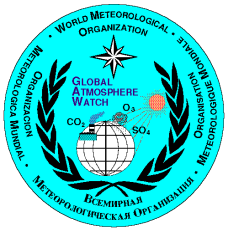

Materials Science & Technology

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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 08/6

Submitted to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE AND CARBON MONOXIDE AT THE GLOBAL GAW STATION AMSTERDAM ISLAND, TERRES AUSTRALES ET ANTARCTIQUES FRANCAISES NOVEMBER 2008

Submitted by
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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The first system and performance audit at the Global GAW station Amsterdam Island (AMS) was conducted by WCC-Empa[1] from 27 November thru 20 December 2008 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The AMS observatory is operated by the French Laboratoire des Sciences du Climat et l'Environnement (LSCE).

The following people contributed to the audit:

Mr. Bruno Seiler	Empa Dübendorf, WCC-Empa
Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Dr. Jean Sciare	LSCE, primary station contact, measurement leader
Dr. Roland Sarda-Estève	LSCE
Mr. Sébastien Devidal	AMS, LSCE, station operator
Mr. José Nicolas	AMS, LSCE, station operator

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

This report is distributed to the GAW Country Contact (Dr. Florence Goutail), the primary station contact (Dr. Jean Sciare) and the World Meteorological Organization in Geneva. The report including 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 Amsterdam Island GAW station (37°29'S, 77°20'W, 70 m a.s.l.) is located on an island of 55 km^2 in the middle of the Indian Ocean. Amsterdam Island is French territory and belongs to the Terres Australes et Antarctiques Françaises (TAAF). It is only accessible by ship. The research vessel Marion Dufrèsne is passing by four times a year, usually in March, August, November and December. The station is only accessible on foot or by tractor, and is located approximately one kilometre away from the base Martin de Viviès, with around 30 inhabitants. The station is situated on top of a 70 m cliff with no obstacles in the surroundings.

Station Facilities

The station complex consists of three buildings. One building is used for aerosol measurements, one for the flask sampling and one for the measurement of carbon monoxide, ozone, radon and carbon dioxide. The laboratory used for carbon dioxide measurements is air-conditioned. In all other rooms the temperature varies from 15 to 28°C. The air inlets are located on a tower at a distance of 20 meters from the buildings. Power is supplied by electric cable from the base Martin de Viviès where it is produced by diesel generators. At an interval of two weeks the generators are switched. This process can lead to short power outages and current fluctuations. A DC converter is used to bridge power outages up to 15 minutes.

Station Management and Operation

The station is managed by the French Laboratoire des Sciences du Climat et l'Environnement (LSCE). The station is visited four to five times per week by one of the two station operators from LSCE.

[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.

Air Inlet System

The air inlets are on top of a metal tower (height: 15 m) at a distance of 20 m from the laboratory building. There are separate air inlets for carbon monoxide, carbon dioxide, ozone, radon and aerosol instruments.

The CO inlet is made of a PVC hood with a diameter of 80 mm that is turned upside down to avoid ingress of rainwater. A cellulose filter is located in the PVC tube. The instrument is connected to the air inlet with Dekabon tubing of 40 m length. An external pump provides for a flow rate that results in a residence time of approximately 35 seconds.

The ozone inlet is made of a Teflon container with an opening of 10 mm at the bottom. No inlet filter is used for ozone. Teflon tubing (inner diameter 4 mm) with a total length of 40 m is used for the connection to the instrument. Only the internal pump of the ozone analyzer is used, which results in a long residence time of more than one minute.

Recommendation 1 (*, immediately)**
The inlet system for ozone needs to be changed. The residence time in the tubing is too long, and ozone is potentially destroyed before the air reaches the instrument. The diameter of the air inlet is too small to guarantee sufficient air-flow. Installation of the air inlet on the roof of the laboratory building would shorten the tubing length considerably and lead to a reasonable residence time. In addition WCC-Empa strongly recommends the use of a Teflon inlet filter to protect the instrument from pollution.

Surface Ozone Measurements

Instrumentation. One ozone analyzer (TEI 49C) is currently used at the station for continuous surface ozone measurements. The instrumentation is adequate for its intended purpose; however, regular instrument checks should be made to ensure proper operation. In case of an instrument failure spare parts should be available at the site to avoid long data gaps.

Recommendation 2 (, 2010)**
It is recommended to purchase spare parts (e.g. pump diaphragm, Teflon valves, ozone scrubber, UV lamp) for immediate instrument repair in the case of instrument failure.

Recommendation 3 (, 2010)**
The instrument should be checked weekly for general operation. In addition, instrument parameters such as temperatures, flow rates etc. should be plotted on QC charts. It is further recommended to follow the preventive maintenance chapter of the TEI 49C manual. The inlet filter needs to be replaced at regular intervals, e.g. every two weeks.

Standards. No ozone standard is available at the site, and a calibration with an external standard is not possible due to the extremely remote location of the station.

Recommendation 4 (, 2010)**
Due to the very remote location it is strongly recommended that an ozone calibrator is available at the site. Regular checks / inter-comparisons should be made every 3 months. Alternatively, parallel measurements with a second ozone analyzer could be made.

Intercomparison (Performance Audit). The inter-comparisons of the station ozone analyzer extended over a period of approx. 22 hours. The result is summarized below, and the following equation characterises the instrument bias:

TEI 49C #54658-300: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.46 ppb)/ 0.9974 (1)

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

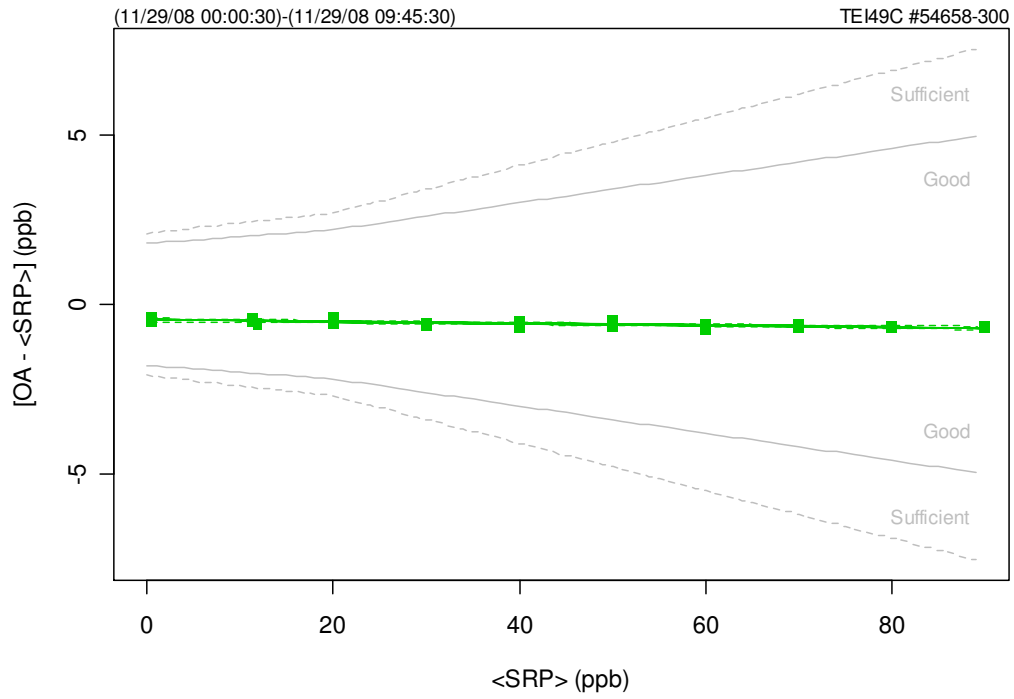

Figure 1. Bias of the Amsterdam Island ozone analyzer (TEI 49C) with respect to the SRP as a function of mixing ratio. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, 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. Amsterdam Island is equipped with a Trace Analytical RGA-3 system for measurement of CO. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with one laboratory standard from NOAA/ESRL, with a mixing ratio of 104.8 ppb (WMO-2000 carbon monoxide scale). In addition, a working standard is available.

Recommendation 5 (*, 2010)**
One laboratory standard is not sufficient to characterize the non-linearity of the measurement system. At least four standards covering the relevant mixing ratios must be used. WCC-Empa recommends purchasing additional standards. The existing laboratory standards needs to be re-calibrated.

Intercomparison (Performance Audit). The inter-comparison involved repeated challenges of the instrument with randomised carbon monoxide mixing ratios from travelling standards. The following equation (2) characterises the instrument bias (cf. Figure 2):

Trace Analytical RGA-3:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 9.9 ppb) / 0.836 (2)

Significant deviations were observed between WCC-Empa and the AMS GAW station, which are most likely due to an insufficient characterization of the RGA-3 calibration function due to a lack of standard gases. It is strongly recommended (cf. Recommendation 2) that at least three additional standards are purchased from NOAA/ESRL, or that the station is provided with standards calibrated at LSCE based on laboratory standards from NOAA/ESRL.

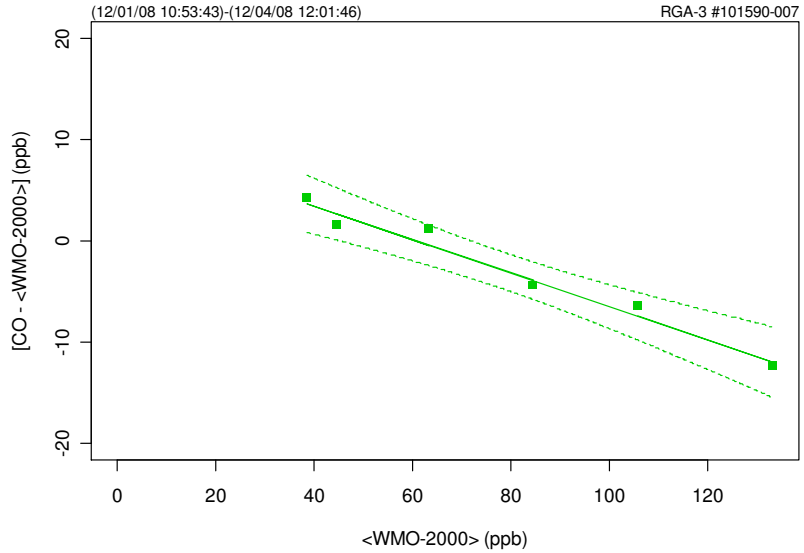

Figure 2. Bias of the AMS carbon monoxide instrument (Trace Analytical RGA-3) with respect to the WMO-2000 reference scale as a function of mixing ratio. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Data Acquisition and Management

Ozone: The TEI 2.2.0 software (Thermo Environmental Instruments Inc.) is used to manually download the data from the internal data logger. This data is transferred to the LSCE by the station operators at the beginning of each month. Final data validation is carried out at LSCE.

GC instrument: The Borwin 1.21.05 software is used to control the GC. At the beginning of each month raw data and 40 example chromatograms for the calibration and air samples are transferred to LSCE. Final data validation is carried out at LSCE.

Data Submission

Data have been partly submitted to the World Data Centre for Greenhouse Gases (WDCGG). By September 2009 data for carbon dioxide (1981 – 2005), carbon monoxide (2004, daily and monthly data only) and VOC flask data (1987-2008) were available at WDCGG. Ozone data have not yet been submitted, but submission is planned for 2009.

Recommendation 6 (, 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. All continuous measurements should be submitted as hourly, daily and monthly averages.

Conclusions

The Global GAW station Amsterdam Island is located in a very remote location in the Indian Ocean and covers a region from where no other data are available. Some time series cover a long period since the early 80s, and are therefore an important contribution to the GAW program. Some technical issues need to be resolved, and it should be considered to expand the measurement program.

Summary Ranking of AMS Station

System Audit Aspect*	Adequacy#	Comment
Access	(4)	Access difficult
Facilities		
Laboratory and office space	(4)	
Air Conditioning	(2)	NA, small temperature changes
Power supply	(4)	Diesel generator (3 km distance)
Internet access	(3)	Only at the main base
General Management and Operation		
Organisation	(4)	
Competence of staff	(4)	Short training period at LSCE
Air Inlet System	(2)	Improvements necessary
Instrumentation		
Ozone	(5)	TEI49C
Carbon monoxide	(4)	RGA-3
Carbon dioxide		Not assessed
Aerosol parameters		Not assessed
Meteo		Not assessed
Standards		
Ozone	(0)	Not available
Carbon monoxide	(2)	Re-calibration / more standards needed
Data Management		
Data acquisition	(3)	Internal data logger (O3)
Data processing	(4)	
Data submission	(3)	Not all data submitted yet

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

_____

Dübendorf, October 2010

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

APPENDIX

Global GAW Station Amsterdam Island

Site description

The Amsterdam Island GAW station is located in the Indian Ocean and is registered in GAWSIS (http://gaw.empa.ch/gawsis). More information can also be found on the station website (http://soon.ipsl.jussieu.fr/fr/RAMCES/SITEams.htm). The station complex consists of three buildings and two towers. Currently only the tall tower is used for measurements.

Measurement Program

The Amsterdam station started its operation in 1967. An overview of the measurement program and its status as of December 2008 is shown in Table 1. Refer to GAWSIS or the station web page for more details.

Table 1. Measurement Program at the AMS Station

Parameter	Current Instrument	Data Coverage (%)[#]		
		<12 m	<3 y	Overall
Aerosol				
Carbonaceous/organic material	thermo-optical analysis / EC-OC			
Light absorption coefficient	AE-9 Magee Scientific			
Major chemical components	Filter sampling + extraction + IC			
Multiwavelength optical depth	AERONET sun photometer			
Ozone				
Surface ozone	UV absorption (TEI 49C)	90		
Greenhouse Gas				
CO_2	NDIR (Siemens Ultramat 5F)			
Reactive Gas				
CO	RGA-3			
C2H6S (dimethylsulfide, DMS)	Chemiluminescence			
Radio Nuclide				
Rn-222				
Meteo				
PTU, wind speed + direction				

[#] Missing information about data coverage: information was not available.

Ozone and Carbon Monoxide Distribution at AMS

The monthly and yearly distributions of one hourly mean values (surface ozone) and daily mean values (carbon monoxide) are shown in Figure 3. The carbon monoxide data is currently re-analysed; at the time of the report, one hourly averages were not yet available.

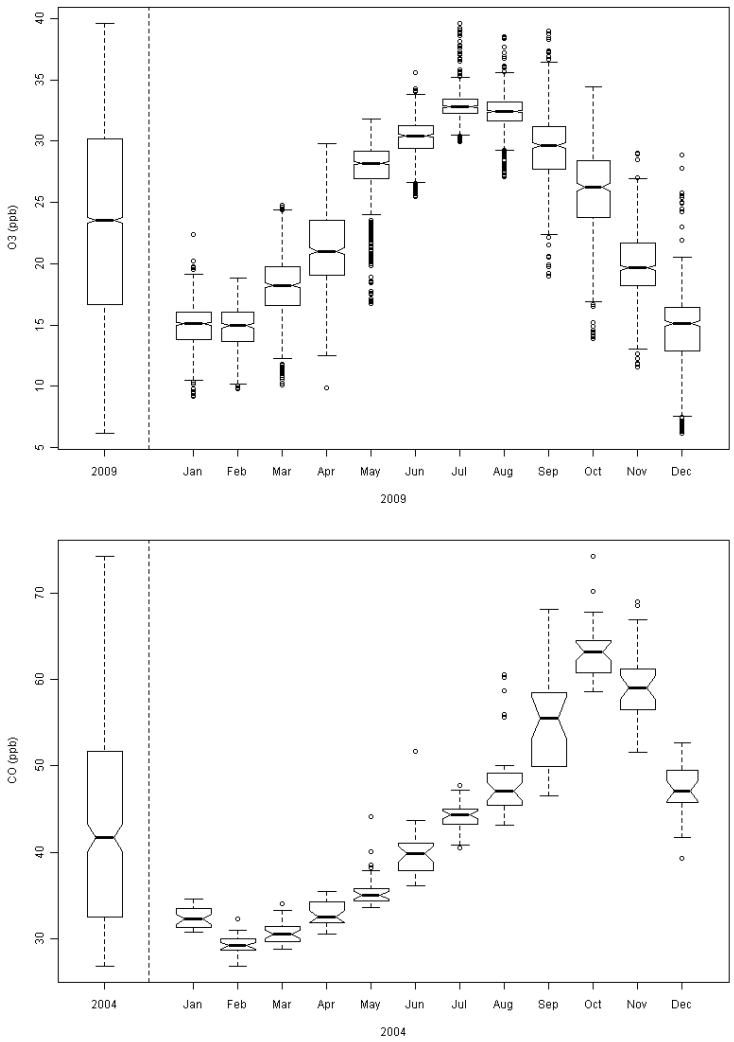

Figure 3. Yearly and monthly box plots for surface ozone (upper panel, year 2009, 1-hourly aggregates) and carbon monoxide (lower panel, year 2004, daily aggregates). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open 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

GAW activities at Amsterdam Island are coordinated by the Laboratoire du Science et de l'Environnement (LSCE). For a complete overview of contact persons and involved institutes refer to GAWSIS.

Surface Ozone Measurements

Surface ozone measurements were made from 1994 to 2004 and started again in October 2008 at the AMS site, just four weeks before the audit. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation]. The current audit assessed only the new instrument that was installed in October 2008, because the previous instrumentation was no longer available. It is recommended that the data until 2004 is carefully reviewed before submission to WDCGG.

Monitoring Set-up and Procedures

Air Conditioning

The laboratory building for surface ozone measurements has no air conditioning.

Air Inlet System

The air inlet is on top of a tower (height: 15 m) at a distance of 20 m from the laboratory building. The ozone air inlet is made of a Teflon container with an opening of 10 mm and is fixed at the metal railing of the tower. No inlet filter is used. 6 mm Teflon tubing (approx. length: 40 m) is used for the connection to the instrument. The inlet line is only flushed by the internal pump of the ozone analyzer.

Overall residence time is estimated to by approximately 30 seconds in the tubing, plus a not well defined residence time in the order of 30 second or more in the Teflon container and the humidify trap. This residence time is clearly too long for ozone measurements. It is recommended to reduce the time by modification of the whole inlet system (cf. Recommendation 1). The following recommendations are made:

- It should be considered to move the air inlet to the smaller tower near the laboratory building.
- The Teflon container should be replaced by a more open inlet design.
- The humidity trap should be removed and Teflon inlet filters should be used.
- The recommended residence time is ten seconds or less.

Instrumentation

The station is equipped with one ozone analyzer (TEI 49C). Instrumental details for the ozone analyzers (OA) are summarized in Table 2 below.

Standards

No ozone standard is available at the site.

Operation and Maintenance

No standard operating procedure was available at the time of the audit. No regular checks other than checks for general instrument operation were made (cf. recommendation 3).

Data Acquisition and Data Transfer

The internal data logger of the instrument is used to acquire data. All data is transferred electronically to LSCE on a monthly basis and additional back-ups on CDs and sent by post to the LSCE four times per year.

Data Treatment

Final data validation is carried out at LSCE and consists of visual inspection of time series.

Data Submission

Ozone data have not yet been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG), but submission is planned for 2009.

Documentation

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

Inter-Comparison of Ozone Analyzer

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

Setup and Connections

Table 2 details the experimental setup during the inter-comparison of the transfer standard with the station analyzer. The data used for the evaluation was recorded by WCC-Empa. No further corrections were applied to the data.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.5; COEFF = 1.008
Ozone analyzer (OA)	Model, S/N	TEI 49C #54658-300
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.5; COEFF = 1.009
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm (WCC-Empa)
Connection between instruments		Ca. 2 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS, OA	One minute aggregates from digital output (custom designed LabView program)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	1013.0 hPa (Station reference)
	TS	1009.3 hPa, adjusted to 1012.4 hPa
	TEI 49C	1010.0 hPa (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 (29 November, 2008)

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. The results are shown in Table 3. These aggregates were used in the assessment of the inter-comparison as described elsewhere [Klausen, et al., 2003]. All results refer to the calibration factors as given in Table 2 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyzer (OA) values.

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the AMS ozone analyzer (OA) TEI 49C #54658-300 with the WCC-Empa transfer standard (TS).

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flags*	sdTS (ppb)	sdOA (ppb)
2008-11-29 00:00	1	0	0.45	0.15	0	0.077	0.031
2008-11-29 00:15	1	40	39.88	39.39	0	0.075	0.023
2008-11-29 00:30	1	70	69.85	69.33	0	0.064	0.030
2008-11-29 00:45	1	30	29.92	29.44	0	0.069	0.027
2008-11-29 01:00	1	90	89.86	89.27	0	0.071	0.049
2008-11-29 01:15	1	20	19.95	19.62	0	0.073	0.059
2008-11-29 01:30	1	10	11.27	10.88	0	0.321	0.083
2008-11-29 01:45	1	60	59.98	59.43	0	0.058	0.041
2008-11-29 02:00	1	50	49.91	49.50	0	0.082	0.040
2008-11-29 02:15	1	80	79.88	79.27	0	0.073	0.048
2008-11-29 02:30	2	0	0.48	0.08	0	0.044	0.030
2008-11-29 02:45	2	90	89.85	89.26	0	0.061	0.040
2008-11-29 03:00	2	70	69.88	69.33	0	0.069	0.046
2008-11-29 03:15	2	40	39.90	39.43	0	0.052	0.037
2008-11-29 03:30	2	50	49.91	49.35	0	0.042	0.042
2008-11-29 03:45	2	20	19.93	19.44	0	0.046	0.033
2008-11-29 04:00	2	30	29.92	29.30	0	0.080	0.020
2008-11-29 04:15	2	60	59.88	59.26	0	0.072	0.047
2008-11-29 04:30	2	10	11.81	11.26	0	0.435	0.146
2008-11-29 04:45	2	80	79.88	79.23	0	0.071	0.054
2008-11-29 05:00	3	0	0.48	0.10	0	0.087	0.012
2008-11-29 05:15	3	30	29.90	29.39	0	0.096	0.027
2008-11-29 05:30	3	60	59.88	59.31	0	0.068	0.033
2008-11-29 05:45	3	40	39.90	39.42	0	0.074	0.036
2008-11-29 06:00	3	90	89.86	89.21	0	0.043	0.035
2008-11-29 06:15	3	50	49.92	49.30	0	0.062	0.043
2008-11-29 06:30	3	10	11.69	11.20	0	0.446	0.111
2008-11-29 06:45	3	20	19.91	19.44	0	0.063	0.027
2008-11-29 07:00	3	80	79.87	79.25	0	0.073	0.041
2008-11-29 07:15	3	70	69.87	69.21	0	0.084	0.029
2008-11-29 07:30	4	0	0.50	0.04	0	0.104	0.026
2008-11-29 07:45	4	40	39.89	39.24	0	0.079	0.027
2008-11-29 08:00	4	70	69.87	69.31	0	0.056	0.041
2008-11-29 08:15	4	30	29.94	29.40	0	0.071	0.038
2008-11-29 08:30	4	90	89.87	89.22	0	0.067	0.033
2008-11-29 08:45	4	20	19.97	19.50	0	0.041	0.031
2008-11-29 09:00	4	10	11.22	10.75	0	1.736	0.468
2008-11-29 09:15	4	60	59.90	59.21	0	0.070	0.033
2008-11-29 09:30	4	50	49.90	49.30	0	0.106	0.038
2008-11-29 09:45	4	80	79.88	79.26	0	0.078	0.039

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

Figure 4 shows the regression residuals of the ozone analyzer with respect to the SRP as a function of ozone mixing ratio for the range 0 – 90 ppb and as a function of time.

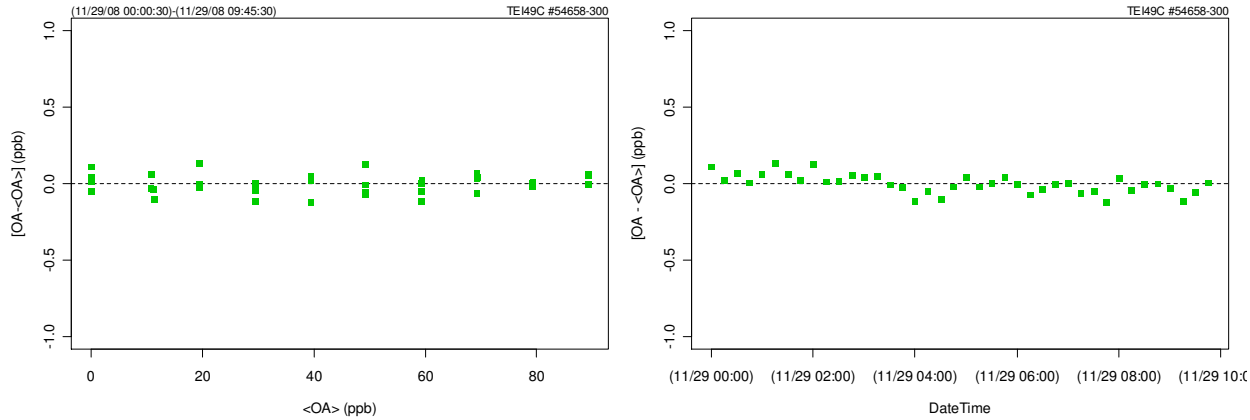

Figure 4. Regression residuals of the AMS ozone analyzer (TEI 49C) as a function of mixing ratio (left panel) and time (right panel).

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 #54658-300:

$$X_{O3}\ (\text{ppb}) = ([\text{OA}] + 0.46\ \text{ppb})/\ 0.9974$$

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

Conclusions

The findings of the performance audit demonstrate good agreement between AMS ozone analyzer and WCC-Empa. Therefore no further recommendations concerning the instrument are proposed by WCC-Empa. However, data should be submitted to WDCGG as soon as possible. In addition, WCC-Empa recommends modifying the inlet system to achieve shorter residence time of the air in the inlet system. The

Carbon Monoxide Measurements

Carbon monoxide measurements started in 1996 at Amsterdam Island. The audit comprised inter-comparison of six traveling standards covering the mixing ratio range from approx. 40 to 135 ppb carbon monoxide in air. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

The laboratory building housing the CO equipment has no air conditioning.

Air Inlet System

The air inlet is on top of a metal tower (height: 15 m) at a distance of 20 m from the laboratory building. The CO inlet is protected with PVC hood with a diameter of 80 mm from rainwater. A cellulose filter is located in the PVC tube. From the manifold the instrument is connected as follows:

- Approx. 41 m 10 mm Dekabon tubing
- KNF Laboport Neuberger pump
- Flow rate to pump 11 l min^{-1}, after pump 400 ml min^{-1}
- Approx. 2 m 10 mm Dekabon tubing to the chemical humidity trap (magnesium perchlorate)
- Approx. 1 m 10 mm Dekabon tubing to instrument

Overall residence time is approximately 35 seconds.

Instrumentation

Amsterdam Island is equipped with a Trace Analytical RGA-3 GC-system. Instrumental details are summarized in **Table 5**.

Standards and Calibration

The carbon monoxide instrument is calibrated using a working standard (pressurised air). The working standard is calibrated at the site using the laboratory standards. Table 4 gives details of the cylinders currently available at the station.

Injections are made every 2.5 minutes, alternating between working standard and ambient air. Two bracketing working standard injections are used to calculate the ambient data.

Table 4. Carbon monoxide standards available at the AMS station

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
NOAA/ESRL CA04839 laboratory standard	104.8 ppb CO[1] CO in air	2004	NOAA/ESRL	2004	cont.
Messer France 597701 working standard	102.0 ppb CO CO in N_2	2006	LSCE	2006	cont.

[1] WMO-2000 carbon monoxide scale, VURF instrument at NOAA/ESRL

Operation and Maintenance

The system is checked for general operation each working day. Remote access is possible from the main base, and instrument parameters and chromatograms are frequently checked. The calibration of the working standard is verified once per month using the laboratory standard.

Data Acquisition and Data Transfer

The entire instrument is controlled by a PC using the GC control software Borwin. The software controls the RGA-3 including all the electrically actuated valves.

Data Treatment

Final mixing ratios are calculated using the peak height of the working standard injections. Chromatograms and final data are stored, and monthly backups of all data are made on an external hard disk.

Data Submission

Carbon monoxide data have not yet is submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG). Submission is planned for 2009.

Documentation

All information is entered in hand-written and electronic log books. The log book entries were comprehensive and up-to-date. Instrument manuals are available at the site.

Inter-Comparison of the Carbon Monoxide Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyzer. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 5 below.

Setup and Connections

The RGA-3 instrument was inter-compared by direct measurements of travelling standards. Details of this experiment are shown in Table 5. The data used for the evaluation was recorded by the AMS data acquisition system.

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

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / FA02479 / 38.44 / 0.51 2 / FA02488 / 44.38 / 0.87 3 / FA02785 / 63.33 / 1.38 4 / FA02466 / 84.57 / 0.66 5 / FA02686 / 105.79 / 1.10 6 / FA02470 / 133.28 / 0.70
Field instrument	Model, S/N	RGA-3, S/N RGA-3-101590-007
	Principle	GC / HgO Reduction Detector. Pre-column: Unibeads 1S 60/80 Analytical column: Mole sieve 5Å 60/80 Carrier: N_2 Column temp. 142°C, Detector temp. 268°C Sample loop 1 ml Sample air dried with magnesium perchlorate
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Duration per level (min)		Injections every 5 min; total 16-21 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (1-4 December, 2008)

Results

The GC system was inter-compared using WCC-Empa travelling standards. Each level was injected between 16 and 21 times. This resulted in a maximum of 21 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 6).

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

Date	TS Identification	TS (ppb)	sdTS (ppb)	AMS CO (ppb)	sdCO (ppb)	No. of inj.
(12/01/08 10:53:43)	FA02686	105.79	1.13	99.39	3.71	21
(12/02/08 05:56:08)	FA02470	133.28	0.55	121.02	3.36	16
(12/02/08 12:03:30)	FA02479	38.44	0.67	42.77	2.99	16
(12/03/08 10:22:00)	FA02785	63.33	1.45	64.56	2.68	17
(12/04/08 10:16:32)	FA02488	44.38	0.98	45.98	1.58	17
(12/04/08 12:01:46)	FA02466	84.57	0.79	80.20	2.04	17

Figure 5 shows the regression residuals of the RGA-3 instrument plotted against time and mole fraction. The absence of a temporal trend (right panel) indicates stable instrument conditions. The absence of mixing ratio dependence (left panel) in the residuals indicates linearity of the current calibration instrument.

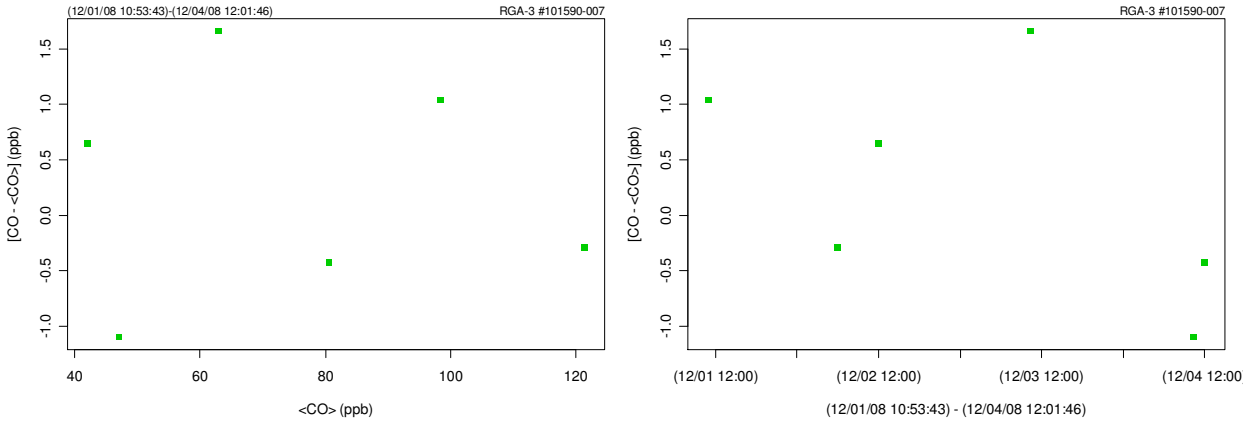

Figure 5. Regression residuals of the AMS RGA-3 based on the inter-comparison with travelling standards. Points represent averages of valid single injections. Left panel: mole fraction dependence; Right panel: time dependence.

Based on these inter-comparison results, unbiased carbon monoxide volume mole fractions of the RGA-3 system X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed using equation (2).

$$X_{CO}\ (\text{ppb}) = ([CO] - 9.9\ \text{ppb}) / 0.836$$

$$u_{CO}\ (\text{ppb}) = \text{sqrt}\ (12.2\ \text{ppb}^2 + 2.37\text{e-}04 * X_{CO}^2) \quad (2)$$

The estimate of the remaining standard uncertainty u_{CO} based on instrument noise and a linear mole fraction dependent contribution of 0.5%.

Changes made to the instrument

No changes were made to the instruments, all settings remained.

Conclusions

The Amsterdam Island CO instrument was working well, however, significant differences were found between the measurements of AMS and WCC-Empa. RGA-3 systems usually have non-linear response functions, and additional laboratory standards are needed for a full characterization of the RGA-3 response function. It is recommended to purchase additional laboratory standards from NOAA/ESRL covering the relevant mole fraction range. Furthermore re-calibration of the current laboratory standard at NOAA/ESRL is recommended.

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 summarized in Table 7, the inter-comparison data is given in Table 8.

Table 7. 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 = -0.5; COEFF = 1.008
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (2008-08-07) 3 runs after return of TS (2009-04-06)

Table 8. Five-minute aggregates computed from 10 valid 30-second values for the inter-comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard (TS).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2008-08-07	1	0	-0.10	0.23	0.06	0.11
2008-08-07	1	190	191.51	0.11	191.48	0.11
2008-08-07	1	90	91.15	0.24	91.18	0.08
2008-08-07	1	140	141.07	0.22	141.04	0.07
2008-08-07	1	60	61.55	0.25	61.42	0.09
2008-08-07	1	30	32.03	0.25	31.83	0.10
2008-08-07	1	0	0.20	0.19	-0.02	0.08
2008-08-07	2	0	-0.03	0.15	-0.07	0.08
2008-08-07	2	90	91.30	0.20	91.27	0.06
2008-08-07	2	60	61.48	0.17	61.27	0.11
2008-08-07	2	140	141.43	0.18	141.35	0.10
2008-08-07	2	190	192.17	0.28	192.04	0.10
2008-08-07	2	30	32.15	0.21	31.84	0.10
2008-08-07	2	0	-0.02	0.21	-0.06	0.08
2008-08-07	3	0	-0.10	0.31	-0.06	0.06
2008-08-07	3	30	31.31	0.32	31.22	0.14
2008-08-07	3	90	91.00	0.26	90.69	0.10
2008-08-07	3	190	191.35	0.33	191.20	0.18
2008-08-07	3	60	61.27	0.30	61.23	0.06
2008-08-07	3	140	141.02	0.49	141.12	0.13
2008-08-07	3	0	-0.15	0.35	-0.01	0.08
2009-04-06	4	0	0.09	0.41	0.00	0.09
2009-04-06	4	140	139.78	0.27	139.85	0.08
2009-04-06	4	30	32.39	0.36	32.25	0.11
2009-04-06	4	90	90.90	0.30	91.04	0.07
2009-04-06	4	190	187.78	0.22	187.92	0.23
2009-04-06	4	60	61.06	0.17	61.09	0.13
2009-04-06	4	0	-0.18	0.24	0.04	0.17
2009-04-06	5	0	-0.01	0.28	-0.09	0.10
2009-04-06	5	60	61.26	0.15	61.24	0.08
2009-04-06	5	140	139.98	0.22	139.89	0.06
2009-04-06	5	90	91.09	0.33	91.05	0.08
2009-04-06	5	190	188.00	0.55	187.87	0.17
2009-04-06	5	30	32.22	0.26	32.17	0.11
2009-04-06	5	0	0.11	0.20	0.02	0.10
2009-04-06	6	0	-0.01	0.16	0.04	0.09
2009-04-06	6	30	32.32	0.34	32.29	0.12
2009-04-06	6	140	140.09	0.28	139.94	0.15
2009-04-06	6	190	188.15	0.39	188.24	0.15
2009-04-06	6	90	90.75	0.24	90.88	0.15
2009-04-06	6	60	61.38	0.27	61.12	0.13
2009-04-06	6	0	0.08	0.13	0.06	0.25

[#]the level is only indicative.

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

$$X_{TS}\ (\text{ppb}) = ([\text{TS}] - 0.04\ \text{ppb}) / 1.0000$$

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

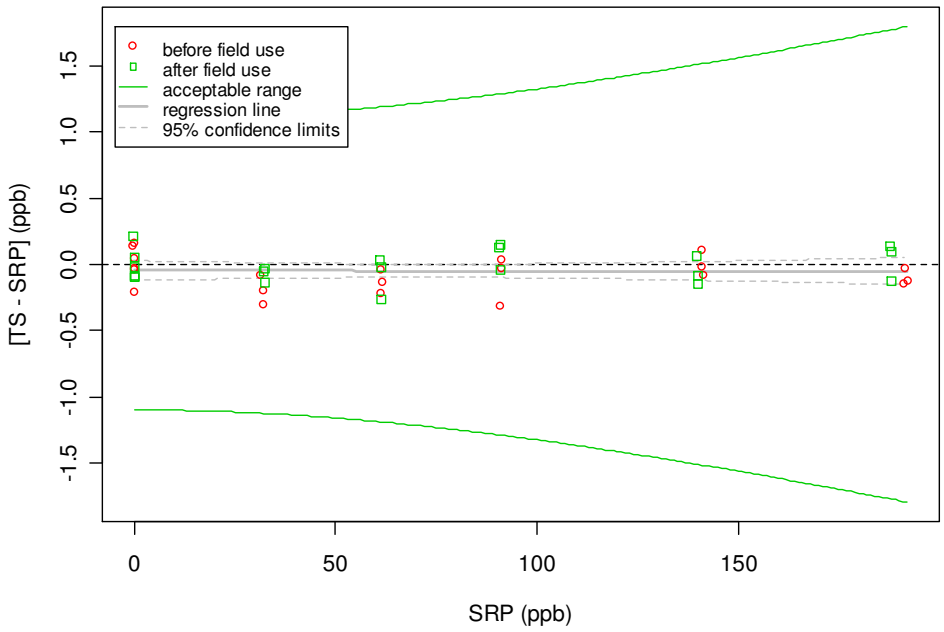

Figure 6. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD; formerly: NOAA/CMDL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly inter-compared with the CCL by way of travelling standards. The scale was transferred to the travelling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. Details are given in Table 9 and Table 10.

Table 9. 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 one specific cylinders, CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Travelling standard (TS)		Carbon monoxide cylinders for direct inter-comparisons. (cf. Table 10)
Connection cylinder - instrument		Ca. 2 meter 1/8" stainless steel tubing (cylinders).
Levels (ppb)		40 – 135 ppb cf. Table 10
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 10. Calibration of the carbon monoxide travelling standards with the WCC-Empa reference before and after the audit.

Date	**050415_FA02470**	sd	**080721_FA02479**	sd	**080814_FA02466**	sd	**080814_FA02488**	sd	**080820_FA02686**	sd	**080820_FA02785**	sd
2008-07-22	**133.11**	0.50	**38.41**	0.54								
2008-07-23			**38.44**	0.36								
2008-08-12			**37.69**	0.50								
2008-08-15					**84.36**	0.53	**43.57**	0.71				
2008-08-21					**83.95**	0.65	**43.76**	0.38				
2008-08-22									**104.97**	0.59	**62.23**	0.45
2008-08-25									**104.93**	0.53	**62.13**	0.46
2009-04-03	**133.44**	0.49	**38.72**	0.34	**84.92**	0.63	**45.25**	0.44	**106.76**	0.57	**64.20**	0.50
2009-05-12					**85.02**	0.63	**44.95**	0.44	**106.49**	0.62	**64.77**	0.70
2009-05-13			**38.95**	0.60								
AVG	**133.28**	0.23	**38.44**	0.47	**84.57**	0.50	**44.38**	0.84	**105.79**	0.97	**63.33**	1.35

A small drift was observed for some of the standards; the average of the analysis before and after the audit was considered for data evaluation.

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Ozone Audit Executive Summary (AMS)

0.1	Station Name:	Amsterdam Island
0.2	GAW ID:	AMS
0.3	Coordinates/Elevation:	37°29'S 77°20'W, 70 m a.s.l.
Parameter:		Surface Ozone

1.1	Date of Audit:	27 - 29 November, 2008
1.2	Auditor:	Bruno Seiler
1.2.1	Station staff involved in audit:	Sébastian Devidal, José Nicolas
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):	$(1.0000\pm0.0010) \times [SRP] - (0.05\pm0.09)$
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C #54658-300
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.5 ppb, SPAN 1.009
1.5.4	Calibration at start of audit (ppb):	$[OA] = (0.9974\pm0.000) \times [SRP] - (0.46\pm0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] + 0.46) / 0.9974$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.61e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 08/6

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

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Carbon Monoxide Audit Executive Summary (AMS)

0.1	Station Name:	Amsterdam Island
0.2	GAW ID:	AMS
0.3	Coordinates/Elevation:	37°29'S 77°20'W, 70 m a.s.l.
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2 – 4 December, 2008	
1.2	Auditor:	Bruno Seiler	
1.2.1	Station staff involved in audit:	Sébastian Devidal, José Nicolas	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	FA02479	38.44±0.51 ppb
		FA02488	44.38±0.87 ppb
		FA02785	63.33±1.38 ppb
		FA02466	84.57±0.66 ppb
		FA02686	105.79±1.10 ppb
		FA02470	133.28±0.70 ppb
1.5	CO analyzer [CA]		
1.5.1	Model:	RGA-3 S/N RGA-3-101590-007	
1.5.2	Range of calibration:	35 – 140 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	$CO = (0.836 \pm 0.012) \times X + (9.9 \pm 1.0)$	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 9.9) / 0.836$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (12.2\ ppb^2 + 2.37e\text{-}04 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	NA	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 08/6	

[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
AMS	Amsterdam Island GAW Station
CCL	Central Calibration Laboratory
DAQ	Data Acquisition System
GAW	Global Atmosphere Watch
GC	Gas Chromatograph
LSCE	Laboratoire des Sciences du Climat et l'Environnement
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyzer
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Travelling Standard
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation