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

Materials Science & Technology

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 07/2

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

OF SURFACE OZONE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION ASSEKREM

ALGERIA, MAY 2007

Submitted by

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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 second system and performance audit at the Global GAW station Assekrem (ASK) in Algeria was conducted by WCC-Empa[1] from 8 thru 14 May 2007 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007]. The ASK observatory is operated by the Office National de la Météorologie (ONM).

A previous audit at the Assekrem GAW observatory was conducted in February 2003 [*Zellweger, et al.*, 2003].

The following people contributed to the audit:

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Dr Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
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Mr Azzedine Sacci	ONM Algiers, Head of Climatology Department
Mr Mohamed Mimouni	ONM Tamanrasset, Station Manager
Mr Bouziane Ouchène	ONM Tamanrasset, Head of Maintenance Group
Mr Mohamed Salah Ferroudj	ONM Tamanrasset, Maintenance Staff
Mr Mohamed Zoukani	ONM Tamanrasset, Station Operator

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

This report is distributed to the GAW Country Contact (ONM, Mr Ferhat Ounnar), the station manager (ONM, Mr Mohamed Mimouni) and the World Meteorological Organization in Geneva. The executive summaries will be posted on the internet.

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

Station Location and Access

The station is located on the summit (plateau) of the second highest point of the Hoggar mountain range at an altitude of 2710 m a.s.l. in the Saharan desert. The site is very remote at a distance of 50 km from Tamanrasset. Tourist activities in the area are limited due to difficult access to several dozen visitors per day, mainly during the winter months. A small hotel at an altitude approx. 100 m lower than the station can accommodate visitors. Vegetation is extremely sparse. Access to the station is possible by 4-wheel drive vehicles, approximately 3 hours drive from Tamanrasset. For transport of material the station can be reached by vehicles, but the upper part of the road beyond the hotel is in bad condition.

[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 facilities at the site consist of a one-story three room building. One room is used for the installation of the equipment, another room serves as an office, and the 3rd room accommodates the solar power conversion unit. The building is not air conditioned in order to save energy. Power is provided by solar panels and batteries are charged for the operation during the night. Communication is possible through the mobile phone network provided by Mobilis. A fixed line telephone is installed at the site but was not working at the time of the audit. Internet access is not possible at the site. A further building at 100 m lower altitude is used to accommodate the station operators. The main offices are located at Tamanrasset, where all data evaluation is done. Details can be found in [*Zellweger, et al.*, 2003].

Recommendation 1 (, 2007)**
The existing telephone line needs to be repaired.

Recommendation 2 (, 2007)**
The ASK site should be connected to the internet, preferably by a permanent broad band connection to allow data transfer and remote access to the site.

Recommendation 3 (*, 2007)**
Some of the equipment needs to be serviced / repaired or replaced:
-The meteorological equipment needs to be replaced. This is already under way.
-The TEOM is currently in France for repair. According to the manufacturer the instrument can not be repaired. Replacement or alternative instrumentation should be considered.

Recommendation 4 (*, 2007)**
At Tamanrasset only a slow and unreliable dial-up internet line is currently available. It is recommended to upgrade this to a permanent internet connection with higher band width at the offices in Tamanrasset.

Station Management and Operation

The station is managed by the Département Météorologique Régional Sud of the Office National de la Météorologie (ONM). The station is visited daily by a station operator. The station operator on duty stays at ASK for two weeks. The management of a Global GAW station requires more flexibility and support compared to traditional meteorological stations. The operators of GAW-related instrumentation need different and additional expertise. Their expertise has to be acknowledged by the management and should be given more extensive training, adequate salaries and other support to maintain long-term motivation.

Recommendation 5 (*, ongoing)**
More attention should be paid to the capacity building and support of the station operators. It is further recommended to have a daily allowance for the station operators to cover additional expenses during their stay at the site.

Recommendation 6 (*, ongoing)**
A budget for the operation and improvement / extension of the station should be allocated. This budget should cover all instruments and should not be limited to meteorological equipment.

Air Inlet System

Each instrument has its own air inlet system or inlet line. The design of these systems is adequate for the intended purpose.

Surface Ozone Measurements

Instrumentation. One ozone analyser is currently installed at the station for continuous surface ozone measurements (TEI 49C). This instrument was provided as an in-kind contribution by Switzerland with financial support from WMO to replace the defective TEI 49 instrument. The instrumentation is adequate for its intended purpose.

Standards. No ozone standard is available in Algeria. The station has been equipped with a TEI 165 ozone generator; however, this instrument does not allow adequate ozone calibrations.

Recommendation 7 (*, 2007)**
It should be considered to purchase an ozone calibrator such as a TEI 49C-PS or TEI 49i-PS.

Recommendation 8 (*, 2007)**
The TEI165 ozone generator can not be used for the calibration of the TEI 49C; however, important quality control checks are possible with this equipment. WCC-Empa recommends to use the generator for regular checks of the A/B ozone ratio and to perform the ozone scrubber test (refer to TEI 49C operation manual for details). This will ensure correct operation of the instrument and helps to identify possible instrument problems such as leaky valves and degradation of the ozone scrubber.

Intercomparison (Performance Audit). The inter-comparisons extended over a period of several days. The TEI 49C analyser was inter-compared during the audit. This instrument was delivered to the station in 2005 and has been the main station analyser since then. The TEI 49C analyser was found to be in good calibration, as summarised below (1a-b). [OA] represents surface ozone readings as delivered by the instrument. The original TEI 49 instrument could not be inter-compared due to an instrument failure in 2005. The following equations characterise the instrument bias:

Initial calibration with unchanged instrument settings:

TEI 49C #56109-306: 0 – 90 ppb: good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.04 ppb) / 0.995 (1a)

Calibration after adjustment of the pressure sensor:

TEI 49C #56109-306: 0 – 90 ppb: good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.11 ppb) / 0.997 (1b)

The results of these inter-comparisons are presented in Figure 1.

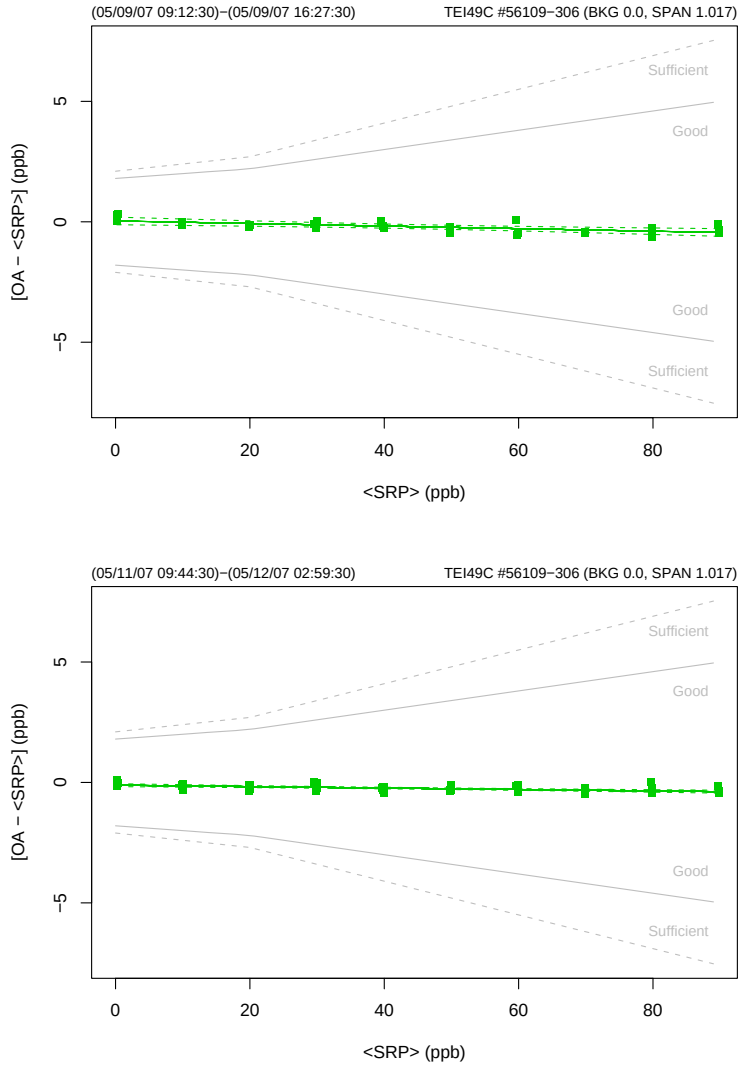

Figure 1. Bias of the Assekrem ozone analyser (TEI 49C) with respect to the SRP as a function of concentration (upper panel: initial calibration with unchanged settings; lower panel: after adjustment of the pressure sensor). Each point represents the average of the last 10 one-minute values at a given 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.

Recommendation 9 (*, 2007)**
The pressure sensor of the TEI 49C instrument needs to be regularly checked (e.g. every three months). For this purpose the station should be equipped with a reference pressure sensor.

Carbon Monoxide Measurements

Instrumentation. Assekrem is currently equipped with a Horiba APMA-360 CE carbon monoxide analyser. The instrument was delivered to the station by QA/SAC Switzerland / WCC-Empa based on a proposal to WMO in 2006. The instrumentation is adequate for the intended purpose.

Standards. The station is normally equipped with two carbon monoxide standards. One standard has a concentration of approx. 1 ppm CO in air and is used for direct calibrations of the instrument. The other standard has a concentration 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 were delivered to the station by WCC-Empa, and no local calibration gas supplier is available.

Recommendation 10 (*, 2007-2010)
For the long term operation of the ASK station, funds need to be made available for calibration gas supply.

Intercomparison (Performance Audit). The instrument was inter-compared during the audit with the calibration factors as they have been set during the installation of the instrument. The inter-comparison involved repeated challenges of the instruments with randomised carbon monoxide concentrations from a travelling standard (dilution unit combined with high concentration carbon monoxide standard). The following equation (2) characterises the instrument bias (cf. Figure 2):

Horiba APMA-360CE #303003 (ZERO 21 SPAN 1.2635):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 3.9 ppb) / 0.998 (2)

The results show that the instrument is in good calibration; however, the individual data points are associated with relatively large uncertainties. This is mainly because the instrument shows a significant short-term noise as expected for an NDIR instrument. However, it was noticed that the noise of this particular instrument is sometimes larger than usual. The reason of this behaviour could not be identified during the audit.

Recommendation 11 (, 2007)**
The instrument noise should be carefully monitored. If periods with excessive noise repeatedly occur the reason for this behaviour needs to be explored.

Recommendation 12 (, 2007)**
The SPAN factor of the instrument is relatively high, but possible for this type of analyser. Nevertheless the calibration of the instrument should be regularly checked with direct inter-comparison with the 1 ppm calibration gas. Action should be taken in case of decreasing sensitivity.

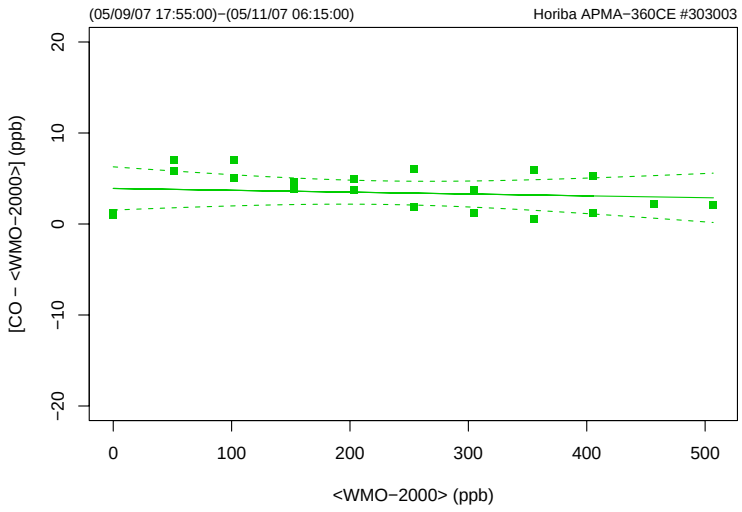

Figure 2. Bias of the Assekrem carbon monoxide analyser (Horiba APMA-360CE) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Other variables / observations

The station runs also a small aerosol programme (aerosol size distribution with a laser particle counter, and TSP with a TEOM). However, these instruments are not fully operational (cf. Recommendation 3), and replacement should be considered. Furthermore NOAA/ESRL flasks are regularly filled at the site.

Data Acquisition and Management

A LabView based data acquisition was installed at ASK for the carbon monoxide and ozone analysers. This DAQ was part of the proposal for CO measurements at ASK by QA/SAC Switzerland. The system, developed by QA/SAC Switzerland, is running on a laptop computer using serial ports for communication with the instruments. One minute averages of all available instrument parameters are stored, including the readings of the mass flow controllers of the dilution system.

Recommendation13 (, 2007)**
The current data acquisition system works well; however, it was noticed during the audit that other USB devices such as USB hubs may cause communications problems. The laptop computer should only be used for data acquisition.

Recommendation14 (*, 2007)**
It is important that the available electronic check list and log files are used and regularly filled in. All relevant information must be entered into these files.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). At the time of the audit data for surface ozone (March 97 – December 05) was available at the data centre. Some of the data however was identified not to be sufficiently quality assured.

Recommendation 15 (, 2007)**
WCC-Empa supports the submission of GAW data to the corresponding data centres; however, all data should undergo thorough quality control before submission. Ozone data which has been submitted needs to be revised. The recommendations for resubmission have been summarised in a separate report [Klausen, 2007] (cf. Appendix 2).

Conclusions

The operational programme of the Global GAW station Assekrem/Tamanrasset consist of continuous carbon monoxide and surface ozone observations. Some of the operations (mainly aerosol measurements) were discontinued mainly due to a lack of resources. Those need to be revived as well as the programme extended. Nevertheless, the existing data sets are a valuable contribution to the GAW programme, especially because they cover a geographical region where only sparse in-situ information about atmospheric composition is available. The continuation of existing measurements on a long term basis and the addition of new parameters are therefore strongly encouraged. All assessed measurements were of sufficiently high quality.

Summary Ranking of Assekrem Station

System Audit Aspect	Adequacy[#]	Comment
Access	(5)	4-weel drive road
Facilities		
Laboratory and office space	(5)	Spacious concrete building
Air Conditioning	(0)	Not available
Power supply	(4)	Solar power / batteries
Internet access	(0)	Not available
General Management and Operation		
Organisation	(3)	No incentives for operators
Competence of staff	(4)	Insufficient science support
Air Inlet System	(4)	Direct lines to instruments
Instrumentation		
Ozone	(5)	TEI 49C
Carbon monoxide	(4)	Horiba APMA-360CE
Aerosol TSP	(0)	Teom, not operational
Aerosol TSP	(0)	Filter sampling, not operational
Aerosol size distribution	(1)	LPC, inadequate instrument
Aerosol Light absorption coef.	(0)	Aethalometer, not operational
Flask sampling	(5)	NOAA/ESRL
Meteo	(3)	Only every 3 hours
Sunshine duration	(3)	Manual system
Standards		
Ozone	(1)	NA, only ozone generator
Carbon monoxide	(4)	Direct and with dilution system
Data Management		
Data acquisition	(5)	LabView based system
Data processing	(4)	More expertise needed
Data submission	(3)	Data need to be revised

[#]0: inadequate thru 5: adequate

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Dübendorf, September 2007

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

APPENDIX 1 – WCC-EMPA AUDIT

Global GAW Station Assekrem

Site description

Information about the Assekrem GAW station can be found in the previous audit report [*Zellweger, et al.*, 2003], and the station is also registered in GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Programme

The observatory Assekrem started its operation in 1995. A short overview of the measurement programme and its status as of May 2007 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the ASK Station

Parameter	Current Instrument	Data Coverage (%) *		
		<12 m	<3 y	Overall
Aerosol				
Light absorption coefficient#	Aethalometer#	0	0	
TSP#	Teom#	0	0	52
TSP#	Filter sampling (Ruprecht Pataschnik)#	0	0	2
Size distribution / number conc.	LPC	>95	>95	>95
Ozone				
Surface ozone	UV absorption (TEI 49C)	>95	>95	>95
Greenhouse Gas				
CO_2, SF_6, N_2O	NOAA/GMD flask sampling	>95	>95	>95
Reactive Gas				
CO	NDIR (Horiba APMA-360)	>95		
CO, H_2	NOAA/GMD flask sampling	>95	>95	>95
Ancillary Measurements				
Sunshine duration		>95	>95	>95
Meteo (TU, wind speed + direction)		>95	>95	>95

*: estimated by station manager based on raw data; actual data coverage may be lower.
#: discontinued; Missing data availability: no data coverage information was available at the time of the audit.

Ozone, Carbon Monoxide and Methane Distribution at Assekrem

The monthly and yearly distributions of one hourly mean values for surface ozone and carbon monoxide for the year 2006 (surface ozone) and for all available carbon monoxide data (September 2006 to April 2007) are shown in Figure 3.

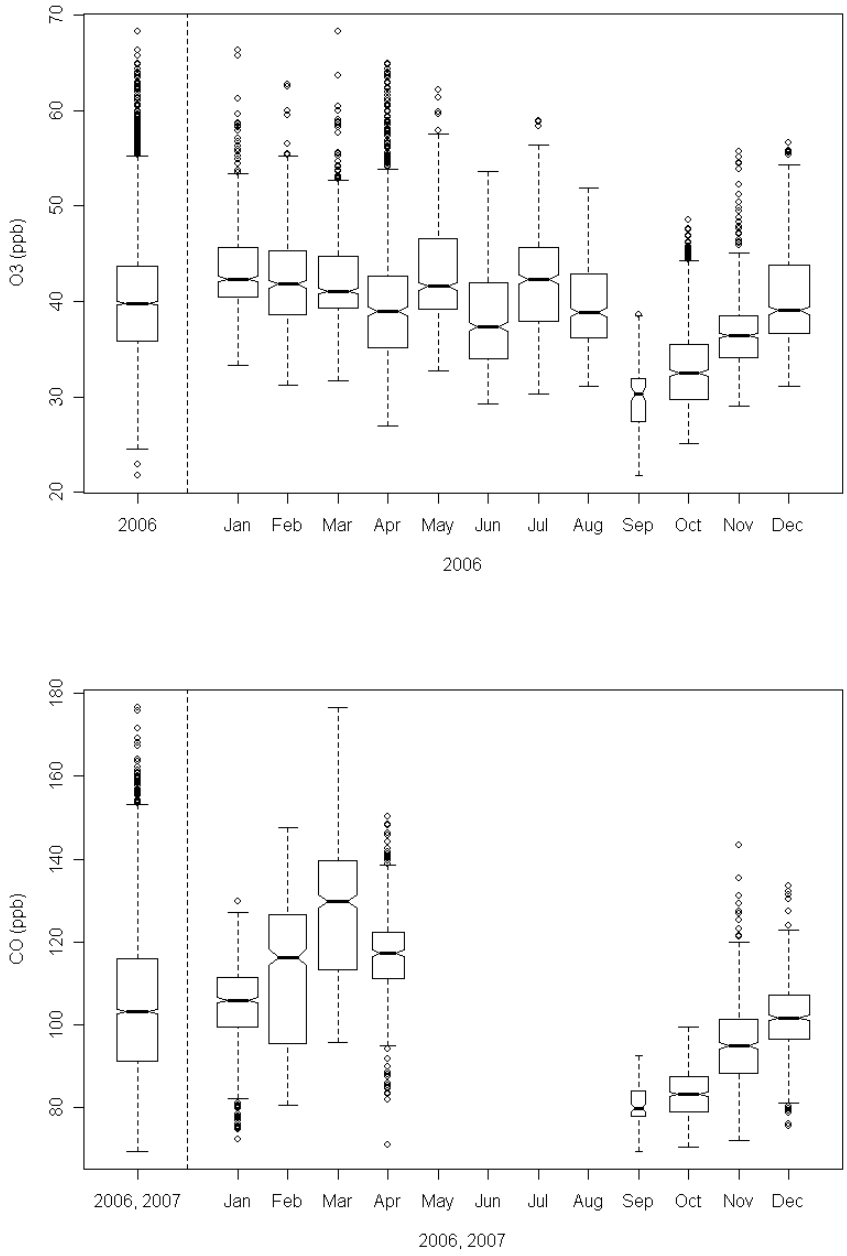

Figure 3. Yearly and monthly box plots of 1-hourly aggregates for the year for surface Ozone (upper panel) and carbon monoxide (lower panel, from September 2006 to April 2007). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, 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 GAW activities of Algeria are coordinated by the Office National de la Météorologie (ONM). An organisational chart of the station is shown in Figure 4.

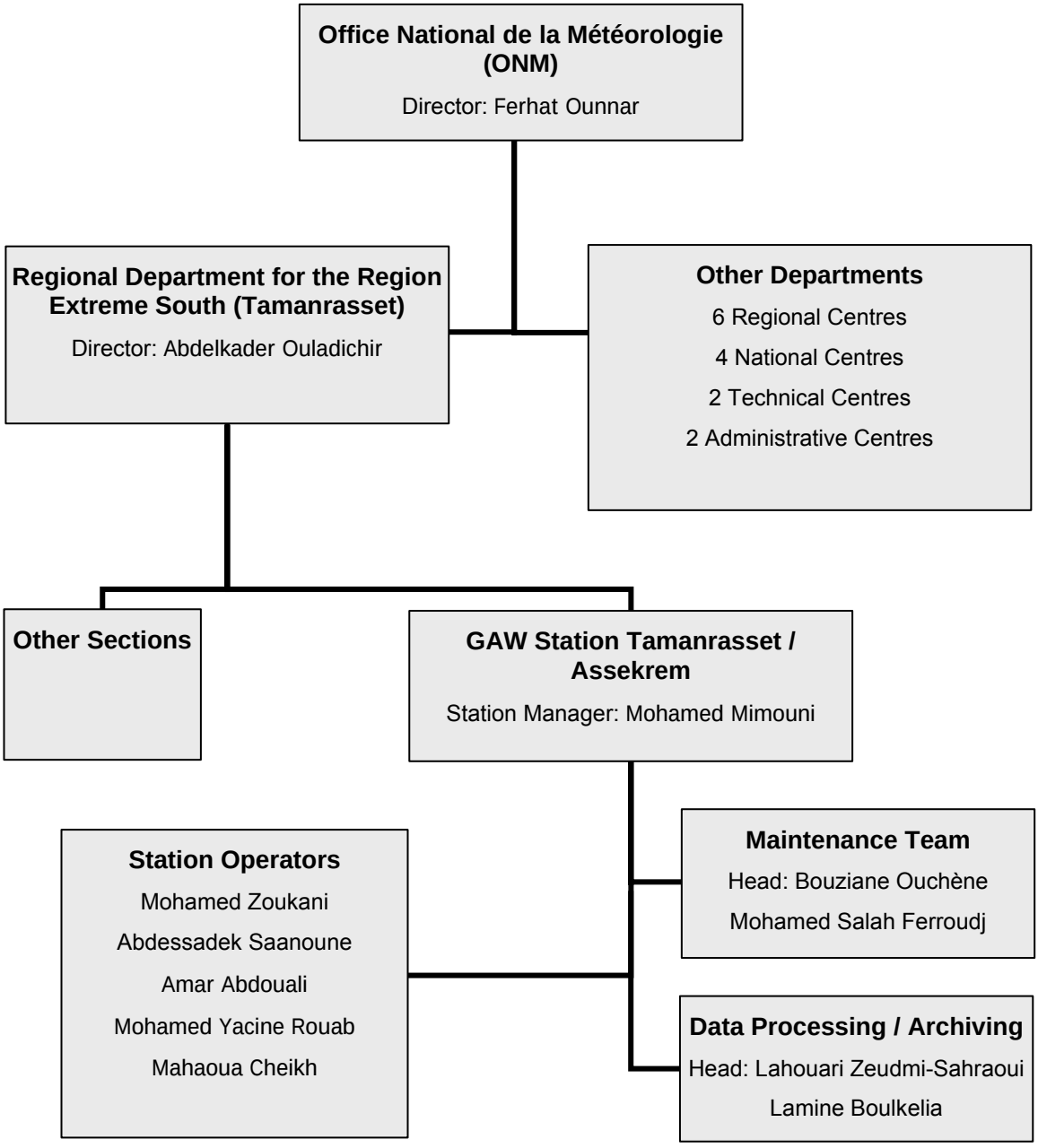

Figure 4. Organisation of the GAW activities in Algeria as of May 2007.

Surface Ozone Measurements

Surface ozone measurements started in 1997 at the Assekrem site, and time series are available since then except for a period between July 2001 and February 2003. During this period the ozone scrubber degraded, and these data can not be corrected and must be flagged as invalid. All existing data has been re-analyzed by QA/SAC Switzerland using a Kolmogorov-Zurbenko adaptive (KZA) filtering technique. The results and recommendations of this work were summarised in a report [*Klausen*, 2007], which was submitted to the station manager and WDCGG. Data should be corrected and re-submitted as recommended in this report.

Major changes since the last audit by WCC-Empa in 2003 include the installation of a new instrument (TEI 49C). This instrument replaces the TEI 49 analyser which failed in 2005. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-a].

Monitoring Set-up and Procedures

Air Conditioning

The laboratory is not air conditioned. The reason for this is mainly the limited capacity of the solar power supply. Under these circumstances the installation of an AC system is currently not of highest priority, because the equipment installed at the site is not sensitive to temperature changes.

Air Inlet System

The air inlet system has been described in the previous audit report [*Zellweger, et al.*, 2003]. The new instrument was connected to the existing inlet line. Residence time is estimated to be approx. 5 seconds.

Instrumentation

The station is equipped with one ozone analyser (TEI 49C). Instrumental details for the ozone analyser (OA) are summarised in Table 2 below. The previous instrument as described in [*Zellweger, et al.*, 2003] failed in 2005 and was decommissioned after installation of the TEI 49C.

Standards

No ozone standard is available at the site. A TEI 165 ozone generator is available for instrument checks (cf. Recommendations 7 and 8).

Operation and Maintenance

A daily check of general operation is performed by the operator in charge, and several instrument parameters are checked weekly. Inlet filters are exchanged monthly. WCC-Empa recommends using the ozone generator for additional preventive checks (cf. recommendation 8).

Data Acquisition and Data Transfer

A custom made LabView based data acquisition system is used to acquire ozone data. All accessible instrument parameters such as flow rates, intensities, temperatures and pressure are recorded by the DAQ, and one minute averages are stored. In case of a DAQ communication problem data can also be manually downloaded using the TEI software (version 2.2.0).

Data Treatment

The raw data is inspected every second week in Tamanrasset (time series plot, check with instrument log book). No further data treatment was done at Tamanrasset. It is recommended to perform additional quality checks of the data before submission to WDCGG (cf. Recommendation 14).

Data Submission

Ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG). Some of these data however was identified not to be sufficiently quality assured. Re-analysis and re-submission is recommended [*Klausen*, 2007].

Documentation

All information was entered in log books. The information was only partly comprehensive and up-to-date. The instrument manuals are available at the site. QA/SAC Switzerland and WCC-Empa trained the station operator in using electronic log files and check lists. These new electronic log files and check lists should be used in future.

Inter-Comparison the Ozone Analyzer

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

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

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

Travelling standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.1; COEFF = 1.010
Ozone analyzer (OA) This instrument is the main ozone analyser since the current audit.	Model, S/N	TEI 49C #56109-306
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.017
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	One minute aggregates from digital output of WCC-Empa data acquisition (custom designed LabView programme)
	OA	Same as TS during the inter-comparison
Pressure readings at beginning of inter-comparison (hPa)	Ambient	NA
	TS	743.3
	OA	746.1 (not adjusted for first inter-comparison, afterwards adjusted to ambient pressure (TS) (743.1) for second inter-comparison)
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		3 runs with unchanged settings (9 May 07) 7 runs with adj. pressure sensor (11-12 May 07)

Results
Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results are valid for the calibration factors as given in Table 2 above. 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.

TEI 49C #56109-306
This instrument was installed at ASK in May 2005. The initial calibration was done against SRP#15 at the laboratory of WCC-Empa in March 2005. Two inter-comparisons were made during the audit. The result of the first assessment (direct comparison between TS and OA without any change of the OA) is shown in Table 3. A final comparison was made after adjustment of the pressure sensor (-0.4%); these results are presented in Table 4.

Figure 5 shows the regression residuals of the TEI 49C ozone analyser for the inter-comparisons described above with respect to the SRP as a function of ozone concentration for the range 0 - 90 ppb and as a function of time.

Table 3. Ten-minute aggregates (initial inter-comparison with unchanged settings) computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the ASK ozone analyser (OA) TEI 49C #56109-306 with the WCC-Empa travelling standard (TS).

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2007-05-09 09:17	1	0	0.41	0.74	0	0.12	0.06
2007-05-09 09:32	1	30	29.58	29.48	0	0.12	0.11
2007-05-09 09:47	1	60	59.56	59.61	0	0.06	0.05
2007-05-09 10:02	1	40	39.60	39.62	0	0.11	0.05
2007-05-09 10:17	1	90	89.66	89.55	0	0.06	0.06
2007-05-09 10:32	1	50	49.78	49.54	0	0.06	0.06
2007-05-09 10:47	1	10	9.86	9.84	0	0.09	0.10
2007-05-09 11:02	1	20	19.87	19.74	0	0.09	0.09
2007-05-09 11:17	1	80	79.82	79.55	0	0.08	0.08
2007-05-09 11:32	1	70	69.92	69.42	0	0.09	0.08
2007-05-09 11:47	2	0	0.20	0.47	0	0.12	0.06
2007-05-09 12:02	2	40	39.96	39.71	0	0.12	0.08
2007-05-09 12:17	2	70	69.89	69.41	0	0.09	0.07
2007-05-09 12:32	2	30	29.95	29.97	0	0.14	0.06
2007-05-09 12:47	2	90	89.84	89.48	0	0.10	0.09
2007-05-09 13:02	2	20	19.96	19.84	0	0.09	0.07
2007-05-09 13:17	2	10	9.98	9.96	0	0.09	0.06
2007-05-09 13:32	2	60	59.89	59.38	0	0.08	0.06
2007-05-09 13:47	2	50	49.88	49.42	0	0.10	0.05
2007-05-09 14:02	2	80	79.86	79.26	0	0.06	0.06
2007-05-09 14:17	3	0	0.22	0.22	0	0.09	0.03
2007-05-09 14:32	3	90	89.84	89.34	0	0.10	0.06
2007-05-09 14:47	3	70	69.87	69.40	0	0.08	0.06
2007-05-09 15:02	3	40	39.90	39.71	0	0.11	0.06
2007-05-09 15:17	3	50	49.87	49.39	0	0.12	0.06
2007-05-09 15:32	3	20	19.92	19.70	0	0.12	0.07
2007-05-09 15:47	3	30	29.83	29.55	0	0.13	0.09
2007-05-09 16:02	3	60	59.78	59.22	0	0.10	0.06
2007-05-09 16:17	3	10	9.93	9.77	0	0.10	0.03
2007-05-09 16:32	3	80	79.82	79.17	0	0.09	0.05

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

Table 4. Ten-minute aggregates (second inter-comparison with adjusted pressure sensor) computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the ASK ozone analyser (OA) TEI 49C #56109-306 with the WCC-Empa travelling standard (TS).

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2007-05-11 09:49	1	0	0.32	0.28	0	0.13	0.09
2007-05-11 10:04	1	30	29.48	29.48	0	0.10	0.08
2007-05-11 10:19	1	60	59.56	59.39	0	0.14	0.06
2007-05-11 10:34	1	40	39.65	39.39	0	0.13	0.07
2007-05-11 10:49	1	90	89.65	89.48	0	0.11	0.10
2007-05-11 11:04	1	50	49.80	49.46	0	0.08	0.04
2007-05-11 11:19	1	10	9.89	9.76	0	0.12	0.05
2007-05-11 11:34	1	20	19.86	19.72	0	0.07	0.08
2007-05-11 11:49	1	80	79.77	79.75	0	0.10	0.08
2007-05-11 12:04	1	70	69.85	69.59	0	0.06	0.07
2007-05-11 12:19	2	0	0.27	0.27	0	0.13	0.07
2007-05-11 12:34	2	40	39.88	39.57	0	0.08	0.07
2007-05-11 12:49	2	70	69.87	69.55	0	0.06	0.07
2007-05-11 13:04	2	30	29.97	29.76	0	0.08	0.05
2007-05-11 13:19	2	90	89.86	89.43	0	0.09	0.04
2007-05-11 13:34	2	20	19.99	19.73	0	0.08	0.09
2007-05-11 13:49	2	10	9.97	9.81	0	0.10	0.05
2007-05-11 14:04	2	60	59.89	59.54	0	0.09	0.07
2007-05-11 14:19	2	50	49.91	49.58	0	0.11	0.06
2007-05-11 14:34	2	80	79.88	79.44	0	0.10	0.08
2007-05-11 14:49	3	0	0.21	0.10	0	0.11	0.06
2007-05-11 15:04	3	90	89.83	89.36	0	0.07	0.08
2007-05-11 15:19	3	70	69.86	69.38	0	0.05	0.05

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2007-05-11 15:34	3	40	39.89	39.65	0	0.07	0.09
2007-05-11 15:49	3	50	49.86	49.48	0	0.08	0.06
2007-05-11 16:04	3	20	19.94	19.58	0	0.14	0.09
2007-05-11 16:19	3	30	29.91	29.52	0	0.10	0.09
2007-05-11 16:34	3	60	59.87	59.53	0	0.11	0.06
2007-05-11 16:49	3	10	9.93	9.81	0	0.12	0.06
2007-05-11 17:04	3	80	79.82	79.36	0	0.07	0.05
2007-05-11 17:19	4	0	0.23	0.06	0	0.12	0.05
2007-05-11 17:34	4	30	29.85	29.69	0	0.11	0.11
2007-05-11 17:49	4	60	59.86	59.54	0	0.15	0.07
2007-05-11 18:04	4	40	39.89	39.63	0	0.06	0.06
2007-05-11 18:19	4	90	89.87	89.43	0	0.12	0.06
2007-05-11 18:34	4	50	49.95	49.84	0	0.12	0.07
2007-05-11 18:49	4	10	9.97	9.81	0	0.13	0.08
2007-05-11 19:04	4	20	19.99	19.81	0	0.08	0.06
2007-05-11 19:19	4	80	79.88	79.61	0	0.06	0.09
2007-05-11 19:34	4	70	69.91	69.54	0	0.08	0.10
2007-05-11 19:49	5	0	0.24	0.16	0	0.13	0.05
2007-05-11 20:04	5	40	39.90	39.71	0	0.07	0.04
2007-05-11 20:19	5	70	69.90	69.61	0	0.10	0.05
2007-05-11 20:34	5	30	29.98	29.83	0	0.13	0.04
2007-05-11 20:49	5	90	89.89	89.46	0	0.06	0.03
2007-05-11 21:04	5	20	20.03	19.92	0	0.11	0.08
2007-05-11 21:19	5	10	10.01	9.70	0	0.06	0.06
2007-05-11 21:34	5	60	59.92	59.51	0	0.10	0.07
2007-05-11 21:49	5	50	49.91	49.57	0	0.11	0.07
2007-05-11 22:04	5	80	79.87	79.56	0	0.05	0.05
2007-05-11 22:19	6	0	0.24	0.26	0	0.12	0.04
2007-05-11 22:34	6	90	89.86	89.48	0	0.06	0.05
2007-05-11 22:49	6	70	69.91	69.52	0	0.13	0.08
2007-05-11 23:04	6	40	39.97	39.75	0	0.06	0.07
2007-05-11 23:19	6	50	49.93	49.71	0	0.10	0.07
2007-05-11 23:34	6	20	20.01	19.73	0	0.05	0.04
2007-05-11 23:49	6	30	29.97	29.74	0	0.12	0.07
2007-05-12 00:04	6	60	59.90	59.77	0	0.10	0.06
2007-05-12 00:19	6	10	9.99	9.92	0	0.08	0.05
2007-05-12 00:34	6	80	79.87	79.49	0	0.10	0.04
2007-05-12 00:49	7	0	0.24	0.32	0	0.16	0.07
2007-05-12 01:04	7	30	29.93	29.90	0	0.11	0.05
2007-05-12 01:19	7	60	59.92	59.71	0	0.06	0.03
2007-05-12 01:34	7	40	39.94	39.46	0	0.10	0.07
2007-05-12 01:49	7	90	89.88	89.42	0	0.08	0.07
2007-05-12 02:04	7	50	49.93	49.78	0	0.10	0.03
2007-05-12 02:19	7	10	10.01	9.80	0	0.08	0.09
2007-05-12 02:34	7	20	19.97	19.67	0	0.16	0.07
2007-05-12 02:49	7	80	79.85	79.53	0	0.09	0.06
2007-05-12 03:04	7	70	69.92	69.42	0	0.04	0.03

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

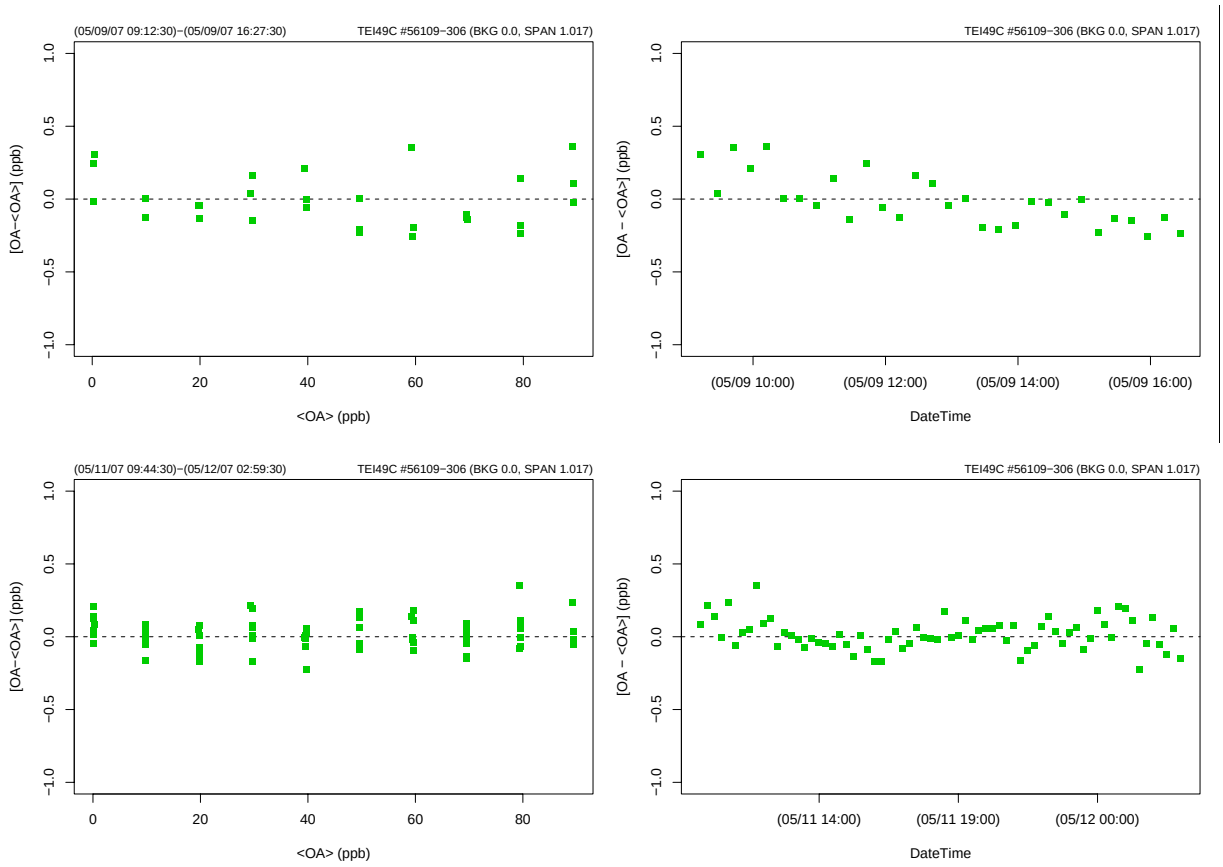

Figure 5. Regression residuals of the ASK ozone analyser (TEI 49C) as a function of concentration (left) and time (right). The upper panel shows the initial inter-comparison (unchanged settings), and the lower panel a second inter-comparison after adjustment of the pressure sensor.

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

TEI 49C #56109-306:

Initial calibration with unchanged settings:

$$\mathbf{X_{O3}\ (ppb) = ([OA] - 0.04\ ppb) / 0.995}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.29\ ppb^2 + 2.67e\text{-}05 * X_{O3}^2)} \qquad \mathbf{(1a)}$$

Calibration after adjustment of the pressure sensor:

$$\mathbf{X_{O3}\ (ppb) = ([OA] + 0.11\ ppb) / 0.997}$$

$$\mathbf{u_{O3}\ (ppb) = sqrt(0.27\ ppb^2 + 2.61e\text{-}05 * X_{O3}^2)} \qquad \mathbf{(1b)}$$

Conclusions

The ASK ozone analyser was found to agree well with the WCC-Empa ozone standard. The initial calibration that was carried out before installation by WCC-Empa in 2005 proved to be still valid.

Carbon Monoxide Measurements

The carbon monoxide instrument was installed at the station in September 2006 by the ASK maintenance staff. The instrument set-up is described in the Standard Operating Procedure (SOP) provided by WCC-Empa. The analyser was funded by WMO, and modifications were made at Empa. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation-b].

Monitoring Set-up and Procedures

Air Conditioning

No air conditioning is available at the site.

Air Inlet System

The carbon monoxide instrument has a inlet comparable to the ozone instrument. It is a ¼" PTFE line, with a length of approx. 4 m. The intake is on top of the roof and approx. 4.6 m above ground. The air intake is located immediately next to the ozone inlet. An inlet filter resides inside the CO analyzer. Residence time is estimated to be approximately 5 seconds.

Instrumentation

The station is equipped with a Horiba APMA-360CE carbon monoxide analyser. Instrumental details for the carbon monoxide analyser are summarised in Table 6 below.

Standards and Calibration

The station has been provided with calibration gases by WCC-Empa. Table 5 gives details of the cylinders currently available at the station. Two types of calibration standards are available: Low concentrations (approx. 1 ppm) for direct calibrations of the instrument, and higher concentrations (50 ppm) for automatic span checks with the dilution system.

Table 5. Carbon monoxide standards available at the ASK station

Manufacturer, S/N, Use	CO Content (ppb) * and matrix	Calibration		In service	
		Date	By	From	To
Messer, 168880, direct calibration	1052.6 ± 10.5 ppb synth. air 5.0	05/12	WCC-Empa	09/06	09/06[#]
Messer, 168879, dilution	50000 ± 500 ppb synth. air 5.0	05/12	WCC-Empa	09/06	09/06[#]
Messer, 8732, dilution	49395 ± 500 ppb synth. air 5.0	12/06	WCC-Empa	04/07	cont.
Messer, 20988, direct calibration	1006.8 ± 10.0 ppb synth. air 5.0	12/06	WCC-Empa	04/07	cont.

** WMO-2000 carbon monoxide scale*
[#] Cylinder accidentally emptied during the installation

Operation and Maintenance

The instrument is daily checked for general operation. In addition, a weekly check list should be filled in. The operators have been trained to use the check list during the audit. The inlet filter is exchanged monthly. All operation and maintenance procedures are further summarised in the Standard Operating Procedure (SOP) -Horiba APMA-360 CO Monitor - GAW Station Assekrem, which was provided to the station by WCC-Empa. Refer to this document for details.

Data Acquisition and Data Transfer

A custom made LabView based data acquisition system is used to acquire carbon monoxide data. In addition to the measurement data the instrument status and the flow rates of the mass flow controllers are recorded by the DAQ. One minute averages are stored. In case of a of a DAQ communication problem data can also be manually downloaded from the internal data logger using another custom made LabView software.

Data Treatment
The first five minute average value after a switch of the zero/span valve is discarded. The remaining five minute average values are used for further data evaluation. Zero values are used to correct for instrument zero drift using a lowess fit. Span values from the automatic span checks are used for quality control purposes but are currently not used for the correction of a span drift. Further experience is needed to clarify if a correction for span drift is necessary.

Data Submission
Carbon monoxide data have not yet been submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG). This is mainly because measurements started only in September 2006. As soon as longer time series become available they will be submitted to WDCGG after quality control in collaboration with QA/SAC Switzerland.

Documentation
The instrument manuals are available at the site. In addition a SOP for the operation of the instrument as well as for the DAQ is available. These documents have been provided by QA/SAC Switzerland and WCC-Empa upon delivery of the instrument. Electronic check lists and log files are available on the DAQ computer. It was noticed during the audit that the station operators were not familiar with these documents. The operator present during the audit has been trained in using the check list and log files. It is important that this knowledge is transferred to the other station operators (cf. Recommendation 14).

Inter-Comparison of Carbon Monoxide Analysers

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 are given in Table 10 below.

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 the ASK data acquisition systems as indicated. All data was corrected for the zero offset as described above.

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

Travelling standard (TS)		One cylinder (Messer Germany, 0651B, 9935.7±30.9 ppb CO 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)
Levels (ppb)		Level / Reference / St.Uncertainty 1 / 0.00 / 0.03 2 / 51.13 / 0.16 3 / 101.83 / 0.32 4 / 152.48 / 0.49 5 / 203.08 / 0.65 6 / 253.84 / 0.81 7 / 304.48 / 0.97 8 / 355.14 / 1.13 9 / 405.61 / 1.29 10 / 456.39 / 1.45 11 / 507.02 / 1.61
Field instrument	Model, S/N	Horiba APMA-360CE #303003
	Principle	NDIR, cross flow modulation technique
	Modification	Nafion drier PERMAPURE PD-50T-12PP
	Range	1 ppm
	Settings	Zero 21 - Span 1.2635
Connection of TS to field instrument		Sample inlet
Data Acquisition		1-minute averages from station data acquisition which were further aggregated to 5 min values
Duration per level (min)		90-120, inclusive of interspersed automatic zero (15') and span (10') checks every second hour
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		2 run (9-11 May, 2007)

Results

Each carbon monoxide level was effectively applied for 90-120 minutes, which resulted in a maximum of 17 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). No span correction was applied to the data for the evaluation of the result.

Table 7. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the ASK Horiba APMA-360CE CO analyser with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	sdTS (ppb)	CO (ppb)	sdCO(ppb)	No. 5' av.
(05/09/07 17:55:00)	0.00	0.03	0.96	2.37	11
(05/09/07 19:10:00)	51.13	0.16	57.00	3.85	10
(05/09/07 20:27:30)	101.83	0.32	108.90	4.96	10
(05/09/07 22:12:30)	152.48	0.49	157.07	4.54	16
(05/09/07 23:55:00)	203.08	0.65	206.85	5.69	11
(05/10/07 01:19:22)	253.84	0.81	259.84	6.58	8
(05/10/07 02:27:30)	304.48	0.97	308.24	4.92	10
(05/10/07 04:10:00)	355.14	1.13	361.06	5.18	17
(05/10/07 05:55:00)	405.61	1.29	410.89	4.09	11
(05/10/07 10:15:00)	0.00	0.03	1.22	7.37	17
(05/10/07 12:15:00)	51.13	0.16	58.13	4.29	17
(05/10/07 14:15:00)	101.83	0.32	106.88	3.58	17
(05/10/07 16:15:00)	152.48	0.49	156.33	3.77	17
(05/10/07 18:15:00)	203.08	0.65	208.01	3.52	17
(05/10/07 20:15:00)	253.84	0.81	255.69	3.24	17
(05/10/07 22:15:00)	304.48	0.97	305.70	2.80	17
(05/11/07 00:15:00)	355.14	1.13	355.68	4.92	17
(05/11/07 02:15:00)	405.61	1.29	406.78	3.99	17
(05/11/07 04:15:00)	456.39	1.45	458.55	2.44	17
(05/11/07 06:15:00)	507.02	1.61	509.12	2.27	17

Figure 6 shows the regression residuals of the analyser over the course of the initial inter-comparison runs. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of concentration dependence (right panel) in the residuals indicates linearity of the instrument, although a relatively large difference was observed between the residuals at zero and low concentrations. However, the individual data points are associated with relatively high uncertainty.

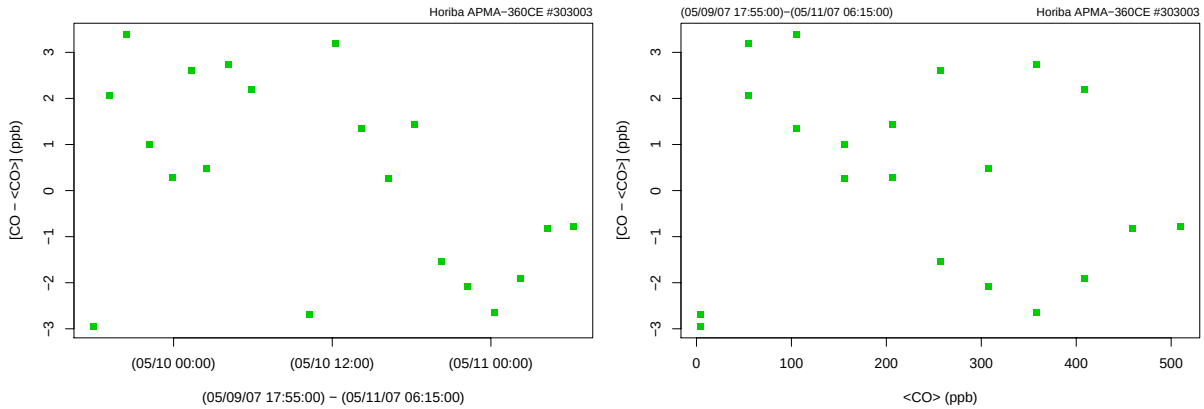

Figure 6. Regression residuals of the ASK carbon monoxide analyser based on the inter-comparison with the dilution unit. Points represent averages of valid 5 minute values. Left panel: time dependence; Right panel: concentration dependence.

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

$$X_{CO}\ (ppb) = ([CO] - 3.9\ ppb) / 0.998$$

$$u_{CO}\ (ppb) = sqrt(26.0\ ppb^2 + 2.91e\text{-}05 * X_{CO}^2) \quad (2)$$

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.

Check of the dilution system (MFCs)
The MFCs used for the automatic span checks were inter-compared with red-y mass flow meters during the audit. These red-y flow meters were compared to the Empa flow reference (Molbloc) before and after the audit. The following results were obtained:

MFC1: Set point 1485 ml/min; Actual flow: 1514.1±1.2 ml/min
MFC2: Set point 15 ml/min; Actual flow: 15.38±0.02 ml/min

This results in an expected CO concentration of 502.7 ppb during span checks with a 50 ppm cylinder. The MFCs were initially compared to the flow reference before delivery. The results of the initial inter-comparison were as follows:

MFC1: Set point 1485 ml/min; Actual flow: 1507.3±0.9 ml/min
MFC2: Set point 15 ml/min; Actual flow: 15.08±0.01 ml/min

With the initial calibration the resulting CO concentration using a 50 ppm span gas would 495.3 ppb, which is slightly lower mainly because of a 2% change of MFC2.

Discussion
The inter-comparison between WCC-Empa and Assekrem showed relatively good agreement between the analyser and the travelling standard. However, individual values are still associated with relatively high uncertainties. The instrument type used at ASK is more stable when compared to other NDIR instruments.

Changes made to the instrument
No changes were made.

Conclusions
The Horiba APMA-360CE 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.

WCC-Empa Travelling Standards

Ozone

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

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

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Travelling standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.1; COEFF = 1.008
Ozone source		Internal generator of SRP
Zero air supply		Pressurised air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (12 March, 2007) 3 runs after return of TS (12 June, 2007)

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

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2007-03-12	1	0	0.09	0.23	0.10	0.08
2007-03-12	1	60	60.37	0.21	60.25	0.15
2007-03-12	1	190	186.70	0.64	186.72	0.09
2007-03-12	1	140	140.22	0.31	140.35	0.15
2007-03-12	1	30	31.82	0.34	31.85	0.06
2007-03-12	1	90	90.13	0.22	89.98	0.09
2007-03-12	1	0	-0.10	0.31	0.16	0.07
2007-03-12	2	0	0.06	0.21	0.10	0.04
2007-03-12	2	30	31.63	0.23	31.74	0.05
2007-03-12	2	190	186.75	0.17	186.77	0.09
2007-03-12	2	60	60.32	0.19	60.33	0.11
2007-03-12	2	140	139.97	0.40	140.10	0.07
2007-03-12	2	90	90.30	0.31	90.20	0.12
2007-03-12	2	0	-0.05	0.32	0.06	0.11
2007-03-12	3	0	-0.09	0.21	-0.19	0.57
2007-03-12	3	60	60.07	0.22	60.38	0.08
2007-03-12	3	30	31.90	0.36	31.94	0.12
2007-03-12	3	140	140.11	0.24	140.09	0.08
2007-03-12	3	90	90.28	0.23	90.13	0.12
2007-03-12	3	190	186.80	0.27	186.96	0.13
2007-03-12	3	0	-0.03	0.30	0.14	0.12
2007-06-12	4	0	-0.10	0.31	-0.08	0.09
2007-06-12	4	140	136.85	0.34	136.63	0.12
2007-06-12	4	90	87.62	0.25	87.70	0.13
2007-06-12	4	30	31.19	0.56	31.06	0.09
2007-06-12	4	190	182.74	0.24	182.88	0.13
2007-06-12	4	60	58.21	0.26	58.16	0.08
2007-06-12	4	0	-0.24	0.46	0.00	0.11
2007-06-12	5	0	0.02	0.30	0.04	0.07
2007-06-12	5	90	87.79	0.27	87.79	0.07
2007-06-12	5	190	182.78	0.48	183.05	0.11
2007-06-12	5	60	58.41	0.25	58.32	0.15
2007-06-12	5	140	135.99	0.50	136.09	0.14
2007-06-12	5	30	31.30	0.40	31.02	0.07
2007-06-12	5	0	0.06	0.39	0.10	0.10
2007-06-12	6	0	0.19	0.27	0.01	0.12
2007-06-12	6	30	31.25	0.29	31.19	0.08
2007-06-12	6	190	183.05	0.26	183.07	0.20
2007-06-12	6	90	87.70	0.25	87.85	0.05
2007-06-12	6	140	135.83	0.41	136.11	0.15
2007-06-12	6	60	58.34	0.34	58.23	0.09
2007-06-12	6	0	0.10	0.38	0.08	0.10

[#]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 7). 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]).

$$X_{TS}\ (\text{ppb}) = ([TS] - 0.01\ \text{ppb}) / 1.0002$$

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

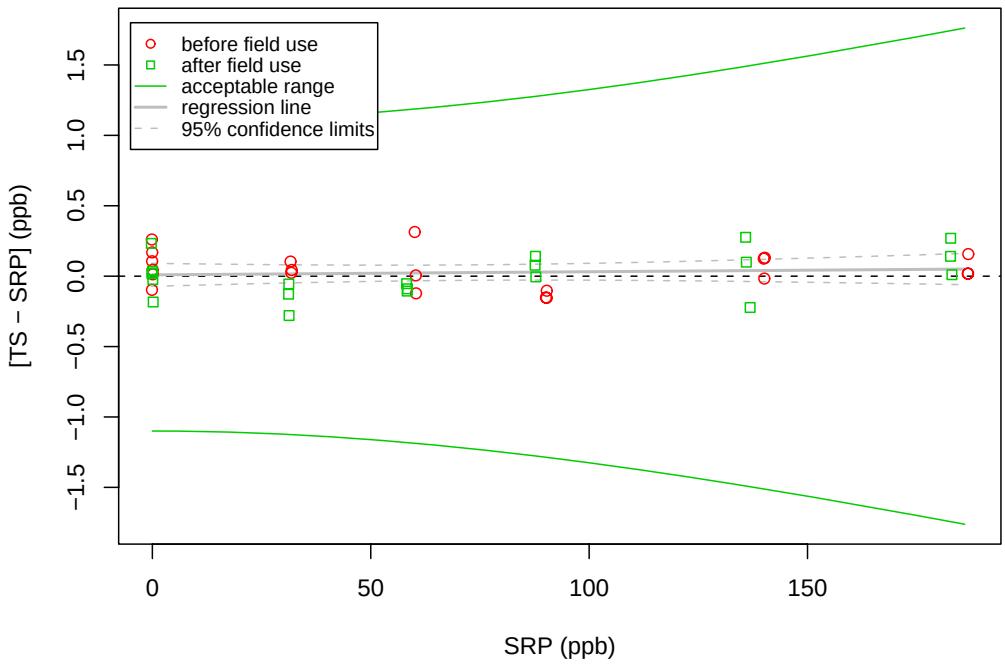

Figure 7. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly inter-compared with the CCL by way of travelling standards. The scale was transferred to the travelling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. Details are given in Table 10 - Table 11.

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

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale 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 – Silicagel PS drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		Messer Germany, 0651B, 9935.7±30.9 ppb CO (α=0.05)
(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 to 500, in steps of 50
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence
Runs		1 run before shipment of TS (21 March, 2007) 1 run after return of TS (15 June, 2007)

Table 11. Calibration of Breitfuss dilution system and carbon monoxide mixing ratios.

	Mass Flow Controller MFC1 (mL min^{-1})		Mass Flow Controller MFC2 (mL min^{-1})		CO Mixing Ratio (ppb)	
Date	**Setpoint**	**Measured**[#]	**Setpoint**	**Measured**[#]	**Expected**	**Measured**[#]
2007-03-21	1800	1784.11 ± 0.59	0.00	0.18 ± 0.01	0.00	0.41 ± 0.21
2007-03-21	1791	1776.64 ± 0.39	9.00	9.13 ± 0.01	50.82	50.70 ± 0.37
2007-03-21	1782	1768.10 ± 0.22	18.00	18.25 ± 0.01	101.49	102.05 ± 0.59
2007-03-21	1773	1758.15 ± 0.22	27.00	27.33 ± 0.00	152.11	152.36 ± 0.50
2007-03-21	1764	1749.38 ± 0.19	36.00	36.43 ± 0.01	202.72	203.01 ± 0.42
2007-03-21	1755	1739.59 ± 0.19	45.00	45.54 ± 0.01	253.45	253.83 ± 0.35
2007-03-21	1746	1730.88 ± 0.19	54.00	54.65 ± 0.01	304.12	304.92 ± 0.65
2007-03-21	1737	1721.11 ± 0.18	63.00	63.74 ± 0.01	354.82	354.75 ± 0.73
2007-03-21	1728	1712.49 ± 0.16	72.00	72.82 ± 0.01	405.28	406.15 ± 0.75
2007-03-21	1719	1702.68 ± 0.25	81.00	81.91 ± 0.01	456.03	456.01 ± 1.16
2007-03-21	1710	1694.00 ± 0.19	90.00	91.02 ± 0.01	506.63	505.09 ± 1.30
2007-06-15	1800	1789.30 ± 0.57	0.00	0.23 ± 0.01	0.00	NA
2007-06-15	1791	1782.53 ± 0.35	9.00	9.28 ± 0.01	51.46	NA
2007-06-15	1782	1774.64 ± 0.23	18.00	18.43 ± 0.01	102.15	NA
2007-06-15	1773	1764.83 ± 0.21	27.00	27.58 ± 0.01	152.88	NA
2007-06-15	1764	1756.39 ± 0.23	36.00	36.72 ± 0.01	203.49	NA
2007-06-15	1755	1746.78 ± 0.17	45.00	45.86 ± 0.01	254.21	NA
2007-06-15	1746	1738.54 ± 0.25	54.00	55.03 ± 0.01	304.87	NA
2007-06-15	1737	1729.38 ± 0.18	63.00	64.16 ± 0.01	355.47	NA
2007-06-15	1728	1720.40 ± 0.23	72.00	73.29 ± 0.01	405.97	NA
2007-06-15	1719	1710.40 ± 0.16	81.00	82.42 ± 0.01	456.77	NA
2007-06-15	1710	1701.70 ± 0.17	90.00	91.58 ± 0.01	507.42	NA

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

APPENDIX 2 – RECTIFICATION OF ASK O3 DATA STORED AT WDCGG

Jörg Klausen, GAW QA/SAC Switzerland, 24 May 2007

Introduction

In 2003, QA/SAC Switzerland and WCC-Empa conducted the first audit of the surface ozone measurements at Assekrem [*Zellweger, et al.*, 2003]. During an initial check, it was found that the readings of the TEI 49 instrument in operation at the time were about 50% too low at 800 ppb. The instrument was checked and an exhausted scrubber was identified as the cause of the problem. The scrubber was replaced and a full inter-comparison of the instrument was conducted. It was found that the instrument was still reading 6% too low, and consequently, the instrument's SPAN calibration factor was adjusted. The final inter-comparison then indicated that the instrument was in calibration.

Calibration history of the instrument

The calibration of this instrument is poorly documented. It was originally purchased and calibrated against a TEI 49 PS in 1996 by P. Perros at LISA (Université Paris 12, France, perros@univ-paris12.fr). Of that initial calibration, no records are available (Perros, personal communication, 2003). The next inter-comparison was conducted by WCC-Empa on 6 February 2003 at Assekrem as mentioned above.

Identification of period affected by faulty scrubber

A statistical analysis of daily aggregates of the data residing at the WDCGG (http://gaw.kishou.go.jp/wdcgg/pub/data/o3/daily/ask123n0.dat) using a Kolmogorov-Zurbenko adaptive (KZA) filtering technique [*R Development Core Team*, 2004; *Zurbenko, et al.*, 1996] was performed in order to identify the beginning of the period affected by the faulty scrubber (Figure 1). KZA is an adaptive moving average filter suitable for detecting systematic biases. The advantage of the adaptive filter over traditional parametric methods is that it is less affected by seasonal patterns and trends. It has been successfully applied to the detection of discontinuities in time series of upper-air data [*Zurbenko, et al.*, 1996]. KZA requires two parameters, namely q (the half length of the window size for the filter), and k (number of iterations to run the filter). As seen in Figure 1, the filter produces a period between mid-2001 and February 2003 that varies little as the parameters for the filter are varied. Visual inspection of the results suggests that a choice of q = 60 days and k = 10 iterations yields a reasonably smooth approximation to the data. The filter found two breaks in the time series of the daily aggregates, spanning the period 2001-07-27 thru 2003-02-02. Note that the second break coincides almost exactly with the replacement of the faulty scrubber. We therefore suggest that the first break found in the series marks the beginning of the break-through of ozone-containing air through the scrubber and, hence, the beginning of the period affected.

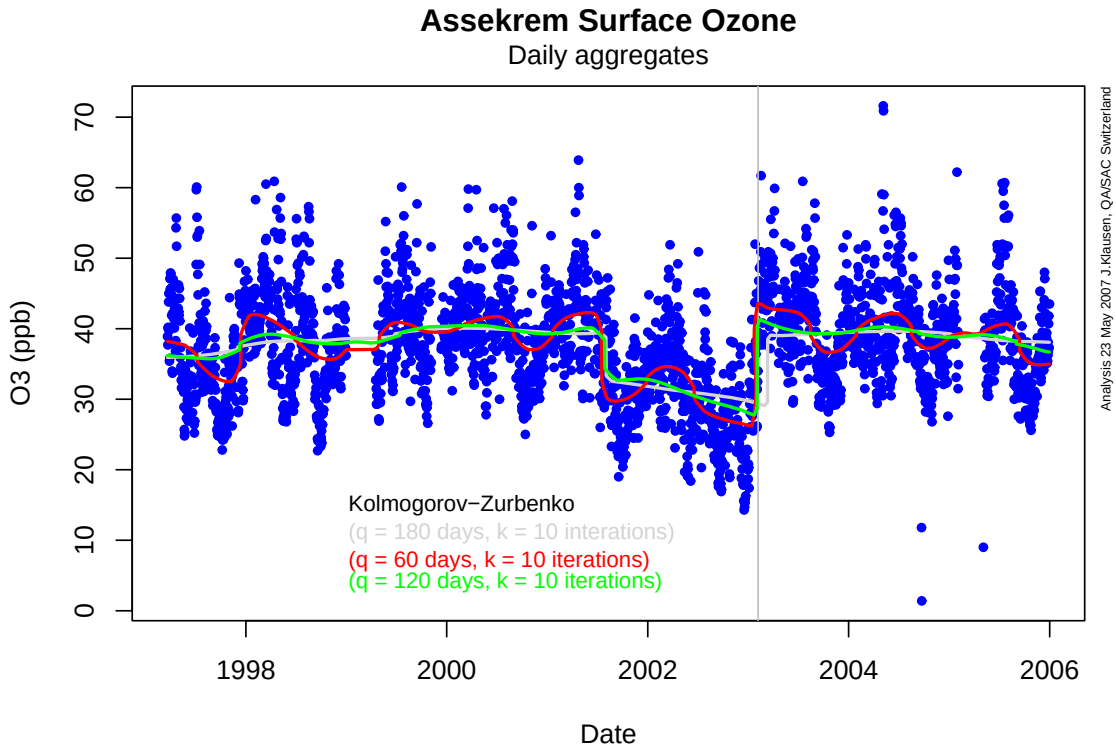

Figure 1. Time series of daily aggregates of surface ozone mixing ratios as observed at Assekrem, Algeria. The smooth curves shown are reconstructions of the time series using the adaptive Kolmogorov-Zurbenko filter with various half lengths of the filter window size. The vertical line indicates the date when the scrubber of the ozone analyzer was replaced.

Identification of other questionable data

Figure 1 shows three days with exceptionally low daily means for the ozone concentration. The hourly data for these days indicate that in all three cases, the data coverage was below 40% due to instrument failure caused by power outages. These data are therefore not representative of the ambient atmosphere and should be flagged.

Data correction due to audit

As mentioned above, the inter-comparison of the analyzer with a transfer standard traceable to the WMO reference scale (NIST SRP) after the replacement of the scrubber indicated that the instrument was reading 6% too low. In the absence of prior inter-comparison results, and in the absence of documented traceability of the TEI 49 PS used originally for calibration of the instrument, it is difficult to decide when the observed bias was introduced. Experience with the TEI 49 instruments suggests that this bias was introduced during the initial calibration at LISA and is not the result of an instrument drift. This judgment is based on the observation that all instruments of this type were reading too low at their factory SPAN calibration factor setting of 500. This setting was 485 (corresponding to a bias of -3%) prior to the adjustment to 515 by WCC-Empa on 6 February 2003.

Unfortunately, no other experimental evidence is available, because the instrument broke down on 3 February 2005 and had to be replaced.

The replacement instrument is a TEI 49C that was calibrated by WCC-Empa prior to shipment to Assekrem, and that audited in May 2007. The inter-comparison indicated that the instrument was still in calibration and the data were unbiased [*Zellweger, et al.*, 2007].

The result of correcting the period indicated above is shown in Figure 2.

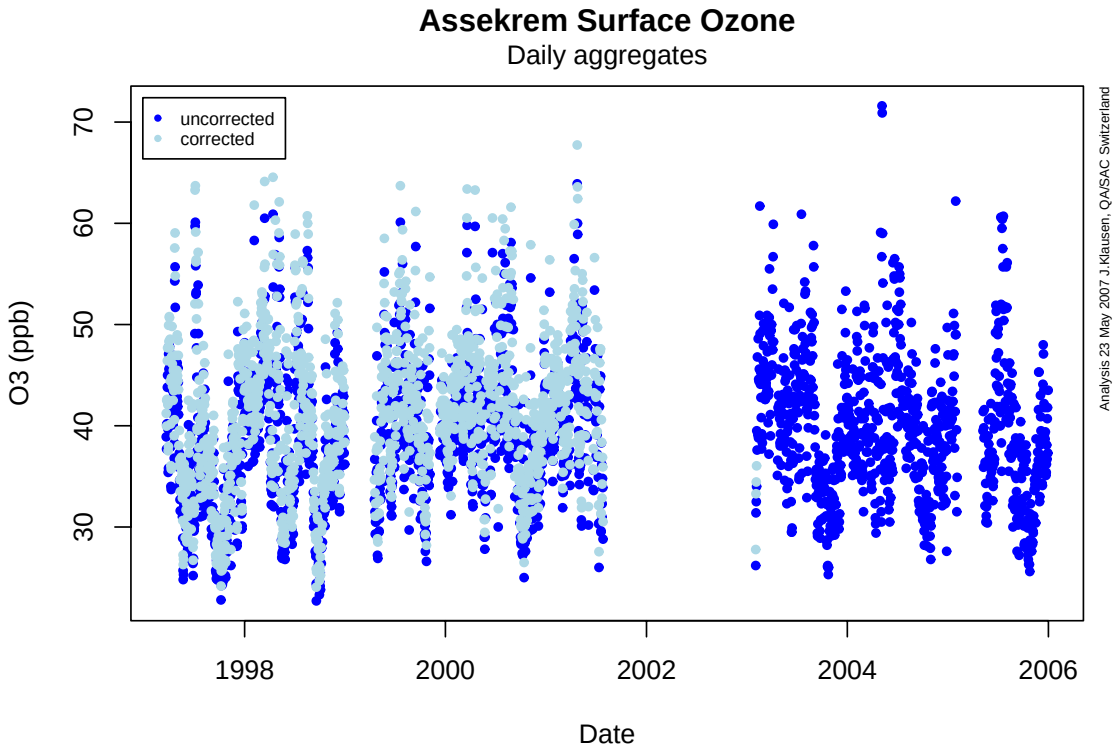

Figure 2. Time series of daily aggregates of surface ozone mixing ratios from Assekrem, Algeria after removal of erroneous data (blue) and compensation of calibration bias of data prior to 6 February 2003 (lightblue).

Recommendations

Based on the above analysis of the time series of surface ozone observations at Assekrem, Algeria, it is recommended to

1) completely discard the period from 2001-07-27 thru 2003-02-02;
2) flag the data of 2004-09-22, 2004-09-23, and 2005-05-05 as invalid;
3) correct the data prior to 2003-02-06 by multiplication with 1.06;
4) re-submit the data (hourly, daily, monthly, yearly aggregates) to WDCGG.

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Ozone Audit Executive Summary (ASK)

0.1	Station Name:	Assekrem
0.2	GAW ID:	ASK
0.3	Coordinates/Elevation:	23.267°N, 5.633°E (2710 m a.s.l)
Parameter:		Surface Ozone

1.1	Date of Audit:	9 – 12 May, 2007
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Mohamed Salah Ferroudj, Mohamed Zoukani
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):	$(1.0002\pm0.0010) \times [SRP] + (0.01\pm0.09)$
1.5	Ozone Analyser [OA]	
1.5.1	Model:	TEI 49C #56109-306
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG: 0.0 SPAN: 1.017
1.5.4	Calibration at start of audit (ppb):	$[OA] = (0.995\pm0.001) \times [SRP] - (0.04\pm0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] + 0.04) / 0.995$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.29\ ppb^2 + 2.67e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	$[OA] = (0.997\pm0.000) \times [SRP] - (0.11\pm0.05)$
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	$X = ([OA] + 0.11) / 0.997$
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.61e\text{-}5 \times X^2)^{1/2}$
1.6	Comments:	-pressure sensor was adjusted during the audit
1.7	Reference:	WCC-Empa Report 07/2

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

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Carbon Monoxide Audit Executive Summary (ASK)

0.1	Station Name:	Assekrem
0.2	GAW ID:	ASK
0.3	Coordinates/Elevation:	23.267°N, 5.633°E (2710 m a.s.l)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	9 – 11 May, 2007
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Mohamed Salah Ferroudj, Mohamed Zoukani
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	Messer 0651B, 9935.7±30.9 (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:	Horiba APMA-360CE #303003
1.5.2	Range of calibration:	0 – 500 ppb
1.5.3	Coefficients at start of audit	Zero 21 - Span 1.2635
1.5.4	Calibration at start of audit (ppb):	$CO = (0.998 \pm 0.002) \times X + (3.9 \pm 0.5)$
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 3.9) / 0.998$
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (26.0\ ppb^2 + 2.91e\text{-}05 \times X^2)^{1/2}$
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:	
1.7	Reference:	WCC-Empa Report 07/2

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

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LIST OF ABBREVIATIONS

AC	Air Conditioning
ASK	Assekrem GAW Station
a.s.l.	above sea level
CCL	Central Calibration Laboratory
DAQ	Data Acquisition System
GAW	Global Atmosphere Watch
GMD	Global Monitoring Division
NA	Not available
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyser
ONM	Office National de la Météorologie
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation