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World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

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World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE AND CARBON MONOXIDE

GLOBAL GAW STATION USHUAIA ARGENTINA, NOVEMBER 2008

Submitted by
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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The third system and performance audit at the Global GAW station Ushuaia (USH) was conducted by WCC-Empa[1] from 25 November thru 3 December 2008 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The USH observatory is operated by the Servicio Meteorológico Nacional (SNM) of Argentina in collaboration with the Government of the Province of Tierra del Fuego.

Previous audits at the Ushuaia GAW station were conducted in November 1998 [*Herzog, et al.*, 1998] and November 2003 [*Zellweger, et al.*, 2003] by WCC-Empa.

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Ing. Maria Elena Barlasina	SMN, Station Manager
Ing. Sergio Luppo	Tierra del Fuego, Senior Station Chief
Dr. Monica Marino	SMN Buenos Aires, Technical director
Mr. Eduardo Piacentini	SMN Buenos Aires, GAW country contact
Mr. Ricardo Sanchez	SMN Buenos Aires, Head of RCC for surface ozone

Our assessment of the Ushuaia 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 SMN, the station manger, the Directorate of Science and Technology of Tierra del Fuego and the station manager of Izaña (twinning partner). 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 Ushuaia Station is located in Tierra del Fuego, Argentina (54° 50' S - 68° 18' W), roughly 10 km south-west of the city of Ushuaia in the vicinity of the Malvinas International Airport. The station is located on a coastal cliff at an altitude of 18 m a.s.l. and exposed to steady winds prevailing from the clean air sector (SW). Easy road access is possible throughout the year with a special permit of the airport security officials.

Station Facilities

The facilities at the site consist of the main building of 150 m^2, which provides space for offices, meeting rooms and laboratories. Attached to this building is a smaller room for the Dobson spectrophotometer. On the platform at the top of the roof, the air inlet and various radiation and meteorological equipment are mounted. The station has no air conditioning, but electrical heating is available. Internet connection is available but only with low bandwidth.

Recommendation 1 (*, 2009)**
The bandwidth of the internet connection should be enlarged to improve data transmission and communication capabilities. A new antenna is currently being installed and the new system should become available in September 2009.

[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 Management and Operation

The GAW activities in Argentina are managed by the Servicio Meteorológico Nacional (SNM) of Argentina in collaboration with the Government of the Province of Tierra del Fuego. The SMN is under the Planning Secretariat of the Ministry of Defence since 2007. Before the SMN was managed by the Air force of Argentina (also within the Ministry of Defence), and the Ushuaia station was under control of a regional air force command. The station is visited daily by the meteorological observers and from Monday to Friday by the station manager. The station manager and observers received only very limited training for the operation of the surface ozone and carbon monoxide instrumentation. It is foreseen that the current station manager will leave the station and positions for a new manger and a technician are currently advertised. Continuous training of existing and new staff is regarded of utmost importance for the successful operation of the measurements.

Recommendation 2 (, ongoing)**
The new organizational structure improved communication between the USH station and SMN. The close cooperation between all involved partners is important and should continue.

Recommendation 3 (*, ongoing)**
SMN should explore all possibilities for operator training. Participation in GAWTEC courses and other means of continuing education is highly recommended, and the knowledge needs to be shared between all station staff.

Recommendation 4 (*, ongoing)**
Additional scientific and technical expertise is needed at the USH site. Future station staff should be selected carefully.

Air Inlet

The air inlet was slightly modified due to recommendations by WCC-Empa in 2003. The current set-up is adequate for its intended purpose.

Surface Ozone Measurements

Instrumentation. The USH station was equipped with two ozone analyzer (TEI 49). During the audit, one of these instrument was decommissioned, and replaced by a TEI 49C provided by WCC-Empa and QA/SAC Switzerland. The current instrumentation is adequate for its intended purpose.

Standards. No ozone standard is available at the site, but a calibrator TEI 49C-PS is available at the Regional Calibration Centre for Surface Ozone (RCC-BsAs) in Buenos Aires. This calibrator has previously been used in irregular intervals for calibration of the USH instruments. The last inter-comparison took place in 2006, and these data were available during the audit. In addition, the ozone calibrator was available at USH for an inter-comparison with WCC-Empa during the audit.

Recommendation 5 (*, ongoing)**
It is strongly recommended to do yearly calibrations / inter-comparisons with a reference instrument at the site. For this purpose the ozone calibrator of the RCC should be shipped to the USH site once per year.

Intercomparison (Performance Audit). The inter-comparisons of the two existing and the new ozone analyzers extended over a period of several days. One of the TEI 49 instruments was found to be faulty and was repaired during the audit. It was decided that data of this instrument should not be used for submission to WDCGG. This instrument was decommissioned and will probably be used in the city of Ushuaia for additional ozone measurements. Data of the faulty instrument are only shown in the appendix.

A full assessment was made of the original main TEI 49 instrument, the new TEI 49C instrument and the TEI 49C-PS ozone calibrator of the RCC Buenos Aires. All instruments were found to be in good calibration, and the results of the inter-comparisons against the WCC-Empa travelling standard are summarised below (1a-c). [OA] represents surface ozone readings as delivered by the ozone analyzer, and [OC] by the ozone calibrator respectively. The following equations characterise the instrument bias:

Ozone analyzer TEI 49 (at USH since 1996)

TEI 49 #47306-278: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.00 ppb) / 1.003 (1a)

The result of this inter-comparison is presented in Figure 1.

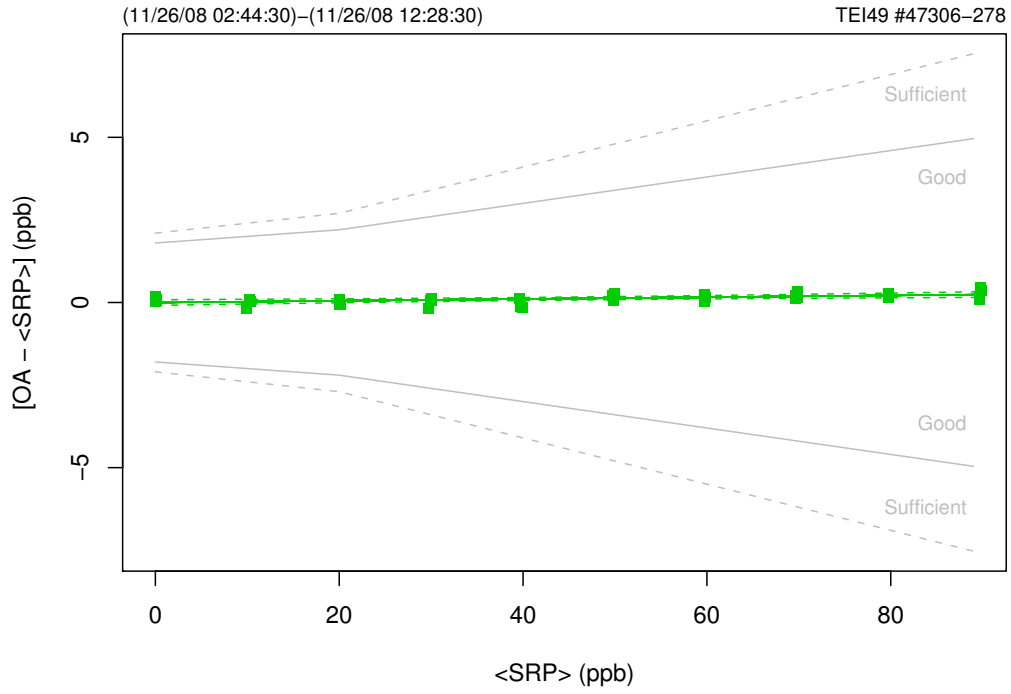

Figure 1. Bias of the original main TEI 49 ozone analyzer with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*,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

New ozone analyzer TEI 49C (at USH since 2008)

TEI 49C #58546-318: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.08 ppb) / 0.996 (1b)

The result of this inter-comparison is presented in **Figure 2**.

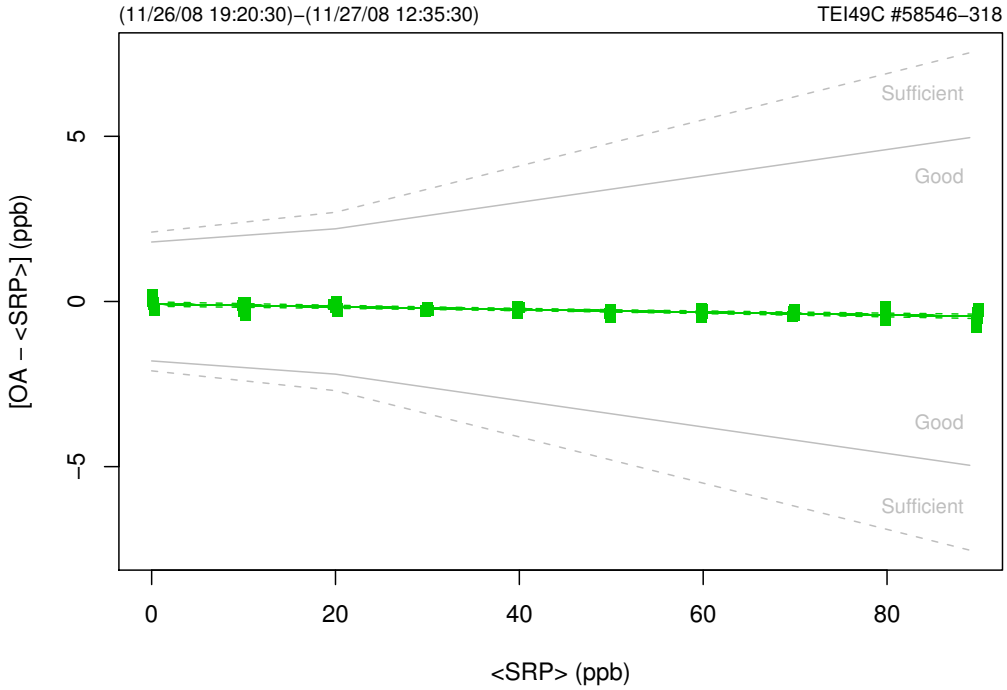

Figure 2. Bias of the new TEI 49C ozone analyzer with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Ozone calibrator TEI 49C-PS of the RCC Buenos Aires

TEI 49C-PS #56084-306: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.17 ppb) / 1.011 (1c)

The result of this inter-comparison is presented in Figure 3.

Recommendation 6 (, ongoing)**
The activities of the Regional Calibration Centre for Surface Ozone in Buenos Aires are an important contribution to the GAW program and should be continued.

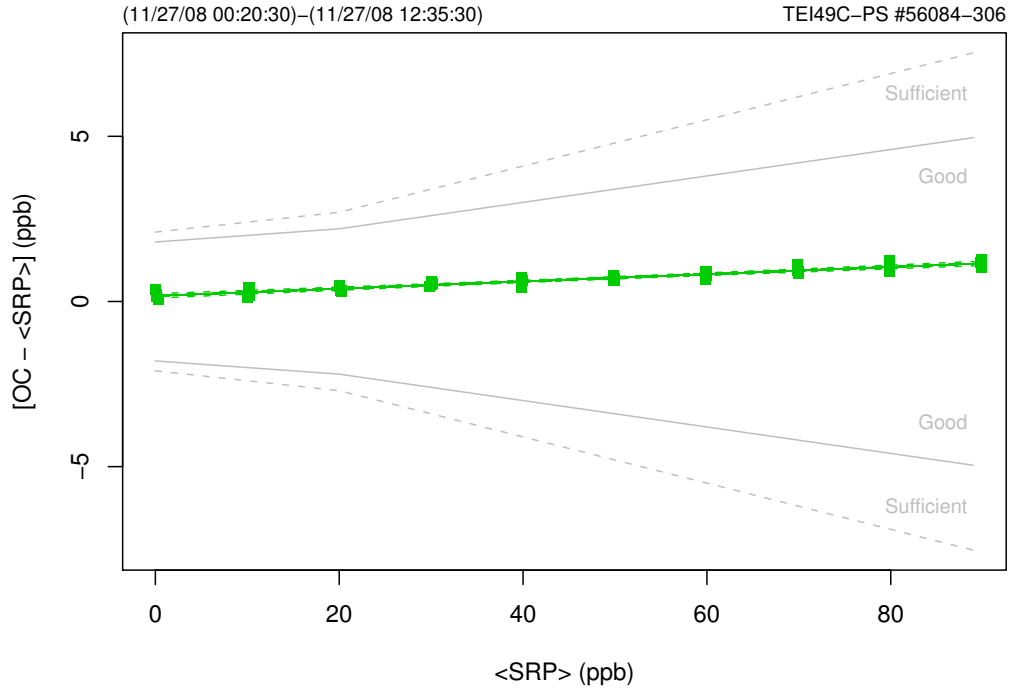

Figure 3. Bias of the TEI 49C-PS ozone calibrator of the RCC Buenos Aires with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Carbon Monoxide Measurements

Instrumentation. Ushuaia is currently equipped with two CO analyzers. One of the original TEI48 (at the site since 1994) is still in operation, but the TEI48 backup instrument failed in 2007. In addition a Horiba APMA-360 CE carbon monoxide analyzer was installed at the station by QA/SAC Switzerland and WCC-Empa. The instrumentation is adequate for the intended purpose.

Standards. The station is currently equipped with four carbon monoxide standards. Two standards (approx. 100 ppm CO in air) were delivered through WCC-Empa in 2004 from remaining funds from the GEF project, and two more standards were delivered as part of the instrument replacement proposal. The new standards were assigned with WMO-2000 traceable carbon monoxide mole fractions by WCC-Empa. One standard has a mole fraction of approx. 2.5 ppm CO in air and is used for direct calibrations of the instrument. The other standard has a mole fraction of approx. 40 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 7 (,2010)**
For the long term operation of the USH station, funding of calibration gas supply needs to be allocated by SMN.

Intercomparison (Performance Audit). Both the TEI48 and the Horiba APMA360 instruments were inter-compared during the audit. The Horiba instrument was calibrated using the 2.5 ppm standard gas before the inter-comparison (initial calibration), while the TEI48 was directly assessed without prior calibration (performance audit). 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 equations (2 and 3) characterise the instrument biases (cf. Figure 4 and Figure 5):

Carbon monoxide analyzer TEI 48 (at USH since 1994)

TEI48 #47169-278 (ZERO 540, SPAN 800)

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 2.4 ppb) / 0.961 (2)

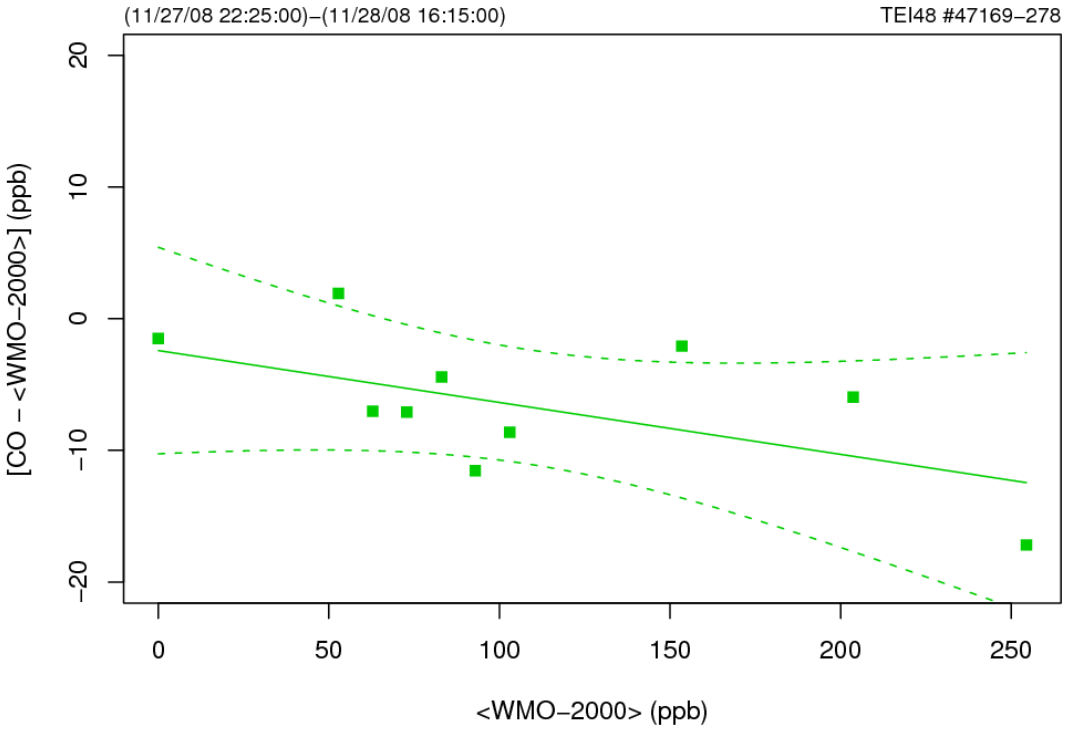

Figure 4. Bias of the Ushuaia carbon monoxide analyzer (TEI 48) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

New carbon monoxide analyzer Horiba APMA-360 (at USH since November 2008)

Horiba APMA-360 #712020 (ZERO -3, SPAN 1.0320):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 2.2 ppb) / 0.992 (3)

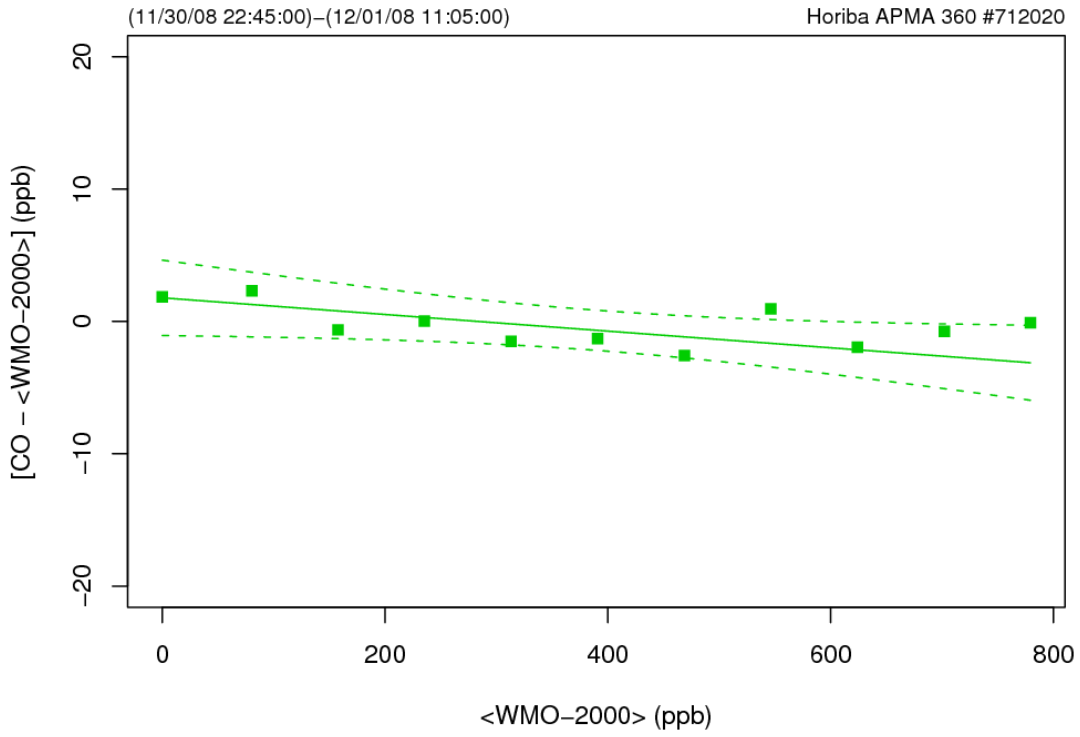

Figure 5. Bias of the new carbon monoxide analyzer (Horiba APMA-360) with respect to the WMO-2000 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

The results show that both instruments are in calibration; however, especially for the TEI 48 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. The new instrument showed a significantly improved repeatability, but averaging times of one-hour are recommended to account for short-term instrument noise.

Recommendation 8 (, 2009)**
Parallel measurements with both the TEI 48 and the new Horiba APMA-360 should be made at least for one year. After this period and when the results confirm equivalency between the two instruments, the TEI 48 may be used at another site, e.g. Ushuaia city.

Recommendation 9 (*, ongoing)
Only data of the new instrument should be used for future CO data submission to WDCGG. Existing data of the TEI 48 instruments need to be revised before final submission to WDCGG (see also recommendation 11).

Other variables / observations

The USH station has a strong ozone program comprising long Dobson time series and the recent addition of weekly ozone sondings. Programs other than CO and surface ozone measurements were discontinued (VOC, aerosol) due to instrument failures, lack of expertise and budgetary constraints for repair or replacement. However, SMN is currently exploring future collaboration, e.g. with CEILAP (http://www.division-lidar.com.ar).

Recommendation 10 (*, ongoing)
All possibilities should be explored to expand the measurement program at the USH site.

Data Acquisition and Management

Analogue signals are acquired for the original TEI48 and TEI49 instruments. This system is adequate for these instruments because no other options are available. For the new ozone and carbon monoxide instruments a LabView based data acquisition system programmed by QA/SAC-Switzerland was installed on a dedicated computer. One minute averages including all available ancillary instrument data are automatically stored in a data base. An additional program transfers the data base incrementally to a remote server (currently at Empa) for near real time data access. However, data transfer is often interrupted due to poor internet connectivity at the USH site.

Recommendation 11 (*, 2009)**
The LabView based data acquisition and the transfer software needs to be improved. Furthermore, the internet bandwidth (both up- and download) needs to be increased to assure continuous and secure data transfer (c.f. recommendation 1, currently being implemented)

Data Submission

CO and ozone data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). At the time of the audit complete data series until 2002 were available at WDCGG. A review of the available data series showed that all submitted data needs to be carefully re-evaluated and re-submitted. Currently questionable data of the USH site can still be accessed at WDCGG. This data has not been flagged invalid or questionable.

Recommendation 12 (*, immediately)**
All submitted data need to be reviewed and further quality controlled. WDCGG needs to be contacted to make sure that invalid data is immediately removed from the data base. Re-submission of quality controlled data is strongly encouraged.

Recommendation 13 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available (quality controlled) data should be submitted to the corresponding data centres, with a submission delay of maximum one year.

Recommendation 14 (, ongoing)**
GAWSIS entries need to be updated at regular intervals. At the time of the audit the information was outdated, and some ongoing programs such as the NOAA/ESRL flask sampling at USH sampling were not registered.

Conclusions

The Global GAW station Ushuaia contributes with long time series of total column and surface ozone, carbon monoxide, radiation and meteorological measurements to the GAW program. The recent addition of vertical ozone soundings is a valuable expansion of the program. It was noticed that the existing time series of the in-situ ozone and carbon monoxide measurements need to be revised for final submission to WDCGG. These data series are a valuable contribution to the GAW program, especially because they cover a geographical region where only sparse information about atmospheric composition is available. The continuation of existing measurements and the addition of new parameters are therefore strongly encouraged. All assessed measurements were of sufficiently high quality.

Summary Ranking of Ushuaia Station

System Audit Aspect	Adequacy[#]	Comment
Access	(4)	Access may difficult in case of snow, 4WD truck needed
Facilities		
Laboratory and office space	(4)	Spacious laboratory building
Air Conditioning	(4)	No cooling but sufficiently constant lab temperature
Power supply	(4)	Repair / replacement of UPS needed
Internet access	(3)	Available but low bandwidth, frequent interruptions
General Management and Operation		
Organisation	(4)	Improved organisation
Competence of staff	(3)	Training needed
Air Inlet System (Ozone and CO)	(4)	
Instrumentation		
Ozone	(5)	TEI49C
Carbon monoxide	(4)	Horiba APMA-360
Total column ozone	(5)	Dobson
Ozone profile	(5)	New program
VOC	(0)	Defective, discontinued
Aerosol (Aethalometer)	(0)	Defective, discontinued
Meteo	(5)	
Standards		
Ozone	(3)	Only at RCC Buenos Aires
Carbon monoxide	(5)	WMO-2000 traceable standards
Data Management		
Data acquisition	(4)	New DAQ being implemented
Data processing	(3)	Training needed
Data submission	(2)	Review of submitted data needed

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

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Dübendorf, September 2009

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

APPENDIX

Global GAW Station Ushuaia

Site description

Information about the Ushuaia GAW station can be found in previous audit reports [*Herzog, et al.*, 1998; *Zellweger, et al.*, 2003], and the station is also registered in GAWSIS (http://gaw.empa.ch/gawsis).

Measurement Program

An overview of the measurement program and its status as of December 2008 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Current measurement Program at the USH Station

Parameter*	**Current Instrument**	**Data Coverage (%)#**		
		<12 m	<3 y	Overall
Aerosol				
Light absorption coefficient	Aethalometer	0	0	>50
Ozone				
Surface ozone	UV absorption (TEI 49 and 49C)	>90	>90	>90
Total column ozone	Dobson	>90	>90	>90
Vertical ozone profile	ECC Sonde	>90	NA	NA
Greenhouse Gas				
CO_2, SF_6, N_2O	NOAA/ESRL flask sampling	>90	>90	NA
Reactive Gas				
CO	NDIR (TEI 48 and Horiba APMA-360)	>90	>90	>90
CO, H_2	NOAA/ESRL flask sampling	>90	>90	NA
Solar radiation				
Global irradiance	Pyranometer (global, broadband)			
Direct irradiance	Pyranometer (global, broadband)			
Diffuse irradiance	Pyranometer (global, broadband)			
UV Broadband	Pyranometer (global, broadband)	>90	>90	>90
Meteo				
PTU, wind speed + direction		>90	>90	>90
Back Trajectories				

* Refer to GAWSIS for more details
\# Missing information about data coverage: information was not available.

Ozone and Carbon Monoxide Distribution at Ushuaia

The monthly and yearly distributions of one hourly mean values for surface ozone and carbon monoxide for the year 2000 are shown in Figure 6. Data for these figures were downloaded from WDCGG. However, a review of the data at WDCGG showed that most of the submitted data needs to be revised. Therefore the distributions shown below should be considered to be preliminary.

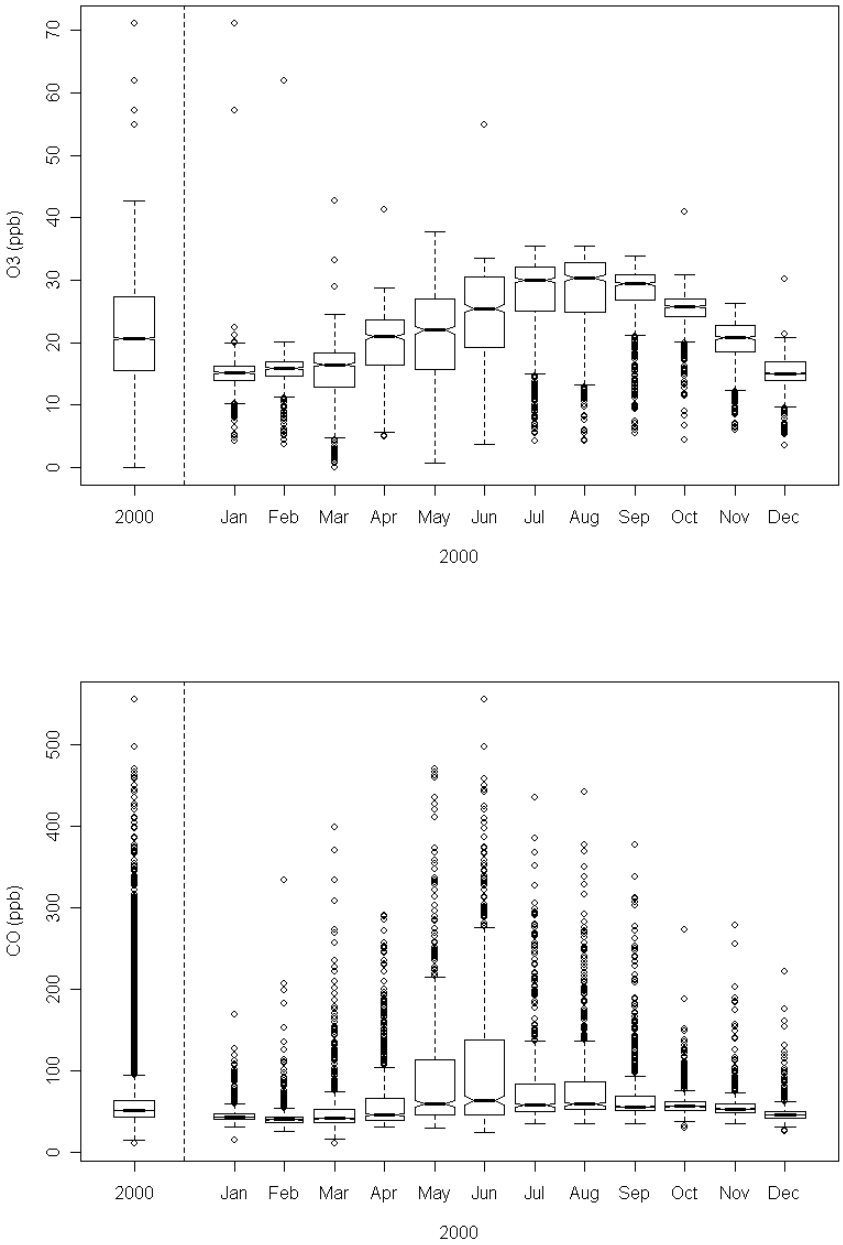

Figure 6. Yearly and monthly box plots of 1-hourly aggregates for the year 2000 for surface Ozone (upper panel) and carbon monoxide (lower panel). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data 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 at Ushuaia are coordinated by SMN and the Province of Tierra del Fuego. An organisational chart is shown in Figure 7 (SMN) and Figure 8 (Tierra del Fuego).

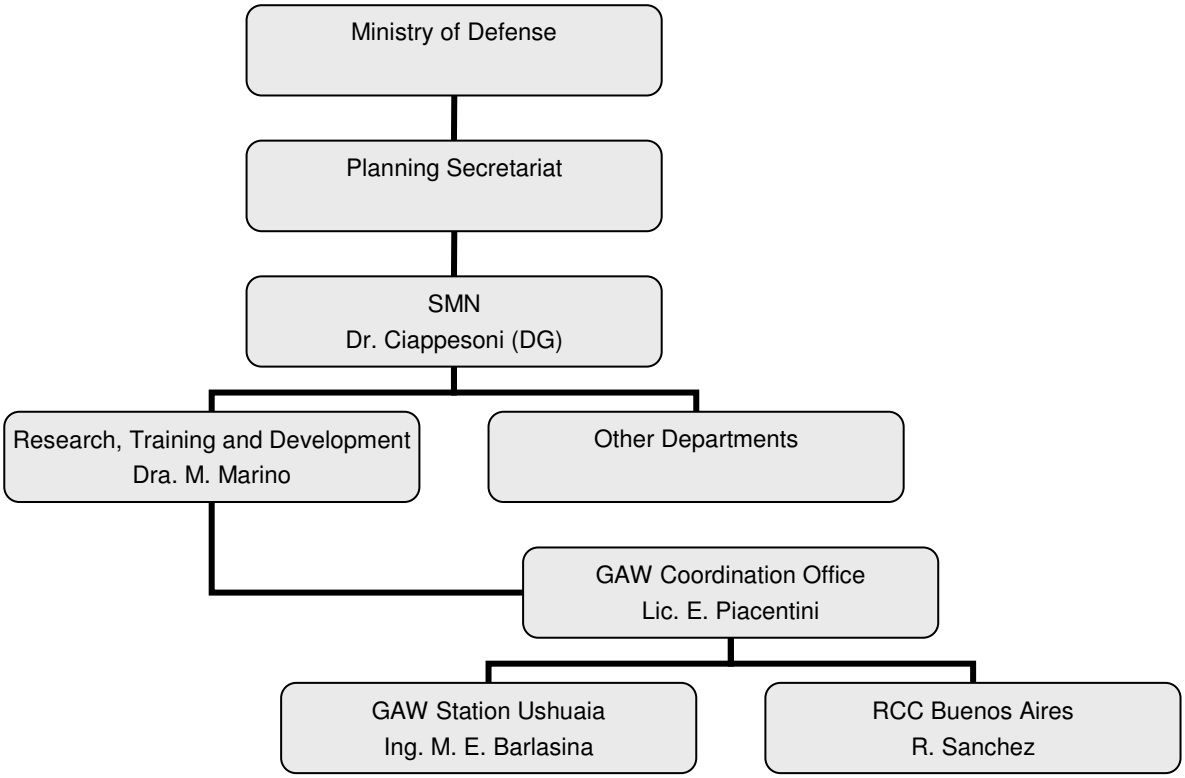

Figure 7. Organisation of the Argentine GAW activities by SMN as of December 2008. Ing. Manuel Cupeiro replaced M. E. Barlasina as the station manager in 2009.

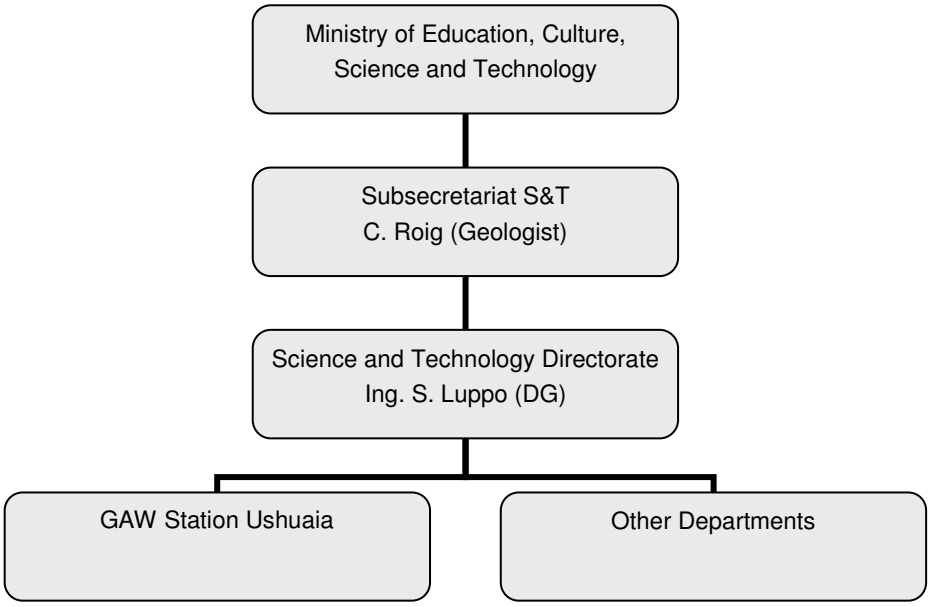

Figure 8. Organisation of the Argentine GAW activities by the Province of Tierra del Fuego as of December 2008.

Surface Ozone Measurements

Surface ozone measurements started in 1994 at the Ushuaia site. These measurements were made with two TEI 49 ozone analyzers running in parallel. During the present audit one of the TEI 49 was replaced by a TEI 49C instrument. Results for all instruments are shown below, including the ozone calibrator of the Buenos Aires Regional Calibration Centre for Surface Ozone. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning

The USH station has only a heating system and is not air-conditioned. Nevertheless the laboratory temperature remains sufficiently constant for the measurements of surface ozone.

Air Inlet System

The inlet system for the surface ozone and carbon monoxide instrument was described in the previous audit report [*Zellweger, et al.*, 2003] and was not significantly changed during the present audit. The new ozone and carbon monoxide instruments were connected with a common sampling line to one branch of the existing ½ inch PFA tubing. No changes were made to the connection of the existing instrumentation (TEI 49 and TEI 48). The residence time was confirmed to be less than 5 seconds for all surface ozone and CO measurements.

Instrumentation

The station was equipped with two ozone analyzer (TEI 49) until the date of the audit. One of these instruments was found to be defective and was decommissioned. A TEI 49C was installed during the audit and will serve as the main ozone analyzer, whereas the remaining TEI 49 is running as a back-up system. Instrumental details for the ozone analyzers (OA) are summarised in Table 2 below.

Standards

No ozone standard is available at the site, but the ozone calibrator of the RCC Buenos Aires was available during the audit. Details are summarised in Table 2.

Operation and Maintenance

The instruments are checked on working days for general operation. These checks include inspection of flow rates and data acquisition. Daily zero checks are performed automatically for the TEI 49 instrument. Inlet filters are exchanged every two to three weeks. No regular calibrations of the instruments were performed, but one of the TEI 49 (O3-1) instruments was calibrated by the RCC Buenos Aires in 2006. However, this calibration was found to be invalid, and the original calibration factors were restored. Another calibration for both TEI 49 instruments was made in March 2008 by Izaña station staff. No changes were made for the main ozone analyzer (O3-1), but significant adjustments were made for the back-up instrument (O3-2). These changes were necessary to compensate for a defective solenoid valve; therefore, data of the O3-2 instrument should be considered invalid.

Data Acquisition and Data Transfer

The data acquisition system as described in the previous audit report [*Herzog, et al.*, 1998; *Zellweger, et al.*, 2003] is still in use for the TEI 49 and TEI 48 instruments. The new ozone and carbon monoxide analyzers are connected via serial interface to a dedicated computer with a custom made LabView data acquisition system (by QA/SAC-Switzerland). One minute averages including all available instrument parameters are stored in a data base and automatically transferred to an FTP server for near real time data access.

Data Treatment

Data processing is done at Ushuaia and consists of a weekly visual inspection of time series. The final data evaluation is done monthly. Currently data analysis is only made by Sergio Luppo. Available data series should be more extensively exploited and need further quality control. Invalid values (i.e. instrument maintenance) are flagged as invalid data but remain in the

database. A filter based on wind direction and velocity is applied to distinguish between “background” and “polluted” air masses.

Data Submission

Ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG). At the time of the audit complete data series until 2002 were available at WDCGG. A review of the available data series showed that all submitted data needs to be carefully re-evaluated and re-submitted. Currently questionable data of the USH site can still be accessed at WDCGG.

Documentation

The instrument manuals are available at the site. In addition station and instrument log books (hand written) are available at the site.

Inter-Comparison of Ozone Analyzer

The inter-comparisons of the two existing and the new ozone analyzers extended over a period of several days. One of the TEI 49 instruments was found to be faulty and was repaired during the audit. It was decided that data of this instrument should not be used for submission to WDCGG. This instrument was decommissioned and will probably be used in the city of Ushuaia for additional ozone measurements. 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 USH ozone analyzers and the calibrator of the RCC Buenos Aires. The data used for the evaluation was recorded by the WCC-Empa data acquisition system (C-Series instruments) and the USH data acquisition system (TEI 49) as indicated. No further corrections were applied to the data.

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. 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 analyzer (OA) values.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #56891-310 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.010
Ozone analyzer (OA) USH internal: O3-1	Model, S/N	TEI 49 #47306-278
	Principle	UV absorption
	Range	1 ppm
	Settings	OFFSET 50; SPAN 510
Ozone analyzer (OA) USH internal: O3-2	Model, S/N	TEI 49 #47312-278
	Principle	UV absorption
	Range	1 ppm
	Settings	OFFSET 51; SPAN 566 after audit OFFSET 50; SPAN 520
Ozone analyzer (OA) (Instrument installed during audit)	Model, S/N	TEI 49C #58546-318
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.012
Ozone calibrator (OC) (normally at RCC Buenos Aires)	Model, S/N	TEI 49C-PS #56084-306
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = -0.5; COEFF = 1.035
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm (WCC-Empa)
Connection between instruments		Ca. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS and OA/OC	One minute aggregates from digital output (custom designed LabView program) for the C-Series instruments, station data acquisition for the TEI 49 (analogue signals)
Pressure readings at beginning of inter-comparison	TS:	0.25% higher than ambient, adjusted to ambient
	OA (O3-1):	0.07% lower than ambient, no adjustment
	OA (O3-2):	0.20% lower than ambient, no adjustment
	OA (TEI 49C)	0.31% lower than ambient, adjusted to ambient
	OC (RCC)	0.36% higher than ambient, adjusted to ambient
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 (2008-11-26), TEI 49 #47306-278 7 runs (2008-11-26 thru 27), TEI 49C #58546-318 5 runs (2008-11- 27), TEI 49C-PS #56084-306

TEI 49 #47306-278 (O3-1)

This instrument was installed at USH in 1994. The result of the assessment (direct comparison between TS and the analyzer) is shown in Table 3.

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the USH ozone analyzer (OA) TEI 49 #47306-278 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-11-26 02:49	1	0	0.05	0.17	0	0.08	0.04
2008-11-26 03:04	1	50	49.76	49.96	0	0.08	0.05
2008-11-26 03:19	1	60	59.78	60.00	0	0.13	0.07
2008-11-26 03:34	1	10	10.26	10.39	0	0.36	0.13
2008-11-26 03:49	1	40	39.63	39.73	0	0.17	0.07
2008-11-26 04:04	1	80	79.76	79.95	0	0.13	0.05
2008-11-26 04:19	1	90	89.87	90.27	0	0.09	0.08
2008-11-26 04:34	1	30	29.94	30.00	0	0.13	0.08
2008-11-26 04:49	1	20	19.97	20.03	0	0.09	0.09
2008-11-26 05:04	1	70	69.71	69.88	0	0.19	0.10
2008-11-26 05:19	2	0	-0.01	0.20	0	0.11	0.04
2008-11-26 05:34	2	70	69.84	70.12	0	0.10	0.06
2008-11-26 05:49	2	90	89.71	89.73	0	0.10	0.06
2008-11-26 06:04	2	20	20.03	20.14	0	0.23	0.10
2008-11-26 06:19	2	50	49.83	49.93	0	0.17	0.08
2008-11-26 06:34	2	10	10.20	10.33	0	0.25	0.12
2008-11-26 06:49	2	40	39.71	39.59	0	0.17	0.05
2008-11-26 07:04	2	80	79.81	80.02	0	0.14	0.09
2008-11-26 07:19	2	30	30.00	30.14	0	0.17	0.08
2008-11-26 07:34	2	60	59.85	59.98	0	0.12	0.05
2008-11-26 07:49	3	0	0.03	0.13	0	0.10	0.06
2008-11-26 08:04	3	10	9.90	9.75	0	0.18	0.10
2008-11-26 08:19	3	30	29.71	29.53	0	0.09	0.06
2008-11-26 08:34	3	90	89.76	89.88	0	0.11	0.06
2008-11-26 08:49	3	50	49.92	50.16	0	0.10	0.12
2008-11-26 09:04	3	60	59.84	59.95	0	0.11	0.08
2008-11-26 09:19	3	20	20.07	20.04	0	0.21	0.13
2008-11-26 09:34	3	80	79.76	79.84	0	0.20	0.10
2008-11-26 09:49	3	70	69.87	69.99	0	0.07	0.07
2008-11-26 10:04	3	40	39.89	39.73	0	0.12	0.08
2008-11-26 10:19	4	0	0.00	0.06	0	0.08	0.03
2008-11-26 10:34	4	50	49.82	49.87	0	0.10	0.06
2008-11-26 10:49	4	60	59.80	59.81	0	0.12	0.04
2008-11-26 11:04	4	10	10.28	10.34	0	0.25	0.12
2008-11-26 11:19	4	40	39.72	39.72	0	0.17	0.06
2008-11-26 11:34	4	80	79.81	79.96	0	0.14	0.06
2008-11-26 11:49	4	90	89.89	90.19	0	0.10	0.06
2008-11-26 12:04	4	30	30.00	30.08	0	0.17	0.09
2008-11-26 12:19	4	20	19.97	19.92	0	0.15	0.09
2008-11-26 12:34	4	70	69.66	69.73	0	0.13	0.11

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

Figure 9 shows the regression residuals of the TEI 49 #47306-278 ozone analyzer with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

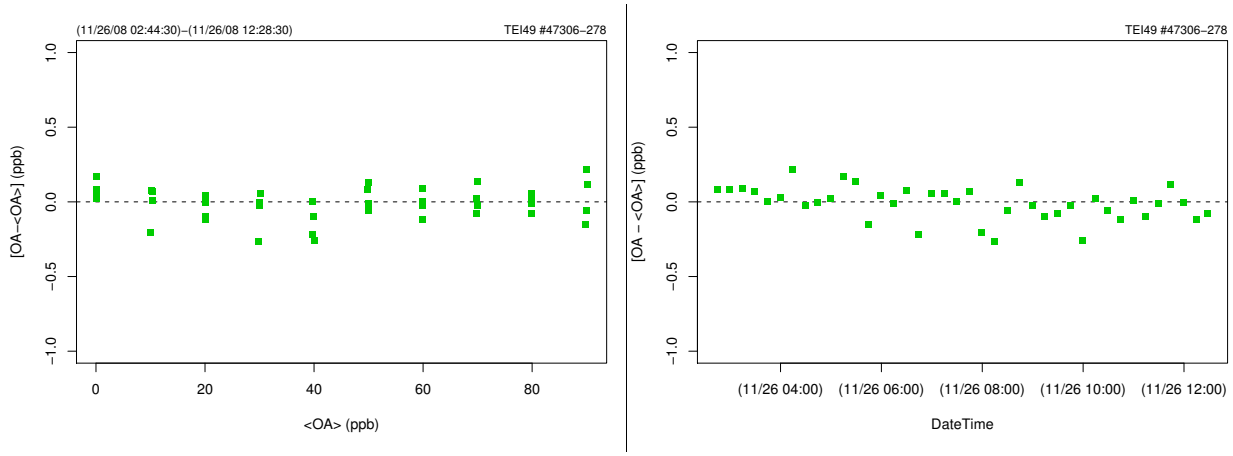

Figure 9. Regression residuals of the USH ozone analyzer (TEI 49 #47306-278) as a function of concentration (left panel) and time (right panel).

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 49 #47306-278:

$$X_{O3}\ (\text{ppb}) = ([\text{OA}] + 0.00\ \text{ppb}) / 1.003$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.27\ \text{ppb}^2 + 2.68\text{e-}05 * X_{O3}^2) \qquad (1a)$$

TEI 49 #47312-278 (O3-2)

This instrument was also installed at USH in 1994. The result of the first assessment (direct comparison between TS and the analyzer) showed a significant bias compared to the SRP (Figure 10). A leaky solenoid valve was identified as the reason and was replaced during the audit. An inter-comparison against the ozone calibrator of the RCC Buenos Aires showed good agreement afterwards. The instrument was decommissioned from the USH site and results are therefore not further discussed here. Furthermore it was decided that data of this instrument should not be used for data submission.

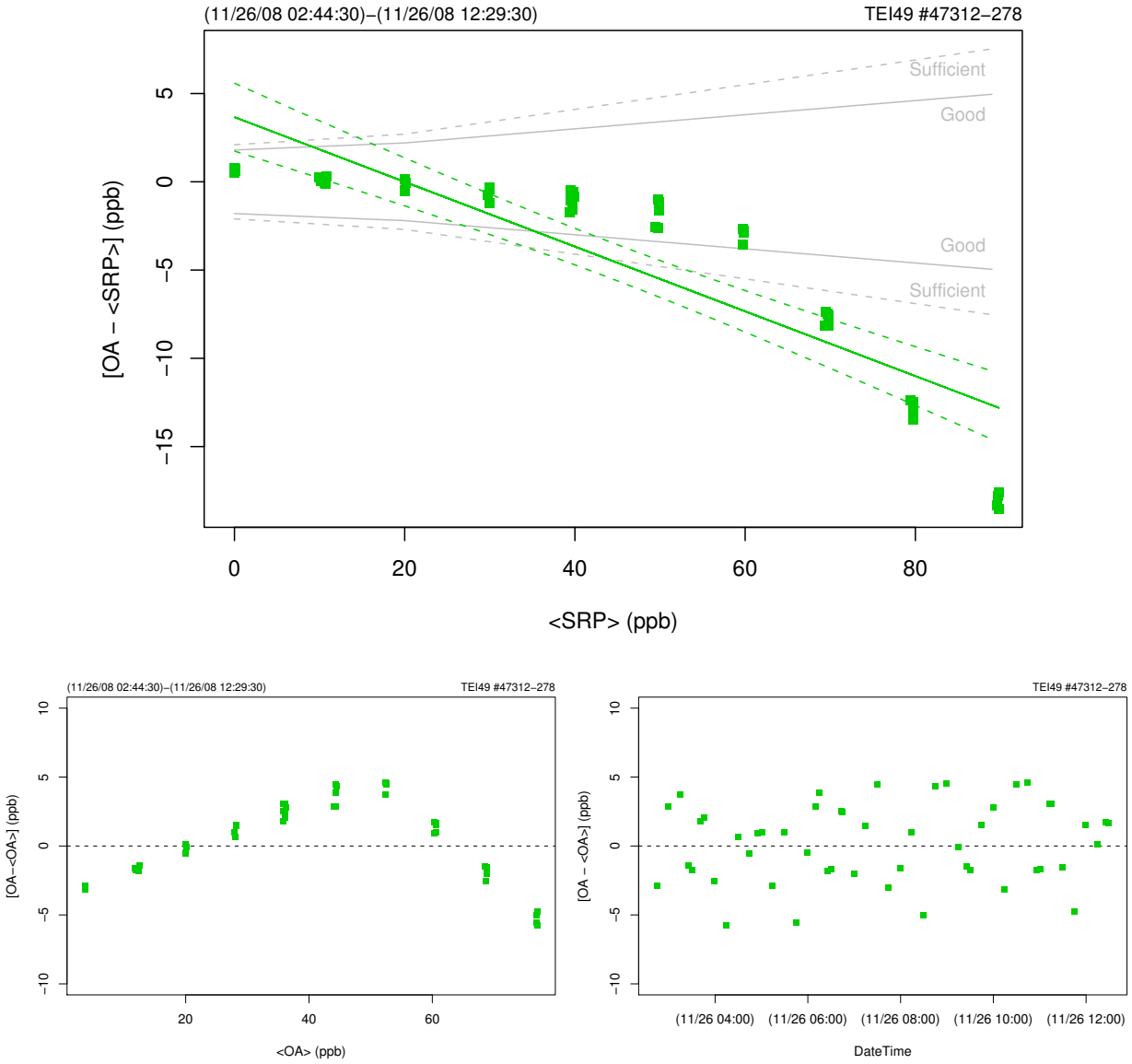

Figure 10. Upper panel: Bias of the TEI 49 #47312-278 ozone analyzer with respect to the SRP as a function of concentration. Lower panel: Regression residuals of the USH ozone analyzer (TEI 49 #47306-278) as a function of concentration (left panel) and time (right panel).

TEI 49C #58546-318

This instrument was installed at USH during the audit. The initial calibration was done against SRP#15 at the laboratory of WCC-Empa in June 2008. The result of the assessment (direct comparison between TS and the analyzer) is shown in **Table 4**.

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the USH ozone analyzer (OA) TEI 49C #58546-318 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-11-26 19:25	1	0	0.08	0.33	0	0.10	0.04
2008-11-26 19:40	1	70	69.77	69.28	0	0.06	0.04
2008-11-26 19:55	1	90	89.76	89.11	0	0.09	0.04
2008-11-26 20:10	1	20	19.82	19.74	0	0.07	0.04
2008-11-26 20:25	1	50	49.78	49.38	0	0.09	0.03
2008-11-26 20:40	1	10	9.99	9.98	0	0.18	0.07
2008-11-26 20:55	1	40	39.76	39.41	0	0.08	0.03
2008-11-26 21:10	1	80	79.83	79.19	0	0.09	0.07
2008-11-26 21:25	1	30	29.89	29.64	0	0.10	0.04
2008-11-26 21:40	1	60	59.89	59.36	0	0.10	0.03
2008-11-26 21:55	2	0	0.14	0.15	0	0.08	0.04
2008-11-26 22:10	2	10	9.83	9.73	0	0.06	0.03
2008-11-26 22:25	2	30	29.79	29.52	0	0.11	0.03
2008-11-26 22:40	2	90	89.81	88.95	0	0.12	0.04
2008-11-26 22:55	2	50	49.88	49.38	0	0.11	0.03
2008-11-26 23:10	2	60	59.91	59.54	0	0.08	0.04
2008-11-26 23:25	2	20	19.99	19.84	0	0.09	0.05
2008-11-26 23:40	2	80	79.84	79.38	0	0.06	0.05
2008-11-26 23:55	2	70	69.91	69.44	0	0.07	0.05
2008-11-27 00:10	2	40	39.96	39.77	0	0.09	0.04
2008-11-27 00:25	3	0	0.05	0.09	0	0.07	0.04
2008-11-27 00:40	3	50	49.92	49.65	0	0.04	0.04
2008-11-27 00:55	3	60	59.90	59.46	0	0.07	0.03
2008-11-27 01:10	3	10	10.11	10.05	0	0.10	0.03
2008-11-27 01:25	3	40	39.82	39.52	0	0.14	0.03
2008-11-27 01:40	3	80	79.90	79.41	0	0.11	0.03
2008-11-27 01:55	3	90	89.98	89.60	0	0.06	0.03
2008-11-27 02:10	3	30	30.05	29.86	0	0.13	0.04
2008-11-27 02:25	3	20	20.06	20.09	0	0.07	0.03
2008-11-27 02:40	3	70	69.87	69.52	0	0.17	0.06
2008-11-27 02:55	4	0	0.02	0.08	0	0.14	0.05
2008-11-27 03:10	4	70	69.95	69.48	0	0.04	0.04
2008-11-27 03:25	4	90	89.91	89.33	0	0.12	0.06
2008-11-27 03:40	4	20	20.18	19.97	0	0.15	0.06
2008-11-27 03:55	4	50	49.92	49.60	0	0.11	0.06
2008-11-27 04:10	4	10	10.20	10.02	0	0.21	0.04
2008-11-27 04:25	4	40	39.84	39.46	0	0.10	0.07
2008-11-27 04:40	4	80	79.94	79.41	0	0.10	0.05
2008-11-27 04:55	4	30	30.11	29.85	0	0.11	0.04
2008-11-27 05:10	4	60	59.99	59.60	0	0.09	0.05
2008-11-27 05:25	5	0	0.27	0.05	0	0.08	0.02
2008-11-27 05:40	5	10	9.99	9.70	0	0.05	0.10
2008-11-27 05:55	5	30	29.84	29.55	0	0.08	0.04
2008-11-27 06:10	5	90	89.88	89.47	0	0.11	0.07
2008-11-27 06:25	5	50	49.99	49.67	0	0.04	0.06
2008-11-27 06:40	5	60	59.98	59.61	0	0.08	0.04
2008-11-27 06:55	5	20	20.17	19.95	0	0.16	0.05
2008-11-27 07:10	5	80	79.86	79.55	0	0.13	0.07
2008-11-27 07:25	5	70	70.00	69.71	0	0.07	0.06
2008-11-27 07:40	5	40	39.98	39.81	0	0.10	0.04

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-11-27 07:55	6	0	0.11	0.06	0	0.11	0.04
2008-11-27 08:10	6	50	49.91	49.62	0	0.07	0.04
2008-11-27 08:25	6	60	59.96	59.70	0	0.08	0.06
2008-11-27 08:40	6	10	10.22	10.21	0	0.13	0.06
2008-11-27 08:55	6	40	39.81	39.64	0	0.14	0.05
2008-11-27 09:10	6	80	79.93	79.73	0	0.09	0.04
2008-11-27 09:25	6	90	89.98	89.70	0	0.10	0.03
2008-11-27 09:40	6	30	30.06	29.88	0	0.07	0.04
2008-11-27 09:55	6	20	20.06	19.97	0	0.06	0.04
2008-11-27 10:10	6	70	69.87	69.52	0	0.18	0.09
2008-11-27 10:25	7	0	0.10	0.13	0	0.11	0.05
2008-11-27 10:40	7	70	69.93	69.55	0	0.07	0.05
2008-11-27 10:55	7	90	89.93	89.47	0	0.12	0.07
2008-11-27 11:10	7	20	20.20	19.90	0	0.12	0.07
2008-11-27 11:25	7	50	49.91	49.62	0	0.10	0.03
2008-11-27 11:40	7	10	10.20	9.80	0	0.21	0.07
2008-11-27 11:55	7	40	39.84	39.49	0	0.12	0.03
2008-11-27 12:10	7	80	79.93	79.59	0	0.12	0.06
2008-11-27 12:25	7	30	30.03	29.75	0	0.12	0.05
2008-11-27 12:40	7	60	59.88	59.65	0	0.08	0.06

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

Figure 11 shows the regression residuals of the TEI 49C #58546-318 ozone analyzer with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

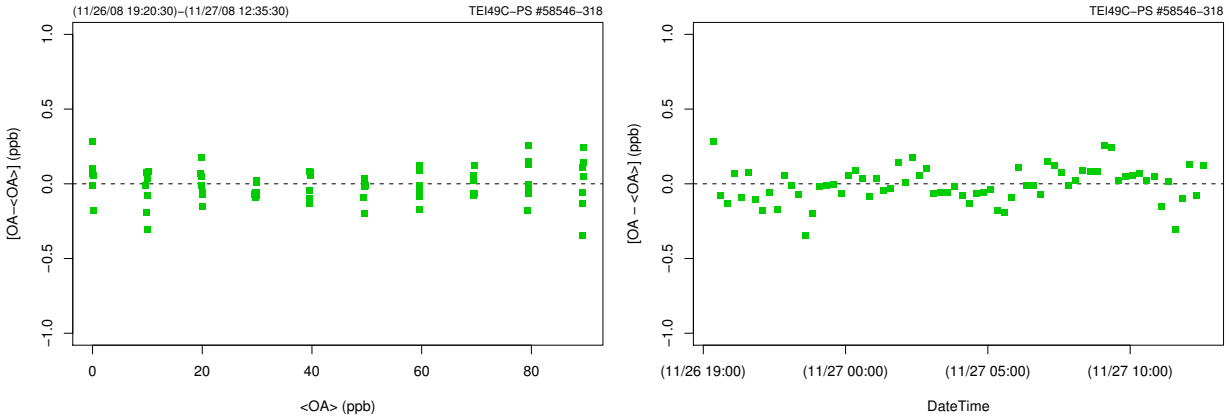

Figure 11. Regression residuals of the new main USH ozone analyzer (TEI 49C #58546-318) as a function of concentration (left panel) and time (right panel).

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 #58546-318:

X_{O3} (ppb) = ([OA] + 0.08 ppb) / 0.996

u_{O3} (ppb) = sqrt (0.28 ppb^2 + 2.62e-05 * X_{O3}^2) (1b)

TEI 49C-PS #56084-306 (Ozone calibrator of the RCC Buenos Aires)

This instrument is usually located at the RCC Buenos Aires but was available at USH during the audit. The result of the assessment is shown in **Table 5**.

Table 5. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the RCC Buenos Aires ozone calibrator (OC) TEI 49C-PS #56084-306 with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOC (ppb)
2008-11-27 00:25	1	0	0.05	0.29	0	0.07	0.07
2008-11-27 00:40	1	50	49.92	50.55	0	0.04	0.06
2008-11-27 00:55	1	60	59.90	60.54	0	0.07	0.05
2008-11-27 01:10	1	10	10.11	10.55	0	0.10	0.05
2008-11-27 01:25	1	40	39.82	40.23	0	0.14	0.08
2008-11-27 01:40	1	80	79.90	80.85	0	0.11	0.05
2008-11-27 01:55	1	90	89.98	91.02	0	0.06	0.09
2008-11-27 02:10	1	30	30.05	30.55	0	0.13	0.07
2008-11-27 02:25	1	20	20.06	20.55	0	0.07	0.06
2008-11-27 02:40	1	70	69.87	70.77	0	0.17	0.07
2008-11-27 02:55	2	0	0.02	0.42	0	0.14	0.05
2008-11-27 03:10	2	70	69.95	70.76	0	0.04	0.07
2008-11-27 03:25	2	90	89.91	90.87	0	0.12	0.09
2008-11-27 03:40	2	20	20.18	20.54	0	0.15	0.06
2008-11-27 03:55	2	50	49.92	50.54	0	0.11	0.07
2008-11-27 04:10	2	10	10.20	10.56	0	0.21	0.07
2008-11-27 04:25	2	40	39.84	40.44	0	0.10	0.09
2008-11-27 04:40	2	80	79.94	80.80	0	0.10	0.07
2008-11-27 04:55	2	30	30.11	30.65	0	0.11	0.08
2008-11-27 05:10	2	60	59.99	60.89	0	0.09	0.07
2008-11-27 05:25	3	0	0.27	0.38	0	0.08	0.07
2008-11-27 05:40	3	10	9.99	10.15	0	0.05	0.05
2008-11-27 05:55	3	30	29.84	30.29	0	0.08	0.06
2008-11-27 06:10	3	90	89.88	90.99	0	0.11	0.04
2008-11-27 06:25	3	50	49.99	50.67	0	0.04	0.06
2008-11-27 06:40	3	60	59.98	60.73	0	0.08	0.06
2008-11-27 06:55	3	20	20.17	20.51	0	0.16	0.09
2008-11-27 07:10	3	80	79.86	80.93	0	0.13	0.11
2008-11-27 07:25	3	70	70.00	70.87	0	0.07	0.06
2008-11-27 07:40	3	40	39.98	40.61	0	0.10	0.08
2008-11-27 07:55	4	0	0.11	0.29	0	0.11	0.06
2008-11-27 08:10	4	50	49.91	50.67	0	0.07	0.05
2008-11-27 08:25	4	60	59.96	60.77	0	0.08	0.04
2008-11-27 08:40	4	10	10.22	10.68	0	0.13	0.10
2008-11-27 08:55	4	40	39.81	40.53	0	0.14	0.08
2008-11-27 09:10	4	80	79.93	81.12	0	0.09	0.07
2008-11-27 09:25	4	90	89.98	91.17	0	0.10	0.08
2008-11-27 09:40	4	30	30.06	30.66	0	0.07	0.05
2008-11-27 09:55	4	20	20.06	20.54	0	0.06	0.08
2008-11-27 10:10	4	70	69.87	70.93	0	0.18	0.10
2008-11-27 10:25	5	0	0.10	0.32	0	0.11	0.09
2008-11-27 10:40	5	70	69.93	70.96	0	0.07	0.08
2008-11-27 10:55	5	90	89.93	91.13	0	0.12	0.05
2008-11-27 11:10	5	20	20.20	20.50	0	0.12	0.06
2008-11-27 11:25	5	50	49.91	50.52	0	0.10	0.07
2008-11-27 11:40	5	10	10.20	10.39	0	0.21	0.08

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOC (ppb)
2008-11-27 11:55	5	40	39.84	40.53	0	0.12	0.10
2008-11-27 12:10	5	80	79.93	80.86	0	0.12	0.07
2008-11-27 12:25	5	30	30.03	30.62	0	0.12	0.06
2008-11-27 12:40	5	60	59.88	60.78	0	0.08	0.07

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

Figure 12 shows the regression residuals of the 49C-PS #56084-306 ozone calibrator with respect to the SRP as a function of ozone concentration for the range 0 – 90 ppb and as a function of time.

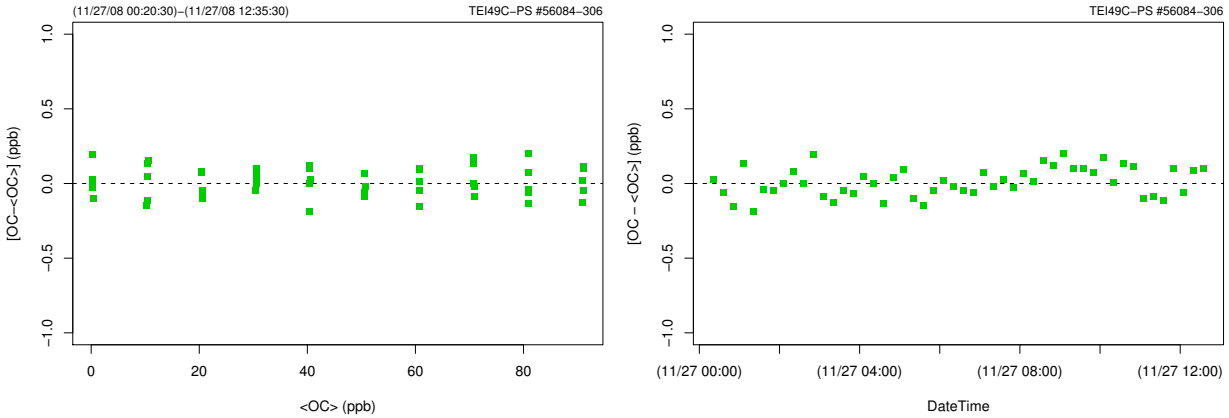

Figure 12. Regression residuals of the new main USH ozone analyzer (49C-PS #56084-306) as a function of concentration (left panel) and time (right panel).

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 [OC] using equation (1) [*Klausen, et al.*, 2003].

TEI 49C-PS #56084-306:

$$X_{O3}\ (\text{ppb}) = ([\text{OA}] - 0.17\ \text{ppb}) / 1.011$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.26\ \text{ppb}^2 + 2.55\text{e-}05 * X_{O3}^2) \qquad (1c)$$

Conclusions

The results of the performance audit demonstrated good agreement between WCC-Empa and one of the original TEI 49 and the new TEI 49C ozone analyzers. Furthermore good agreement was found between the ozone calibrator of the RCC Buenos Aires and the measurements of WCC-Empa. However, one of the TEI 49 instrument was found to be defective and was decommissioned. Data of this instrument should not be used for data submission. It is strongly suggested that the calibrator of the RCC Buenos Aires is now used to check / calibrate the USH ozone analyzers as well as other ozone instruments in South America.

Carbon Monoxide Measurements

Carbon monoxide measurements are available at the USH site since 1994. The measurements were made with two TEI48 gas filter correlation NDIR monitors. During the present audit an additional cross flow modulation NDIR instrument (Horiba APMA360) was installed, and one of the TEI 48 analyzers was decommissioned due to instrument failure. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

The USH station has only a heating system and is not air-conditioned. Temperature fluctuations affect the performance of the TEI 48 instruments, but the laboratory temperature remains sufficiently constant for the measurements of carbon monoxide with the new Horiba APMA360 instrument.

Air Inlet System

Same as for surface ozone, see above.

Instrumentation

The station is equipped with two TEI 48 and a Horiba APMA-360CE carbon monoxide analyzers. One of the TEI 48 instruments was not working (probably defective electronics, no start-up) and could not be assessed. It was the same instrument (TEI 48 #47168-278) that already showed a poor performance in the previous audit by WCC-Empa. Therefore data of this instrument should not be used for submission to WDCGG. Instrumental details for the carbon monoxide analyzer are summarised in Table 7 below.

Standards and Calibration

The station has been provided with calibration gases by WCC-Empa. Table 6 gives details of the cylinders currently available at the station. Two types of calibration standards are available: A lower concentration (approx. 2.5 ppm) for direct calibrations of the instruments, and higher concentrations (approx. 50 ppm) for automatic span checks with the dilution system.

Table 6. Carbon monoxide standards available at the USH station

Manufacturer, S/N, Use	CO Content (ppm) and matrix	Calibration		In service	
		Date	By	From	To
SMI CA08220, direct calibration	2.582 ± 0.026 ppm natural / synth. air	08/08	WCC-Empa*	08/11	cont.
SMI CA08263, dilution	38.39 ± 0.38 ppm natural / synth. air	08/08	WCC-Empa*	stock	
SMI CA05308, dilution	98.8 ± 0.99 ppm natural. air	02/09	SMI#	08/11	cont.
SMI CA05309, dilution	98.9 ± 0.99 ppm natural. air	02/09	SMI#	stock	

** WMO-2000 carbon monoxide scale*
 # NIST traceable

Operation and Maintenance

The instruments are daily checked for general operation. In addition, a weekly check list should be filled in for the Horiba instrument. The inlet filter is exchanged every 3 months or earlier when necessary.

Data Acquisition and Data Transfer

Same as for surface ozone, see above.

Data Treatment

General aspects: See surface ozone. Data of the TEI 48 is corrected for zero drift by using the five minute zero value before a 5 minute ambient measurement. The last 3 minutes of each period are used to calculate averages. The corrected data is further averaged to one hour mean values. This data is filtered using wind direction and speed. Invalid data is flagged (instrument failures and maintenance, calibrations, etc.). Data evaluation of the Horiba APMA360 will also include a correction for the zero drift.

Data Submission

Carbon monoxide data have been submitted to the WDCGG. At the time of the audit complete data series until 2002 were available at WDCGG. A review of the available data series showed that all submitted data needs to be carefully re-evaluated and re-submitted. Currently questionable data of the USH site can still be accessed at WDCGG.

Documentation

The instrument manuals are available at the site. In addition a SOP for the operation of the Horiba APMA360 has been provided by QA/SAC Switzerland upon delivery of the instrument. Electronic check lists and log files are available on the DAQ computer for the Horiba instrument.

Inter-Comparison of Carbon Monoxide Analyzers

Both the TEI 48 and the new Horiba AMPA360 were inter-compared during the audit. For the TEI 48 instrument the main purpose of the inter-comparison was to assess the bias with respect to the WMO-2000 carbon monoxide scale, whereas an initial calibration was made for the Horiba instrument. This is the reason why the Horiba instrument was inter-compared over a wider concentration range. 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 12 below.

Setup and Connections

Table 7 shows details of the experimental setup during the inter-comparison of transfer standard and station analyzer. The data used for the evaluation was recorded by the USH data acquisition systems as indicated. All data of the TEI 48 analyzer was corrected for zero drift as described above. No further corrections were applied to the Horiba APMA360 data.

Table 7. Experimental details of the carbon monoxide inter-comparison.

Travelling standard (TS)		One cylinder (SMI, CA08263, 38.39±0.39 ppm CO in a mixture of synthetic and natural air) and a zero-air generator (silica gel - inlet filter 5 µm - metal bellow pump - Sofnocat - outlet filter 5 µm) custom-built by WCC-Empa, in combination with a dilution system (Breitfuss, MGM)
Levels (ppb)		10 different concentrations levels ranging from 0-250 ppb (TEI 48) 11 different concentrations levels ranging from 0-1000 ppb (Horiba APMA360)
Old field instrument	Model, S/N	TEI 48 #47169-278
	Principle	NDIR, gas filter correlation
	Modification	External zero / span unit
	Range	1 ppm
	Settings	Zero 540 - Span 800
New field instrument	Model, S/N	Horiba APMA-360 #712020
	Principle	NDIR, cross flow modulation technique
	Modification	Nafion drier PERMAPURE PD-50T-12PP, external zero / span unit
	Range	1 ppm
	Settings	Zero -3, Span 1.0320
Connection of TS to field instrument		Sample inlet
Data Acquisition		1-minute averages (Horiba) and zero corrected 1-minute averages (TEI 48) from station data acquisition systems
Duration per level (min)		75 min, inclusive of interspersed automatic zero (15') and span (10') checks every second hour (Horiba) 120 min, including automatic zero checks (5') every 10 minutes (TEI 48)
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		TEI 48: 1 run (2008-11-27 thru 28) Horiba APMA360: 1 run (2008-11-30 thru 2008-12-01)

Results

TEI 48 #47169-278

Each carbon monoxide level was applied for 120 minutes, which resulted in a maximum of 12 useable 3-min averages per level and run. These were corrected for zero-drift and further aggregated by level before use in the assessment (cf. Table 8).

Table 8. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the USH TEI 48 CO analyzer with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	CO (ppb)	sdCO(ppb)	No. 3' av.
(11/27/08 22:25:00)	52.80	1.00	54.73	10.06	11
(11/28/08 00:20:00)	203.69	2.04	197.72	8.96	12
(11/28/08 02:25:00)	72.82	1.00	65.73	7.92	11
(11/28/08 04:25:00)	103.00	1.03	94.36	7.14	11
(11/28/08 06:20:00)	153.45	1.53	151.37	11.23	10
(11/28/08 08:20:00)	83.03	1.00	78.60	6.23	10
(11/28/08 10:15:00)	254.46	2.54	237.27	10.90	11
(11/28/08 12:15:00)	0.00	1.00	-1.52	12.25	11
(11/28/08 14:15:00)	92.92	1.00	81.36	8.43	11
(11/28/08 16:15:00)	62.84	1.00	55.82	12.33	11

Figure 13 shows the regression residuals of the TEI 48 analyzer over the course of the 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. However, the individual data points are associated with relatively high uncertainty.

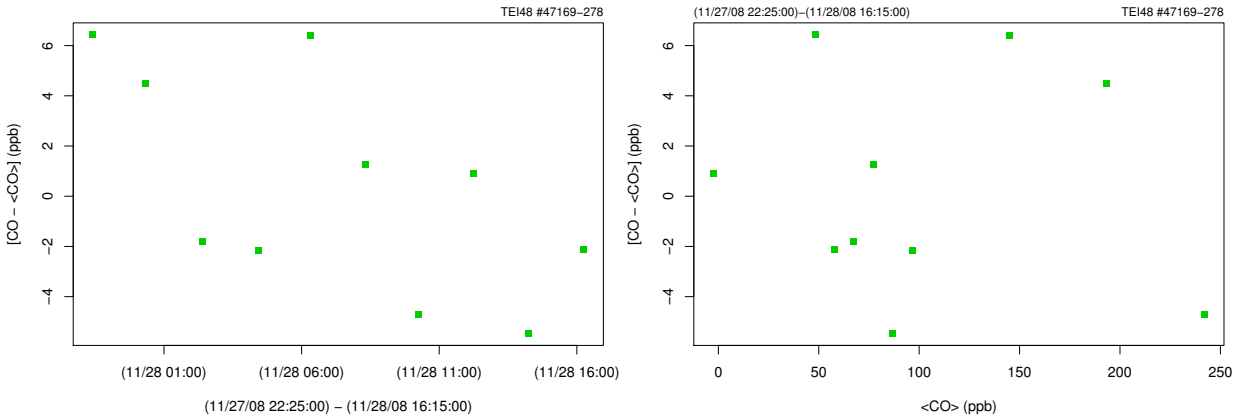

Figure 13. Regression residuals of the TEI 48 carbon monoxide analyzer based on the inter-comparison with the dilution unit. Points represent averages of valid 3 minute values. Left panel: time dependence; Right panel: concentration dependence.

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 3 min averages can be computed from the zero corrected three-minute CO data that was taken initially of the analyzer using equation (2).

TEI48 #47169-278

$$\mathbf{X_{CO}\ (ppb) = ([CO] + 2.4\ ppb) / 0.961}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(111.6\ ppb^2 + 3.08e\text{-}04 * X_{CO}^2)} \qquad \mathbf{(2)}$$

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.

Changes made to the instrument

No changes were made.

Horiba APMA360 #712020

Each carbon monoxide level was applied for 75 minutes, which resulted in a maximum of 75 useable 1-min averages per level and run. These values were averaged 5-min means and further aggregated by level before use in the assessment (cf. Table 9).

Table 9. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the USH Horiba analyzer with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	CO (ppb)	sdCO(ppb)	No. 5' av.
(11/30/08 22:47:30)	157.80	1.58	157.19	4.41	12
(11/30/08 23:51:45)	0.00	1.00	2.45	2.24	8
(12/01/08 01:08:30)	623.93	6.24	622.06	4.65	14
(12/01/08 02:38:00)	390.75	3.91	389.33	3.28	9
(12/01/08 03:25:00)	779.26	7.79	779.15	5.33	9
(12/01/08 04:52:30)	313.12	3.13	311.37	4.23	14
(12/01/08 06:13:40)	468.66	4.69	466.09	6.10	9
(12/01/08 07:16:00)	546.36	5.46	548.18	6.31	11
(12/01/08 08:43:55)	80.49	1.00	82.85	3.59	12
(12/01/08 09:47:00)	702.00	7.02	701.36	7.61	9
(12/01/08 11:05:30)	235.26	2.35	234.89	4.21	14

Figure 14 shows the regression residuals of the Horiba APMA360 analyzer over the course of the 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.

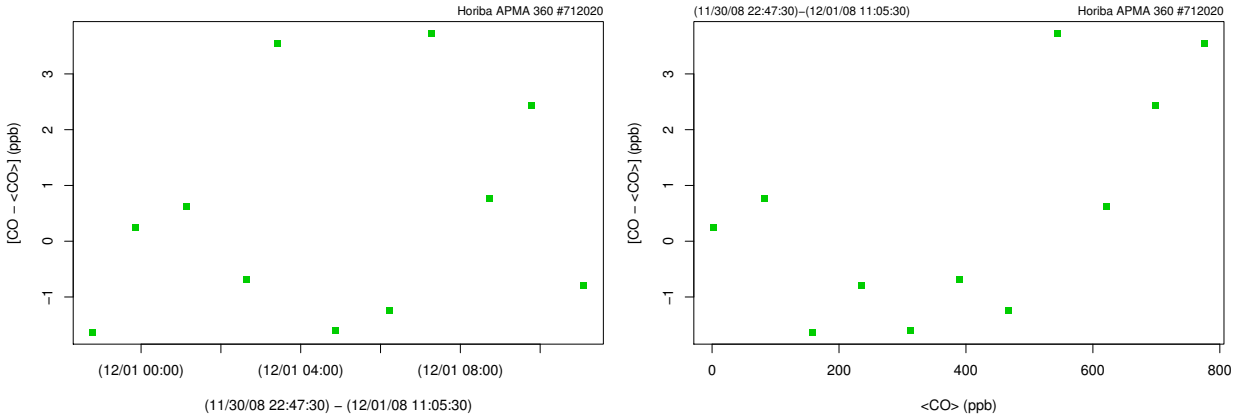

Figure 14. Regression residuals of the Horiba APMA360 carbon monoxide analyzer based on the inter-comparison with the dilution unit. Points represent averages of valid 5 minute values. Left panel: time dependence; Right panel: concentration dependence.

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 5-minute CO data that was taken initially of the analyzer using equation (2).

Horiba APMA360 #712020

$$\mathbf{X_{CO}\ (ppb) = ([CO] - 2.2\ ppb) / 0.992}$$

$$\mathbf{u_{CO}\ (ppb) = sqrt(23.3\ ppb^2 + 4.83e\text{-}05 * X_{CO}^2)} \qquad \mathbf{(3)}$$

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

Changes made to the instrument

No changes were made.

Conclusions

The audit demonstrated that both the existing TEI 48 and the new Horiba APMA360 CO analyzers agreed well compared to the WCC-Empa reference within the limits of the instrument specifications. However, especially data of the TEI 48 system was associated with high uncertainties. Data (of both instruments) should therefore be aggregated to hourly mean values for any further use. It is further recommended to use data of the Horiba APMA360 for data submission. The TEI 48 should run in parallel for at least one year.

WCC-Empa Traveling Standards

Ozone

The WCC-Empa traveling 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 10, the inter-comparison data is given in Table 11.

Table 10. 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 #56891-310 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.010
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 ten 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 (2009-01-15)

Table 11. 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	0.13	0.11
2008-08-07	1	190	191.51	0.11	191.50	0.15
2008-08-07	1	90	91.15	0.24	91.23	0.12
2008-08-07	1	140	141.07	0.22	141.11	0.12
2008-08-07	1	60	61.55	0.25	61.39	0.04
2008-08-07	1	30	32.03	0.25	31.93	0.09
2008-08-07	1	0	0.20	0.19	0.00	0.07
2008-08-07	2	0	-0.03	0.15	0.07	0.10
2008-08-07	2	90	91.30	0.20	91.52	0.09
2008-08-07	2	60	61.48	0.17	61.49	0.06
2008-08-07	2	140	141.43	0.18	141.54	0.08
2008-08-07	2	190	192.17	0.28	192.33	0.09
2008-08-07	2	30	32.15	0.21	32.04	0.06
2008-08-07	2	0	-0.02	0.21	-0.03	0.10
2008-08-07	3	0	-0.10	0.31	-0.01	0.11
2008-08-07	3	30	31.31	0.32	31.38	0.08
2008-08-07	3	90	91.00	0.26	90.97	0.19
2008-08-07	3	190	191.35	0.33	191.52	0.17
2008-08-07	3	60	61.27	0.30	61.28	0.08
2008-08-07	3	140	141.02	0.49	141.47	0.09
2008-08-07	3	0	-0.15	0.35	0.13	0.10
2009-01-15	4	0	0.10	0.37	0.04	0.09
2009-01-15	4	140	139.71	0.26	139.73	0.10
2009-01-15	4	30	32.66	0.14	32.44	0.08
2009-01-15	4	60	61.54	0.24	61.62	0.13
2009-01-15	4	190	187.83	0.22	188.24	0.17
2009-01-15	4	90	91.08	0.26	91.10	0.11
2009-01-15	4	0	0.22	0.25	0.09	0.10
2009-01-15	5	0	0.03	0.16	0.04	0.08
2009-01-15	5	30	32.30	0.24	32.34	0.13
2009-01-15	5	140	139.62	0.19	139.57	0.11
2009-01-15	5	190	187.89	0.26	188.25	0.11
2009-01-15	5	60	61.48	0.31	61.50	0.11
2009-01-15	5	90	90.73	0.18	90.79	0.07
2009-01-15	5	0	0.07	0.32	0.01	0.14
2009-01-15	6	0	0.00	0.27	-0.05	0.14
2009-01-15	6	60	61.36	0.28	61.43	0.09
2009-01-15	6	140	139.24	0.32	139.46	0.08
2009-01-15	6	30	32.46	0.33	32.42	0.10
2009-01-15	6	190	187.53	0.14	187.61	0.11
2009-01-15	6	90	90.75	0.21	90.81	0.10
2009-01-15	6	0	0.20	0.28	-0.12	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 15). 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]).

$$X_{TS}\ (\text{ppb}) = ([TS] + 0.04\ \text{ppb}) / 1.001$$

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

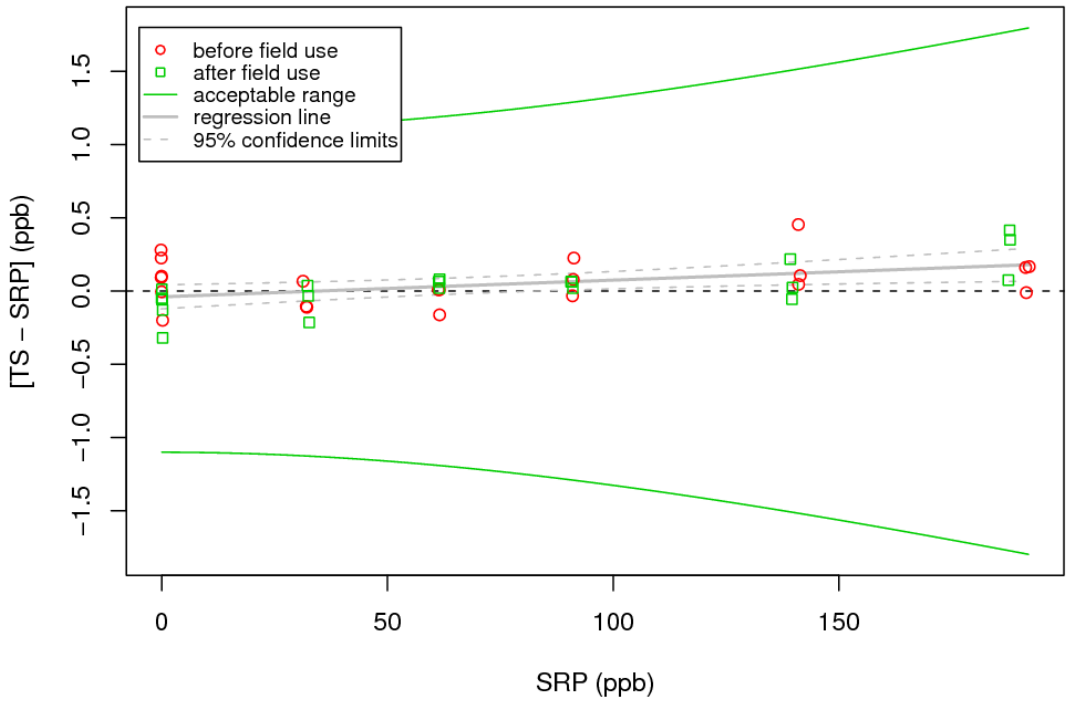

Figure 15. Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 12 - Table 14.

Table 12. 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 cylinder, CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Travelling standard (TS)		zero air (1) and a high concentration carbon monoxide cylinder (2), in combination with a dilution unit (3)
(1) Zero air supply		Ambient air – Silicagel PS drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		SMI, D94 4280, CA08263, 38.39±0.39 ppm CO (α=0.05). Cylinder remained at the station.
(3) Dilution unit		Breitfuss MGM #2262/91/1. The levels used were calibrated before and after the field inter-comparison against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851).
Connection between instruments		Ca. 5 meter 6 mm Sertoflex tubing
Data acquisition		Aerolaser 1-min averages
Levels (ppb)		0 to 1000, in steps of 100, and 0 to 250
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 (August 2008) 1 run after return of TS (January 2009)

Table 13. Calibration of Breitfuss dilution system and carbon monoxide mixing ratios.

	Mass Flow Controller MFC 1 (mL min^{-1})			Mass Flow Controller MFC 2 (mL min-1)			Carbon Monoxide Mixing Ratio (ppb)		
Date	**Setpoint**	**Measured#**	**sd**	**Setpoint**	**Measured**	**sd**	**Expected**	**Measured#**	**sd**
2008-08-25	2988.0	3004.1	0.8	12.00	12.33	0.01	156.9	156.9	0.6
2008-08-25	3000.0	3015.1	0.4	0.00	0.18	0.01	0.0	0.2	0.3
2008-08-25	2952.0	2968.1	0.4	48.00	48.91	0.01	622.3	622.2	0.6
2008-08-25	2970.0	2986.1	0.4	30.00	30.62	0.01	389.6	390.1	1.3
2008-08-25	2940.0	2954.3	0.4	60.00	61.09	0.01	777.7	777.6	1.8
2008-08-25	2976.0	2990.0	0.3	24.00	24.51	0.01	312.1	312.6	0.6
2008-08-25	2964.0	2977.4	0.3	36.00	36.70	0.01	467.4	467.7	1.0
2008-08-25	2958.0	2971.0	0.2	42.00	42.79	0.01	545.0	545.7	1.8
2008-08-25	2994.0	3006.8	0.3	6.00	6.25	0.01	79.7	80.0	0.2
2008-08-25	2946.0	2958.1	0.2	54.00	54.99	0.01	700.5	699.4	1.2
2008-08-25	2982.0	2994.5	0.2	18.00	18.39	0.01	234.3	234.7	0.5
2009-01-22	2988.0	2987.2	0.7	12.00	12.40	0.01	158.7	NA	NA
2009-01-22	3000.0	2997.4	0.6	0.00	0.36	0.07	0.0	NA	NA
2009-01-22	2952.0	2949.7	0.3	48.00	48.86	0.02	625.6	NA	NA
2009-01-22	2970.0	2968.2	0.3	30.00	30.62	0.01	391.9	NA	NA
2009-01-22	2940.0	2937.0	0.3	60.00	60.98	0.01	780.8	NA	NA
2009-01-22	2976.0	2972.3	0.5	24.00	24.53	0.01	314.2	NA	NA
2009-01-22	2964.0	2959.3	0.3	36.00	36.67	0.01	469.9	NA	NA
2009-01-22	2958.0	2953.1	0.5	42.00	42.74	0.01	547.7	NA	NA
2009-01-22	2994.0	2988.8	0.2	6.00	6.34	0.01	81.3	NA	NA
2009-01-22	2946.0	2940.4	0.3	54.00	54.89	0.02	703.5	NA	NA
2009-01-22	2982.0	2976.0	0.3	18.00	18.43	0.01	236.3	NA	NA

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

Table 14. Calibration of Breitfuss dilution system and carbon monoxide mixing ratios.

	Mass Flow Controller MFC 1 (mL min^{-1})			Mass Flow Controller MFC 2 (mL min-1)			Carbon Monoxide Mixing Ratio (ppb)		
Date	**Setpoint**	**Measured#**	**sd**	**Setpoint**	**Measured**	**sd**	**Expected**	**Measured#**	**sd**
2008-09-04	3994.8	4035.7	0.4	5.21	5.59	0.01	53.1	52.1	0.9
2008-09-04	3979.2	4017.9	0.8	20.84	21.48	0.01	204.1	204.7	0.7
2008-09-04	3992.7	4028.3	0.5	7.29	7.68	0.03	73.1	73.0	0.4
2008-09-04	3989.6	4023.4	0.7	10.42	10.86	0.01	103.4	103.6	0.5
2008-09-04	3984.4	4015.6	0.3	15.63	16.16	0.01	153.8	154.0	0.5
2008-09-04	3991.7	4022.6	0.3	8.34	8.75	0.01	83.3	83.2	0.3
2008-09-04	3973.9	4005.1	0.2	26.05	26.77	0.01	254.9	254.9	0.6
2008-09-04	4000.0	4032.7	1.3	0.00	0.43	0.16	0.0	0.0	0.4
2008-09-04	3990.6	4027.7	0.9	9.38	9.80	0.01	93.1	93.0	0.4
2008-09-04	3993.7	4031.1	0.6	6.25	6.63	0.01	63.1	63.0	0.5
2009-01-23	3994.8	4014.8	0.9	5.21	5.50	0.02	52.5	NA	NA
2009-01-23	3979.2	3996.0	0.7	20.84	21.27	0.01	203.3	NA	NA
2009-01-23	3992.7	4007.1	0.9	7.29	7.59	0.01	72.6	NA	NA
2009-01-23	3989.6	4002.0	0.4	10.42	10.73	0.01	102.6	NA	NA
2009-01-23	3984.4	3993.6	0.7	15.63	15.99	0.01	153.1	NA	NA
2009-01-23	3991.7	3999.5	0.3	8.34	8.64	0.01	82.7	NA	NA
2009-01-23	3973.9	3981.5	0.3	26.05	26.52	0.01	254.0	NA	NA
2009-01-23	4000.0	4006.3	0.3	0.00	0.24	0.01	0.0	NA	NA
2009-01-23	3990.6	3997.7	0.7	9.38	9.68	0.01	92.7	NA	NA
2009-01-23	3993.7	4002.5	0.4	6.25	6.54	0.02	62.6	NA	NA

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

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution / Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary (USH)

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.850°S 68.283°W (18 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2008-11-26
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Ricardo Sanchez, Maria Elena Barlasina, Sergio Luppo
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #56891-310
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(1.0011 \pm 0.0010) \times [SRP] - (0.04 \pm 0.09)$
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49 #47306-278 (O3-1)
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	OFFSET 50; SPAN 510
1.5.4	Calibration at start of audit (ppb):	$[OA] = (1.003 \pm 0.001) \times [SRP] - (0.00 \pm 0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] + 0.00) / 1.003$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.69e\text{-}5 \times X^2)^{1/2}$
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:	TEI 49, at USH since 1994
1.7	Reference:	WCC-Empa Report 08/4

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

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Ozone Audit Executive Summary (USH)

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.850°S 68.283°W (18 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2008-11-26 thru 2008-11-27
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Ricardo Sanchez, Maria Elena Barlasina, Sergio Luppo
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #56891-310
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(1.0011 \pm 0.0010) \times [SRP] - (0.04 \pm 0.09)$
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C #58546-318
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG = 0.0; COEFF = 1.012
1.5.4	Calibration at start of audit (ppb):	$[OA] = (0.996 \pm 0.000) \times [SRP] - (0.08 \pm 0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] + 0.08) / 0.996$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.62e\text{-}5 \times X^2)^{1/2}$
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:	Instrument installed at USH during audit
1.7	Reference:	WCC-Empa Report 08/4

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

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Ozone Audit Executive Summary (USH)

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.850°S 68.283°W (18 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2008-11-26 thru 2008-11-27
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.1	Station staff involved in audit:	Ricardo Sanchez, Maria Elena Barlasina, Sergio Luppo
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #56891-310
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(1.0011 \pm 0.0010) \times [SRP] - (0.04 \pm 0.09)$
1.5	Ozone Calibrator [OC]	
1.5.1	Model:	TEI 49C-PS #56084-306
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG = -0.5; COEFF = 1.035
1.5.4	Calibration at start of audit (ppb):	$[OC] = (1.011 \pm 0.000) \times [SRP] + (0.17 \pm 0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OC] - 0.17) / 1.011$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.26\ ppb^2 + 2.55e\text{-}5 \times X^2)^{1/2}$
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:	Ozone calibrator of the Regional Calibration Centre for Surface Ozone (RCC Buenos Aires)
1.7	Reference:	WCC-Empa Report 08/4

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

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Carbon Monoxide Audit Executive Summary (USH)

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.850°S 68.283°W (18 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2008-11-27 thru 2008-11-28
1.2	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.2	Station staff involved in audit:	Ricardo Sanchez, Maria Elena Barlasina, Sergio Luppo
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	SMI CA08263, 38.39±0.39 (ppm) (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 – 250 ppb
1.5	CO analyzer	
1.5.1	Model:	TEI 48 #47169-278
1.5.2	Range of calibration:	0 – 250 ppb
1.5.3	Coefficients at start of audit	Zero 540 - Span 800
1.5.4	Calibration at start of audit (ppb):	CO = (0.961±0.016) × X - (2.4±1.9)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 2.4) / 0.961
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (111.6\ ppb^2 + 3.08e\text{-}04 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 08/4

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

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Carbon Monoxide Audit Executive Summary (USH)

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.850°S 68.283°W (18 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2008-11-30-2008-12-01
1.1	Auditor:	Dr. C. Zellweger, Dr. J. Klausen
1.2.3	Station staff involved in audit:	Ricardo Sanchez, Maria Elena Barlasina, Sergio Luppo
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	SMI CA08263, 38.39±0.39 (ppm) (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 – 250 ppb
1.5	CO analyzer [CA]	
1.5.1	Model:	Horiba APMA360 #712020
1.5.2	Range of calibration:	0 – 800 ppb
1.5.3	Coefficients at start of audit	Zero -3 / Span 1.0320
1.5.4	Calibration at start of audit (ppb):	$CO = (0.992 \pm 0.005) \times X + (2.2 \pm 1.0)$
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO - 2.2) / 0.992$
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (23.3\ ppb^2 + 4.83e\text{-}05 \times X^2)^{1/2}$
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 08/4

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

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LIST OF ABBREVIATIONS

a.s.l.	above sea level
DAQ	Data Acquisition System
GAW	Global Atmosphere Watch
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyzer
OC	Ozone Calibrator
PFA	Teflon (**p**er**f**luoro**a**lkoxy copolymer)
PTFE	Teflon (**p**oly**t**etra**f**luoro**e**thylene)
RCC	Regional Calibration Centre
SOP	Standard Operating Procedure
SMN	Servicio Meteorológico Nacional
SRP	Standard Reference Photometer
TS	Travelling Standard
USH	Ushuaia GAW Station
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation