times of approx. 1 second (main inlet) to 3 seconds (8 m inlet). All materials as well as the residence time are adequate for CO_2 and CH_4 measurements.

Instrumentation

A Picarro G1301 analyser was installed during the current audit. The installation includes peripherals (valve box) for sample air drying and calibration. Further details can be found in Appendix III.

Standards and Calibration

The station has been provided with one calibration gas (working standard) by WCC-Empa. In addition, 4 NOAA laboratory standards were sent to the station; however, these standards arrived only after the current audit and are still at KMD. Furthermore, CO_2 standards are available from the Aircoa project.

Table 8 gives details of the cylinders currently available at the station.

Table 8. CO_2 and CH_4 standards available at the MKN station

Manufacturer, S/N, Use	Mole fractions	Calibration		In service	
		Date	By	From	To
SMI - Empa, 091124_CB08863, Working standard	538.94±0.10 ppm CO_2 2292.91±0.30 ppb CH_4 270.3±2.7 ppb CO	2009-2010	WCC-Empa	Jul 2010	continued
CC324465	390.57±0.00 ppm CO_2 1847.68±0.14 ppb CH_4	2010	NOAA/ESRL	Aug 2010	continued
CC325133	381.04±0.00 ppm CO_2 1802.38±0.30 ppb CH_4	2010	NOAA/ESRL	Aug 2010	continued
CC1788	409.09±0.04 ppm CO_2 1941.31±0.48 ppb CH_4	2010	NOAA/ESRL	Aug 2010	continued
CC324480	370.12±0.02 ppm CO_2 1750.60±0.20 ppb CH_4	2010	NOAA/ESRL	Aug 2010	continued
SMI, CA07933	409 ppm CO_2	2008	Univ. Colorado	2008	
SMI, CA07941	473 ppm CO_2	2008	Univ. Colorado	2008	
SMI, CA07990	350 ppm CO_2	2008	Univ. Colorado	2008	
SMI, CA07917	379 ppm CO_2	2008	Univ. Colorado	2008	
SMI, JJ23428	384 ppm CO_2	2008	NOAA, Britt Stevens	2008	

Scales: WMO-2000 (CO), NOAA04 (CH_4), WMO X2007 (CO_2)

Data Acquisition and Data Transfer

The internal data acquisition software of the Picarro system is used for data acquisition. The Picarro instrument is connected to the GAWDAQ PC over a local area network. Data are automatically transferred to the GAWDAQ PC, and data increments are automatically transferred to Empa. The automatic transfer to KMD is planned as soon as internet connectivity and power supply at MKN are re-established.

Operation and Maintenance

The Picarro G1301 system is set up to run fully automated. Required maintenance includes the exchange of inlet filters (every 6 months), as well as monitoring the instrument and pump performance, and check the remaining pressure of the calibration gases during station visits.

Data Treatment

No data has been acquired so far except for a few hours during the installation of the instrument.

Data Submission

Data submission is planned once long enough time series become available.

Documentation

The MKN station has been provided with the instrument manual and a documentation of the valve box (cf. Appendix III). Furthermore, documentation of the automatic data transfer is available. As for the instruments, the operators should enter all relevant information in electronic log books and checklists. This process has been initiated during the audit but needs to be improved.

Calibration of the instrument

The Picarro instrument has not been calibrated; the picarrocrds.ini file has not been changed, and no user calibration settings were made. The original settings are shown below:

[CALIBRATION]
CONCENTRATION_CH4_GAL_INTERCEPT=-0.000346858
CONCENTRATION_CH4_GAL_SLOPE=0.990677619
CONCENTRATION_CH4_USER_INTERCEPT=0.000
CONCENTRATION_CH4_USER_SLOPE=1.000

CONCENTRATION_H2O_CONC_INTERCEPT=0.00
CONCENTRATION_H2O_CONC_SLOPE=1.00
CONCENTRATION_H2O_USER_INTERCEPT=0.000
CONCENTRATION_H2O_USER_SLOPE=1.000

CONCENTRATION_CO2_GAL_INTERCEPT=-0.2739
CONCENTRATION_CO2_GAL_SLOPE=0.707918134
CONCENTRATION_CO2_GAL_H2O_RATIO_SLOPE=0.01244
CONCENTRATION_CO2_USER_INTERCEPT=0.000
CONCENTRATION_CO2_USER_CONC_SLOPE=1.000

Table 9 (CO_2) and Table 10 (CH_4) summarises the results of several standards measured at WCC-Empa in May 2010. The standards were measured directly with the Picarro instrument; three standards were also measured including the valve box. These results confirmed that the valve box has a significant influence on the observed mole fractions. In contrast to the results presented in **Error! Reference source not found.**, significantly lower values were also found for methane. Therefore, it is absolutely essential that all standards pass through the valve box.

Table 9. CO_2 standards measured with the MKN Picarro

Tank ID	CO_2 (ppm) WMO X2007	sd (ppm)	MKN Picarro direct (ppm)	sd (ppm)	MKN Picarro over box (ppm)	sd (ppm)
Zero Air	-0.03	0.01	-0.23	0.02		
CA04590	392.21	0.02	390.61	0.03	389.78	0.02
100519_CB08835	294.37	0.02	293.14	0.01		
CA05373	326.96	0.02	325.61	0.01	325.14	0.01
091124_CB08870	537.10	0.02	534.97	0.02	534.01	0.02
CA05316	348.32	0.02	346.89	0.02		
CA04462	368.96	0.02	367.46	0.01		

Table 10. CH_4 standards measured with the MKN Picarro

Tank ID	CH_4 (ppb) NOAA04	sd (ppb)	MKN Picarro direct (ppb)	sd (ppb)	MKN Picarro over box (ppb)	sd (ppb)
Zero Air	0.00	0.04	0.59	0.16		
CA04590	1905.97	0.11	1897.38	0.18	1896.62	0.19
100519_CB08835	1987.35	0.08	1978.30	0.16		

CA05373	1607.82	0.08	1600.70	0.10	1600.20	0.12
091124_CB08870	2287.65	0.11	2277.16	0.15	2276.30	0.13
CA05316	1712.44	0.07	1704.81	0.14		
CA04462	1817.81	0.06	1809.74	0.13		

Based on these measurements, the following functions were obtained for the MKN Picarro excluding the valve box:

CO_2 (WMO X2007) = 1.0035 * CO_2 (Picarro MKN) + 0.21 ppm (4)

CH_4 (NOAA04) = 1.0049 * CH_4 (Picarro MKN) - 0.62 ppb (5)

The working standard (091124_CB08863) provided by WCC-Empa was also measured at MKN after the installation of the instrument. The following results were obtained:

CO_2 (ppm):
WCC-Empa assigned: 538.94±0.10
Measured at MKN (direct): 537.28±0.04
Measured at MKN after correction with (4): 539.37±0.04
Measured at MKN (over valve box): 535.89±0.03

CH_4 (ppb):
WCC-Empa assigned: 2292.91±0.30
Measured at MKN (direct): 2281.71±0.24
Measured at MKN after correction with (5): 2292.27±0.24
Measured at MKN (over valve box): 2281.10±0.19

These results show that the calibration of the MKN Picarro slightly changed at MKN compared to the initial calibration at WCC-Empa. Especially the CO_2 loss over the valve box seems to depend on the actual pressure difference in the Nafion drier. Therefore, frequent measurements of the working standard are necessary for accurate determination of the ambient air mole fractions.

Conclusions

The Picarro G1301 is a state of the art instrument for the measurement of atmospheric carbon dioxide and methane. The valve box designed by QA/SAC-Switzerland allows fully automated sequences of different sample inlets and calibration gases. However, issues related to the Nafion drier need further measurements for final conclusions; it might be advisable to bypass the drier and to apply a correction for water vapour.

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 comparisons at the Empa calibration laboratory are summarised in Table 11, the comparison data is given in Table 12.

Table 11. Experimental details of the 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 #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
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, 40, 80, 120, 160, 200
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 (2010-05-14) 3 runs after return of TS (2010-07-20)

Table 12. Five-minute aggregates computed from 10 valid 30-second values for the 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)
2010-05-14	1	0	0.03	0.31	-0.02	0.21
2010-05-14	1	40	41.01	0.22	40.32	0.20
2010-05-14	1	200	201.64	0.19	202.32	0.27
2010-05-14	1	120	120.40	0.23	120.25	0.19
2010-05-14	1	160	161.44	0.42	160.97	0.16
2010-05-14	1	80	79.65	0.14	78.98	0.44
2010-05-14	1	0	0.00	0.31	-0.20	0.12
2010-05-14	2	0	-0.05	0.33	-0.51	0.32
2010-05-14	2	120	120.07	0.37	120.05	0.29
2010-05-14	2	200	202.25	0.18	202.23	0.25
2010-05-14	2	40	40.83	0.33	40.60	0.49
2010-05-14	2	160	161.00	0.17	160.86	0.30
2010-05-14	2	80	79.56	0.16	79.52	0.20
2010-05-14	2	0	0.22	0.33	0.04	0.17
2010-05-14	3	0	-0.25	0.14	0.02	0.29
2010-05-14	3	120	119.95	0.26	120.12	0.24
2010-05-14	3	200	202.49	0.25	202.07	0.24
2010-05-14	3	40	40.71	0.39	40.81	0.18
2010-05-14	3	160	161.19	0.35	160.94	0.27
2010-05-14	3	80	79.58	0.47	79.51	0.16
2010-05-14	3	0	0.09	0.19	0.02	0.24
2010-07-20	4	0	-0.12	0.60	0.01	0.34
2010-07-20	4	120	117.65	0.47	117.51	0.37
2010-07-20	4	200	198.08	0.21	198.02	0.20
2010-07-20	4	40	39.54	0.40	39.46	0.17
2010-07-20	4	160	157.04	0.33	156.95	0.31
2010-07-20	4	80	77.77	0.22	77.59	0.28
2010-07-20	4	0	-0.22	0.48	-0.03	0.38
2010-07-20	5	0	-0.04	0.46	0.08	0.17
2010-07-20	5	120	118.49	0.36	118.42	0.30
2010-07-20	5	200	198.22	0.40	198.08	0.46
2010-07-20	5	40	39.71	0.45	39.77	0.22
2010-07-20	5	160	157.58	0.36	157.75	0.16
2010-07-20	5	80	77.98	0.34	77.85	0.24
2010-07-20	5	0	-0.11	0.39	0.05	0.19
2010-07-20	6	0	0.05	0.41	-0.04	0.26
2010-07-20	6	40	39.93	0.38	39.83	0.18
2010-07-20	6	160	159.14	0.49	158.74	0.19
2010-07-20	6	80	78.11	0.30	77.81	0.16
2010-07-20	6	120	117.79	0.26	117.95	0.18
2010-07-20	6	200	197.92	0.27	198.04	0.11
2010-07-20	6	0	0.23	0.26	-0.11	0.23

[#]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 9). 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] + 0.09 ppb) / 1.000

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

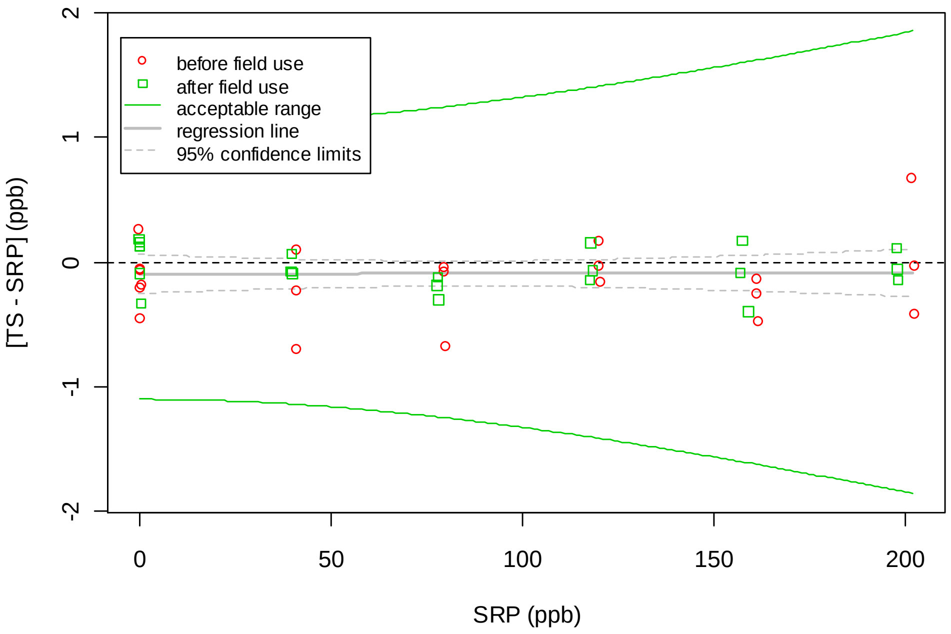


Figure 9. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 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 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 13.

Table 13. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the travelling standard (TS) used during the field 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, 080304_CA06112 51.02±0.50 ppm CO in natural air (α=0.05). The cylinder was calibrated against the WCC-Empa reference scale 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 = 1.0081±0.0002 * Reference Redy2 = 1.0099±0.0032 * Reference
Connection between instruments		Ca. 2.5 meter 1/4" Dekabon tubing
Sequence of Levels		Repeated runs of randomised sequence
Calibrations of MFCs		1 run before shipment of TS (2010-02-09)

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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:	2010-06-15 to 2010-06-25
1.2	Auditor:	Dr. C. Zellweger and Dr. J. Klausen
1.2.1	Station staff involved in audit:	Mr. C. Okuku, Mr. C. Kioko, Mr. J. Aseyo and Mr. K. Thiong'o
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49i-PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(1.0000±0.0010) × [SRP] - (0.09±0.14)
1.5	Ozone Analyzer [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; COEFF = 1.013
1.5.4	Calibration at start of audit (ppb):	[OA] = (0.999±0.001) × [SRP] + (0.29±0.12)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] - 0.29) / 0.999
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.32\ ppb^2 + 2.70e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	NA
1.5.8	Calibration after audit (ppb):	NA
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 10/4

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

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Carbon Monoxide Audit Executive Summary (MKN)

0.4	Station Name:	Mt. Kenya
0.5	GAW ID:	MKN
0.6	Coordinates/Elevation:	0.033°S, 37.217°E (ca. 3678 m a.s.l)
Parameter:		Carbon Monoxide
1.1	Date of Audit:	2010-06-15 to 2010-06-25
1.2	Auditor:	Dr. C. Zellweger and Dr. J. Klausen
1.2.1	Station staff involved in audit:	Mr. C. Okuku, Mr. C. Kioko, Mr. J. Aseyo and Mr. K. Thiong'o
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	080304_CA06112 51.02 ppm ±0.51 ppm CO
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 = (0.97815±0.007) × X - (6.8±1.3)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 6.8) / 0.978
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (62.5\ ppb^2 + 7.94e\text{-}05 \times X^2)^{1/2}$
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:	Main station analyser since November 2008
1.7	Reference:	WCC-Empa Report 10/4

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

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LIST OF ABBREVIATIONS

a.s.l	above sea level
CCL	Central Calibration Laboratory
DANDI	GAW Data Analysis and Data Integration
DAQ	Data Acquisition System
GAWSIS	GAW Station Information System
KMD	Kenya Meteorological Department
KPLC	Kenya Power & Lighting Company
KWS	Kenya Wildlife Service
MFC	Mass Flow Controller
MKN	Mt. Kenya GAW station
NDIR	Non-Dispersive Infrared
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
UoN	University of Nairobi
WCC-Empa	World Calibration Centre at Empa
WDC	World Data Centre
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation

APPENDIX II – MEETING MINUTES

Minutes of meeting with EMPA Twinning Partners at KMD's Headquarters (Nairobi) on Thursday 24 June 2010.

Present:

1.	Dr. Joseph Mukabana	-	Director, KMD
2.	Mr. Peter Ambenje	-	KMD
3.	Dr. Charles Mutai	-	KMD
4.	Mr. Kennedy Thiongo	-	KMD
5.	Mr. Constance Okuku	-	KMD
6.	Mr. Njeria Chito	-	KMD
7.	Mr. John Aseyo	-	KMD
8.	Dr. Jörg Klausen	-	EMPA, WMO/GAW QA/SAC Switzerland
9.	Dr. Christoph Zellweger	-	EMPA, WMO/GAW World Calibration Centre

Dr. Joseph Mukabana welcomed all to his office and thanked the EMPA partners for visiting Kenya for GAW biannual instruments calibration and audit mission.

Dr. Christoph Zellweger explained GAW's biannual mission to Kenya. He informed the meeting that inter-comparison of both CO and O_3 instruments are within allowable standards. He also mentioned the installation of new equipment for monitoring CO_2 and CH_4.

Dr. Klausen on behalf of Dr. Calpini (MeteoSwiss) congratulated KMD for its hospitality in hosting the MeteoSwiss delegation who visited a week earlier to install the new Ozonesonde sounding equipment.

Dr. Klausen then explained the other activities conducted during this mission. In particular, efforts were made to improve the central data acquisition system (GAWDAQ), and to re-initiate the automatic data transfer of station raw data.

The meeting discussed at length on the challenges facing Mt. Kenya GAW Station. The power is one of the main challenges that have significantly affected its operations. Previous meetings (on 15 and 18 June 2010) between the consumer (KMD) and the power provider (KPLC) suggested a replacement of overhead cables, and KPLC promised to address the issue. The UPS broke down on 17 June 2010 due to power surges and it requires urgent repair or replacement since power is directly connected to the instruments.

On the improvement and sustainability of Mt. Kenya GAW station, the following were agreed upon or proposed:

a) GAW Division created in the KMD's structure with a view of expansion;
b) KPLC proposal on PVC-isolated power cable attached to the poles using spreaders;
c) Automatic data transfer to KMD headquarters before sending EMPA ;
d) Promotion of internships programmes ;
e) Construction of Sanitation facilities
f) Purchase of mountain gears for GAW staff (Bunk beds, warm clothing, thermal wear, boots, gloves, etc) for ;
g) Installation of Air conditioning to stabilize temperature variations;
h) Purchase of a robust 4WD vehicle;
i) Back-up hybrid solar/wind power generation;
j) Acquisition of land for Office, Observatory, Laboratory, and Hostel construction at Nanyuki town;
k) Improvement of computing resources and internet facilities;

1

l) Installation of a new mast for hosting Automatic Instruments
m) Future GAW Conference to be held in Kenya
n) Enhance collaborative research in GAW activities;
o) For smooth continuity, former Mt. Kenya GAW staff to assist new deployed staff, when need be ;
p) Monitoring of Mercury Hg in near future with collaboration with European Commission (information);

On closing remarks, the Director (KMD) thanked the members for attending the meeting, and highlighted the importance of Mt. Kenya GAW station to the country and the international community. There being no other business, the meeting adjourned at 12.45 p.m.

In a follow-up meeting, Dr. Klausen and other group members with Mr. Peter Mutai and Samwel Machua (KMD ICT and Data Management, respectively) to discuss the processes involved in facilitating direct near-real time access to the raw data collected at MKN, and use of these data at KMD. It was agreed that the database increments (binary files, MS Access records) should be sent to KMD first and then to Empa at every hour. KMD would open an ftp directory to receive these files (As of 13 July 2010, this ftp directory has not been communicated). Sample VB scripts were discussed that can be used to read the binary files and to either re-construct the GAWDAQ database at KMD or else to generate text files from them. A number of sample files were given to KMD.

Note:

1. *The meeting later between KPLC, KMD and EMPA took place on 25 June 2010. Eng Mwaniki (Regional Manager Mt. Kenya) promised to follow up with his senior KPLC staff on the power outages at Mt. Kenya GAW Station. He assured of the KPLC commitment in maintaining the power line and the plan to replace the whole cable with a better one.*

2. *Telephone conversation between Thiongo (KMD) and Eng Mureithi (Chief Distribution Manager, KPLC) on 5 July 2010 indicated an approval of KPLC budget (Kh. 23 million) for installing a new ABC cable with concrete poles. However, procurement procedures may take about six months. He (Mureithi) also promised to officially respond to Director's (KMD) letter.*

Signed:

Dr. J. Mukabana: 26/7/2010

Dr. C. Mutai (taking minutes): 15/7/2010

APPENDIX III – VALVE BOX DOCUMENTATION

Reference jkl134

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ValveBox for PICARRO G1301 Multigas Analyzer (MKN)

Jörg Klausen, Martin Steinbacher and Christoph Zellweger

Laboratory for Air Pollution / Environmental Technology, GAW QA/SAC Switzerland, Empa, Dübendorf, Switzerland, joerg.klausen@empa.ch

Plumbing Diagram

The setup is based on a Picarro G1301 analyzer. This will be equipped with the peripherals for drying and calibration (Figure 1).

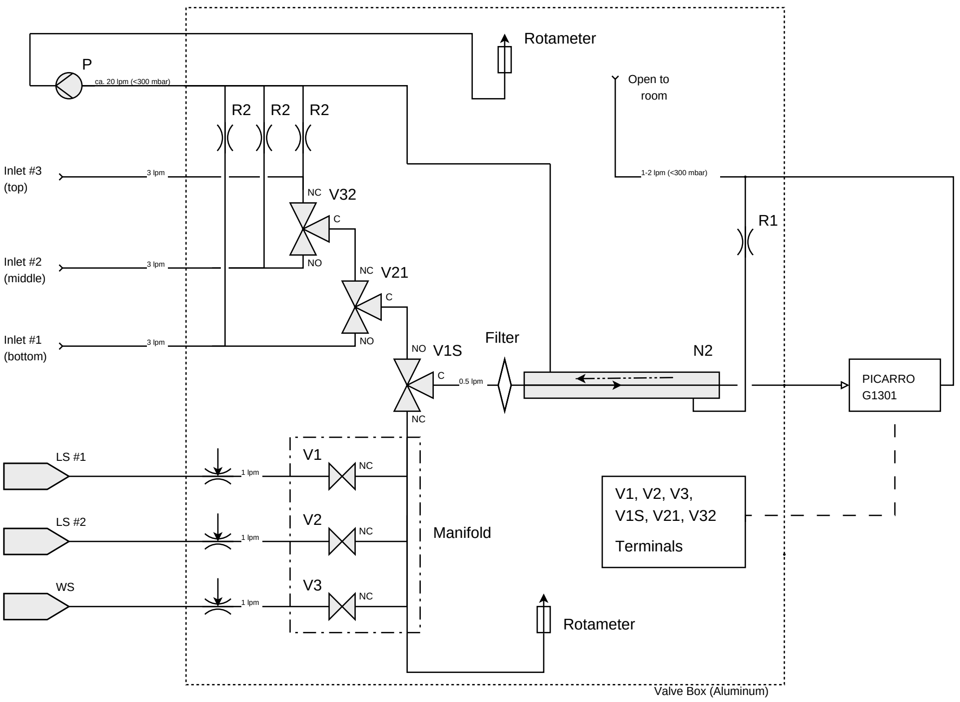

Figure 1. Schematic of set-up (R1: 100 µm, R2: 700 µm). A single pump is used to drive the samples from 3 inlets as well as the Nafion dryer. R2 controls the overall flow of the sample gases, while R1 controls the vacuum in the Nafion dryer.

This 'valve box' allows three inlets as well as three standard gas cylinders to be connected and controlled by the Picarro instrument. It uses only one pump to minimize power consumption. One Nafion dryer is used to dry the sample gases (and, in fact, slightly humidify the standard gases). The drying achieved is largely controlled by the pressure gradient inside the Nafion unit. The smaller R1, the lower the pressure, and the lower the humidity of the gas downstream of the Nafion dryer. The trade-off is that humidity removed from the gas stream is transported out of the dryer rather slowly at the low flows obtained at small pressures (small R1). Based on initial tests at Empa, moist ambient air at ca. 20℃ is dried to about 0.03% by volume water content, equivalent to a dew point of ca. -35℃ (cf. Vaisala humidity calculator, http://www.vaisala.com/humiditycalculator/). At an inlet pressure of 670 mbar, the volumetric flows at the sample inlets was determined to be 2.45 lpm. With R1 = 400 µm, the flow through the Nafion dryer was 0.85 lpm and the pressure at the pump 180 mbar (Note: With this size of the critical orifice, the performance of the dryer was insufficient, and a smaller orifice was eventually used.)

Physical Layout of Components

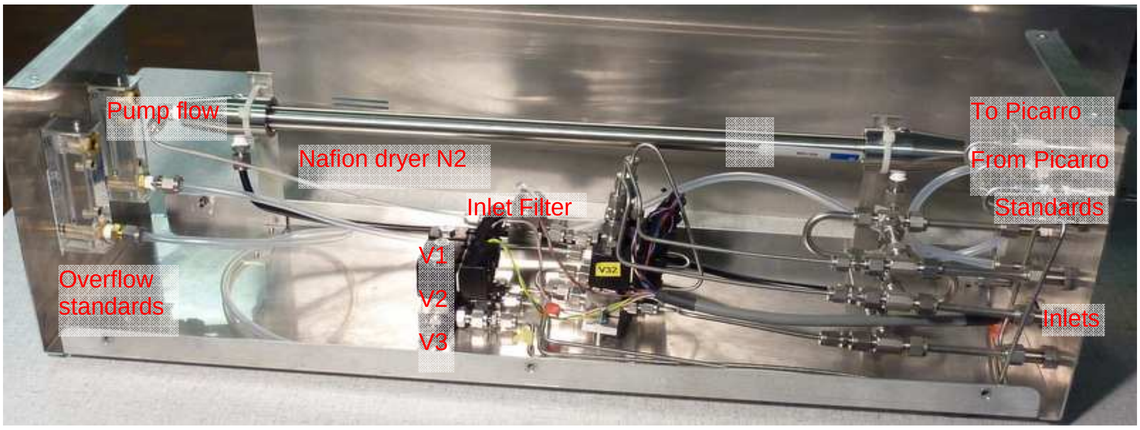

Figure 1. Layout of components inside Valve Box (note: the rotameter for the pump is still missing)

Color Codes of Interface Cable inside box

Pins	Color	Valve
1, 9	blue, red	V1S
2, 10	white, brown	V21
3, 11	black, violet	V32
4, 12	blue/red, gray/pink	V1
5, 13	gray, pink	V2
6, 14	green, yellow	V3

Itemized List of Components

Item	Units	Supplier
Pump, Thomas 2688CHI44	1	GardnerDenver
Service kit	1	
Rubber support	1	
Calibration gases, 30 L each	4 cyl	NOAA/ESRL
Regulators, Scott Specialty Model 5114D590 (Output is 2 to 100 psig; 1/8” Swagelok fittings	4	NOAA/ESRL
Solenoid valves 2/2 134138(#134106)	4	Bürkert
Solenoid valves 3/2 Type 2506 (#008353)	4	
Manifold 2/2 (3 valves)	1	
Cable plug	8	
Nafion dryer, PD-50T-24SS	1	Müller
Inlet filter holder, Swagelok SS-4TF-LE	1	Arbor
Inlet filters (7µm), Swagelok SS-2F-K4-7	10	
Needle valves, Swagelok	3	
Standard 1/4" Orifices, SS-1/4-TUBE-100	1	Lenox Laser
Standard 1/4" Orifices, SS-1/4-TUBE-700	3	
Rotameter Cole Parmer 0.1-1 lpm, W27265	1	Fisher Sci.
Rotameter Cole Parmer 4-20 lpm, W2726…	1	
Tubing (SERTOflex), 1/4"	100 m	Serto
Fittings (Swagelok) and other small items		

Picarro Valve Sequencer Setup

The Picarro instrument offers a so-called 'valve sequencer' that allows to control six (6) external valves with 2 states. For operation with three inlet lines and 3 standards, the following configuration can be used to generate sequences:

Section	Duration (min)	Picarro valve port (physical valve)						Action (Solenoid Code)
		#1 (V1)	#2 (V2)	#3 (V3)	#4 (V32)	#5 (V21)	#6 (V1S)	
1	20	X					X	Standard LS#1 (33)
	20		X				X	Standard LS#2 (34)
	20			X			X	Standard WS (36)
2	20							Sample 1 (Manifold 5 m)
	20					X		Sample 2 (5 m)
	20				X	X		Sample 2 (8 m)
3	15							Sample 1 (Manifold 5 m)
	15					X		Sample 2 (5 m)
	15				X	X		Sample 2 (8 m)
	15			X			X	Standard WS (36)

For initial performance testing at the site, the following sequence is recommended:

$1 – \{2 – 2 – 2 – 3\}_6$

This is a sequence that is recycled after 25 hrs involving one full calibration and a check using WS every 4 hrs. In order to save calibration gas, a sequence involving fewer calibration steps can be applied, for example

$1 – \{2 – 2 – 2 – 2 – 2 – 3\}_8$

Results of Initial Tests

Initial tests comprised of leak tests as well as performance checks.

For leak tests, the entire box was flushed with 10% CO_2 test gas. Since the box operates at pressures below ambient, increases of the CO_2 signal indicated leaks in the system. When leaks were found, the box was opened, and the leak localized by exposing one fitting after the other to an external stream of 10% CO_2 test gas.

Particular attention was paid to leak-checking the connections of the calibration gases, since even small losses of calibration gas would amount to large losses in the long term and would be unacceptable. A calibration gas cylinder was connected to a calibration gas port on the box, and the relevant port was closed (valve not actuated). The regulator attached to the cylinder was then pressurized to approx. 40 psi (ca. 3 bar), and the main cylinder valve was closed. A pressure drop of the high-pressure gauge on the regulator within 30' was indicative of a leak. This test was repeated until all ports were considered leak-tight.

Note: The solenoids are specified for pressures up to 6 bar. However, it is strictly recommended to apply **input pressures below 2 bar (28 psi)** to avoid leaks due to over-pressure.

A series of test measurements was conducted to characterize the performance of the box. Three different compressed ambient air gases were used to investigate the response times of the three different calibration ports until stable CO_2 and CH_4 levels are observed.

Mixing ratios of standard gases used for the performance tests:

calibration port	Solenoid valve output value	CO_2 mixing ratio [ppm]	CH_4 mixing ratio [ppb]
1	33	384.5	1881
2	34	439.6	2306
3	36	469.1	3166

All cylinders were equipped with the same type of pressure regulator. Repeated tests switching from the bottom inlet (measuring laboratory air passing the valve box and the Nafion dryer) to the different calibration ports were conducted. Fig. 2 illustrates the changes in CO_2 and CH_4 when switching from laboratory air to the various calibration gases.

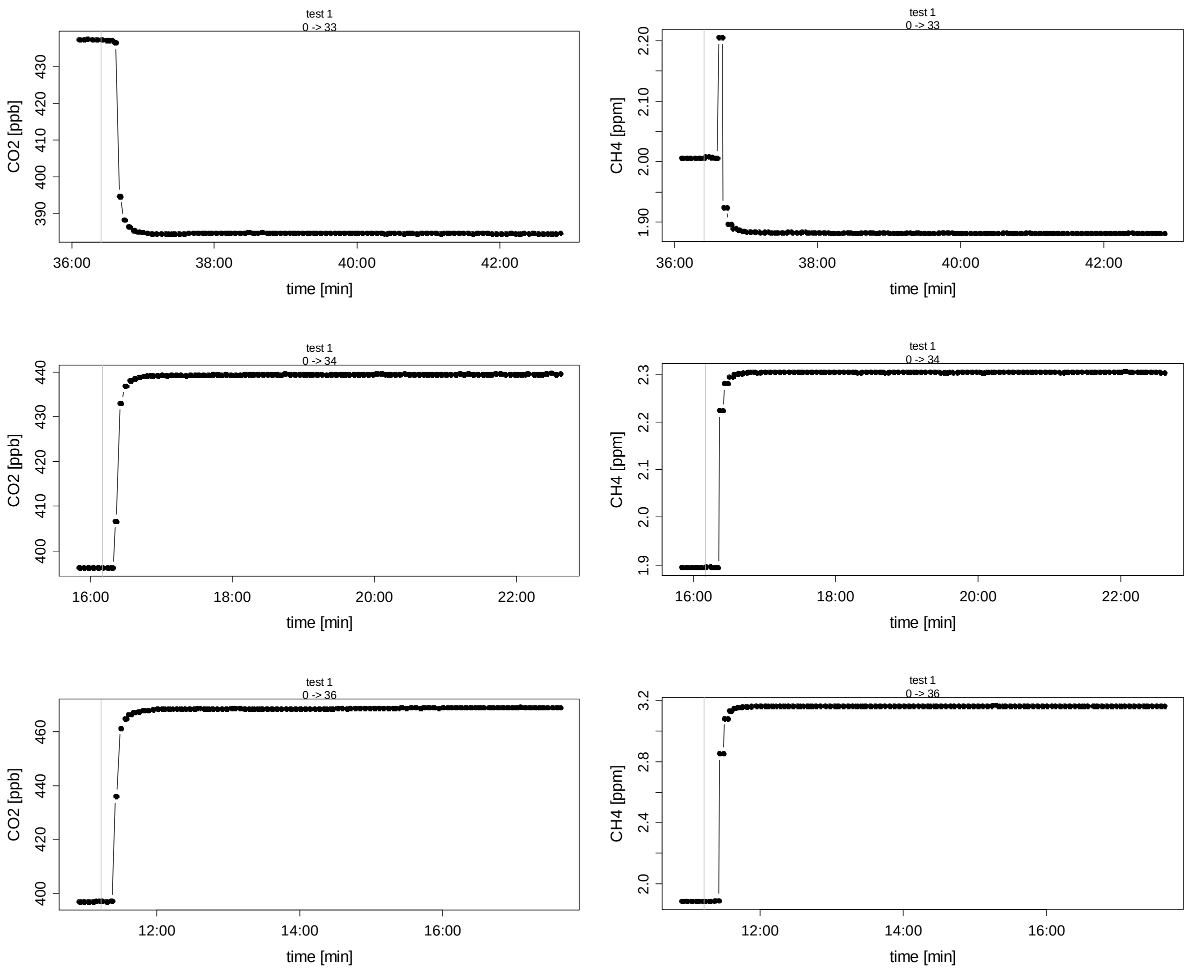

Figure 2. Changes in CO_2 (left) and CH_4 (right) when switching from laboratory air to different calibration gases using the three different calgas ports. The grey lines mark the time of switching.

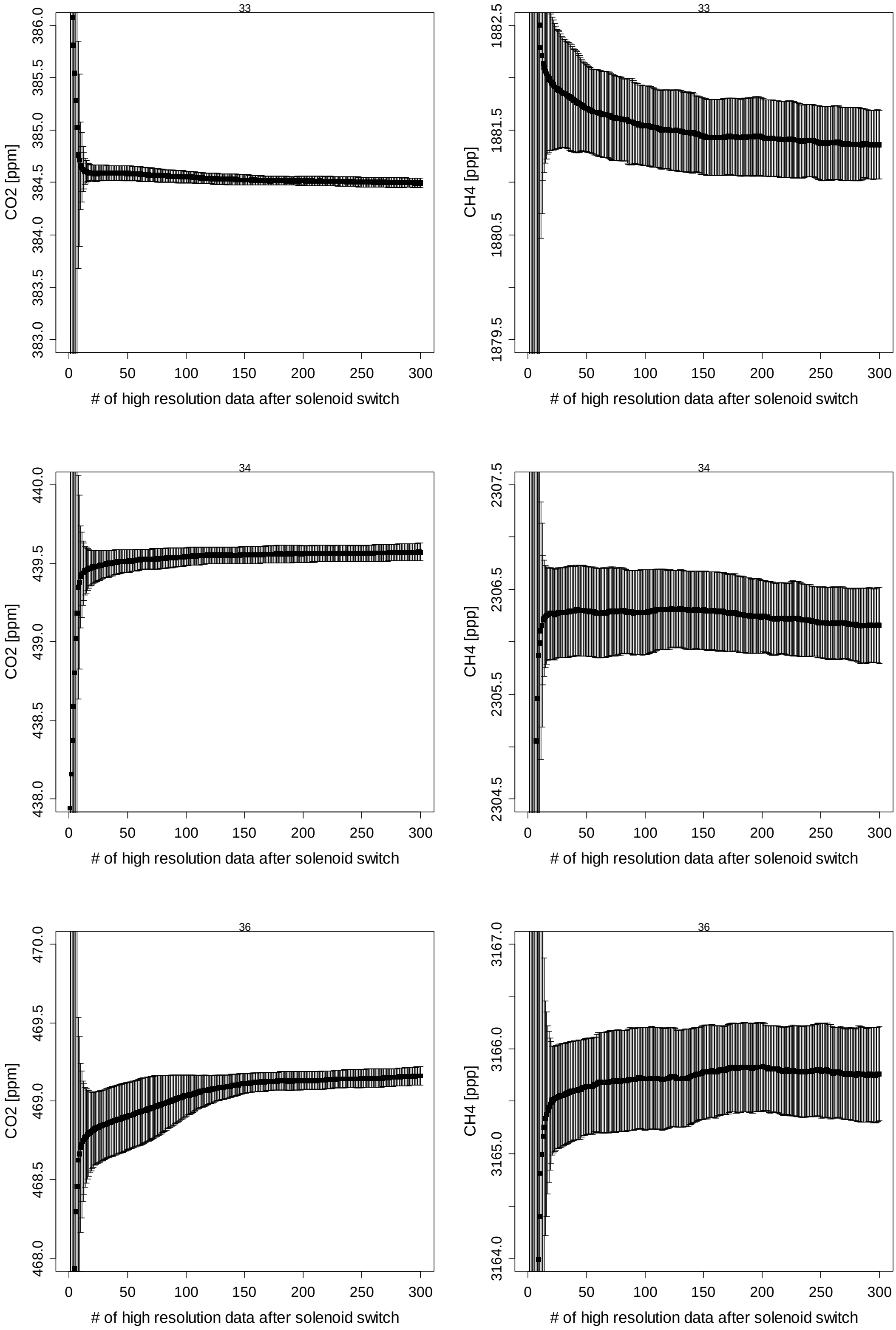

Figure 3. Mean (± standard deviation of the mean) CO_2 (left) and CH_4 (right) mixing ratios over 200 high resolution data after solenoid switch. The mean values were averaged over the shown x-value plus 199 consecutive data. Data are usually acquired every 2-3 seconds.

Fig. 2 shows that it takes several seconds after the valve switch until the new gas gets to the measurement cell, followed by several seconds until the new gas concentration is approximately reached. Fig. 3 shows the mean ± standard deviation of the mean of 200 data points and allows a qualitative assessment of the response times.. The x-axis displays the first data point of each averaging window. Large standard deviations (i.e. error bars) illustrate distinct changes of the observed mixing ratios during the averaging period. Small error bars correspond to stable readings.

The following table summarizes the results visualized in Fig. 3. It takes about 30-140 data points and 15-40 data points for CO_2 and CH_4, respectively, until stable conditions, i.e. standard deviations over 200 data points < 0.07ppm and < 0.5ppb for CO_2 and CH_4, are reached. The threshold levels are set somehow arbitrarily but are in the range of the GAW recommendations of the inter-laboratory comparabilities of ± 0.1ppm (Northern Hemisphere, ± 0.05ppm on Southern Hemisphere) for CO_2. For CH_4, the threshold level is even lower than the GAW recommendations of ± 2ppb.

Summary of response times until stable mixing ratio reading are reached:

calibration port	Solenoid valve output value	# of high resolution data until CO2 std < 0.07 ppm	# of high resolution data until CH4 std < 0.5 ppb
1	33	32 (~ 80 sec)	38 (~ 100 sec)
2	34	54 (~ 135 sec)	15 (~ 40 sec)
3	36	140 (~ 350 sec)	24 (~ 60 sec)

In conclusion, a flush time of about 350 sec (nearly 6 minutes) is recommended before considering the data for calibration purposes. Averages over 200 data points (~ 500 sec, 8.3 minutes) seem to be appropriate to achieve mean values of sufficient precision.

Another tests was conducted by measuring the same cylinder on all three standard ports and the three inlet ports, as well as directly at the inlet of the Picarro, shortcutting the valve box and the Nafion dryer. All data were humidity corrected according to an experimental determination before (see below). Fig. 4 shows a very good agreement between the three standard (cal) ports and the three inlet, whereas the CO_2 mixing ratio measured directly at the inlet port of the Picarro leads to a significantly higher reading. Most likely this can be attributed to CO_2 specific losses in the valve box (in the Nafion dryer) since all 7 measurements for CH_4 agree well within their precisions. That means that – even if a humidity correction is applied after the measurements – all samples (standards, air samples) have to be measured through the valve box.

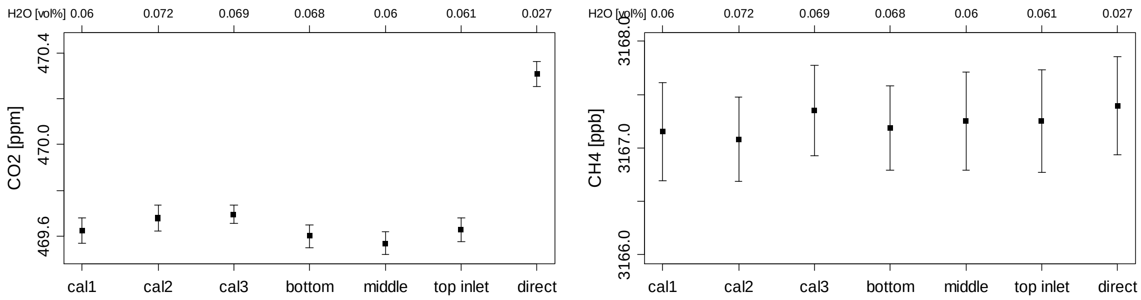

Figure 4. Calibration gas measured on all three calibration ports as well as on all three inlet ports and directly at the Picarro inlet. CO_2 (left) and CH_4 (right) are humidity-corrected. Corresponding mean H_2O readings [in volumen %] are displayed on top of the panels. Data show mean ± standard deviation over 200 data points, i.e. over about 8.3 minutes.

The applied humidity correction was experimentally determined by adding water (range 0-3.4%) to a dry sample gas with known and stable CO_2 and CH_4 mole fraction. CO_2, CH_4 and H_2O mole fractions were measured with the Picarro G1301 analyzers. Fig. 5 shows the corresponding results for CO_2 obtained at Empa before shipment of the instrument.

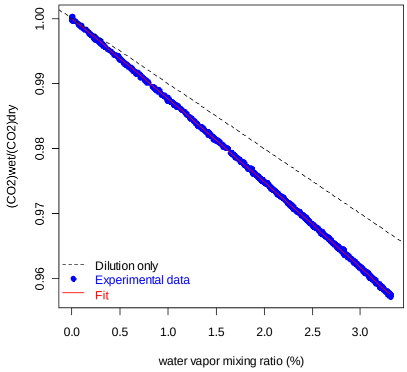

Figure 5. Experimental results of the water vapour correction.

The black dotted line shows the expected response function if dilution alone contributes to the measured CO_2 mole fraction. Blue points are observed measurements for different mole fractions, and the red line the corresponding fit:

$$\frac{(CO_2)_{wet}}{(CO_2)_{dry}} = 1 + a \cdot H_2O + b \cdot (H_2O)^2$$

$$\frac{(CH_4)_{wet}}{(CH_4)_{dry}} = 1 + c \cdot H_2O + d \cdot (H_2O)^2$$

with a = -0.012241815, b = -0.0001997, c = -0.01087, d = -0.00000157.