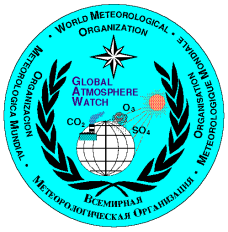

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Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 08/1

Submitted to the
World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GLOBAL GAW STATION BARROW USA, MARCH 2008

Submitted by
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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The first system and performance audit at the Global GAW station Barrow (BRW) was conducted by WCC-Empa[1] from 10 thru 12 March 2008 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The BRW observatory is operated by the Earth System Research Laboratory (ESRL) / Global Monitoring Division (GMD) at the National Oceanic and Atmospheric Administration (NOAA),. Other global GAW stations operated by NOAA/ESRL include Mauna Loa (Hawaii), South Pole (Antarctica) and American Samoa. These Stations are part of the United States contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program.

Previous audits at Barrow: none.

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr Daniel J. Endres	NOAA/ESRL, Primary station contact
Mr Brad Halter	NOAA/ESRL, Station operator (temporary)
Mr Samuel J. Oltmans	NOAA/ESRL, Surface Ozone program
Dr Paul C. Novelli	NOAA/ESRL, Carbon monoxide
Dr Ed Dlugokencky	NOAA/ESRL, Methane
Dr Geoff Dutton	NOAA/ESRL, Nitrous oxide

Our assessment of the Barrow observatory in general, as well as the surface ozone, carbon monoxide, methane and nitrous oxide 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 NOAA/ESRL-GMD, the primary station contact (Mr Daniel J. Endres) and the World Meteorological Organization in Geneva. The report including executive summaries will be posted on the internet.

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

Station Location and Access

Barrow (BRW) Observatory, established in 1973, is located near sea level 8 km east of Barrow, Alaska (71.323°N 156.612°W). This facility is manned year around by 2 engineers/scientists. BRW is located so that it receives minimal influence from anthropogenic effects. It is about 8 km northeast of the village of Barrow and has a prevailing east-northeast wind off the Beaufort Sea. It is attended at least 5 days a week for routine inspection and maintenance of the instrumentation. In addition, the National Weather Service (NWS) maintains a weather observatory in Barrow. Although the measurements at Barrow are made over open tundra, there are large lagoons and a number of lakes in the vicinity, and the Arctic Ocean is less than 3 km northwest of the site. Because of its proximity to these bodies of water and the fact that the prevailing winds are off the Beaufort Sea, BRW is perhaps best characterized as having an Arctic maritime climate affected by variations of weather and sea ice conditions in the Central Arctic (Köppen classification ET – polar tundra). The station is reached over an access road.

Station Facilities

The BRW site consists of several buildings. The main laboratory was built in 1973, and has one room for instrumentation and one workshop / storage room. It has limited office space on the corridor. The station has permanent internet access, although the bandwidth is rather low. It is an

[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.

ideal platform for continuous atmospheric monitoring as well as measurement campaigns. A new station building is planned for the near future.

Recommendation 1 (*, 2010)
WCC-Empa supports the plan to establish a new station building. The current facility is becoming too small for the large number of ongoing measurements and cooperative research programs.

Station Management and Operation

The station is managed by the National Oceanic & Atmospheric Administration, Earth System Laboratory, Global Monitoring Division (NOAA/ESRL-GMD). The station is visited daily from Monday to Friday by the station manger and the station operator. Both permanent positions were vacant after the audit, but could be filled in the mean time with Steve Groove (station manager) and Jason Johns (station operator).

Recommendation 2 (*, 2010)**
Due to the remoteness of the location it may be difficult to find permanent staff for the site. It is important that the knowledge is transferred to new staff. If the positions cannot be filled, alternative scenarios such as half yearly / yearly shifts with sufficient overlap during staff changes have to be considered.

Air Inlet System

Each analytical system has its own air inlet. The system is functional but it should be considered to renew the whole inlet systems when the new laboratory building is planned. In addition, stainless steel parts on one of the surface ozone inlet lines need to be replaced by PTFE or PFA parts.

Recommendation 3 (, 2010)**
The inlet systems should be upgraded when the new station building will be established.

Recommendation 4 (*, 2010)**
Stainless steel parts in the inlet line of the TEI 49i ozone instrument need to be replaced by PTFE or PFA parts.

Surface Ozone Measurements

Instrumentation. Two ozone analyzers (TEI 49i and TEI 49C) are currently used at the station for continuous surface ozone measurements. The instrumentation is adequate for its intended purpose.

Standards. No ozone standard is available at the site. Instruments are usually only calibrated before installation at the site. In case the two analyzers show diverging results, further action is taken.

Recommendation 5 (, ongoing)**
It should be considered to do yearly calibrations / inter-comparisons with a reference instrument at the site. The reference instrument could be shipped to the site, and the inter-comparison be made by the station operator.

Intercomparison (Performance Audit). The inter-comparisons of the two station instruments TEI 49C and TEI 49i station ozone analyzers extended over a period of 15-20 hours. The results are summarised below and the following equations characterises the instrument bias:

TEI 49C #75572-380: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.17 ppb) / 1.002 (1a)

TEI 49i # 629719159: 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.15 ppb) / 1.012 (1b)

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

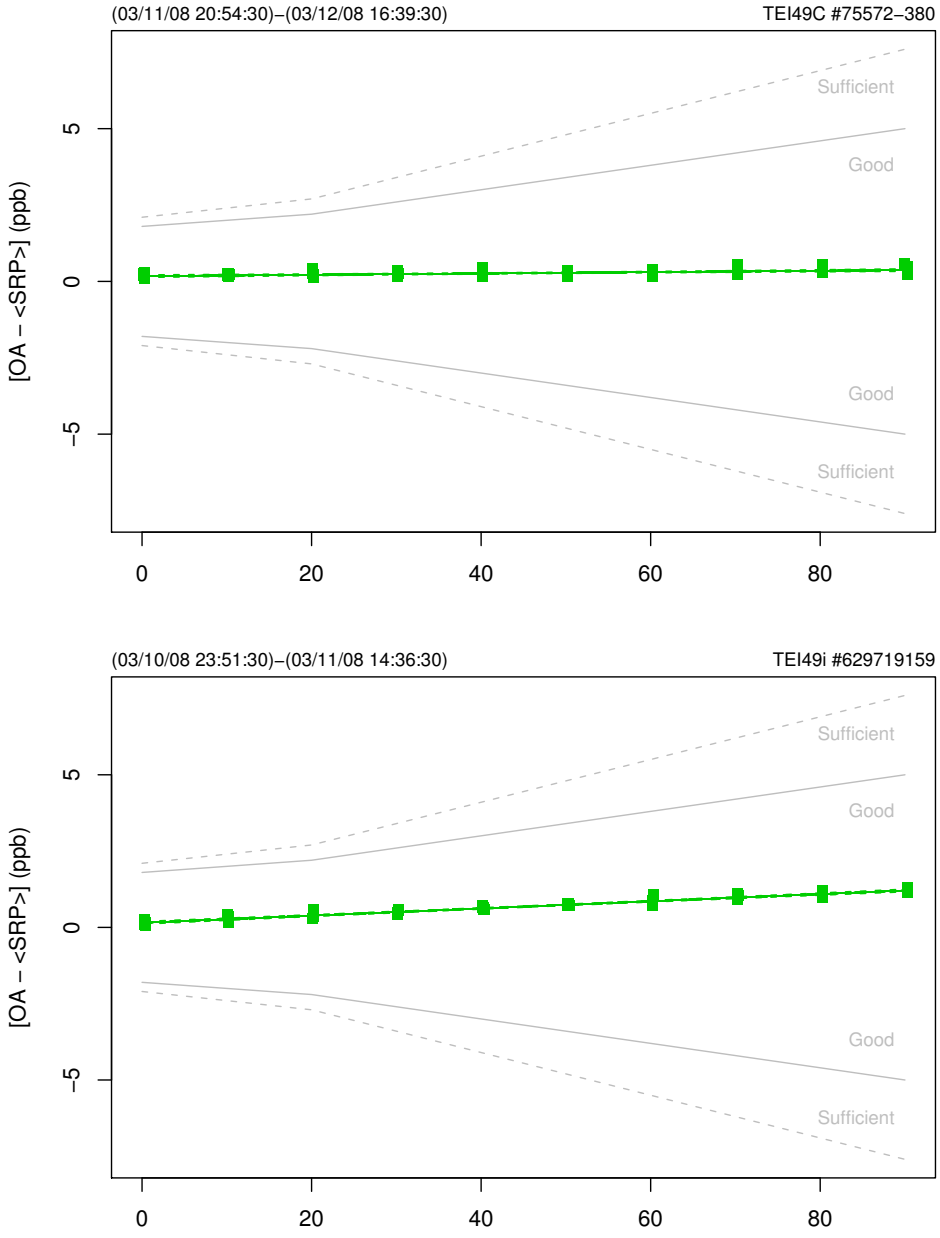

Figure 1. Bias of the Barrow ozone analyzers TEI 49C (upper panel) and TEI 49i (lower panel) with respect to the SRP as a function of mixing ratio. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment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

Carbon Monoxide Measurements

Instrumentation. Barrow is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2. The GC system was built in analogy to the system installed at Mauna Loa [*Zellweger, et al.*, 2003]. The instrumentation is adequate for the intended purpose and shows a good reproducibility for multiple injections of a gas sample.

Standards. The station is equipped with three laboratory standards, which span the mixing ratio range between 58 and 220 ppb. All standards have been certified by NOAA/ESRL based on the WMO-2000 carbon monoxide calibration scale.

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

RGA-3 S/N 070188-008:

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 1.5 ppb) / 1.005 (2)

The results show that the measurements of the Barrow instrument are fully comparable to WCC-Empa. No significant differences were found between WCC-Empa and BRW.

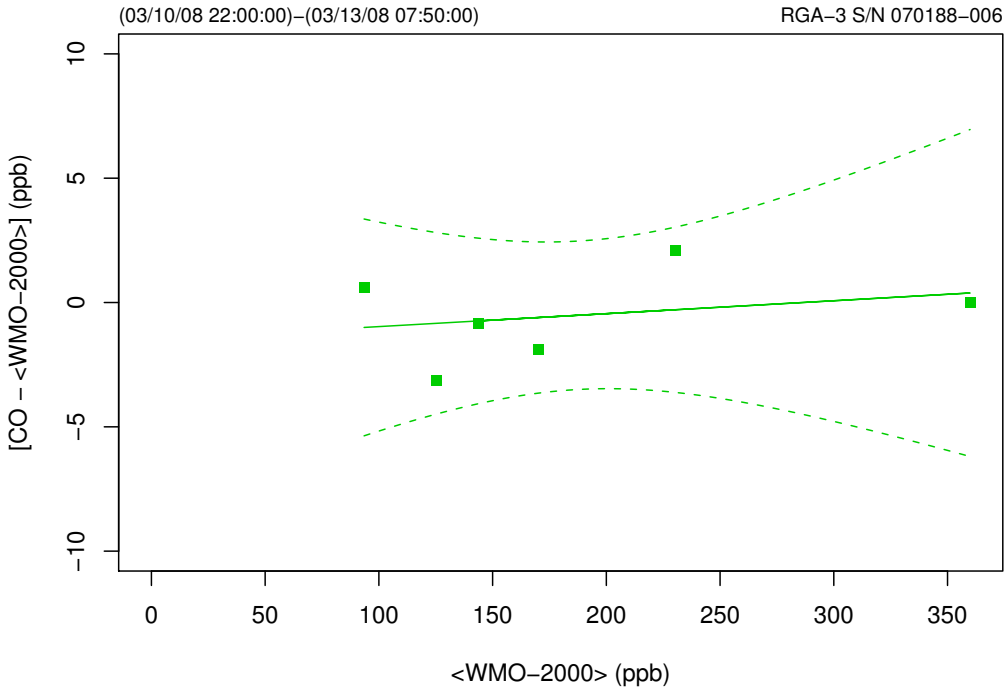

Figure 2. Bias of the Barrow carbon monoxide instrument (RGA-3) with respect to the WMO-2000 reference scale as a function of mixing ratio. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence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

Methane Measurements

Instrumentation. A HP 6890 gas chromatograph with an FID detector is used for ambient methane measurements at Barrow.

Standards. The station is equipped with one laboratory standard with a mixing ratio of the current cylinder of 1832.84 ppb. The standard has been certified by NOAA/ESRL based on the NOAA04 methane calibration scale.

Intercomparison (Performance Audit). The inter-comparison involved repeated measurements of WCC-Empa traveling standards with the BRW instrument. No significant deviations between the Barrow instrument and WCC-Empa were found. The following equation characterises the instrument bias (cf. Figure 3):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 0.99997 (3)

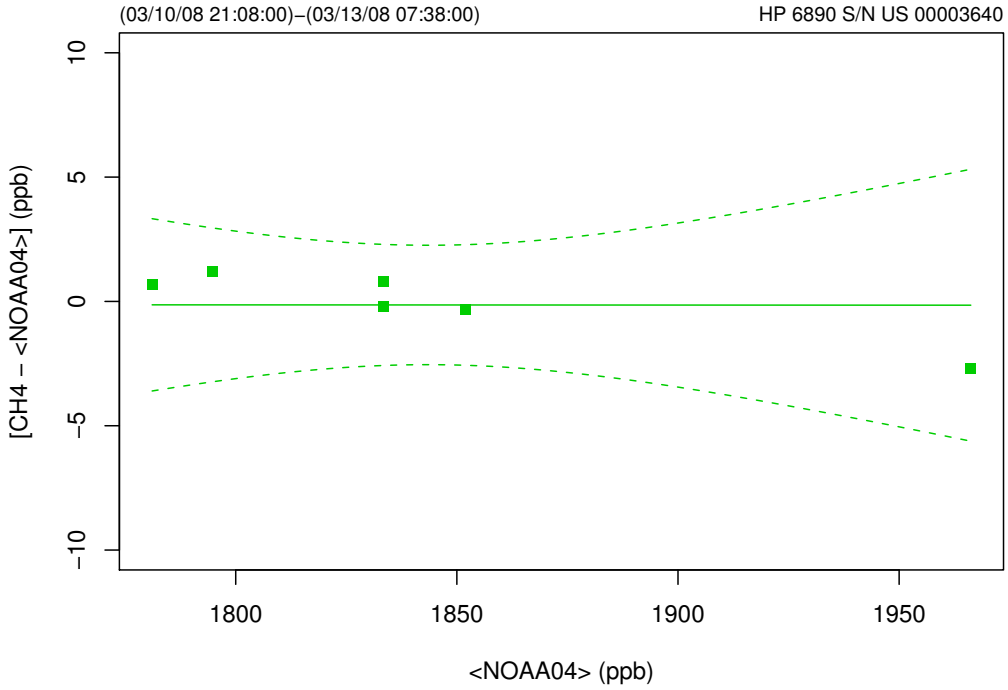

Figure 3. Bias of the Barrow methane GC with respect to the NOAA04 reference scale as a function of mixing ratio. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Nitrous Oxide Measurements

Instrumentation. A custom built 4-channel GC system (Chromatograph for Atmospheric Trace Species – CATS) is used for the detection of nitrous oxide and a number of other trace species. Details are available from the Halocarbons & other Atmospheric Trace Species (HATS) website (www.esrl.noaa.gov/gmd/hats).

Standards. The station is equipped with a number of laboratory standards that cover the relevant mixing ratio range. All standards have been certified by NOAA/ESRL based on the NOAA-2006 N_2O scale calibration scale.

Intercomparison (Performance Audit). At the time of the audit WCC-Empa had only one traveling standard. This standard was initially calibrated by Eckhart Scheel from the WCC-N_2O at IMK-IFU and was assigned a value of 315.86 ± 0.30 ppb (NOAA-2000 N_2O scale), which translates into 315.73 ± 0.30 ppb on the NOAA-2006 scale. This traveling standard was analyzed by the BRW instrument during the audit. Based on the NOAA-2006 N_2O scale a value of 315.74

± 0.30 ppb (1σ) (11 injections) was obtained, which is in perfect agreement with the value assigned by the WCC- N_2O.

Data Acquisition and Management

Ozone: The TEI iPort Software is used to manually download data of both instruments.

CO and CH_4 GC: The data acquisition consists of a workstation and a GC control software package developed at NOAA/ESRL. All chromatograms are stored and automatically transferred via internet to the main database at NOAA. Peak integration is carried out both for area and height but peak area is used for the final data set.

N_2O GC: A custom built system remote control and near real time data access is available. More details of the system are available on the HATS website (www.esrl.noaa.gov/gmd/hats).

Recommendation 6 (*, 2010)
It should be considered to use a dedicated data acquisition system for the ozone instruments, preferably with remote access.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone (1973 – 2005), methane (1986 – 2008) and nitrous oxide (1993 – 2009) have been submitted by NOAA/GMD. All data are reported in UTC. No in-situ CO data have been submitted.

Recommendation 7 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year.

Recommendation 8 (*, ongoing)**
In-situ CO data needs to be submitted to WDCGG.

Conclusions

The Global GAW station Barrow carries out a comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the BRW station an important contribution to the GAW program. All assessed measurements were of high quality.

Summary Ranking of Barrow Station

System Audit Aspect	Adequacy[#]	Comment
Access	(5)	Year-round access possible
Facilities		
Laboratory and office space	(3)	Becoming old / small
Air Conditioning	(3)	Only heating is necessary
Power supply	(5)	
Internet access	(4)	Low bandwidth
General Management and Operation		
Organisation	(5)	
Competence of staff	(5)	
Air Inlet System	(4)	Each system uses own inlet, steel parts in ozone sample line
Instrumentation		
Ozone	(5)	TEI49i and TEI49C
Carbon monoxide	(4)	RGA-3
Methane	(5)	HP 6890
Nitrous Oxide	(5)	Custom built CATS GC
Other gases*	(5)	CO_2, SF_6, CFCs, HCFCs
Aerosol parameters*	(5)	Comprehensive program
Flask sampling	(5)	NOAA / SIO / Univ. of California
Meteo	(5)	
Standards		
Ozone	(1)	Not available, but two analyzers
Carbon monoxide	(5)	
Methane	(5)	
Nitrous Oxide	(5)	
Data Management		
Data acquisition	(4)	O_3 (3), others (5)
Data processing	(5)	
Data submission	(3)	CO in-situ data not submitted yet

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

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Dübendorf, January 2010

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

APPENDIX

Global GAW Station Barrow

Site description

BRW is located near sea level 8 km east of Barrow, Alaska at 71.32 degrees north and receives minimal influence from anthropogenic effects. Further information can be found from the station website (www.esrl.noaa.gov/gmd/obop/brw) and GAWSIS (www.empa.ch/gaw/gawsis).

Measurement Program

An overview of the measurement program and its status as of March 2008 is shown in Table 1. Refer to GAWSIS or the station web page for more details.

Table 1. Measurement Program at the BRW Station

Parameter*	**Current Instrument**	**Data Coverage (%)#**		
		<12 m	<3 y	Overall
Aerosol				
CCN concentration spectra	Cloud condensation nuclei counter			
Hemispheric backscattering coef.	TSI Nephelometer 3563			
Light absorption coefficient	PSAP, 3-wavelength 467/530/660 nm			
Light scattering coefficient	TSI Nephelometer 3563			
Size distribution	SPMS with range of 13-811 nm			
Total number concentration	Condensation particle counter (CPC)			
Ozone				
Surface ozone	UV absorption (TEI 49i and 49C)			95.1
Total column ozone	Dobson			
Vertical ozone profile	ECC Sonde			
Greenhouse Gas				
CO_2	Li-COR 6251			90.4
CH_4	HP 6890 with FID	81.2	83.3	87.1
N_2O, SF_6, CFCs, HCFCs, CCl4, CH_3Cl, $CHCl_3$, CH_3CCl_3, CH_3Br, COS	CATS GC			83.5 (N_2O)
Reactive Gas				
CO	RGA-3			
Flask Sampling				
VOC, CFCs, HCFs, CO_2, N_2O, CH_4, CO, H_2, SF_6, CO_2 isotopes	NOAA/GMD flask sampling program			
Isotopes				
CO_2 and CH_4 isotopes	Flask Sampling			
Solar radiation				
Global irradiance	Pyranometer (Eppley)			
Direct irradiance	Pyrheliometer (direct broadband)			
IR (direction unspecified)	Pyrgeometer (infrared)			
Meteo				
PTU, wind speed + direction				
Precipitation	Rain gauge			

* Refer to GAWSIS or NOAA/GMD website for more details
# Missing information about data coverage: information was not available, but general high data availabilities (>90%) are expected for most parameters.

Ozone, Carbon Monoxide and Methane Distribution at Barrow

The monthly and yearly distributions of one hourly mean values for surface ozone, carbon monoxide, methane and nitrous oxide are shown in Figure 4.

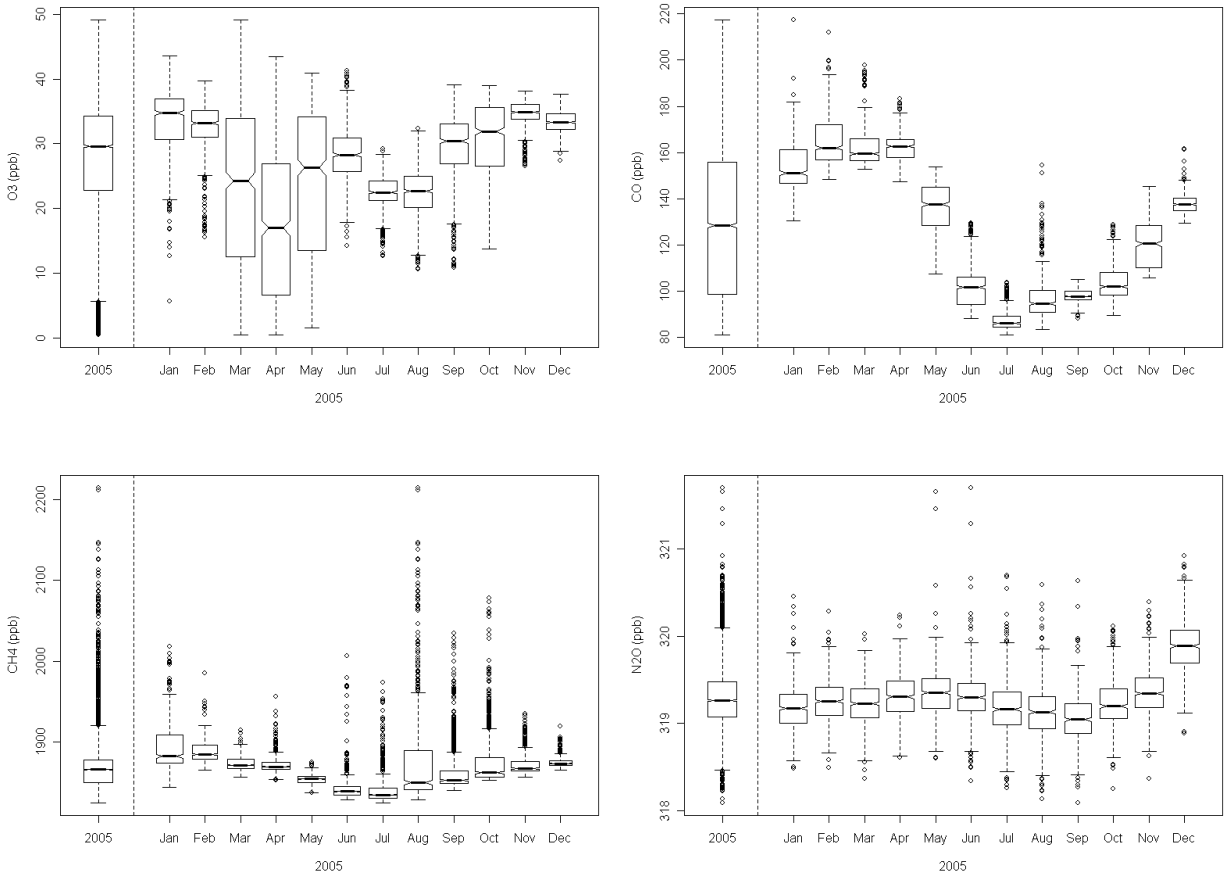

Figure 4. Yearly and monthly box plots of 1-hourly aggregates for surface Ozone, carbon monoxide, methane and nitrous oxide for 2005. The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month. CO data is preliminary.

Organisation and Contact Persons

The GAW activities of the United States are coordinated by the National Oceanic & Atmospheric Administration's (NOAA) Earth System Research Laboratory (ESRL). Most of the GAW relevant activities are under the Global Monitoring Division (GMD). Detailed information including organisational charts and contact persons can be accessed on the NOAA/ERL web site (www.esrl.noaa.gov).

Surface Ozone Measurements

Surface ozone measurements started in March 1973 at the Barrow site, and continuous one-hourly time series are available since then. Two ozone analyzers are running in parallel at the BRW site.

All inter-comparisons were done according to Standard Operating Procedures [*WMO*, in preparation].

Monitoring Set-up and Procedures

Air Conditioning

The BRW station is heated to approximately 20°C. Due to the extreme cold temperatures, no cooling is necessary. However, the temperature inside the laboratory is not very stable and ranges between 10 and 35°C.

Air Inlet System

The two ozone analyzers share a common inlet dedicated for surface ozone measurements. The inlet consists of an unheated stainless steel tube with an inner diameter of approx. 4 cm. The inlet is protected by an upside-down beaker. A blower is used to achieve high flow rates. The flow speed was measured using an Anemometer during the audit (4.3 m/sec). Instruments are connected by individual PTPE sampling lines with a length of approximately 3 meters. The inlet filters are mounted in these lines. The connection of one instrument (TEI 49i) was made using stainless steel parts, whereas the other instrument was connected with Teflon parts (Figure 5). Total residence time in the inlet system is less than 3 seconds.

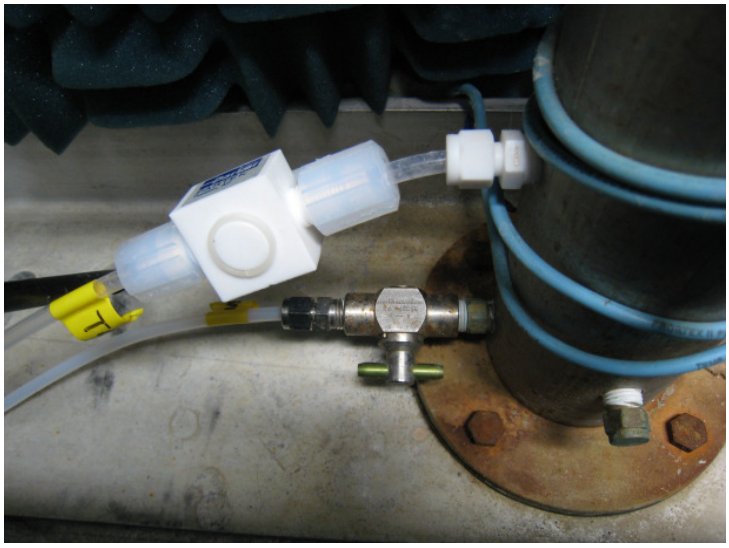

Figure 5. Sampling line connections of the BRW ozone instruments.

Instrumentation

The station is equipped with two ozone analyzers (TEI 49i and TEI 49C). Instrumental details for the ozone analyzers (OA) are summarised in Table 2 below.

Standards

No ozone standard is available at the site, and calibrations were until now only made before installation of a new analyzer.

Operation and Maintenance

The station is visited daily from Monday to Friday, and the instruments are checked for general operation. A zero and span (25 and 50 ppb) check using the internal ozone generator is performed once per week. All other maintenance including inlet filter change is performed only on a case by case basis.

Data Acquisition and Data Transfer

The TEI iPort Software is used for manual data download (weekly). Only five minute and one-hourly averages are saved. The file with the one-hourly averages includes all available instrument parameters. Data is manually transferred to NOAA by e-mail.

Data Treatment

Data validation is carried out at NOAA. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries. All data is re-calculated using the last calibration of the instrument. Currently the following corrections are applied:

TEI 49C: O_3 final [pbb] = 0.46 + 1.018 *(TEI 49C)
TEI 49i: O_3 final [pbb] = 0.50 + 1.019 *(TEI 49i)

These corrections were also applied for the evaluation of the audit results.

Data Submission

At the time of the audit ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (WDCGG) covering the period from 1973 to 2005.

Documentation

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

Inter-Comparison of Ozone Analyzer

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

Setup and Connections

Table 2 details the experimental setup during the inter-comparison of the transfer standard with the station analyzers. The data used for the evaluation was recorded by the WCC-Empa data acquisition system as indicated. Raw data was corrected using the data of the last calibration (see above), which is the usual treatment for all data.

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

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.4; COEFF = 1.002
Main ozone analyzer (OA)	Model, S/N	TEI 49C #75572-380
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.000
Backup ozone analyzer (OA)	Model, S/N	TEI 49i #0629719159
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.000
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm (WCC-Empa)
Connection between instruments		Ca. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS and OA	One minute aggregates from digital output (custom designed LabView program of WCC-Empa)
Pressure readings at beginning of inter-comparison (hPa)	Ambient	1018.2 (Station reference)
	TS	1017.1, adjusted to 1018.2
	TEI 49C	no adjustments were made
	TEI 49i	no adjustments were made
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90
Duration per level (min)		15
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		TEI 49i: 6 runs (10 thru 11 March, 2008) TEI 49C: 8 runs (11 thru 12 March, 2008)

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. The results are shown in Table 3 (TEI 49C) and Table 4 (TEI 49i). These aggregates were used in the assessment of the inter-comparison as described elsewhere [Klausen, et al., 2003]. All results refer to the calibration factors as given in Table 2 above and were corrected using the formulas described under “data treatment”. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyzer (OA) values.

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the BRW ozone analyzer (OA) TEI 49C #75572-380 with the WCC-Empa transfer standard (TS).

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-03-11 21:00	1	0	0.12	0.43	0	0.11	0.02
2008-03-11 21:15	1	30	29.96	30.40	0	0.09	0.04
2008-03-11 21:30	1	60	59.91	60.54	0	0.06	0.02
2008-03-11 21:45	1	40	39.93	40.62	0	0.07	0.03
2008-03-11 22:00	1	90	89.96	90.70	0	0.07	0.03
2008-03-11 22:15	1	50	49.98	50.53	0	0.09	0.06
2008-03-11 22:30	1	10	10.19	10.56	0	0.15	0.04
2008-03-11 22:45	1	20	19.97	20.51	0	0.11	0.03
2008-03-11 23:00	1	80	79.96	80.64	0	0.05	0.02
2008-03-11 23:15	1	70	69.93	70.77	0	0.10	0.03
2008-03-11 23:30	2	0	0.22	0.43	0	0.09	0.03
2008-03-11 23:45	2	40	39.93	40.56	0	0.10	0.03
2008-03-12 00:00	2	70	69.98	70.57	0	0.05	0.04
2008-03-12 00:15	2	30	29.95	30.49	0	0.12	0.06
2008-03-12 00:30	2	90	89.94	90.61	0	0.05	0.05
2008-03-12 00:45	2	20	19.92	20.50	0	0.23	0.05
2008-03-12 01:00	2	10	9.98	10.37	0	0.12	0.03
2008-03-12 01:15	2	60	59.96	60.58	0	0.07	0.06
2008-03-12 01:30	2	50	49.93	50.53	0	0.08	0.05
2008-03-12 01:45	2	80	79.90	80.79	0	0.04	0.05
2008-03-12 02:00	3	0	0.10	0.48	0	0.11	0.03
2008-03-12 02:15	3	90	89.90	90.73	0	0.11	0.05
2008-03-12 02:30	3	70	69.96	70.62	0	0.11	0.07
2008-03-12 02:45	3	40	39.99	40.52	0	0.07	0.04
2008-03-12 03:00	3	50	49.99	50.55	0	0.07	0.04
2008-03-12 03:15	3	20	20.04	20.35	0	0.07	0.03
2008-03-12 03:30	3	30	30.02	30.45	0	0.10	0.06
2008-03-12 03:45	3	60	59.95	60.55	0	0.07	0.06
2008-03-12 04:00	3	10	10.03	10.35	0	0.12	0.04
2008-03-12 04:15	3	80	79.93	80.68	0	0.04	0.04
2008-03-12 04:30	4	0	0.18	0.40	0	0.08	0.03
2008-03-12 04:45	4	30	29.97	30.35	0	0.07	0.03
2008-03-12 05:00	4	60	59.91	60.48	0	0.12	0.05
2008-03-12 05:15	4	40	39.97	40.42	0	0.07	0.03
2008-03-12 05:30	4	90	89.90	90.55	0	0.08	0.03
2008-03-12 05:45	4	50	49.99	50.42	0	0.05	0.05
2008-03-12 06:00	4	10	10.04	10.42	0	0.09	0.03
2008-03-12 06:15	4	20	20.06	20.46	0	0.14	0.05
2008-03-12 06:30	4	80	79.90	80.58	0	0.07	0.04
2008-03-12 06:45	4	70	69.97	70.54	0	0.08	0.06
2008-03-12 07:00	5	0	0.16	0.44	0	0.08	0.04
2008-03-12 07:15	5	40	39.95	40.50	0	0.09	0.04
2008-03-12 07:30	5	70	69.93	70.45	0	0.06	0.04
2008-03-12 07:45	5	30	29.98	30.37	0	0.08	0.02
2008-03-12 08:00	5	90	89.92	90.48	0	0.06	0.04
2008-03-12 08:15	5	20	20.02	20.33	0	0.06	0.04
2008-03-12 08:30	5	10	10.05	10.44	0	0.12	0.03
2008-03-12 08:45	5	60	59.94	60.53	0	0.06	0.03
2008-03-12 09:00	5	50	49.97	50.47	0	0.06	0.04
2008-03-12 09:15	5	80	79.91	80.59	0	0.05	0.05

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-03-12 09:30	6	0	0.13	0.53	0	0.09	0.04
2008-03-12 09:45	6	90	89.89	90.71	0	0.08	0.05
2008-03-12 10:00	6	70	69.95	70.52	0	0.10	0.07
2008-03-12 10:15	6	40	40.00	40.40	0	0.07	0.04
2008-03-12 10:30	6	50	49.95	50.44	0	0.07	0.06
2008-03-12 10:45	6	20	20.07	20.38	0	0.12	0.04
2008-03-12 11:00	6	30	29.99	30.35	0	0.07	0.04
2008-03-12 11:15	6	60	59.96	60.46	0	0.10	0.06
2008-03-12 11:30	6	10	10.07	10.36	0	0.11	0.05
2008-03-12 11:45	6	80	79.90	80.50	0	0.07	0.04
2008-03-12 12:00	7	0	0.18	0.43	0	0.06	0.02
2008-03-12 12:15	7	30	29.97	30.40	0	0.11	0.05
2008-03-12 12:30	7	60	59.93	60.37	0	0.06	0.04
2008-03-12 12:45	7	40	39.97	40.41	0	0.08	0.05
2008-03-12 13:00	7	90	89.90	90.64	0	0.07	0.05
2008-03-12 13:15	7	50	49.97	50.49	0	0.07	0.04
2008-03-12 13:30	7	10	10.07	10.37	0	0.10	0.03
2008-03-12 13:45	7	20	19.92	20.33	0	0.10	0.04
2008-03-12 14:00	7	80	79.92	80.55	0	0.07	0.03
2008-03-12 14:15	7	70	69.93	70.52	0	0.06	0.04
2008-03-12 14:30	8	0	0.10	0.48	0	0.25	0.03
2008-03-12 14:45	8	40	39.94	40.42	0	0.04	0.03
2008-03-12 15:00	8	70	69.93	70.56	0	0.05	0.04
2008-03-12 15:15	8	30	30.00	30.50	0	0.07	0.03
2008-03-12 15:30	8	90	89.59	90.54	0	0.95	0.04
2008-03-12 15:45	8	20	20.03	20.39	0	0.08	0.04
2008-03-12 16:00	8	10	9.94	10.27	0	0.12	0.04
2008-03-12 16:15	8	60	59.92	60.58	0	0.07	0.04
2008-03-12 16:30	8	50	49.95	50.36	0	0.08	0.07
2008-03-12 16:45	8	80	79.90	80.51	0	0.05	0.04

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

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the inter-comparison of the BRW back-up ozone analyzer (OA) TEI 49i #0629719159 with the WCC-Empa transfer standard (TS).

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-03-10 23:56	1	0	0.22	0.60	0	0.07	0.04
2008-03-11 00:11	1	30	30.08	30.82	0	0.07	0.04
2008-03-11 00:26	1	60	60.03	61.37	0	0.06	0.04
2008-03-11 00:41	1	40	40.15	40.95	0	0.07	0.04
2008-03-11 00:56	1	90	90.00	91.58	0	0.07	0.04
2008-03-11 01:11	1	50	50.13	51.11	0	0.05	0.04
2008-03-11 01:26	1	10	9.94	10.49	0	0.16	0.05
2008-03-11 01:41	1	20	20.10	20.87	0	0.12	0.04
2008-03-11 01:56	1	80	79.99	81.29	0	0.07	0.05
2008-03-11 02:11	1	70	70.00	71.26	0	0.09	0.06
2008-03-11 02:26	2	0	0.23	0.53	0	0.10	0.03
2008-03-11 02:41	2	40	40.03	40.91	0	0.07	0.04
2008-03-11 02:56	2	70	70.01	71.34	0	0.10	0.03
2008-03-11 03:11	2	30	30.05	30.82	0	0.07	0.02
2008-03-11 03:26	2	90	89.99	91.55	0	0.04	0.05
2008-03-11 03:41	2	20	20.04	20.62	0	0.11	0.04
2008-03-11 03:56	2	10	10.12	10.63	0	0.09	0.02

DateTime (UTC)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2008-03-11 04:11	2	60	59.99	61.14	0	0.10	0.03
2008-03-11 04:26	2	50	49.99	51.01	0	0.10	0.04
2008-03-11 04:41	2	80	79.95	81.47	0	0.10	0.03
2008-03-11 04:56	3	0	0.28	0.57	0	0.09	0.03
2008-03-11 05:11	3	90	89.91	91.57	0	0.08	0.05
2008-03-11 05:26	3	70	69.96	71.17	0	0.09	0.04
2008-03-11 05:41	3	40	40.05	40.90	0	0.08	0.04
2008-03-11 05:56	3	50	50.01	51.03	0	0.10	0.05
2008-03-11 06:11	3	20	20.01	20.63	0	0.10	0.04
2008-03-11 06:26	3	30	30.03	30.80	0	0.08	0.04
2008-03-11 06:41	3	60	59.96	60.99	0	0.07	0.03
2008-03-11 06:56	3	10	10.10	10.39	0	0.11	0.03
2008-03-11 07:11	3	80	79.93	81.35	0	0.06	0.03
2008-03-11 07:26	4	0	0.29	0.48	0	0.09	0.04
2008-03-11 07:41	4	30	29.98	30.65	0	0.07	0.04
2008-03-11 07:56	4	60	59.98	61.05	0	0.09	0.04
2008-03-11 08:11	4	40	39.98	40.93	0	0.09	0.05
2008-03-11 08:26	4	90	89.93	91.46	0	0.05	0.03
2008-03-11 08:41	4	50	49.99	50.96	0	0.05	0.04
2008-03-11 08:56	4	10	10.05	10.37	0	0.09	0.04
2008-03-11 09:11	4	20	19.98	20.44	0	0.14	0.05
2008-03-11 09:26	4	80	79.92	81.34	0	0.06	0.04
2008-03-11 09:41	4	70	69.94	71.35	0	0.08	0.03
2008-03-11 09:56	5	0	0.23	0.45	0	0.07	0.04
2008-03-11 10:11	5	40	39.98	40.84	0	0.08	0.04
2008-03-11 10:26	5	70	69.91	71.21	0	0.09	0.04
2008-03-11 10:41	5	30	30.00	30.61	0	0.08	0.05
2008-03-11 10:56	5	90	89.92	91.42	0	0.05	0.05
2008-03-11 11:11	5	20	20.05	20.57	0	0.07	0.06
2008-03-11 11:26	5	10	10.02	10.41	0	0.11	0.03
2008-03-11 11:41	5	60	59.97	60.97	0	0.09	0.05
2008-03-11 11:56	5	50	49.99	50.94	0	0.04	0.04
2008-03-11 12:11	5	80	79.93	81.41	0	0.04	0.05
2008-03-11 12:26	6	0	0.25	0.49	0	0.06	0.03
2008-03-11 12:41	6	90	89.91	91.42	0	0.07	0.06
2008-03-11 12:56	6	70	69.97	71.20	0	0.05	0.03
2008-03-11 13:11	6	40	40.03	40.84	0	0.09	0.04
2008-03-11 13:26	6	50	50.00	50.98	0	0.05	0.04
2008-03-11 13:41	6	20	20.02	20.55	0	0.09	0.03
2008-03-11 13:56	6	30	29.99	30.65	0	0.05	0.03
2008-03-11 14:11	6	60	59.96	61.06	0	0.06	0.04
2008-03-11 14:26	6	10	10.01	10.29	0	0.08	0.04
2008-03-11 14:41	6	80	79.90	81.37	0	0.07	0.06

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

Figure 6 and Figure 7 show the regression residuals of the ozone analyzers with respect to the SRP as a function of ozone mixing ratio for the range 0 – 90 ppb and as a function of time.

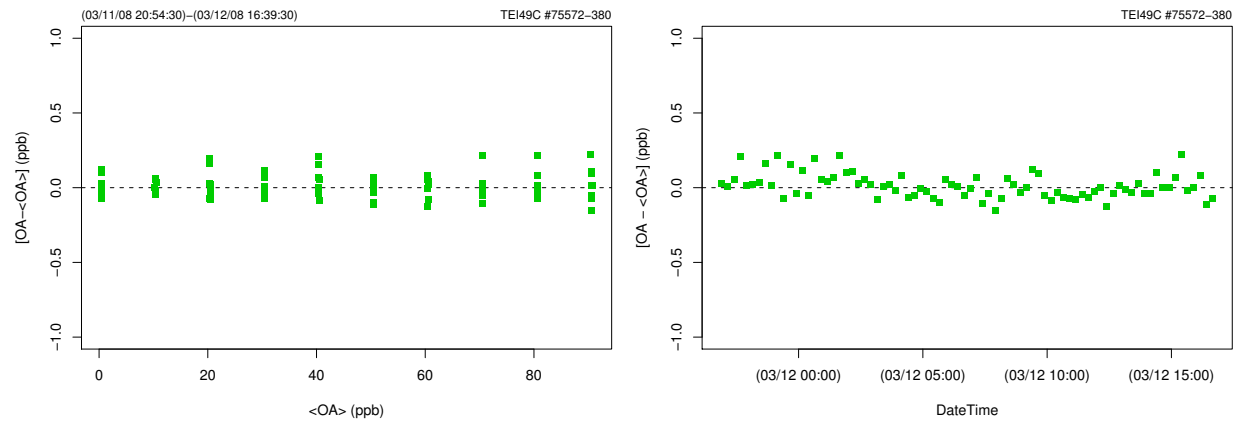

Figure 6. Regression residuals of the BRW ozone analyzer (TEI 49C) as a function of mixing ratio (left panel) and time (right panel).

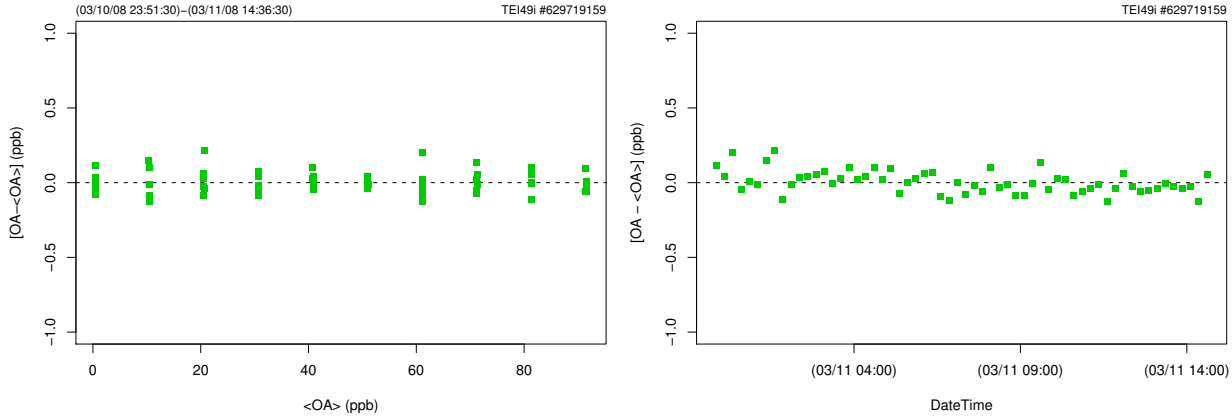

Figure 7. Regression residuals of the BRW ozone analyzer (TEI 49i) as a function of mixing ratio (left panel) and time (right panel).

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

TEI 49C #75572-380:

$$X_{O3}\ (\text{ppb}) = ([OA] - 0.17\ \text{ppb}) / 1.002$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.28\ \text{ppb}^2 + 2.59\text{e-}05 * X_{O3}^2) \quad (1a)$$

TEI 49i # 629719159:

$$X_{O3}\ (\text{ppb}) = ([OA] - 0.15\ \text{ppb}) / 1.012$$

$$u_{O3}\ (\text{ppb}) = \text{sqrt}\ (0.27\ \text{ppb}^2 + 2.54\text{e-}05 * X_{O3}^2) \quad (1b)$$

Conclusions

The findings of this audit demonstrate good agreement between BRW main ozone analyzer and WCC-Empa. Slightly higher readings but still good agreement was observed with the BRW backup analyzer. A few mainly technical recommendations were made by WCC-Empa addressing mainly inlet material and calibration frequency issues (cf. Executive Summary).

Carbon Monoxide Measurements

Carbon monoxide measurements started in February 1993 at Barrow, and a complete time series is available since then. The audit comprised inter-comparison of six traveling standards covering the mixing ratio range from approx. 90 to 360 ppb carbon monoxide in air. These traveling standards were also analyzed at the central calibration laboratory at NOAA after the audit. All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

The air inlet system for carbon monoxide is located on top of the tower at a height of 15 m above ground. The following tubing is used:

- ca 50 m long Dekabon tube (outer diameter ⅓ inch) - pump and overflow (4 l/min)
- 1/16'' SS tubing, length approx. 5 m. Flow rate ca. 100 ml/min to stream selection valve.
- Cold trap -57°C

The overall residence time is estimated to be approximately 30 seconds. The inlet system is adequate for analyzing CO and CH_4 concerning materials and residence time.

Instrumentation

Barrow is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2. The GC system was built in analogy to the system installed at Mauna Loa [*Zellweger, et al.*, 2003].

Standards and Calibration

The carbon monoxide instrument is calibrated using three working standard (natural air). These working standards have been calibrated at NOAA before use at the site on the WMO-2000 carbon monoxide scale. Table 5 gives details of the cylinders currently available at the station.

Injections are made every 5 minutes. All tree working standards are injected followed by one sample injection. The working standard injections are used to calculate the ambient data.

Table 5. Carbon monoxide working standards available at the BRW station (WMO-2000 carbon monoxide scale)

Manufacturer, S/N, Use	CO Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
NOAA/ESRL CA05692 (WS)	61.0 ppb CO	2006	NOAA/ESRL	06-12-01	07-12-18
NOAA/ESRL CA01794 (WS)	178.7 ppb CO	2006	NOAA/ESRL	06-12-19	08-02-26
NOAA/ESRL CA07001 (WS)	120.7 ppb CO	2007	NOAA/ESRL	07-06-14	present
NOAA/ESRL CA07522 (WS)	58.0 ppb CO	2006	NOAA/ESRL	07-12-18	present
NOAA/ESRL CA07522 (WS)	220.3 ppb CO	2006	NOAA/ESRL	08-02-26	present

Operation and Maintenance

The system is checked for general operation each working day. Remote access is possible, and instrument parameters and chromatograms are frequently checked. All working standards are re-calibrated against the WMO-2000 carbon monoxide scale at NOAA after deployment. The cooling trap is changed in weekly intervals.

Data Acquisition and Data Transfer

The data acquisition consists of a workstation and a GC control software package developed at NOAA/ESRL. All chromatograms are stored and automatically transferred to the main database at NOAA. Peak integration is carried out both for area and height but peak area is used for the final data set.

Data Treatment

The station operator plots the data and examines the chromatograms. Comments and notes are made in electronic log files. The final data evaluation is done at NOAA and includes again plausibility checks and the application of the appropriate calibration factors based on the working standard results. One hourly and daily averages are calculated for the final data set.

Data Submission

Data of the in-situ carbon monoxide measurements have not yet been submitted to the GAW World Data Centre for Carbon Monoxide at JMA (World Data Centre for Greenhouse Gases, WDCGG). To date only flask CO data is available from WDCGG.

Documentation

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

Inter-Comparison of the Carbon Monoxide Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included inter-comparisons of the traveling standards at Empa before and after the inter-comparison of the analyzer. Details of the traceability of the traveling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 6 below.

Setup and Connections

The RGA-3 instrument was inter-compared by direct measurements of traveling standards. Details of this experiment are shown in Table 6. The data used for the evaluation was recorded by the BRW data acquisition system.

Results

The GC system was inter-compared using WCC-Empa traveling standards. Each level was injected between 9 and 54 times. This resulted in a maximum of 54 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 7).

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

Traveling standard (TS)		WCC-Empa Traveling standards (6 l aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 070927_FA02482 / 93.48 / 1.03 2 / 070808_FA02686 / 125.41 / 1.47 3 / 050415_FA02476 / 143.59 / 0.72 4 / 050701_FA02464 / 170.34 / 0.82 5 / 070807_FA02785 / 230.43 / 0.98 6 / 050701_FA02505 / 359.85 / 1.41
Field instrument	Model, S/N	RGA-3, S/N 070188-006
	Principle	GC with HgO Reduction Detector Pre-column: Unibeads 60/80, 18", 1/8" o.d. Analytical column: Mole sieve 5Å, 24"t, 1/8" o.d. Carrier: N_2 4.5 Column temp. 105°C, Detector temp. 265°C Sample loop 3 ml Sample air dried to dew point -57°C
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Duration per level (min)		Injections every 20 min; total 9-54 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (10-13 March, 2008)

Table 7. CO aggregates computed from single injections for each level and repetition during the inter-comparison of the BRW GC with WCC-Empa traveling standards (TS).

Date	**TS Identification**	**TS (ppb)**	**sdTS (ppb)**	**BRW CO (ppb)**	**sdCO (ppb)**	**No. of inj.**
(03/10/08 22:00:00)	070927_FA02482	93.48	1.03	94.09	0.32	9
(03/11/08 08:10:00)	070808_FA02686	125.41	1.47	122.25	0.40	50
(03/11/08 20:20:00)	050701_FA02464	170.34	0.82	168.43	0.37	21
(03/12/08 08:20:00)	050701_FA02505	359.85	1.41	359.91	1.26	51
(03/12/08 19:50:00)	050415_FA02476	143.59	0.72	142.77	0.73	18
(03/13/08 07:50:00)	070807_FA02785	230.43	0.98	232.51	4.40	54

Figure 8 shows the regression residuals of the RGA-3 instrument plotted against time and mole fraction. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of mixing ratio dependence (right panel) in the residuals indicates linearity of the instrument.

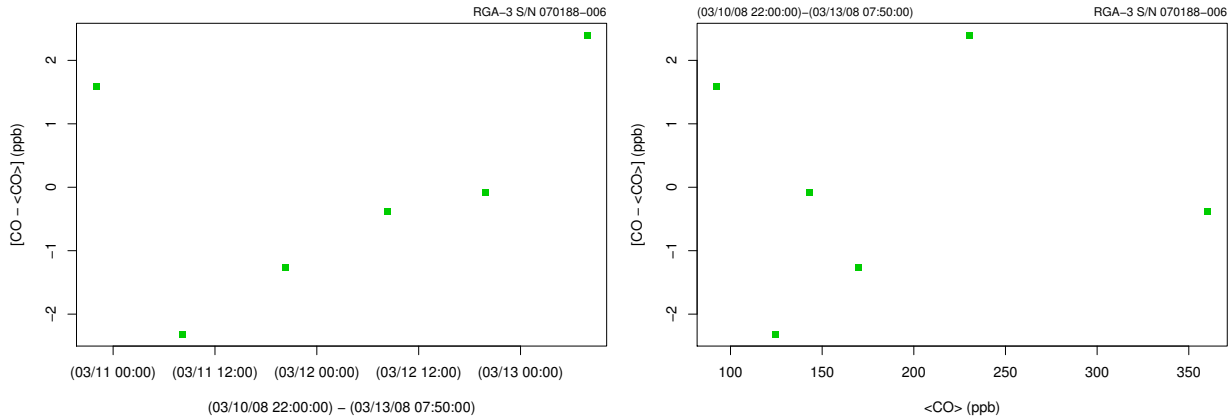

Figure 8. Regression residuals of the BRW RGA-3 based on the inter-comparison with traveling standards. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

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

$$X_{CO}\ (\text{ppb}) = ([CO] + 1.5\ \text{ppb}) / 1.005$$

$$u_{CO}\ (\text{ppb}) = \text{sqrt}\ (4.2\ \text{ppb}^2 + 5.91\text{e-}05 * X_{CO}^2) \qquad (2)$$

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

Changes made to the instrument

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

Analysis of the WCC-Empa CO traveling standards at NOAA

The WCC-Empa CO traveling standards were also analyzed on the Vacuum UV Fluorescence analyzer (Aerolaser 5001) at NOAA/ESRL after the audit at BRW. The analysis was carried out against the WMO-2000 carbon monoxide reference scale of NOAA. The results are shown in Table 8.

Table 8. Inter-comparison of the WCC-Empa traveling standards at NOAA/ESRL. Each cylinder was measured 8 times for 2 minutes on the NOAA Aerolaser system.

TS Identification	TS (ppb)	sdTS (ppb)	NOAA CO (ppb)	sdCO (ppb)
070927_FA02482	93.48	1.03	93.2	0.2
070808_FA02686	125.41	1.47	124.2	0.2
050415_FA02476	143.59	0.72	142.0	0.3
050701_FA02464	170.34	0.82	168.7	0.4
070807_FA02785	230.43	0.98	229.2	0.4
050701_FA02505	359.85	1.41	357.2	0.5

The NOAA/ESRL results were on average 0.77% lower compared to WCC-Empa, with no significant mixing ratio dependency. This result is in line with other inter-comparisons between WCC-Empa and NOAA/ESRL.

Conclusions

Good agreement was found between WCC-Empa traveling standards and the Barrow CO instrument. Some of the WCC-Empa traveling standards contained high H_2 mixing ratios, which complicated the analysis with the BRW analytical system.

Methane Measurements

Methane measurements started at BRW in January 1986, and a complete time series is available since then.

All inter-comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

The same air inlet system as for carbon monoxide is used for methane measurements. The overall residence time is estimated to be approximately 30 seconds. The inlet system is adequate for analyzing CO and CH_4 concerning materials and residence time.

Instrumentation

Barrow is equipped with a HP 6890 gas chromatograph with an FID detector for ambient methane. Instrument details are summarised in Table 10. The GC system was built in analogy to the system installed at Mauna Loa [*Zellweger, et al.*, 2003].

Standards and Calibration

The BRW methane scale is directly linked to the CCL at NOAA. Table 9 shows details of the cylinders currently available at the station.

Calibration of the instrument is performed using the working standard. Injections are made every 7.5 minutes, alternating between sample and standard. Peak height is used for data evaluation.

Table 9. Methane working standards (WS) available at Barrow (NOAA-04 methane scale)

Manufacturer, S/N, Use	CH_4 Content (ppb)	Calibration		In service	
		Date	By	From	To
NOAA/ESRL ALM-024310 (WS)	1826.53 ppb CH_4	2006	NOAA/ESRL	06-12-11	08-02-28
NOAA/ESRL CC64031 (WS)	1832.84 ppb CH_4	2007	NOAA/ESRL	08-02-28	cont.

Operation and Maintenance

Same as for carbon monoxide.

Data Acquisition and Data Transfer

Same as for carbon monoxide, but peak height is used for final data evaluation.

Data Treatment

Same as for carbon monoxide.

Data Submission

Data of the in-situ methane measurements have been submitted to the GAW World Data Centre for Methane at JMA (World Data Centre for Greenhouse Gases, WDCGG). Currently the complete time series covering the period from 1986 to 2007 is available at WDCGG.

Documentation

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

Inter-Comparison of Methane Analyzers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included inter-comparisons of the traveling standards at Empa before and after the inter-comparison of the analyzer. Details of the traceability of the traveling standard to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 10 below.

Setup and Connections

Table 10 shows details of the experimental setup during the inter-comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the BRW data acquisition system, and no further corrections were applied.

Table 10. Experimental details of the methane inter-comparison.

Traveling standard (TS)		WCC-Empa Traveling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 070808_FA02686 / 1781.1 / 0.8 2 / 070927_FA02482 / 1794.8 / 1.3 3 / 050701_FA02505 / 1833.4 / 1.1 4 / 05070_FA02464 / 1832.9 / 1.0 5 / 070807_FA02785 / 1850.0 / 1.5 6 / 050415_FA02476 / 1966.2 / 0.7
Field instrument	Model, S/N	HP 6890, S/N US00003640
Connection of TS to field instrument		TS were connected to the sample selection valve of the BRW system
Data Acquisition		Station data acquisition
Number of injections		Injections every 15 min; total 10-36 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (10 thru 13 March, 2008)

Results

Each TS was injected between 10 to 36 times, which resulted in a maximum of 36 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 11).

Table 11. CH_4 aggregates computed from single injections (mean and standard uncertainty of mean) for each level during the inter-comparison of the BRW methane analyzer with the WCC-Empa traveling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	CH_4 (ppb)	uCH_4 (ppb)	No. of inj.
2008-03-10 21:08	1781.1	0.8	1781.8	0.7	10
2008-03-10 08:08	1794.8	1.3	1796.0	0.7	34
2008-03-11 20:08	1833.4	1.1	1834.2	0.8	14
2008-03-12 08:23	1832.9	1.0	1833.2	0.7	33
2008-03-12 19:53	1852.0	1.5	1851.7	0.5	11
2008-03-13 07:38	1966.2	0.7	1963.5	0.8	36

Figure 9 shows the regression residuals of the HP 6890 GC plotted against time and mixing ratio. From these data both a temporal trend (left panel) and mixing ratio dependence (right panel) cannot be excluded; however, the regression residuals are small, and not significantly different from zero except for the highest mixing ratio.

Based on the inter-comparison results, unbiased methane volume mixing ratios of the HP 6890 analyzer X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed from the single injection inter-comparison data using equation (3).

$$X_{CH4}\ (\text{ppb}) = (CH_4) / 0.99997$$

$$u_{CH4}\ (\text{ppb}) = \text{sqrt}\ (2.0\ \text{ppb}^2 + 1.37\text{e-}07 * X_{CH4}^2) \qquad (3)$$

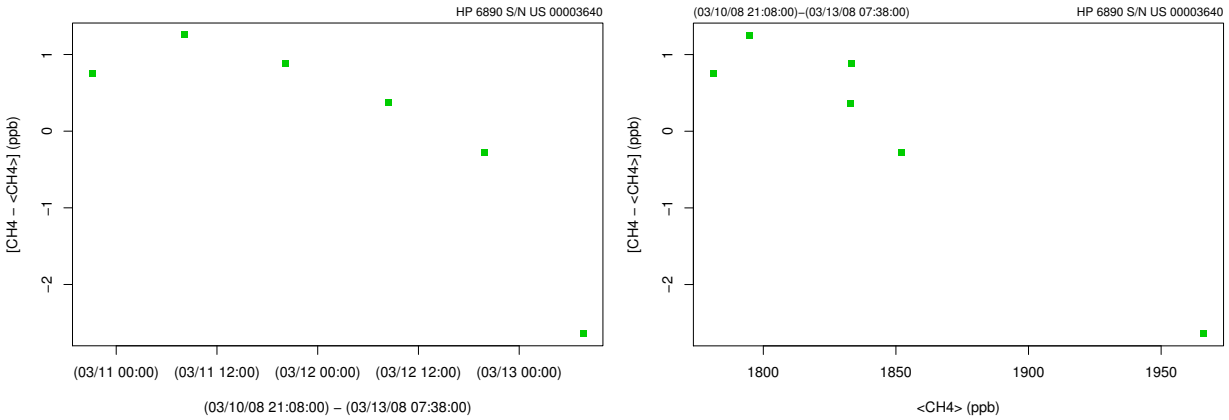

Figure 9. Regression residuals of the BRW methane GC. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mixing ratio dependence.

Conclusions

No significant deviations between Barrow and WCC-Empa were found. The good result of the inter-comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. The repeatability of the Barrow GC was good, with an average standard deviation of 0.04% (10-36 injections). This value is comparable to the best GC-FID systems at GAW stations. Therefore no further technical recommendations are made by WCC-Empa.

Nitrous Oxide Measurements

Nitrous oxide measurements started at BRW in October 1986 under NOAA's Radiatively Important Trace Species (RITS) program. Besides N_2O the RITS instrument measured CFC-12, CFC-11, CFC-113, methyl chloroform and carbon tetrachloride. In 1999 the RITS instrument was replaced by a CATS (Chromatograph for Atmospheric Trace Species) system with 4 channels and the capability of measuring the previous chemicals as well as sulfur hexafluoride (SF_6), Halon-1211 ($CBrClF_2$), HCFC-22 ($CHClF_2$), HCFC-142b ($CClF_2$-CH_3), carbonyl sulfide (OCS), methyl chloride (CH_3Cl), and methyl bromide (CH_3Br). A continuous N_2O time series of one-hourly averages is available from BRW since the start in 1986. Details of the measurement setup can be found on the HATS website (www.esrl.noaa.gov/gmd/hats).

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

The CATS GC system has a dedicated air inlet system, which is adequate for analyzing N_2O concerning materials and residence time.

Instrumentation

A custom built 4-channel GC system (Chromatograph for Atmospheric Trace Species – CATS) is used for the detection of nitrous oxide and a number of other trace species.

Standards and Calibration

The station is equipped with laboratory standards that cover the relevant mixing ratio range. All standards have been certified by NOAA/ESRL based on the NOAA-2006 N_2O scale calibration scale.

Operation and Maintenance

A detailed SOP is available.

Daily: A daily check list with engineering parameters and chromatogram status is filled in.

Weekly: Carrier gas consumption is compared to previous week.

Monthly: Check and adjustment of sample flow rates.

Other: Exchange of purifier traps and de-icing of cooling trap according to the SOP.

Data Acquisition and Data Transfer

A custom build data acquisition software running under QNX Windows graphical user interface is used. Full remote control is possible, and data are transferred in near-real time to the data base. More information is available on the HATS website (www.esrl.noaa.gov/gmd/hats).

Data Submission

Data of the in-situ N_2O measurements have been submitted to the GAW World Data Centre for Methane at JMA (World Data Centre for Greenhouse Gases, WDCGG). Currently the complete time series covering the period from 1987 to 2008 is available at WDCGG.

Documentation

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

Inter-Comparison of Nitrous Oxide Measurements

At the time of the audit WCC-Empa had only one traveling standard. This standard was initially calibrated by Eckhart Scheel from the WCC- N_2O at IMK-IFU and was assigned with a value of 315.86 ± 0.30 ppb (NOAA-2000 N_2O scale), which translates into 315.73 ± 0.30 ppb on the NOAA-2006 scale [*Hall, et al.*, 2007]. This traveling standard was analyzed by the BRW instrument during the audit. Based on the NOAA-06 N_2O scale a value of 315.74 ± 0.30 ppb (1σ) (11 injections) was obtained, which is in perfect agreement with the value assigned by the WCC-N_2O.

Conclusions

No significant deviations between the Barrow measurements and WCC-Empa traveling standard were found. The excellent result of the inter-comparison measurement shows that the whole analytical system is appropriate for the measurement of N_2O. Therefore no further technical recommendations are made by WCC-Empa.

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 12, the inter-comparison data is given in Table 13.

Table 12. Experimental details of the inter-comparison of traveling standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Traveling standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = -0.4; COEFF = 1.002
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (2008-01-31) 3 runs after return of TS (31 2008-05-26)

Table 13. Five-minute aggregates computed from 10 valid 30-second values for the inter-comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2008-01-31	1	0	0.06	0.31	0.04	0.06
2008-01-31	1	90	90.25	0.17	90.33	0.12
2008-01-31	1	190	182.43	0.26	182.44	0.28
2008-01-31	1	30	32.10	0.22	31.97	0.07
2008-01-31	1	140	137.56	0.32	137.45	0.36
2008-01-31	1	60	60.00	0.15	60.12	0.08
2008-01-31	1	0	0.09	0.18	0.10	0.07
2008-01-31	2	0	-0.13	0.09	0.06	0.08
2008-01-31	2	90	90.57	0.18	90.72	0.15
2008-01-31	2	190	182.89	0.40	183.11	0.20
2008-01-31	2	30	31.99	0.19	32.14	0.10
2008-01-31	2	140	137.65	0.31	137.85	0.16
2008-01-31	2	60	59.93	0.16	60.25	0.09
2008-01-31	2	0	0.02	0.20	0.12	0.10
2008-01-31	3	0	0.00	0.20	0.04	0.11
2008-01-31	3	30	31.88	0.20	31.88	0.08
2008-01-31	3	140	138.24	0.53	138.58	0.46
2008-01-31	3	60	59.98	0.16	60.05	0.10
2008-01-31	3	90	89.97	0.15	90.35	0.13
2008-01-31	3	190	183.34	0.33	183.50	0.33
2008-01-31	3	0	0.02	0.09	0.08	0.10
2008-05-26	4	0	-0.06	0.20	-0.51	0.07
2008-05-26	4	90	93.39	0.30	92.34	0.07
2008-05-26	4	190	186.63	0.45	185.17	0.29
2008-05-26	4	60	60.58	0.40	59.81	0.14
2008-05-26	4	140	140.48	0.21	139.27	0.11
2008-05-26	4	30	30.22	0.27	29.69	0.13
2008-05-26	4	0	0.25	0.16	-0.33	0.09
2008-05-26	5	0	0.06	0.23	-0.27	0.08
2008-05-26	5	30	30.04	0.21	29.51	0.12
2008-05-26	5	190	185.79	0.28	184.62	0.48
2008-05-26	5	90	91.70	0.26	90.75	0.11
2008-05-26	5	140	139.61	0.24	138.51	0.09
2008-05-26	5	60	60.48	0.28	59.99	0.06
2008-05-26	5	0	0.04	0.24	-0.27	0.07
2008-05-26	6	0	-0.19	0.15	-0.23	0.12
2008-05-26	6	90	92.51	0.30	91.81	0.20
2008-05-26	6	190	184.88	0.26	183.81	0.25
2008-05-26	6	30	30.09	0.25	29.76	0.11
2008-05-26	6	140	138.93	0.30	137.92	0.10
2008-05-26	6	60	60.45	0.23	59.86	0.08
2008-05-26	6	0	-0.14	0.25	-0.11	0.12

[#]the level is only indicative.

The traveling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 10). 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]).

$$X_{TS}\ (\text{ppb}) = ([TS] + 0.11\ \text{ppb}) / 0.997$$

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

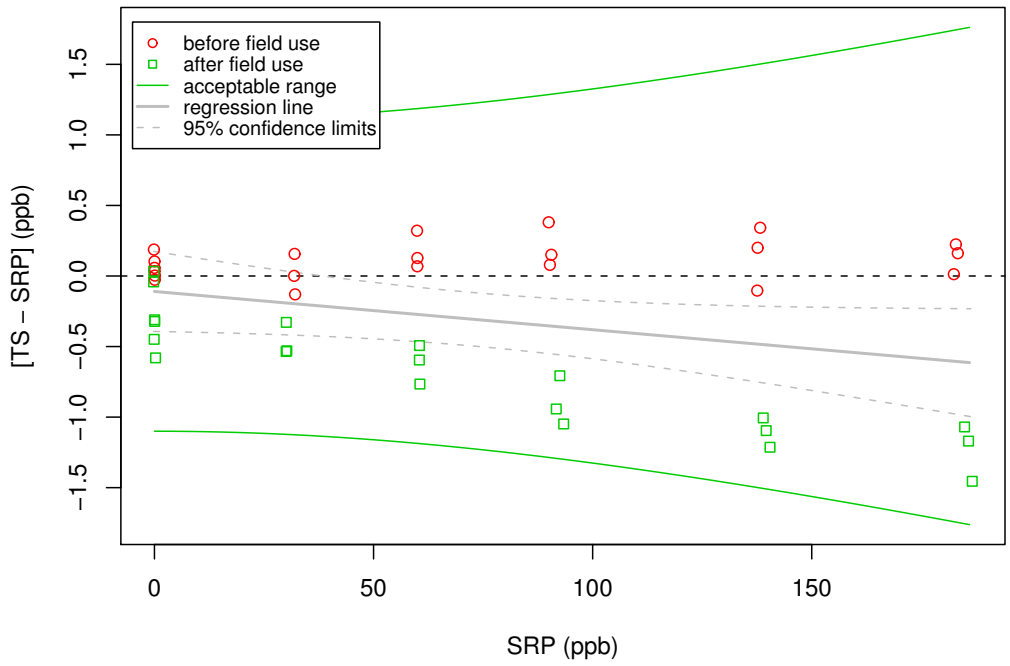

Figure 10. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

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 traveling standards. The scale was transferred to the traveling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. Details are given in Table 14 and Table 15.

Table 14. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the traveling standard (TS) used during the field inter-comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. Due to remaining minor inconsistencies in the WMO-2000 scale below 150 ppb, the transfer of the scale is based on one specific cylinders, CA02854 (295.5±3.0 ppb)
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Traveling standard (TS)		Carbon monoxide cylinders for direct inter-comparisons. (cf. Table 15)
Connection between instruments		Ca. 2 meter 1/8” stainless steel tubing (cylinders).
Range (ppb)		90 – 360 ppb cf. Table 15
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 15. Calibration of the carbon monoxide traveling standards with the WCC-Empa reference before and after the audit.

Date	2008-01-31			2008-05-28		
Cylinder identification	CO (ppb)			CO (ppb)		
070927_FA02482	93.2	±	0.6	93.8	±	0.7
070808_FA02686	124.5	±	0.4	126.3	±	0.6
050415_FA02476	143.7	±	0.5	143.5	±	0.5
050701_FA02464	170.2	±	0.5	170.5	±	0.6
070807_FA02785	230.3	±	0.6	230.6	±	0.8
050701_FA02505	359.4	±	0.9	360.3	±	0.9

[#] Average±sd (n = approx. 100)

No significant drift was observed over the period of the audit except for 070808_FA02686. The average of the two measurements was used for the evaluation of the audit results.

Methane

WCC-Empa refers to the latest WMO/GAW methane scale (hereafter: NOAA04 scale) [*Dlugokencky, et al.*, 2005] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 16). The scale was transferred to the traveling standards using a Varian 3400 gas chromatograph with an FID detector. Details of the traveling standards are given in Table 17.

Table *16*. NOAA/ESRL CH4 laboratory standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Cylinder#	Methane [ppb]* (NOAA04)
CA05316	1712.5 ± 0.30 ppb
CA04462	1817.4 ± 0.19 ppb
CA04580	1905.1 ± 0.24 ppb

*Certificates (CMDL83) from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316). Values were converted to NOAA04 scale by applying a factor of 1.0124.

Table 17. Calibration of the methane traveling standards with the WCC-Empa reference (Average mole fraction in ppb ± sd (n = 10)).

Date	050415_FA02476	sd	050701_FA02464	sd	050701_FA02505	sd	070807_FA02785	sd	070808_FA02686	sd	070927_FA02482	sd
2005-06-08	**1965.7**	1.3										
2005-07-15			**1832.1**	1.2	**1833.6**	1.2						
2005-08-04	**1965.5**	1.5										
2005-10-04	**1966.2**	1.0	**1832.1**	1.3	**1832.7**	1.9						
2005-12-14	**1966.8**	1.7	**1834.0**	1.3	**1832.6**	1.8						
2006-04-28					**1832.7**	0.9						
2006-05-02	**1966.7**	1.2	**1833.6**	1.7								
2006-06-26	**1967.0**	0.8	**1832.2**	0.8	**1833.3**	1.2						
2006-08-07					**1831.1**	1.4						
2006-11-22					**1833.2**	1.7						
2007-06-14	**1966.5**	1.2	**1832.6**	1.2	**1833.8**	1.1						
2007-09-25	**1965.6**	1.3	**1832.3**	1.1	**1833.2**	1.2						
2007-09-28											**1795.1**	1.8
2007-10-02											**1794.7**	1.3
2007-10-25							**1850.3**	1.3	**1781.1**	1.0	**1796.3**	1.4
2007-11-26							**1851.1**	1.4				
2007-12-17							**1850.8**	1.3	**1780.0**	1.3	**1793.9**	1.1
2008-01-30			**1833.9**	1.4							**1792.3**	0.9
2008-01-31	**1966.1**	1.8	**1833.2**	1.4	**1834.7**	1.4	**1852.7**	1.0	**1780.9**	0.8		
2008-05-23	**1964.9**	1.2	**1831.3**	1.8	**1835.0**	1.4	**1853.8**	1.7	**1781.6**	1.1	**1795.3**	1.9
2008-05-26	**1967.1**	2.1	**1834.6**	1.4	**1834.5**	1.2	**1853.3**	1.3	**1782.1**	1.0	**1795.7**	1.0
avg	**1966.2**	0.7	**1832.9**	1.0	**1833.4**	1.1	**1852.0**	1.5	**1781.1**	0.8	**1794.8**	1.3

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Ozone Audit Executive Summary (BRW)

0.1	Station Name:	Barrow
0.2	GAW ID:	BRW
0.3	Coordinates/Elevation:	71.323 °N 156.612 °W (11 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2008-03-10 thru 2008-03-12
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Daniel J. Endres
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #54509-300
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(0.9973 \pm 0.0010) \times [SRP] - (0.11 \pm 0.12)$
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C # 75572-380
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.0 ppb, SPAN 1.000
1.5.4	Calibration at start of audit (ppb):	$[OA] = (1.002 \pm 0.000) \times [SRP] + (0.17 \pm 0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] - 0.17) / 1.002$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.59e\text{-}5 \times X^2)^{1/2}$
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:	Main station analyzer O3 final [pbb] = 0.46 + 1.018 *(TEI 49C) Data were corrected for bias according to normal station method.
1.7	Reference:	WCC-Empa Report 08/1

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

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Ozone Audit Executive Summary (BRW)

0.1	Station Name:	Barrow
0.2	GAW ID:	BRW
0.3	Coordinates/Elevation:	71.323 °N 156.612 °W (11 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2008-03-10 thru 2008-03-12
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Daniel J. Endres
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #54509-300
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	$(0.9973 \pm 0.0010) \times [SRP] - (0.11 \pm 0.12)$
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49i #629719159
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.0 ppb, SPAN 1.000
1.5.4	Calibration at start of audit (ppb):	$[OA] = (1.012 \pm 0.000) \times [SRP] + (0.15 \pm 0.05)$
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	$X = ([OA] - 0.15) / 1.012$
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.27\ ppb^2 + 2.54e\text{-}5 \times X^2)^{1/2}$
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:	Secondary station analyzer O3 final [pbb] = 0.50 + 1.019 *(TEI 49i) Data were corrected for bias according to normal station method.
1.7	Reference:	WCC-Empa Report 08/1

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

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Carbon Monoxide Audit Executive Summary (BRW)

0.1	Station Name:	Barrow
0.2	GAW ID:	BRW
0.3	Coordinates/Elevation:	71.323 °N 156.612 °W (11 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2008-03-10 thru 2008-03-12	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Daniel J. Endres	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	070927_FA02482	93.48±1.03 ppb
		070808_FA02686	125.41±1.47 ppb
		050415_FA02476	143.59±0.72 ppb
		050701_FA02464	170.34±0.82 ppb
		070807_FA02785	230.43±0.98 ppb
		050701_FA02505	359.85±1.41 ppb
		CO analyzer [CO]	
1.4.2	Model:	RGA-3, S/N 070188-006	
1.4.3	Range of calibration:	90 – 360 ppb	
1.4.4	Coefficients at start of audit	NA	
1.4.5	Calibration at start of audit (ppb):	$CO = (1.005 \pm 0.006) \times X - (1.5 \pm 1.1)$	
1.4.6	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO + 1.5) / 1.005$	
1.4.7	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (4.2\ ppb^2 + 5.91e\text{-}05 \times X^2)^{1/2}$	
1.4.8	Coefficients after audit	NA	
1.4.9	Calibration after audit (ppb):	unchanged	
1.4.10	Unbiased CO mixing ratio (ppb) after audit:	unchanged	
1.4.11	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged	
1.5	Comments:		
1.6	Reference:	WCC-Empa Report 08/1	

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

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Methane Audit Executive Summary (BRW)

0.1	Station Name:	Barrow
0.2	GAW ID:	BRW
0.3	Coordinates/Elevation:	71.323 °N 156.612 °W (11 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2008-03-10 thru 2008-03-12	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Daniel J. Endres	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02686	1781.1±0.8 ppb
		070927_FA02482	1794.8±1.3 ppb
		05070_FA02464	1832.9±1.0 ppb
		050701_FA02505	1833.4±1.1 ppb
		070807_FA02785	1850.0±1.5 ppb
		050415_FA02476	1966.2±0.7 ppb
1.5	CH_4 analyzer [CA]		
1.5.1	Model:	HP 6890, S/N US00003640	
1.5.2	Range of calibration:	1780 –1970 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (0.99997 \pm 0.00035) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 0.99997$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (2.0\ ppb^2 + 1.37e\text{-}07 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (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 08/1	

[CH_4]: Instrument readings; X: mole fractions on the NOAA04 CH_4 scale.

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LIST OF ABBREVIATIONS

a.s.l.	above sea level
CCL	Central Calibration Laboratory
DAQ	Data Acquisition System
GAW	Global Atmosphere Watch
GC	Gas Chromatograph
NIST	National Institute of Standards and Technology
NOAA/ESRL	National Oceanic & Atmospheric Administration / Earth System Research Laboratory
OA	Ozone Analyzer
BRW	Barrow GAW Station
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Traveling Standard
WCC-Empa	World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organisation