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

EMPA

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

WCC-EMPA REPORT 03/4

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

GLOBAL GAW STATION USHUAIA

ARGENTINA, NOVEMBER 2003

Submitted by

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

EMPA Dübendorf, Switzerland

Contents:

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

S C S	SCHWEIZERISCHER KALIBRIERDIENSTDIENST SERVICE SUISSE D'ETALONAGE SERVIZIO SVIZZERA DI TARURA SWISS CALIBRATION SERVICE	**ISO/IEC accredited calibration service** SCS accreditation-No.	**SCS 089**

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Ushuaia from 8. to 15. November 2003 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane and QA/SAC Switzerland. The first audit was carried out by WCC-EMPA in 1998. The results of the second audit can be summarized as follows:

System Audit of the Observatory

The Ushuaia global GAW station offers excellent facilities for atmospheric research and measurement campaigns. It was however recognized that some of the measurements were discontinued (e.g. CFCs, Flask sampling), apparently due to a lack of funding and not sufficiently well defined responsibilities. It is regarded as important that as many as possible of the available instruments are operated on a continuous basis to ensure the long-term value of the station within the Global Atmosphere Watch and to add to the scientific importance of this observatory.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and main and backup ozone instruments of the station, demonstrated good agreement between the station analyzers and the transfer standard after adjustment of the calibration factors and without the use of the new data acquisition. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1). An inlet loss for ozone was discovered by the station staff, and corrections should be applied according to the recommendations of WCC-EMPA.

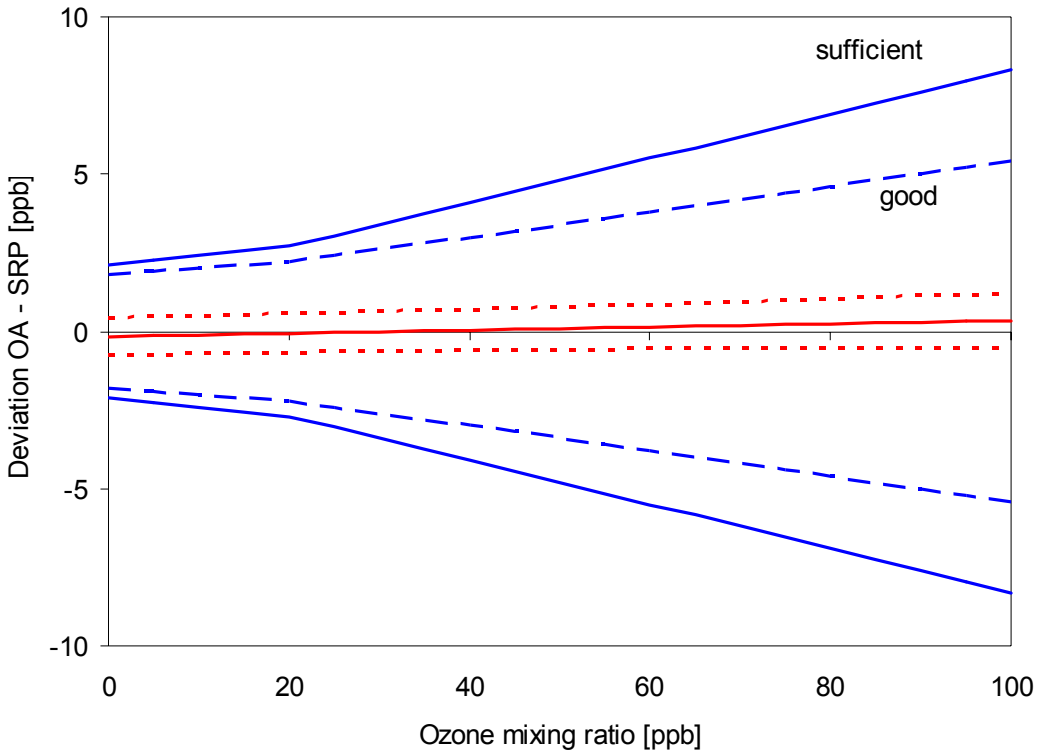

Figure 1: Inter-comparison of instrument TEI 49 #47306-278 (main instrument) valid for the new calibration factors (OFFSET 50, SPAN 510).

Due to the facts that the new data acquisition was influencing the analog output, the inlet loss and the correction of the instrument calibration, several recommendations were made by WCC-EMPA concerning ozone measurements. Part of the recommendations address correction of previous acquired data, and part are of general nature. An executive summary of the audit results for surface ozone is given in Appendix V.

Audit of the Carbon Monoxide Measurement

Despite the fact that the carbon monoxide analyzers could not be calibrated for several years due to a lack of calibration gas and other instrumental problems, the inter-comparison results with WCC-EMPA showed a good agreement between the main station instrument and WCC-EMPA (Figure 2). The results were less convincing for the back-up instrument, which is in need of calibration and servicing.

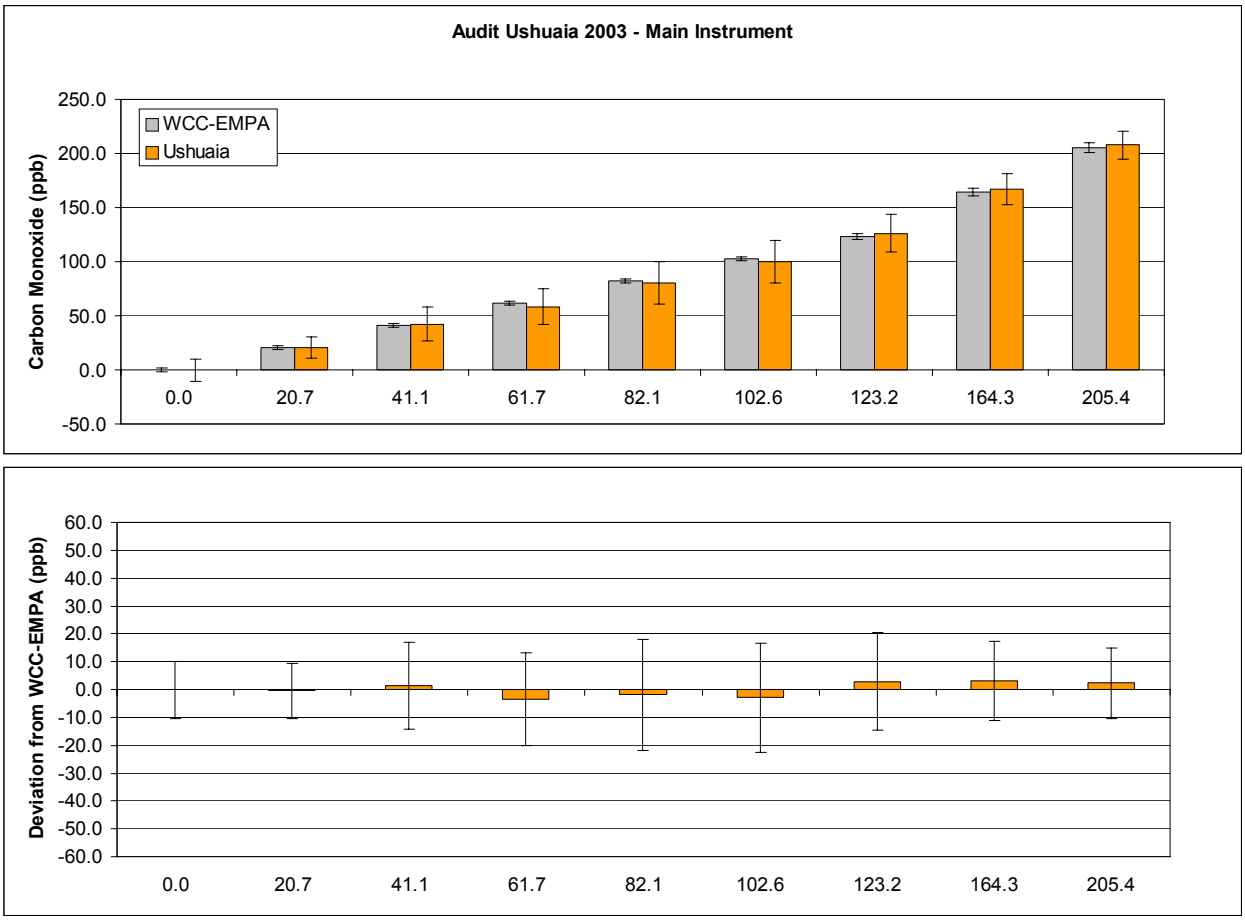

Figure 2: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the main CO analyzer of Ushuaia (orange).
lower panel: deviation of the Ushuaia station from the conventional true value.
The error bars represent the 95% confidence interval. Data are one hour averages.

Recommendations of WCC-EMPA address mainly calibration issues and the state of the back-up analyzer.

General Recommendations

- Different national institutions participate in the operation of the GAW station Ushuaia. It is important that responsibilities are clearly defined and communicated. It was recognized during the audit that especially the communication and exchange between SNM Buenos Aires and the Ushuaia staff should be improved.
- Collaboration with external partners, both national and international, is regarded as important. Ushuaia hosts other research institutes such as CADIC (Centro Austral de Investigaciones Científicas), and the possibilities for a cooperation should be explored.
- Continuing education and training of the station staff (e.g. GAWTEC) is encouraged. At present, the station staff both from SMN and the local authorities is rather isolated, and training activities are mainly offered for SMN Buenos Aires staff.
- A budget, for example in accordance to the GAW measurement guide, should be available for the long-term operation and maintenance of the station. Part of the budget should be at the immediate disposal of the Ushuaia staff to support purchase of consumables and to allow necessary maintenance of equipment.

Conclusions

The global GAW station Ushuaia was established under the Global Environment Facility (GEF) program in 1994. Since then, many parameters have been measured over long time periods, but some measurements were discontinued due to an apparent lack of funding and a lack of communication between the partners involved. Appropriate budgetary as well as managerial measures to ensure continuation of these measurements should be given high priority and internal review of the process is recommended.

The Ushuaia station is of great importance within the GAW program for its geographical location, and because ground based measurements of air pollutants from such remote regions are limited. Furthermore, the station offers excellent infrastructure concerning accessibility and laboratory facilities. To take advantage of this, national and international co-operation of both technical and scientific staff (training, workshops, exchange programs, scientific partnerships) is regarded as important and should be intensified.

The results of the inter-comparisons for surface ozone and carbon monoxide showed good agreement between WCC-EMPA and the station instruments. Previously acquired ozone data need to be corrected for calibration bias and inlet loss.

Dübendorf, 4. August 2004

Project scientist

Dr. C. Zellweger

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Project manager

Dr. B. Buchmann

2. Introduction

The **Global GAW Station Ushuaia** is part of Argentina's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program. The observatory was established within the framework of UNDP's Global Environment Facility (GEF) and is designated for long-term measurements of several chemical compounds and physical and meteorological parameters in the troposphere and stratosphere. The station has started its operation in 1994. The leading office is the Servicio Meteorológico Nacional (SNM) of Argentina. The Province of Tierra del Fuego and the city of Ushuaia also participates in the project.

The air pollution and environmental technology laboratory of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the GAW **World Calibration Centre** (WCC) for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a coordinated quality assurance program for this part of GAW. The detailed goals and tasks of the WCC concerning surface ozone are described in the GAW report No. 104. System and performance audits at global GAW stations are conducted regularly based on mutual agreement about every two to four years.

In agreement with the station manager, Mayor Osvaldo Barturen of the Servicio Meteorológico Nacional (SNM), and the measurement leaders for CO and surface ozone, Mr. Sergio Luppo and Mr. Miguel Pereyra, a **system and performance audit** at the Ushuaia observatory was conducted by WCC-EMPA between 8. and 15. November 2003.

The scope of the audit was the whole measurement system in general and surface ozone and carbon monoxide measurements in particular. The entire system from the air inlet to the data processing and the quality assurance was reviewed during the audit procedure. The assessment criteria for the ozone inter-comparison have been developed by WCC-EMPA and QA/SAC Switzerland [Hofer et al., 2000; Klausen et al., 2003]. The present audit report is distributed to the station, to SNM and the World Meteorological Organization in Geneva.

Staff involved in the audit

Ushuaia	My Osvaldo Barturen	contacts, general program
	Mr. Sergio Luppo	contacts, general program technical assistance at the observatory
	Mr. Miguel Pereyra	technical assistance at the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
QA/SAC Switzerland	Dr. Jörg Klausen	

Previous audits at the GAW station Ushuaia:

- November 1998 by WCC-EMPA for surface ozone and carbon monoxide

3. Global GAW Site Ushuaia, Argentina

The measurement program of the site was undergoing several changes since its establishing in 1994. A short overview of the measurement program and its status as of November 2003 is given below.

Surface Ozone

Two instruments were running in parallel at the site. Both instruments were in a good condition. Problems with the inlet system were recognized by the station operators and could be solved during the audit of WCC-EMPA. In addition, a data acquisition problem was identified and solved. At the end of the audit, surface ozone measurements were fully operational, and long time series are available.

Carbon Monoxide

Two instruments were running in parallel at the site. The main instrument was in a good condition. The backup instrument was in need of service. The main instrument was found to be in calibration, neither CO instrument had been calibrated recently. Calibration gas for the standard addition was lacking and the valves for automated standard addition were defective. Both problems were solved and CO measurements are now fully operational. The good inter-comparison results with WCC-EMPA also support the quality of the existing long time series. However, calibration of the measurements remains a problem and requires more attention in future.

Total Ozone and UVB

The total ozone (Dobson) and UVB measurements were active and well under control.

Meteorological Parameters

Ancillary meteorological parameters were measured, but the anemometer was in need of repair.

Aerosol Measurements

Black carbon measurements (aethalometer) were not in operation. According to log-book, operation was stopped in August 1999. A thorough check of the instrument did indicate that the instrument itself should be fine, although the newest software version available at the site (3.53) did stall. With version 3.51 the instrument itself seemed to work fine. The problem was eventually located with the flow settings of the instrument and the pump that needed servicing. Spare membranes and gaskets were, however, not available on site.

In addition, there is a TEOM at the site whose origin is not exactly known and that was never in operation. The station manager, Osvaldo Barturen, was requested to contact Ali Wiedensohler and/or Julian Wilson for assistance with regards to placement and operation.

CFC Measurements

The GC-ECD to measure CFCs in-situ had not been operating for about a year or so due to a lack of carrier gas (and the apparent lack of funds to replace it). The instrument is placed in a dedicated room and looks fully functional.

Flask Sampling

The CFC flask sampling program was never started. The sampling pump and valves are properly mounted and the flasks ready for use.

The greenhouse gases flask sampling program seemed to have been interrupted. At the time of the audit, 16 flasks were waiting to be taken to the U.S. embassy in BsAs.

Solar Radiation

Solar radiation measurements were partly operational, but the solar tracker was defective and had been taken off the measurement platform. Apparently, one of the power supply units was defective.

3.1. Description of the Site

The Ushuaia Station is located roughly 10 km south-west of the city of Ushuaia on the “Isla Grande de la Tierra del Fuego”, Argentina (54° 51' S – 68° 17' W).
The station is located in a coastal cliff at an altitude of 18 m above sea level, on a remote sub-Antarctic marine coast. Steady winds blow prevailing from the clean air sector (SW) down the Beagle Channel. The ground in the vicinity around the station is covered with pasture and bush. The vegetation in the surrounding area is consisting mainly of shrub and southern beech (Nothofagus species) forest.

Figure 3: Map showing the location of the Ushuaia station

Ozone and Carbon Monoxide Levels at Ushuaia

The frequency distribution of 1 hour mean values of surface ozone and carbon monoxide is shown in Figures 4 and 5.

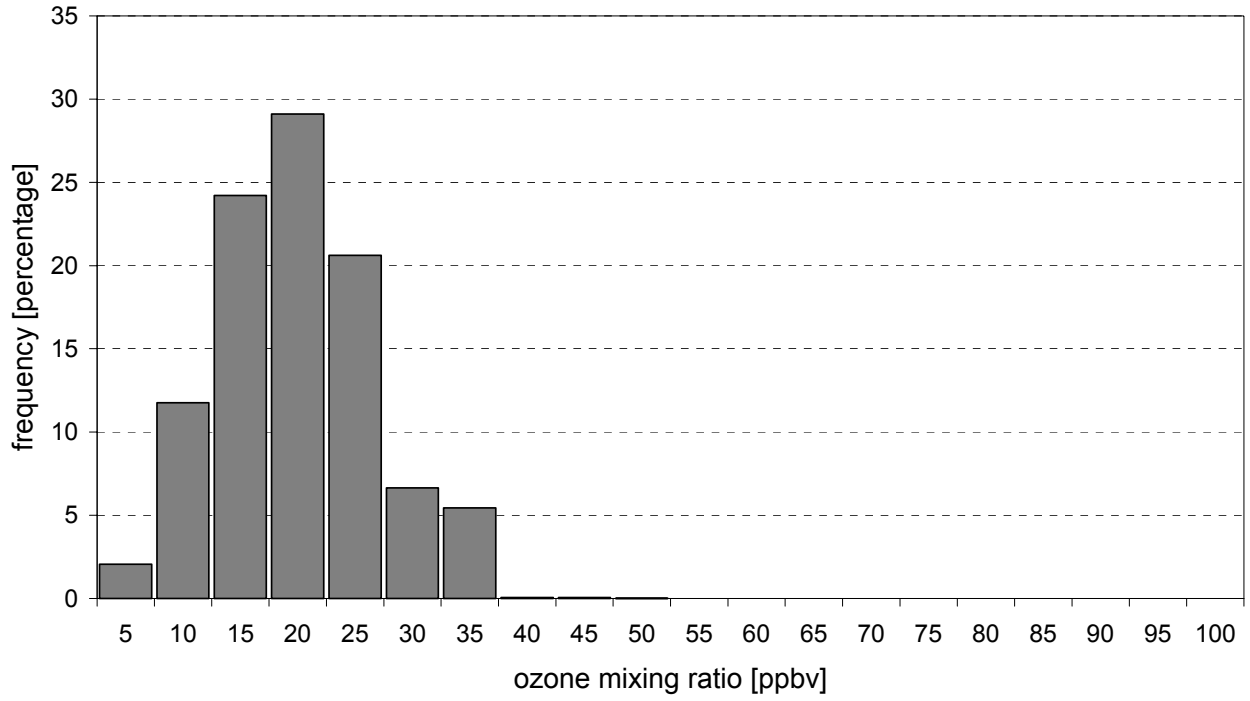

Figure 4: Frequency distribution of the 60 minutes mean ozone mixing ratio (2001) at Ushuaia. Availability of data: 88.5%.

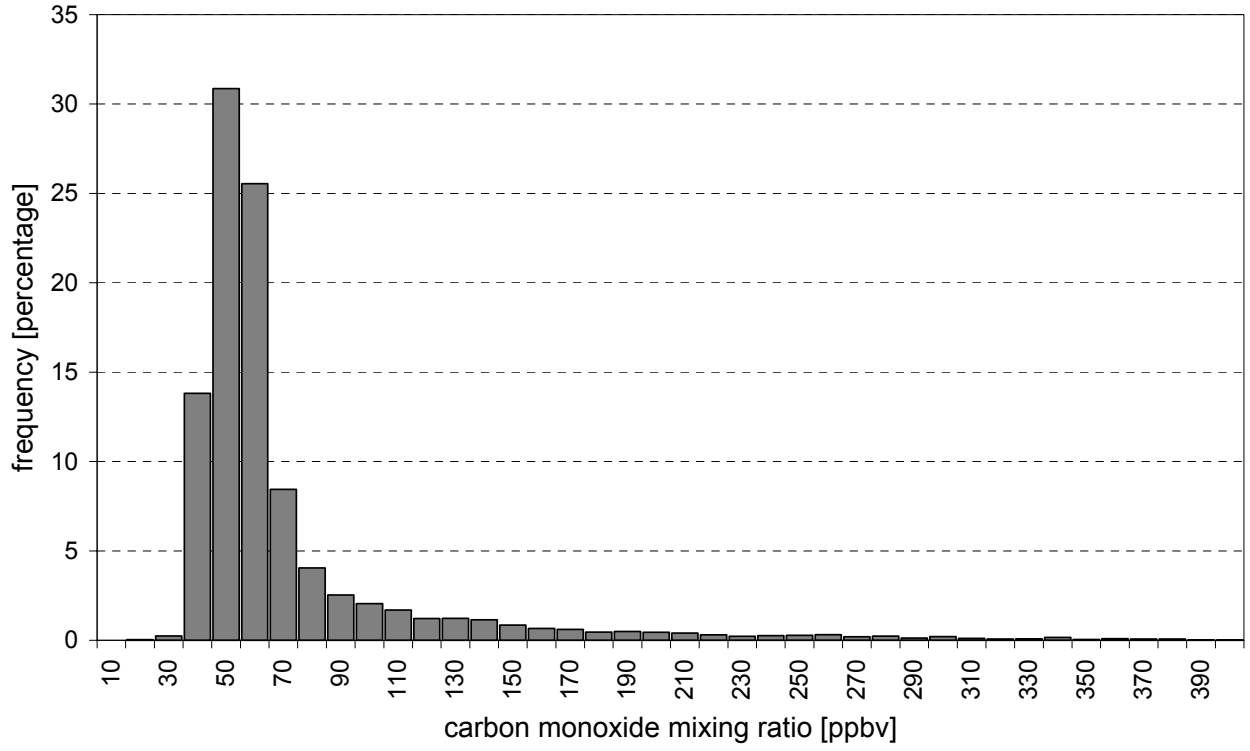

Figure 5: Frequency distribution of the 1 hour mean carbon monoxide mixing ratio (2000) at Ushuaia. Availability of data: 99.4%.

3.2. Description of the Observatory

The facilities at the site consist of the 150 m^2main building (Figure 6), which provides space for offices, meeting rooms and laboratories (Figure 7). Attached to this building is the Dobson spectrophotometer. On the platform at the top of the roof, the air inlet and several radiation and meteorological equipment are mounted. The station is currently expanded with a new part to launch meteo and ozone sondes in the future.

In addition to the main facility, a remote island sampling site with a 12 m tower on Isla Redonda (54° 51' S – 68° 28' W) is available for special projects. However, this site has not been used for the past few years.

Figure 6: View of the laboratory building at the Ushuaia GAW station

Figure 7: Ozone and carbon monoxide instruments at the Ushuaia GAW station

3.3. Staff / Operators

The main responsibility for the Ushuaia GAW station is with the Meteorological Service of Argentina (SNM). In addition a contract between SNM and the government of Tierra del Fuego assures the day-to-day operation of the station.

Table 1: Staff responsible for the GAW site Ushuaia (as of December 2003)

Name	**Position and duty**
SNM (Buenos Aires)	
Com. Ricardo A. Grünert	Director General of SNM
Com. Miguel A. Rabiolo	Permanent Representative of WMO
Vcom. Carlos A. Villanueva	Logistic Director
My Osvaldo M. Barturen	Station Manager; Head of Regional Calibration Center
Operators (Ushuaia)	
Government of Tierra del Fuego	
Mr Sergio Luppo	Chemical Engineer; Operator Carbon Monoxide
Ms Lilian Riebel	Technician; Data Management
Mr Claudio Izetta	Technician; Data Management
Municipality of Ushuaia	
Mr Miguel Pereyra	Chemical Engineer; Operator Surface Ozone
SMN	
Mr Juan Muños	Technician; Sounding Program
Mr Marcelo Sosa	Technician; Observer total ozone
Ms Erica Picaluga	Technician; Observer total ozone
Mr Eduardo Vitale	Technician; Observer total ozone

Comment

- The collaboration of different institutions and organizations is regarded as an advantage for the GAW program. However, specific responsibilities must be clearly defined and communicated. Furthermore, the program needs support from all involved partners.

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

4.1.1. Air Inlet System

Sampling-location: 7 m above ground on top of the station building, 2 m above the roof.

Sample inlet:

Rain protection: The Inlet is protected against rain and snow by an up-side-down electro polished stainless steel intake.

Inlet/Manifold: 2x5 m ½ inch PFA tubing inside the stainless steel inlet. From there connections CO and ozone instruments by ¼ inch PFA tubing, length approx. 3 m for each instrument. Additional pump to increase flow rate. Total flow rate 11 liter per minute with current set-up.

Inlet-filter: Teflon inlet filter before analyzer, exchanged monthly.

Residence time in the sampling line: approx. 5 s

The inlet used at the Ushuaia station was provided by the Izaña GAW station. It was noticed by the station operators that the inlet showed a significant ozone loss after renovation of the station building in 2001. As a consequence, a direct PFA sampling inlet line was used since September 2003 for parallel measurements. Inspection of the inlet showed that the distance between the rain protection and the stainless steel tube was very short (approx. 2 cm). The PFA tubing was partly inside the stainless steel tube. This may have happened during renovation work in 2001. The inlet was again fixed during the audit, and the distance between rain protection and the end of the steel tube was enlarged to approx. 10 cm. This allows the PFA tubing to stick out sufficiently. All of the ½ inch PFA tubing was replaced during the audit.

Materials as well as the residence time of the inlet system as after the audit are adequate for surface ozone measurements.

4.1.2. Instrumentation

Ozone Analyzer

Two TEI 49 ozone analyzers are running at the Ushuaia GAW station. They were running parallel using the same inlet for most of the time, but since September 2003 two different inlets were used (see above). Instrument details are summarized in Table 2. All instrumentation is installed inside the laboratory and is protected from direct sunlight. The laboratory has a heating system but is not air-conditioned. However, due to the relatively small variations of ambient temperatures the variation inside the building is expected to be small.

Table 2: Ozone analyzers at the Ushuaia Research Station

Instrument model	TEI 49 #47306-278 "O3-1"	TEI 49 #47312-278 "O3-2"
Instrument options	internal ozone generator	internal ozone generator
Used as	main station instrument	back-up instrument
Method	UV absorption	UV absorption
at Ushuaia	since September 1994	since November 1994
Range	0-100 ppb	0-100 ppb
Analog output	0-10 V	0-10 V
Span Coefficient before audit	507	500
Zero Offset before audit	50	50
Span Coefficient after audit	510	503
Zero Offset after audit	50	51

Ozone Calibrator

No ozone calibrator is available at the site. However, an ozone calibrator is available at the regional calibration center (RCC) in Buenos Aires. Nevertheless, calibrations or inter-comparisons were not performed on a regularly basis between the Ushuaia station and the RCC Buenos Aires. The calibration standard of the RCC Buenos Aires was available at the site during the audit. An inter-comparison with the WCC-EMPA reference is shown in Appendix I.

Operation and Maintenance

The instruments are checked on working days for general operation. These checks include inspection of flow rates and data acquisition. A full monthly instrument check includes a span check with the internal ozone generator. Daily zero checks are performed automatically. Inlet filters are exchanged every two to three weeks. No regular calibrations of the instrument were performed (last time during the WCC-EMPA audit in 1998).

4.1.3. Data Handling

Data Acquisition and –transfer

During the audit two data acquisition system were used by the Ushuaia station. The original acquisition as described in the WCC-EMPA audit report 98/8 (12-bit AD converter and a self-made Qbasic software) was running in addition to the data acquisition delivered by the Izaña GAW station. It was noticed during the audit that the new data acquisition had an influence on the analog output of the instruments. The analog output was 4% lower with the new system in use. This was probably due to an impedance problem. It was decided to abandon the new system and include the valve control for the automatic ozone zero check in the “old” software. With the help of the station operators, the necessary changes to the software were implemented. In addition the UPS detection signal was moved from an otherwise unused PC to the data acquisition system PC.

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. Invalid values (i.e. instrument maintenance) are flagged as invalid data but are not removed from 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 recently established data center for surface ozone at JMA (World Data Center for Greenhouse Gases, WDCGG).

4.1.4. Documentation

Logbooks

Station and instrument logbooks are available at the site. The notes are up to date and describe all important events.

Standard Operation Procedures (SOPs)

No specific SOPs but instrument manuals are available at the site.

Comment

The frequent instrument checks and the up-to-date logbooks support the quality of the data. No change of the current practice is suggested.

4.2. Inter-comparison of the Ozone Instruments

The WCC-EMPA audit was confined to both operational ozone instruments at the Ushuaia station. The results shown below are valid for the new calibration factors (see Table 2) and without the new data acquisition connected. Corrections for the old data should be made accordingly. An inter-comparison was also performed with the calibrator TEI 49C-PS from the RCC Buenos Aires. These results are shown in Appendix I.

4.2.1. Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix II-III) was operated in stand-by mode to warm up for 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 400 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 8 the experimental set-up during the audit. No modifications of the ozone analyzers which could influence the measurements were made for the inter-comparisons. However, the new data acquisition was disconnected before the start of the final inter-comparisons.

The audit procedure included a direct inter-comparison of the WCC-EMPA transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in Appendix III.

Table 3: Experimental details of the ozone inter-comparison

reference:	WCC: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49 #47306-278 "O3-1" TEI 49 #47312-278 "O3-2"
ozone source:	WCC: TEI 49C-PS, internal ozone generator
zero air supply:	EMPA: silica gel - inlet filter 5 μm - metal bellows pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm
data acquisition system:	16-channel ADC with acquisition software
pressure transducer readings:	Ambient pressure: 1006.0 hPa TEI 49C-PS (WCC): 1007.0 hPa (not adjusted) TEI 49 "O3-1": 1002.4 hPa (not adjusted) TEI 49 "O3-2": 995.0 hPa (not adjusted)
concentration range	0 - 100 ppb
number of concentrations:	5 plus zero air at start and end
approx. concentration levels:	10 / 20 / 30 / 50 / 90 ppb
concentration sequence:	random
averaging interval per concentration:	5 minutes
number of runs:	3 x between 11 and 14 November 2003
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

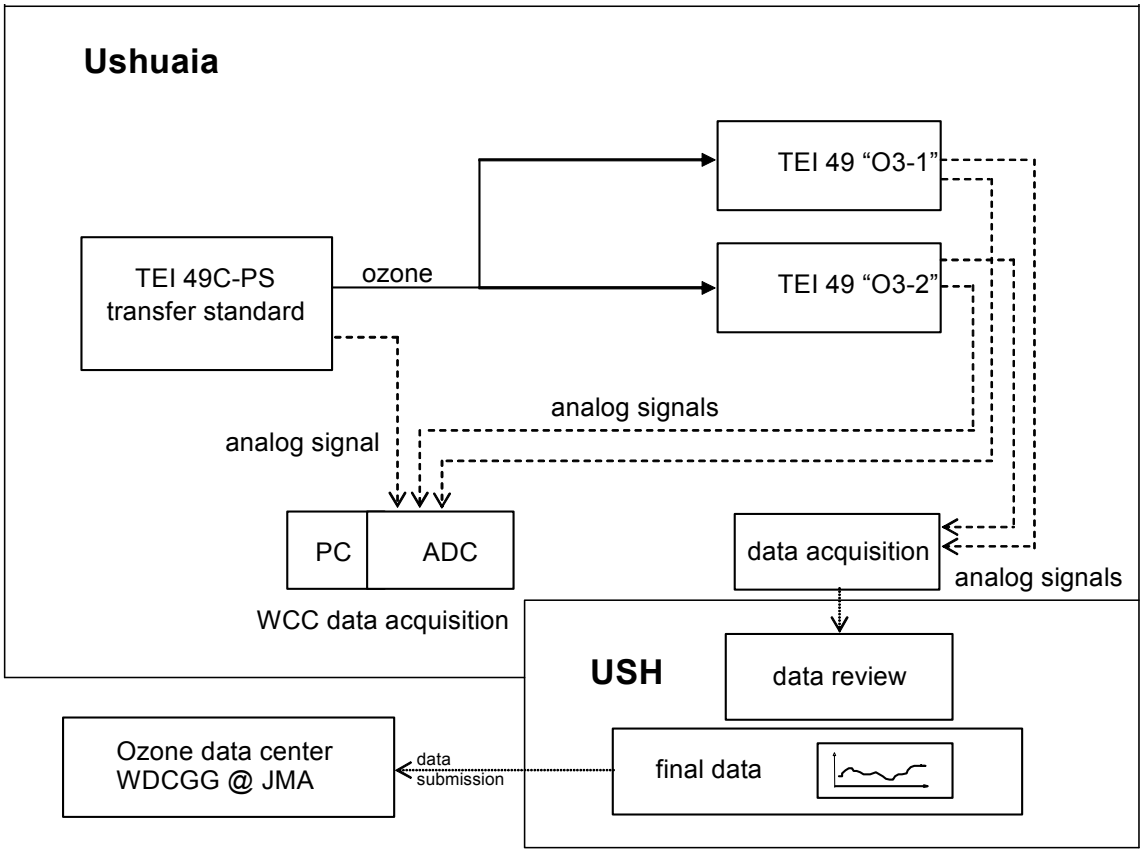

Figure 8: Experimental set up for the ozone inter-comparison

4.2.2. Results

The assessment of the inter-comparison was done according to Klausen et al. (2003). The results shown below refer to the new calibration factors as given in Table 2. It was noticed that the data acquisition provided by Izaña influenced the analog output of the instruments. Refer to Section 4.3 for suggested corrections of previously acquired data.

Ozone Analyzer

The results comprise the inter-comparison between the TEI 49 #47306-278 and TEI 49 #47312-278 field instruments and the WCC transfer standard TEI 49C-PS, carried out between 11. and 14. November 2003.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 4. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

Figures 9 to 12 show the residuals of the linear regression analysis of the field instruments compared to the EMPA transfer standard. The residuals versus the run index are shown in Figures 9 and 10 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figures 11 and 12 (concentration dependence). The result is presented for both instruments in a graph with the assessment criteria for GAW field instruments (Figures 13 and 14).

The data used for the evaluation was recorded by both EMPA and Ushuaia data acquisition systems. Note that only the old station data acquisition was used during the inter-comparison. The new system provided by Izaña influenced the analog output and is no longer in use. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 4: Inter-comparison of the ozone field instruments TEI 49 #47306-278 and TEI 49 #47312-278

	TEI 49C-PS WCC-EMPA		**TEI 49 #47306-278 Ushuaia**				**TEI 49 #47312-278 Ushuaia**			
run index	conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.50	0.07	0.08	0.17	-0.42		0.52	0.16	0.02	
2	10.32	0.43	9.78	0.58	-0.54	-5.23	10.26	0.49	-0.07	-0.64
3	30.19	0.43	29.81	0.46	-0.38	-1.27	30.12	0.45	-0.07	-0.22
4	19.78	0.23	19.49	0.24	-0.30	-1.50	19.79	0.21	0.00	0.02
5	89.91	0.09	89.99	0.20	0.09	0.10	90.04	0.22	0.13	0.15
6	49.93	0.13	49.74	0.15	-0.19	-0.39	49.98	0.17	0.05	0.10
7	0.53	0.06	-0.01	0.17	-0.54		0.49	0.12	-0.04	
8	0.54	0.07	-0.01	0.17	-0.55		0.46	0.13	-0.08	
9	29.97	0.18	29.65	0.30	-0.32	-1.07	30.03	0.26	0.06	0.19
10	89.87	0.08	89.59	0.25	-0.29	-0.32	89.95	0.14	0.08	0.09
11	20.10	0.23	19.67	0.26	-0.43	-2.12	20.17	0.29	0.07	0.34
12	49.92	0.10	49.73	0.16	-0.18	-0.36	49.78	0.14	-0.14	-0.27
13	10.23	0.31	9.83	0.34	-0.40	-3.94	10.15	0.30	-0.08	-0.74
14	0.50	0.11	0.06	0.16	-0.44		0.39	0.11	-0.11	
15	0.49	0.11	0.09	0.17	-0.41		0.41	0.11	-0.09	
16	10.25	0.33	9.99	0.38	-0.26	-2.52	10.26	0.41	0.01	0.10
17	89.93	0.13	90.14	0.30	0.21	0.23	90.01	0.17	0.08	0.09
18	20.07	0.14	19.82	0.17	-0.25	-1.25	20.14	0.21	0.07	0.33
19	50.01	0.12	49.97	0.27	-0.04	-0.08	49.98	0.19	-0.02	-0.05
20	30.06	0.14	29.74	0.24	-0.33	-1.08	29.84	0.24	-0.23	-0.75
21	0.44	0.12	0.11	0.20	-0.33		0.55	0.18	0.11	

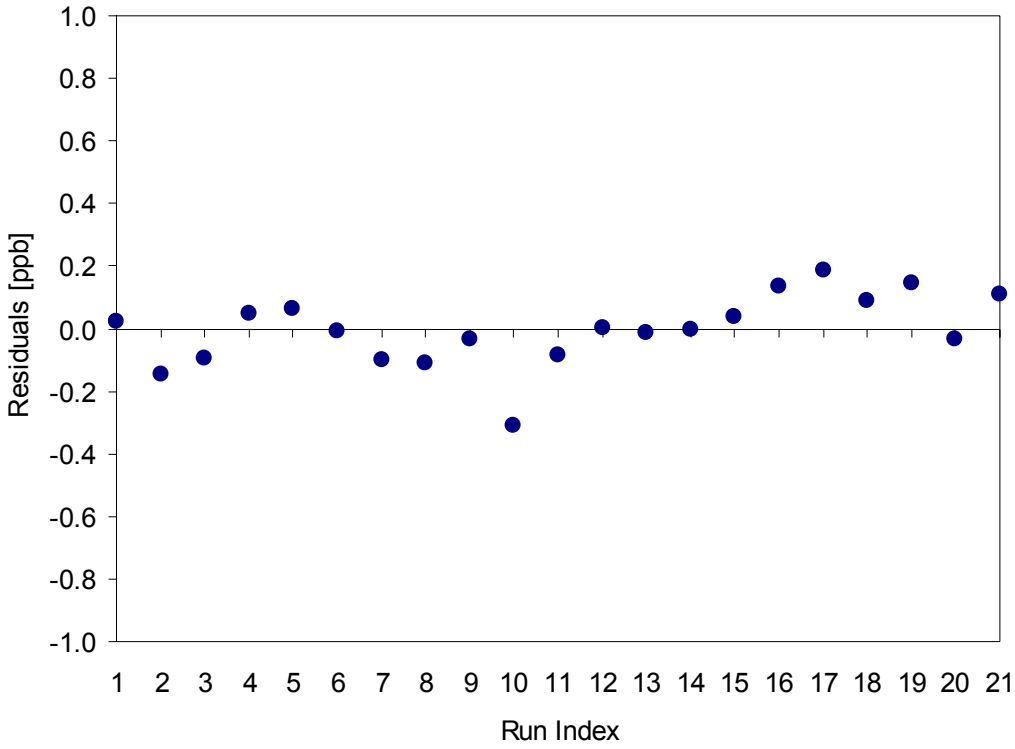

Figure 9: Residuals to the linear regression function (TEI 49 #47306-278) vs. the run index (time dependence)

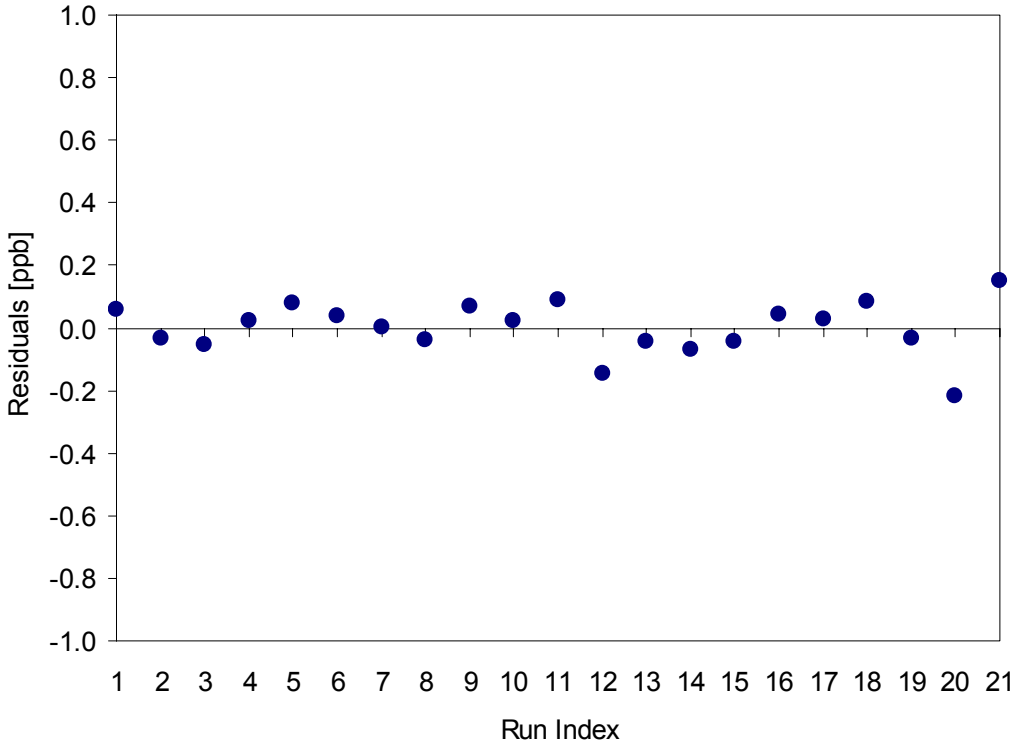

Figure 10: Residuals to the linear regression function (TEI 49 #47312-278) vs. the run index (time dependence)

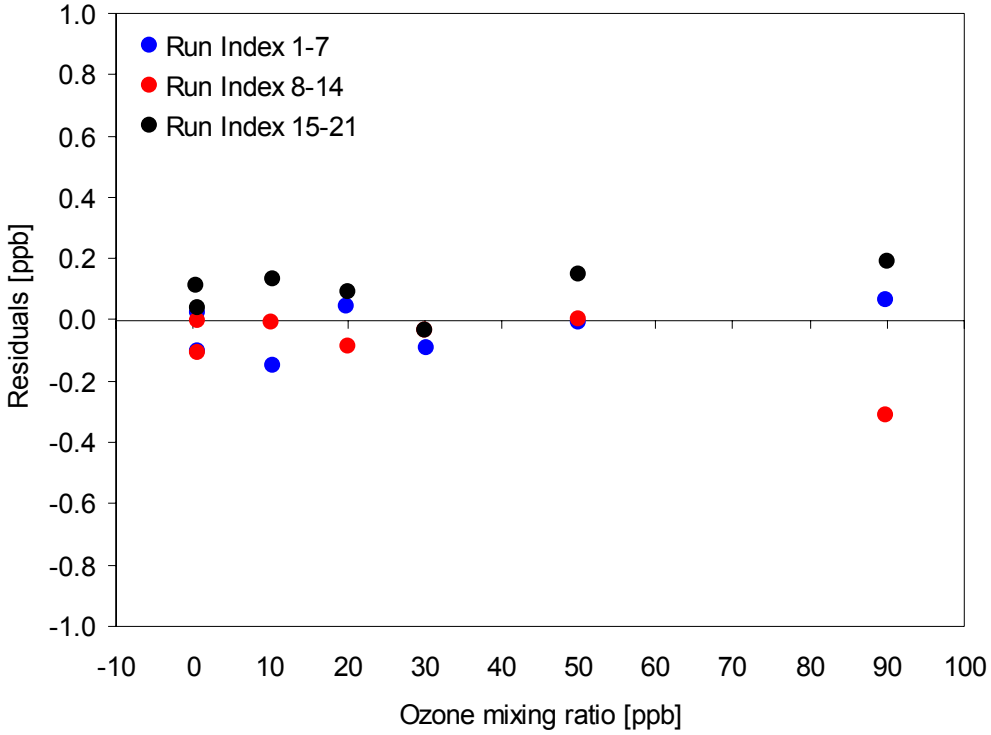

Figure 11: Residuals to the linear regression function (TEI 49 #47306-278) vs. the concentration of the WCC transfer standard (concentration dependence)

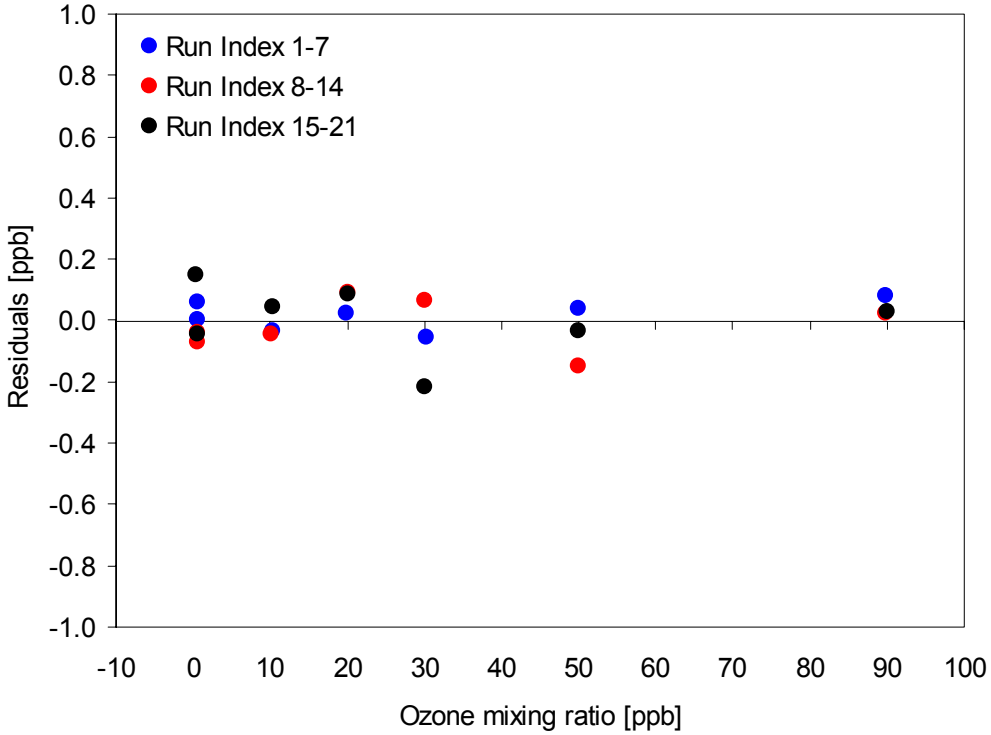

Figure 12: Residuals to the linear regression function (TEI 49 #47312-278) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of Klausen et al. (2003). The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

TEI 49 #47306-278:

$$\text{Unbiased } O_3 = (\text{TEI 49} + 0.16) / 1.0051$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49 = O_3 mixing ratio in ppb, determined with TEI49 #47306-278

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.60 \text{ ppb})^2 + (0.00618 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 13 shows the deviation of the TEI 49 #47306-278 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

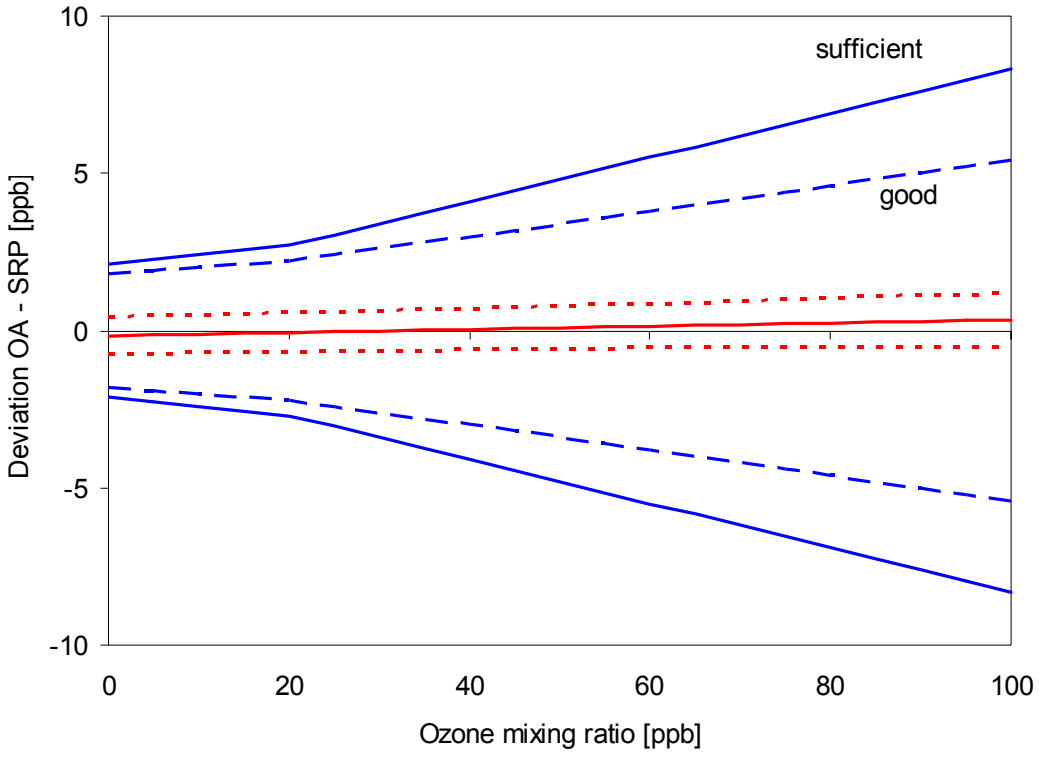

Figure 13: Inter-comparison of instrument TEI 49 #47306-278

TEI 49 #47312-278:

$$\text{Unbiased } O_3 = (\text{TEI 49} - 0.25) / 1.0010$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49 = O_3 mixing ratio in ppb, determined with TEI49 #47312-278

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.58 \text{ ppb})^2 + (0.00615 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 14 shows the deviation of the TEI 49 #47312-278 from SRP#15 with the assessment criteria for "good" and "sufficient" agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

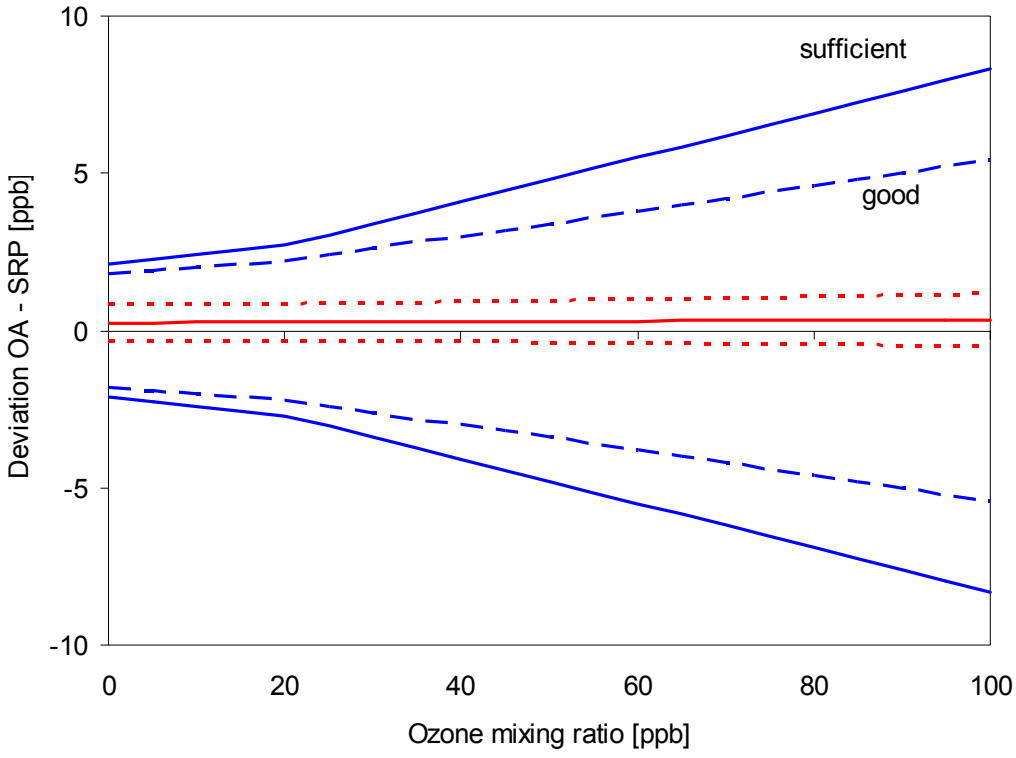

Figure 14: Inter-comparison of instrument TEI 49 #47312-278

Comment

The ozone concentrations observed at Ushuaia (2001) ranged between 7 and 31 ppb (5- and 95-percentile of 60 min mean values). Both ozone analyzers of Ushuaia fulfill the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone. No significant bias in the intercept and the slope was observed with the new calibration factors and the old data acquisition system. Both analyzers were also inter-compared with the original settings. Data observed with these settings should be corrected as described in Section 4.3.

4.3. Recommendation for Ozone Measurements

With the new calibrations factors both TEI 49 ozone instruments at Ushuaia fulfill the assessment criteria as "good" over the tested range of 0 to 100 ppb. The recommendations of WCC-EMPA are split into two parts, “corrections of previous data” and “general recommendations”.

Correction of previous data

It was recognized during the audit that the previously acquired data needs to be corrected for a) inlet loss, b) influence of new data acquisition, and c) calibration settings.

a) Inlet loss

Ozone loss, most likely due to an accidental change of the new inlet during renovation work in 2001, was recognized in September 2003. Since then, parallel measurements using an alternative inlet are available. Data from the period beginning 2001 until the date of the audit should be corrected for the inlet loss using the results of the parallel measurements, and uncertainties should be increased accordingly.

b) Influence of the new data acquisition

WCC-EMPA made a direct inter-comparison with the instrumental set-up encountered at the beginning of the audit. It was recognized that the new data acquisition had an influence on the acquired ozone data. The following relationship can be used to correct data from the period with the new data acquisition in use. This correction also accounts for the bias due to the old calibration settings. This correction should be applied for the period with the new data acquisition in use:

TEI 49 #47306-278: Unbiased O_3 = (TEI 49 + 0.06) / 0.9491

TEI 49 #47312-278: Unbiased O_3 = (TEI 49 + 0.32) / 0.9458

c) Calibration settings

The calibration settings were changed during the audit (details see Table 2). To account for the change of the calibration factors, the following correction can be applied:

TEI 49 #47306-278: Unbiased O_3 = (TEI 49 + 0.20) / 0.9851

TEI 49 #47312-278: Unbiased O_3 = (TEI 49 + 0.61) / 0.9837

This correction should be made for the period between the WCC-EMPA audit in 1998 and the installation of the new data acquisition. The uncertainty budget should consider the calibration results of the current audit compared to the 1998 audit which suggests a small instrumental drift.

General recommendations

- Frequent checks (at least yearly) for ozone loss in the inlet system are encouraged.
- WCC-EMPA recommends not to use the new (INPE) data acquisition until the impedance problem is solved.
- Calibrations (with a reference instrument) are only performed on a very irregular basis. In fact, the last calibration dated back to the WCC-EMPA audit in 1998. It is recommended to perform calibrations at least in yearly intervals. A calibrator is available at the Regional Calibration Center for Surface Ozone in Buenos Aires.
- Quality assurance and control of the ozone data should be improved. Thorough inspection of the time series and a comparison using data from both instruments is encouraged.
- Submission of ozone data to the World Data Center for Greenhouse Gases (WDCGG) at JMA is encouraged after data have been quality controlled.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Ushuaia in 1994. A more or less continuous time series is available since then. Two NDIR analyzers are running in parallel, but one instrument is considered to be more stable and is the designated main CO analyzer.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO

The same inlet system and manifold as for ozone are used (see 4.1.1.). The estimated residence time in the sampling line is approx. 5 s.

5.1.2. Instrumentation

Two TEI48 NDIR monitors are used as in-situ CO analyzers. Instrumental details are listed in Table 5.

Table 5: Carbon monoxide instruments at Ushuaia

instrument	Thermo Environmental Inc.	Thermo Environmental Inc.
model, S/N	TEI 48 #47169-278	TEI 48 #47168-278
used as	main instrument	backup instrument
at Ushuaia	since November 1994	
method	NDIR / Gas Filter Correlation	
Range	0 – 1000 ppb	
analog output	0 – 10 V	
calibration interval	manual calibration with station standards, irregular intervals	
zero check	automatic, every 5 minutes for a duration of 5 minutes	
zero trap	Degussa Type E221 P/D 0.5% at 180°C	

Gas Standards

Table 6 shows the gas standards available at Ushuaia. The CMDL standards still refer to the old CO scale. A calibration of the station instruments using the CMDL standards was not performed because of the high gas consumption. In addition to the CMDL standards, two high concentration CO standards (approx. 100 ppm) from Scott-Marrin are available at the site. These standards should be used for the daily standard addition. However, due to a defective valve, the standard addition was not performed since many years.

Table 6: Station CO cylinders

Gas cylinder	Description	Concentration
CA02556	CMDL certified (26.07.1996) CO standard	44.2 ppb
CA02538	CMDL certified (26.07.1996) CO standard	97.6 ppb
CA02546	CMDL certified (26.07.1996) CO standard	147.5 ppb
CA02518	CMDL certified (26.07.1996) CO standard	198.7 ppb
CA01102	CMDL certified (26.07.1996) CO standard	250.0 ppb
CA02554	CMDL certified (26.07.1996) CO standard	317.4 ppb
CA05309	Scott Marin CO standard	98.9 ± 1.0 ppm
CA05308	Scott Marin CO standard	98.8 ± 1.0 ppm

Operation and Maintenance

Analysis: The system is alternating between sample and zero check every five minutes. The last three minutes of each five minute period are averaged, and the sample (ambient) value is corrected by subtracting the previous zero value. This results in one measurement value every ten minutes. These ten minute values are further averaged to one hourly and daily values.

5.1.3. Data Handling

Data Acquisition and –transfer

The same data acquisitions as for ozone were used. Due to an impedance problem the new system provided by Izaña was disconnected during the audit.

Data Treatment

A correction of the zero drift is made using the five minute zero measurement 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 Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA.

5.1.4. Documentation

Logbooks

A logbook is available for the carbon monoxide instrument. The notes are up-to-date and describe all important events.

Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site.

Comment

The frequent instrument checks and the up-to-date logbook support the quality of the data. However, the instruments are not calibrated in regular intervals.

5.2. Inter-comparison of the in-situ Carbon Monoxide Analyzer

5.2.1. Experimental Procedure

WCC-EMPA provided different CO concentrations using and high concentration CO standard and a dilution unit. Details and traceability to CMDL are described in Appendix IV. Each concentration was measured by the station instrument for two hours. The second one hour average was used for the inter-comparison. This allowed the system to stabilize for one hour for each concentration. The data was acquired by the station software and the WCC-EMPA data acquisition. The experimental details are summarized in Table 7.

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

Field instruments:	TEI 48 #47169-278 (main instrument) TEI 48 #47168-278 (backup instrument)
Reference:	WCC-EMPA dilution unit (see Appendix IV)
Data acquisition system:	Station and WCC-EMPA data acquisitions
Approx. concentration levels:	0 to 200 ppb

5.2.2. Results

The CO concentrations determined by the main station instrument TEI 48 #47169-278 for nine different concentrations provided by the WCC-EMPA dilution system are shown in Table 8. For each one hour mean value the difference between the tested instrument and the dilution unit is calculated in ppb and %. Figure 15 shows the absolute differences (ppb) between the measurements of the TEI 48 #47169-278 and WCC-EMPA (conventional true value). The results for the station backup instrument TEI 48 #47168-278 are also shown (Table 9 and Figure 16). The WCC-EMPA dilution system was calibrated before and after the audit against a flow reference and tested with an Aerolaser AL5001 CO instrument which was calibrated with a CMDL certified standard (CMDL CA02854, 295.5 pbb). The error bars represent the combined 95% confidence interval for the calibration of the dilution system against the CMDL standard and of the one hourly average values at Ushuaia.

Table 8: Carbon monoxide inter-comparison measurements at Ushuaia

No.	**WCC standard**	**Ushuaia analysis (TEI 48 #47169-278)**				
	conc. ± uncertainty*	conc.	s_d	No. of 10	deviation from reference	
	ppb	ppb	ppb	min values	ppb	%
1	0.0 ± 2.0	-0.1	4.2	6	-0.1	N/A
2	20.7 ± 2.0	20.2	4.0	6	-0.5	-2.4
3	41.1 ± 2.0	42.4	6.4	6	1.3	3.2
4	61.7 ± 2.0	58.3	6.8	6	-3.4	-5.5
5	82.1 ± 2.0	80.2	8.1	6	-1.9	-2.3
6	102.6 ± 2.0	99.7	8.0	6	-2.9	-2.8
7	123.2 ± 2.5	126.1	7.2	6	2.9	2.4
8	164.3 ± 3.3	167.3	5.8	6	3.0	1.8
9	205.4 ± 4.1	207.7	5.2	6	2.3	1.1

* uncertainties were estimated to be ± 2 ppb (conc. ≤ 100 ppb) or 2 % (conc. > 100 ppb)

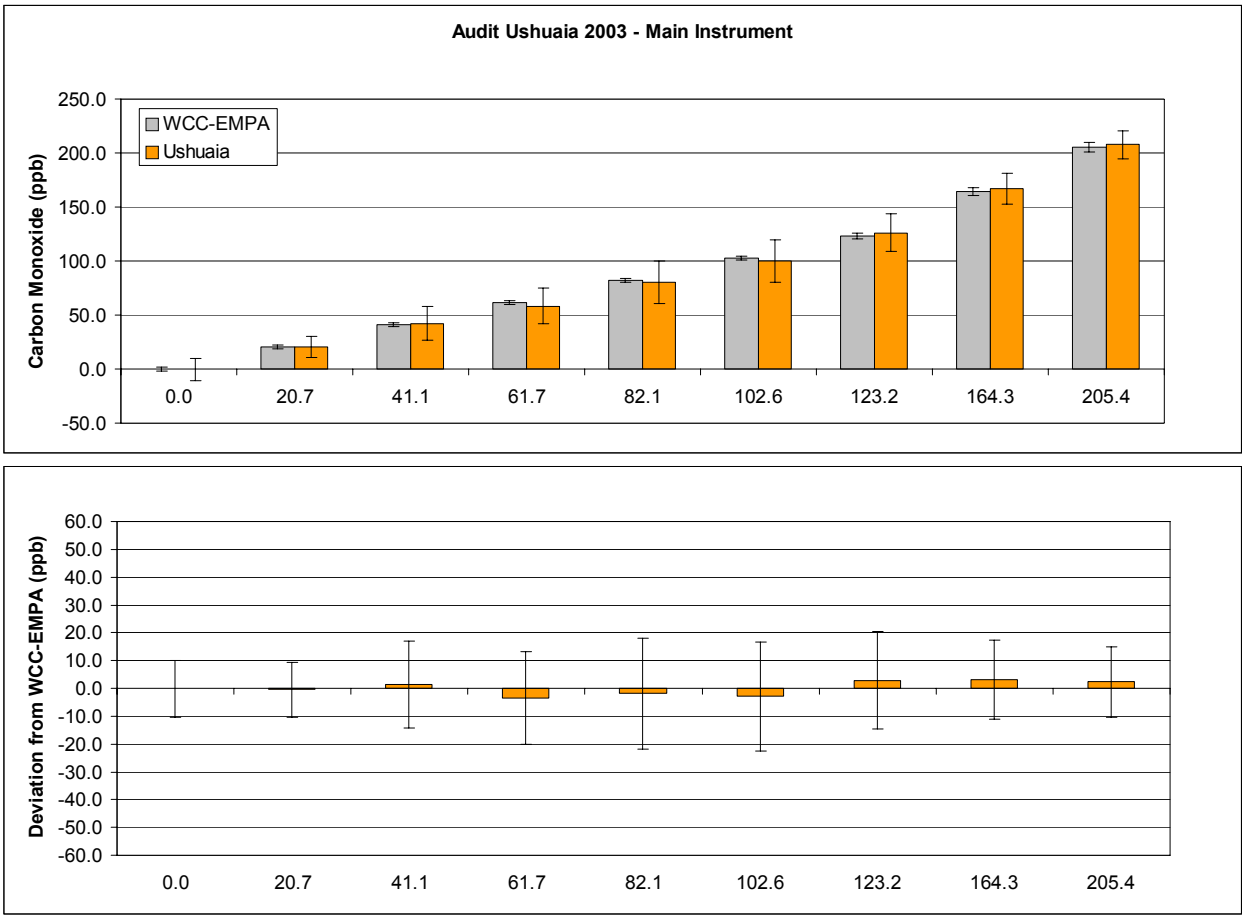

Figure 15: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the main CO analyzer of Ushuaia (orange).
lower panel: deviation of the Ushuaia station from the conventional true value.
The error bars represent the 95% confidence interval. Data are one hour averages.

Table 9: Carbon monoxide inter-comparison measurements at Ushuaia

No.	**WCC standard**	**Ushuaia analysis (TEI 48 #47168-278)**				
	conc. ± uncertainty*	conc.	s_d	No. of 10	deviation from reference	
	ppb	ppb	ppb	min values	ppb	%
1	0.0 ± 2.0	1.2	9.9	6	1.2	N/A
2	20.7 ± 2.0	16.7	11.1	6	-4.0	-19.3
3	41.1 ± 2.0	35.9	9.1	6	-5.2	-12.7
4	61.7 ± 2.0	51.8	10.7	6	-9.9	-16.0
5	82.1 ± 2.0	73.0	5.2	6	-9.1	-11.1
6	102.6 ± 2.0	99.6	22.1	6	-3.0	-2.9
7	123.2 ± 2.5	119.7	9.9	6	-3.5	-2.8
8	164.3 ± 3.3	144.6	14.1	6	-19.7	-12.0
9	205.4 ± 4.1	190.4	7.8	6	-15.0	-7.3

* uncertainties were estimated to be ± 2 ppb (conc. ≤ 100 ppb) or 2 % (conc. > 100 ppb)

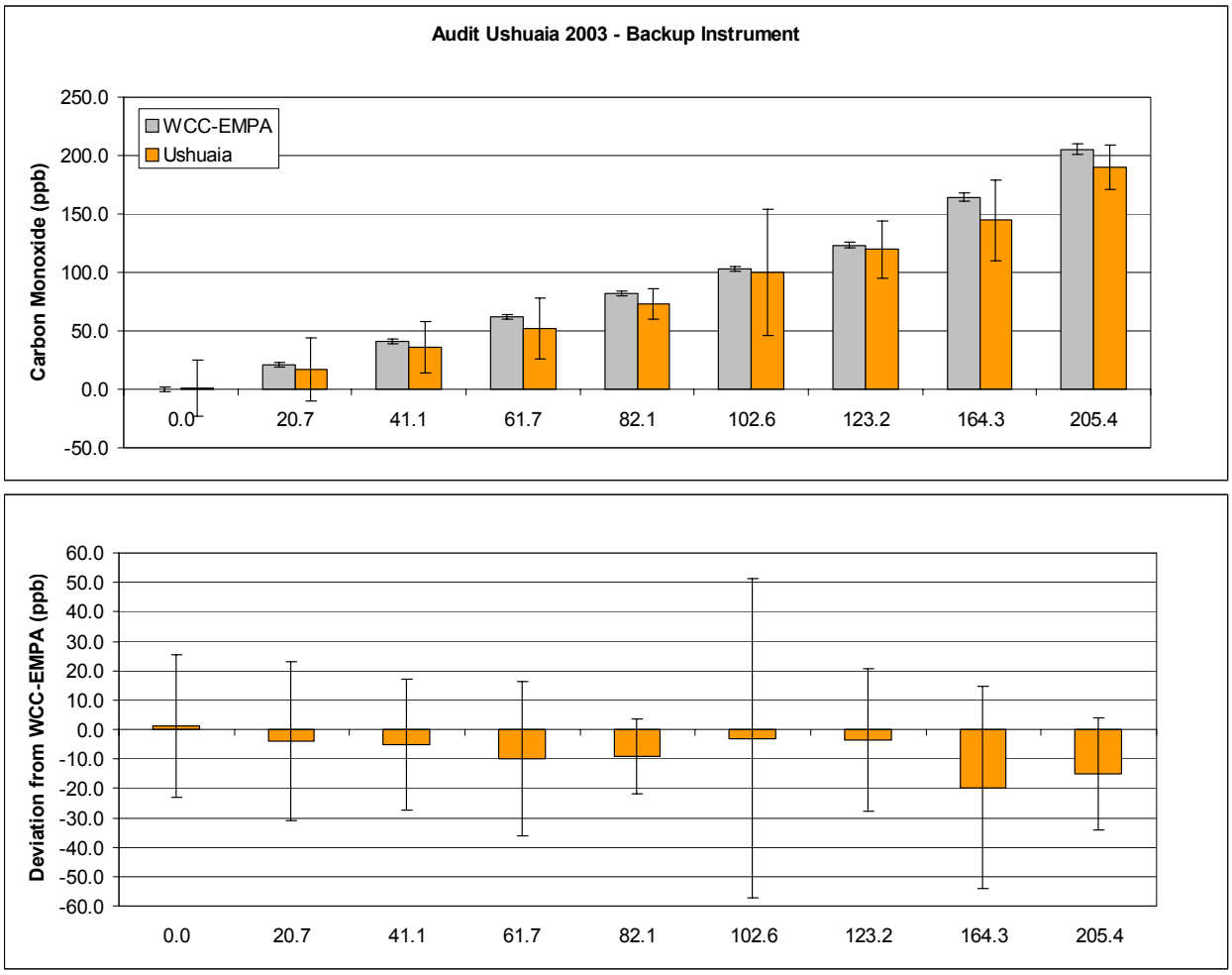

Figure 16: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the backup CO analyzer of Ushuaia (orange).
lower panel: deviation of the Ushuaia station from the conventional true value.
The error bars represent the 95% confidence interval. Data are one hour averages.

5.3. Discussion of the Inter-comparison Results

The agreement between the main station CO instrument and WCC-EMPA was good despite the fact that the analyzer was not calibrated since a long time. The instrument noise was higher than with other analytical techniques, but in the order of a normally expected value for the NDIR / GFC technique.

The agreement between the station backup instrument and WCC-EMPA was significantly worse compared to the main instrument. First, this instrument shows excessive noise. Second, concentrations measured with this instrument tend to be significantly too low. This instrument may not be in calibration, and the reason for the noise and the slow response to concentration changes should be explored.

5.4. Recommendation for Carbon Monoxide Measurements

The good agreement between the main station analyzer and WCC-EMPA shows that the system is operated with great care. However, calibrations could not be performed over the last past years due to a lack of calibration gases and spare parts. Specific recommendations for carbon monoxide are summarized below.

- Standard additions (daily) should again be performed. The calibrations standards are available at the site, and the valve needed will be delivered by WCC-EMPA (storehouse project).
- WCC-EMPA recommends not to adjust calibration factors based on the results of the standard addition. Calibrations should be done using a standard gas directly (e.g. CMDL 300 ppb).
- The backup instrument needs to be serviced. It should also be considered to change the current sequence of 5 min zero / 5 min ambient measurements to a cycle with 10 min. This would allow a longer stabilizing time before the actual averaging.
- The CMDL standards at the site refer to the old CMDL scale. A re-calibration at CMDL is encouraged.

8. References

Hofer, P., B. Buchmann, and A. Herzog, Traceability, Uncertainty and Assessment Criteria of Surface Ozone Measurements, *EMPA-WCC Report 98/5*, 19 pp., Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf, Switzerland, 2000.

Klausen, J. C. Zellweger, B. Buchmann, and P. Hofer, Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res*, in Press, 2003

Novelli, P.C., K.A. Masarie, P.M. Lang, B.D. Hall, R.C. Myers, and J.W. Elkins, Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires, *J. Geophys. Res.* 108, 4464, doi:10.1029/2002JD003031, 2003.

Press, W.H., S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C: The Art of Scientific Computing*, 994 pp., Cambridge University Press, Cambridge, U.K., 1995.

Appendix

I TEI 49C-PS of the Regional Calibration Center (RCC) Buenos Aires

In addition to the two analyzers of the Ushuaia station, the calibrator of the Regional Calibration Center (RCC) for Surface Ozone Buenos Aires was at the station during the audit. This calibrator is normally located in Buenos Aires and usually does not travel, but was made available for calibration by SMN.

The last calibration of the instrument was performed in 1998 by Alex Herzog from WCC-EMPA. The calibration settings (OFFSET 1.5, SPAN 1.021) proved to be no longer valid. The instrument was not in use until the start of the RCC in 2003. Due to the fact that the calibration of the instrument had to be adjusted, all data of previous calibrations done in 2003 should be corrected. The following correction can be applied for calibrations performed with TEI 49C-PS # 56084-306 (OFFSET 1.5, SPAN 1.021):

Unbiased O_3 = (TEI 49C-PS + 2.02) / 0.9859

The calibration of the instrument was changed (new: OFFSET -0.5, SPAN 1.035), and the following relationship between TEI 49C-PS # 56084-306 and SRP#15 (Reference) was observed:

TEI 49C-PS # 56084-306:

$$\text{Unbiased } O_3 = (\text{TEI 49C-PS} - 0.16) / 0.9998$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS # 56084-306

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.63 \text{ ppb})^2 + (0.00548 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 17 shows the deviation of the TEI 49C-PS # 56084-306 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

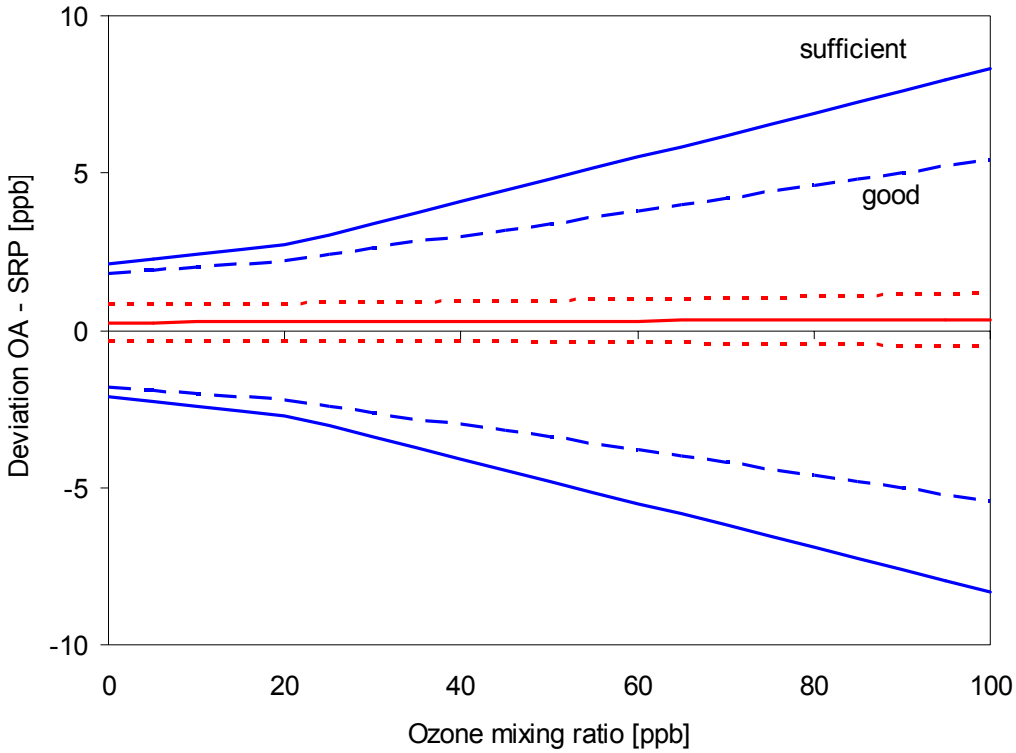

Figure 17: Inter-comparison of instrument TEI 49C-PS # 56084-306

II EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The UV absorption is proportional to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 18. One gas stream flows through a pressure regulator to the reference solenoid valve to become the zero reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. After the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS then determines the ozone concentration for each cell and outputs the average concentration.

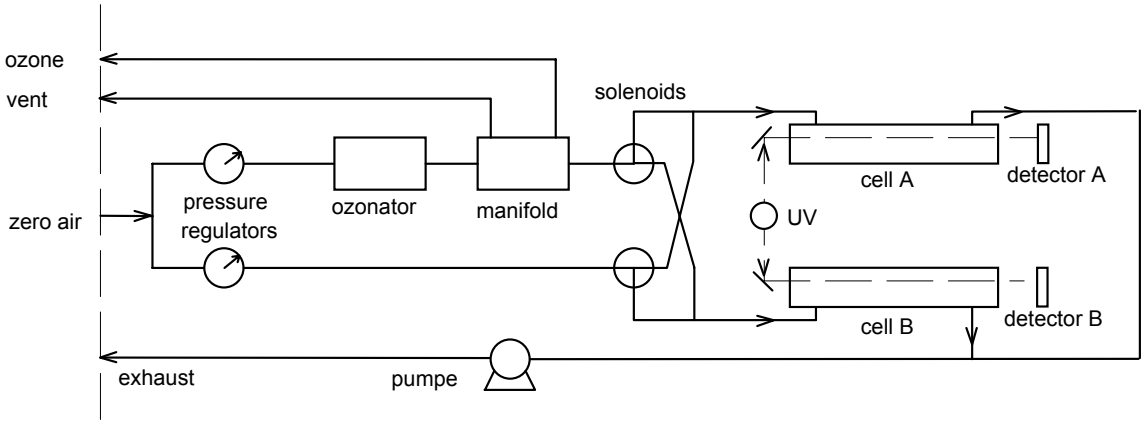

Figure 18: Flow schematic of TEI 49C-PS

III Stability of the Transfer Standard TEI 49C-PS

To exclude errors that might result from transportation of the transfer standard, the TEI 49C PS #54509-300 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this inter-comparison at the EMPA calibration laboratory are summarized in Table 10 and Figure 19.

Table 10: Inter-comparison procedure SRP - TEI 49C-PS

pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 140 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurized air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

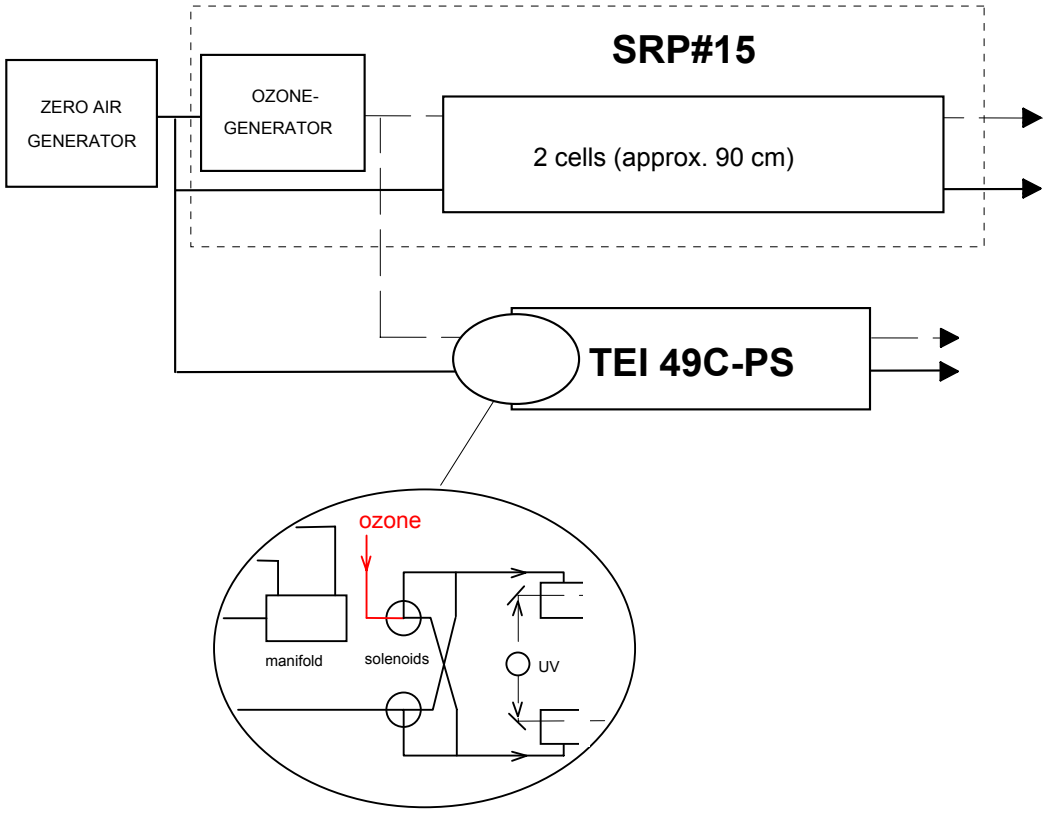

Figure 19: Instruments set up SRP -TEI 49C-PS

The transfer standard fulfilled the criteria given in Klausen et al. (2003), which means that neither intercept nor slope were different from 0 and 1,respectively, on the 95% confidence level.
Figure 20 shows the deviation of the transfer standard from SRP#15 before and after the audit. The maximum allowed deviation is also shown in this figure. The regression statistics between the WCC-EMPA transfer standard and SRP#15 were calculated using the procedure `fitexy` given in Press et al. (1995). The following relationship was found for the pooled data of the inter-comparisons before and after the audit:

$$\text{TEI 49C-PS \#54509-300} = 0.9999 \times \text{SRP\#15} + 0.29 \text{ ppb}$$

This relationship was used for the calculation of the unbiased ozone concentrations.

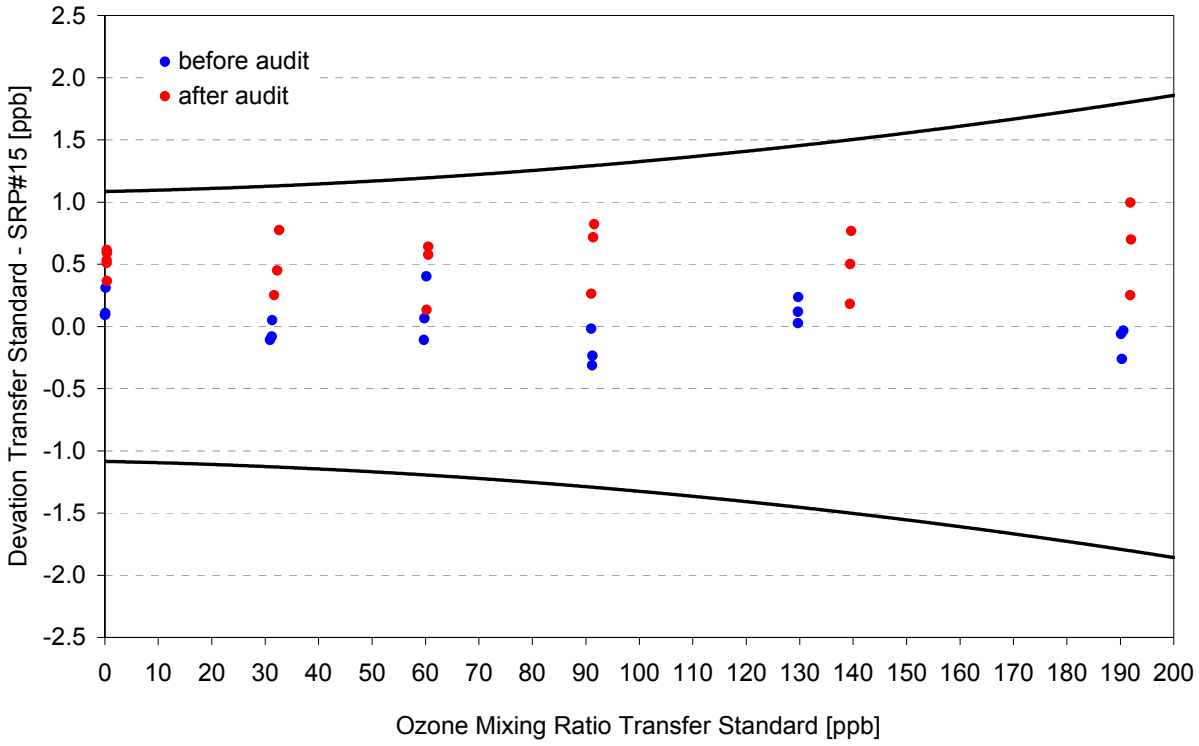

Figure 20: Deviation of the WCC-EMPA transfer standard from SRP#15 before and after the audit

IV WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at WCC-EMPA are listed in Table 11:

The CO scale of the CMDL was recently revised (Novelli et al., 2003). WCC-EMPA refers to the **new** scale. A MGM dilution unit (Breitfuss, Serial # 2262/91/1) was used. This dilution unit was calibrated against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851) before and after the audit. Zero air was generated using a zero air generator (Ambient Air – Rubingel – Sofnocat – Filter – Pump – Purafil – Sofnocat – Filter). This zero air system was tested before the audit and completely removed CO from ambient levels of > 1 ppm at 3.5 liters per minute. A CO standard (Sauerstoffwerk Lenzburg) in synthetic air was used for the dilution system. This standard was calibrated against CMDL revised scale CA02854 with the Aerolaser AL5001, resulting in a concentration of 7256.0 ppb CO. In addition, the whole dilution system was checked by measuring the resulting concentrations with the AL5001. The results (flows, expected and measured CO concentrations) are listed in Table 12. The average expected concentration was assigned to be the conventional true value.

Table 10: CMDL CO Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Standard (Gas Cylinders)	CMDL old scale*	CMDL new scale**	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard (")	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	CA02854

* Certificates from 5.8.97 (97.6, 189.3, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)
** Revised scale (by P. Novelli), re-calibrated at CMDL, 23.01.01

Table 12: MGM dilution system

Mass Flow Controller Setpoint [ml/min]		Mass Flow Controller Actual value before audit [ml/min]		Expected CO concentration before audit	Measured CO concentration before audit	Mass Flow Controller Actual value after audit [ml/min]		Expected CO concentration after audit	Measured CO concentration after audit	Average expected concentration
MFC1	MFC2	MFC1	MFC2	[ppb]	[ppb ± 1σ]	MFC1	MFC2	[ppb]	[ppb ± 1σ]	[ppb]
3500.0	0.0			0.0	-0.1 ± 0.4			0.0	0.2 ± 0.4	**0.0**
3490.4	9.6	3488.9	9.8	20.6	21.4 ± 0.6	3498.6	9.9	20.8	20.6 ± 0.6	**20.7**
3480.7	19.3	3492.5	19.6	41.0	41.7 ± 1.1	3495.8	19.7	41.3	41.3 ± 0.6	**41.1**
3471.1	28.9	3479.7	29.3	61.6	62.1 ± 0.7	3476.0	29.4	61.9	61.3 ± 1.1	**61.7**
3461.4	38.6	3474.9	39.1	82.0	82.3 ± 0.8	3464.0	39.1	82.3	81.1 ± 1.1	**82.1**
3451.8	48.2	3468.8	48.9	102.4	102.7 ± 0.8	3457.1	48.9	102.8	102.6 ± 1.0	**102.6**
3442.1	57.9	3454.0	58.6	122.9	123.0 ± 0.9	3439.8	58.7	123.6	123.2 ± 0.8	**123.2**
3422.8	77.2	3427.6	78.1	164.1	163.8 ± 1.0	3438.3	78.5	164.4	163.5 ± 1.1	**164.3**
3403.5	96.5	3407.5	97.6	205.1	204.1 ± 0.6	3415.1	98.1	205.7	204.8 ± 0.9	**205.4**

V System and Performance Audits Executive Summary

GAW World Calibration Centre for Surface Ozone
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System and Performance Audits Executive Summary

0.1	Station Name:	Ushuaia
0.2	GAW ID:	
0.3	Coordinates/Elevation:	54° 51' S – 68° 17' W (18 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1	Date of Audit:	08.11.2003 –15.11.2003
1.2	Auditors:	Dr. C. Zellweger and Dr. J. Klausen
1.3	Station staff involved in audit:	My Osvaldo Barturen, Station Manager; Head of Regional Calibration Center Mr. Sergio Luppo, Chemical Engineer; Operator Surface Ozone Mr. Miguel Pereyra, Chemical Engineer; Operator Carbon Monoxide
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS S/N: 54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	$(0.9999\pm0.0010) \times [SRP] + (0.29\pm0.11)$
1.6	Ozone Analyzer [OA]	
1.6.1	Model:	TEI49 S/N: 47306-278
1.6.2	Coefficients prior to audit	OFFSET: 50 SPAN: 507
1.6.3	Coefficients during and after audit	OFFSET: 50 SPAN: 510
1.6.4	Range of calibration: 0 – 100 ppb	
1.6.5	Calibration after audit (ppb):	$[OA] = (1.005\pm0.0035) \times [TS] + (-0.45\pm0.16)$
1.6.6	Unbiased ozone concentration (ppb):	$C = ([OA] + 0.1554)/1.0051$
1.6.7	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.60\ ppb)^2 + (0.0062 \times C)^2\}^{1/2}$
1.7	Comments	Calibration valid for a direct Intercomparison between TS and OA. Complete bias assessment should include other effects described in WCC-EMPA Report 03/4.
1.8	Reference:	WCC-EMPA Report 03/4