SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION USHUAIA ARGENTINA FEBRUARY 2016

Submitted to the World Meteorological Organization by

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WCC-Empa Report 16/1

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The fourth system and performance audit by WCC-Empa[1] at the Global GAW station Ushuaia was conducted from 3 - 10 February 2016 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). The measurements and the operation of the Ushuaia GAW station are coordinated by the Servicio Meteorológico Nacional (SNM) of Argentina in collaboration with the Government of the Province of Tierra del Fuego.

Previous audits at Ushuaia GAW station were conducted in November 1998 (Herzog et al., 1998), November 2003 (Zellweger et al., 2003) and November 2008 (Zellweger et al., 2008).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr. Stefan Bugmann	Empa Dübendorf, National Air Pollution Monitoring Network
Ing. Manuel Cupeiro	SMN Ushuaia, Station Manager
Mr. Marcelo Sosa	SMN Ushuaia, Station Operator
Dr. M. Paula Etala	SMN Buenos Aires, Technical director
Mr. Gerardo Carbajal Benítez	SMN Buenos Aires, Head of GAW Department

This report summarises the assessment of the Ushuaia GAW station in general, as well as the surface ozone and carbon monoxide measurements in particular.

The report is distributed to SMN Buenos Aires, the USH station manager and the World Meteorological Organization in Geneva. The report will also be made publicly available on the internet.

The recommendations found in this report are graded as minor, important and critical and are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Management and Operation

The USH GAW station is jointly managed by Argentinian Weather Service (SMN) and the Government of the Tierra del Fuego province. The station is visited daily by a meteorological observer and, from Monday to Friday, by a GAW station operator.

Recommendation 1 (, important, ongoing)**
The financial planning for the USH operation must include a budget for maintenance and repair of the existing instrumentation, as well as provisions for future instrument replacements and measurement programme expansions.

Recommendation 2 (, important, ongoing)**
SMN should explore all possibilities for operator training. Participation in GAWTEC courses and other means of continuing education is highly recommended.

[1] WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide. 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 based on mutual agreement.

Station Location and Access

The Ushuaia Station is located in Tierra del Fuego, Argentina (54.845°S, 68.311°W), roughly 10 km south-west of the city of Ushuaia in the vicinity of the Malvinas International Airport. The station is located on a coastal cliff at an altitude of 18 m a.s.l., on a remote sub-Antarctic marine coast. Steady winds blow prevailing from the clean air sector (SW). Tierra del Fuego and its adjacent oceanic area are under the westerlies influence. The ground in the vicinity around the station is covered with pasture and bush. The vegetation in the surrounding area (30 Km) is consisting mainly of Nothofagus forest. Access to the station is possible throughout the year with a special permit of the airport security.

Further information about the USH station is available from the GAW Station Information System (GAWSIS) (gawsis.meteoswiss.ch/GAWSIS//index.html#/search/station/stationReportDetails/470).

> **Recommendation 3 (**, important, ongoing)**
> *The USH station is located in the immediate vicinity of the international airport and close to the city of Ushuaia. This location enables both research focusing on the local and regional pollution and the remote marine troposphere. However, it is important that the processes influencing the station are well understood, and corresponding studies are strongly encouraged.*

Station Facilities

The facilities at the site consist of the main building of 230 m^2, which provides space for offices, meeting rooms and laboratories. 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 main laboratory is air conditioned, and internet connection is available but with limited bandwidth.

Measurement Programme

Measurements from four different WMO/GAW focal areas are performed at USH. An overview of the measurement programme is available from GAWSIS. It should be noted that all greenhouse gas (GHG) measurements are only performed as part of the NOAA/ESRL flask network. The current suite of measurements is regarded as too small for a station with a global status in the GAW programme. It is strongly encouraged that the programme is enlarged.

> **Recommendation 4 (***, important, 2017)**
> *The continuous measurements of GHGs as part of this audit (see further below) showed that the addition of GHG instrumentation would be beneficial for the USH station and the GAW programme. WCC-Empa strongly supports the current intention of SMN to enlarge the measurement programme at USH by purchasing a Picarro G2401 analyser.*

Air Inlet System

The current air inlet system for carbon monoxide and surface ozone with the air intake located 7 m above ground (details see previous audit reports), consisting of ½" PTFE tubing flushed at 11 l/min by a diaphragm pump, is adequate for these measurements. However, if the measurement programme is enlarged, additional inlet lines with appropriate material will be necessary, since the current PTFE system will not be suitable for GHG measurements.

Surface Ozone Measurements

The surface ozone measurements at Ushuaia were established in 1994 and continuous time series are available since then.

Instrumentation. The station is equipped with one ozone analyser (TEI 49C). The instrumentation is adequate for its intended purpose, but has reached the end of its expected lifetime.

Standards. An ozone transfer standard (TEI 49C-PS) is available at the Regional Calibration Centre for Surface Ozone in Buenos Aires (RCC-BsAs). The transfer standard has full traceability to the WMO/GAW reference (Standard Reference Photometer SRP#15) maintained at Empa and was available at USH during the audit.

> **Recommendation 5 (***, important, 2017)**
> *The ozone instrumentation of both the USH station and the RCC-BsAs has reached the end of its expected lifetime. Therefore, a budget for the replacement of the instruments needs to be allocated.*

Intercomparison (Performance Audit). The ozone analyser of USH and the transfer standard of the RCC-BsAs were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system, and no further corrections were applied. The following equations characterise the bias of the instruments:

USH station analyser:

TEI 49C #58546-318 (BKG +0.0 ppb, COEF 1.012):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.06 ppb) / 1.0008 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.28 ppb^2 + 2.53e-05 * X_{O3}^2) (1b)

RCC-BsAs ozone calibrator:

TEI 49C-PS #56034-306 (BKG -0.5 ppb, COEF 1.015):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.43 ppb) / 0.9993 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.54-05 * X_{O3}^2) (1d)

The result of the comparison is further illustrated in the figures below.

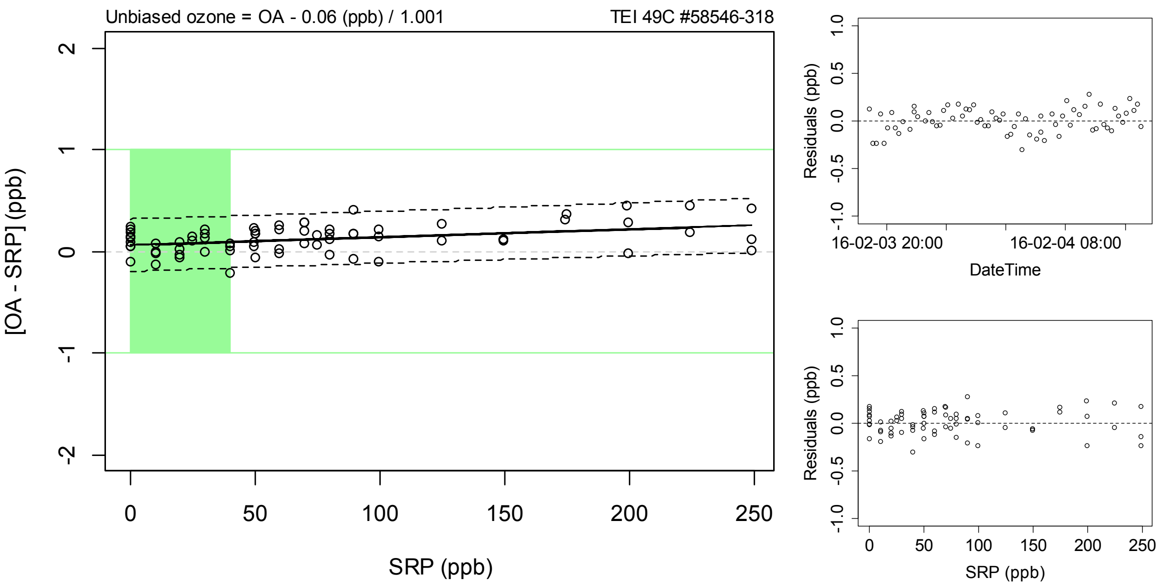

Figure 1. *Left: Bias of the USH ozone analyser (OA) (TEI 49C #58546-318) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The green lines correspond to the DQOs and the green area to the mole fraction range relevant for USH. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

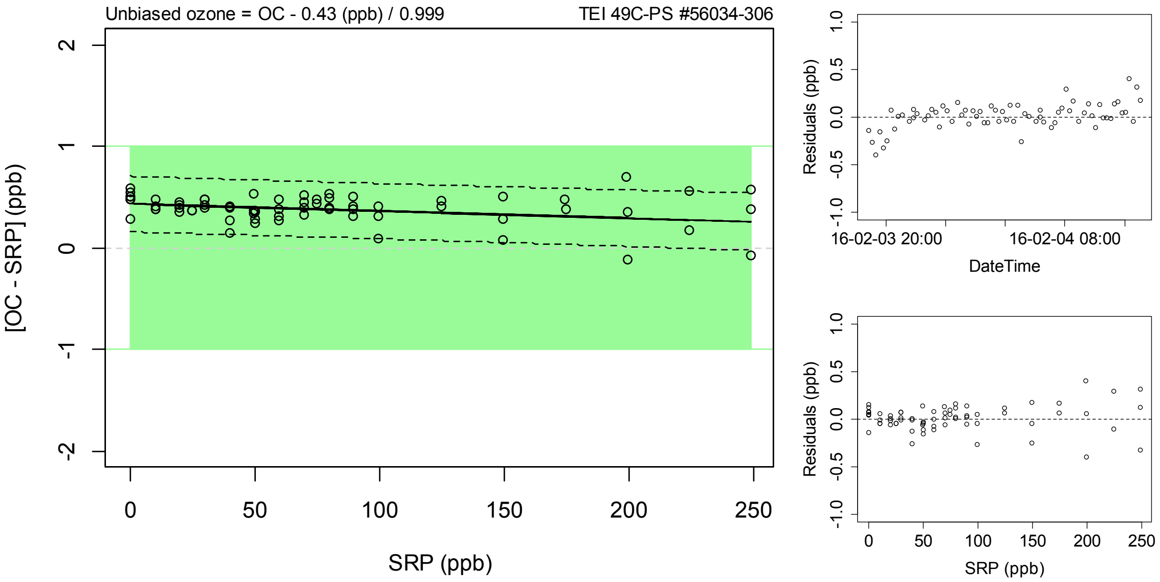

Figure 2. *Same as above for the backup ozone calibrator (OC) TEI 49C-PS #56034-306.*

The results of the comparison can be summarised as follows:

Both the TEI 49C #58546-318 ozone analyser and the TEI 49C-PS #56034-306 ozone calibrator are in good calibration, and the bias is within the WMO/GAW DQOs for the relevant mole fraction range. The instrumentation at USH is adequate for ozone measurements; however, both instruments have reached the end of their expected lifetime.

Carbon Monoxide Measurements

Carbon monoxide measurements at Ushuaia were established in 1994, and continuous time series are available since then.

Instrumentation. The measurements were initially made with two TEI48 gas filter correlation Non-dispersive Infrared (NDIR) monitors. These instruments were complemented by a cross flow modulation NDIR instrument (Horiba APMA-360) during the WCC-Empa audit in 2008, and one of the TEI48 instruments was decommissioned at that time. Shortly after that, the second TEI48 was also decommissioned; and currently, only the Horiba APMA-360 is available for CO measurements.

Standards. Calibration standards provided by WCC-Empa are available at USH. Automatic zero and span checks are daily carried out using a Sofnocat 423 scrubber (zero check) a high ppm CO standard diluted with CO free air (span check). Details and a list of available standards are given in the Appendix. At the time of the audit, USH was equipped with four carbon monoxide standards. Two standards (approx. 100 ppm CO in air) were delivered through WCC-Empa in 2004, and two standards (2.582 and 38.39 ppm CO in air) were delivered during the last audit in 2008. These standards were assigned with WMO-2000 traceable carbon monoxide mole fractions by WCC-Empa. The standard with a mole fraction of 2.582 ppm CO in air and is used for direct calibrations of the instrument. The other standard with the mole fraction of 38.39 ppm CO in air and is used for automatic span checks after dilution with zero air. With this equipment, adequate calibration of the carbon monoxide measurements is possible. However, all standards were delivered to the station by WCC-Empa, and no local calibration gas supplier is available.

Recommendation 6 (, important, ongoing)**
For the long term operation of the USH station, funding of calibration gas supply needs to be allocated by SMN.

Recommendation 7 (, important, ongoing)**
Manual checks using the low ppm standards were discontinued at the time of the audit. It is important that these checks are resumed in monthly intervals.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the USH instrument with randomised carbon monoxide concentrations from a travelling standard (dilution unit combined with high concentration carbon monoxide standard). The USH instrument was calibrated using the 2.582 ppm CO in air standard and zero air before the comparison. Based on this calibration, a zero correction of +6.32 ppb CO and a span factor of 0.9687 was applied to the HORIBA raw data. The following equation characterises the instrument bias, and the results is further illustrated in Figure 3 with respect to the WMO GAW DQOs (WMO, 2014):

HORIBA APMA-360 SN 712020:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 1.0) / 1.0006 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (10.1 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

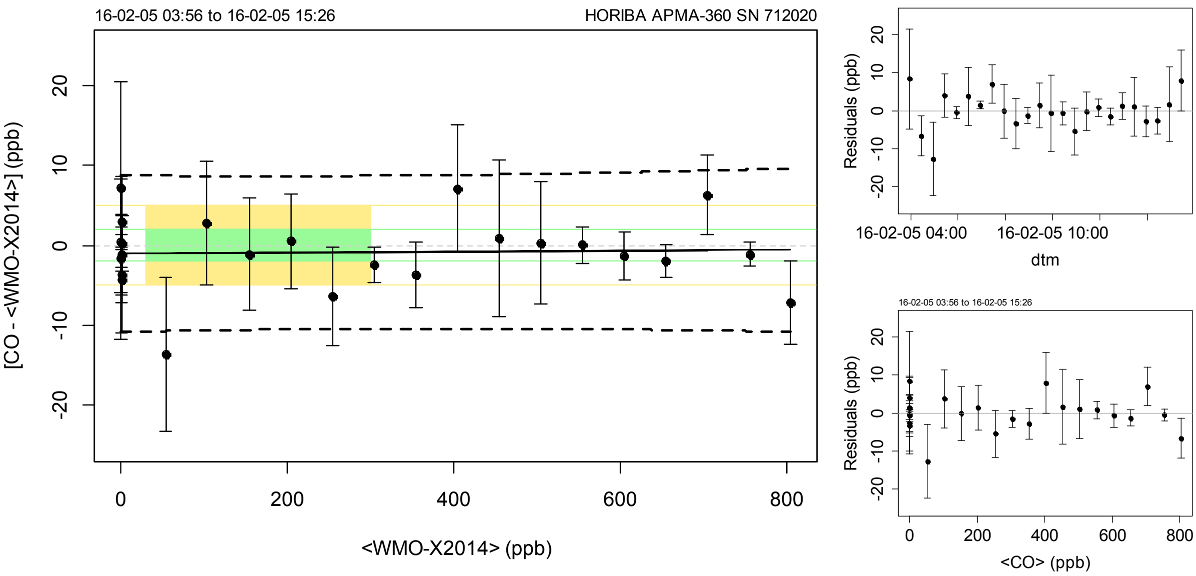

Figure 3. *Left: Bias of the USH HORIBA APMA-360 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for USH. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The results of the comparisons can be summarised as follows:

On average, the agreement of the HORIBA APMA-360 analyser was well within the WMO/GAW compatibility goals of ±2 ppb over the entire relevant mole fraction range. However, due to instrumental noise, the corresponding uncertainties are much higher than the compatibility goals. The instrument is able to capture long term variations and trends but lacks accuracy on shorter time scales. Therefore, instrument replacement by a measurement technique with better repeatability should is highly recommended.

Recommendation 8 (, important, 2017)**
The current CO instrument has reached the end of its expected lifetime and only partly complies with the requirements for Global GAW station. WCC-Empa recommends replacement by a newer generation instrument, preferably in combination with the addition of new measurement parameters (e.g. CH_4 and CO_2, or N_2O).

The standards available at USH were calibrated by WCC-Empa on the WMO-X2000 carbon monoxide scale. The comparison showed that the deviation between the WMO-X2000 and the current WMO-X2014A was small and not significant considering the relatively high uncertainty due to the measurement technique.

Parallel Measurements of Ambient Air

The audit included parallel measurements of CO with a WCC-Empa travelling instrument (TI) (Picarro G2401 SN # 617-CFKADS2001). The TI was running from 5 February 2016 through 9 May 2016. The TI was connected to the station inlet which is also used for the USH CO and ozone measurements. This was appropriate since the focus of the comparison was carbon monoxide. The TI was sampling using the following sequence: 1810 min ambient air followed by 30 min measurement of two standard gases (15 min each). To account for the effect of water vapour a correction function (Rella et al., 2013; Zellweger et al., 2012) was applied to the WCC-Empa CRDS data. Details of the calibration of the TI are given in the Appendix.

The CO comparison (1h data) between the WCC-Empa TI and the USH HORIBA APMA-360 analyser is shown in Figure 4. The temporal variation was well captured by both instruments. The average deviation was within the extended WMO/GAW compatibility goal, and considering the uncertainty of the HORIBA APMA-360, the results also confirm the findings of the performance audit with travelling standards.

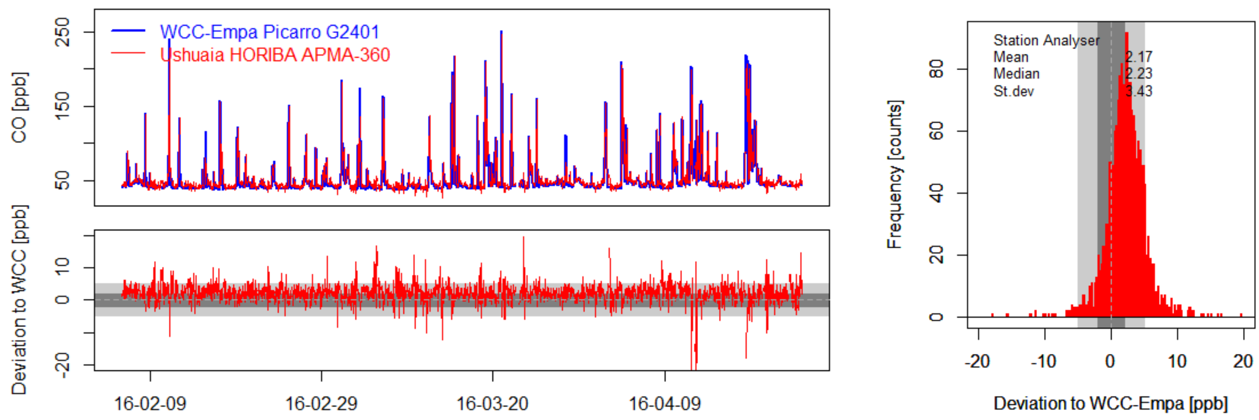

Figure 4. *CO comparison at USH between the WCC-Empa travelling instrument and the USH HORIBA APMA-360 analyser. Upper panel: CO time series (1 h data). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.*

The results confirm that the station CO analyser is still in a good working condition. It should further be noted that the ambient variability of CO at USH was high during the period of the measurement campaign. The station is partly influenced by significant pollution from nearby sources. This was also confirmed by the measurements of CH_4 and CO_2 made by the TI during the audit. These are the first available continuous in-situ observations of CO_2 and CH_4 at USH. The following figures show an overview of the CO, CO_2 and CH_4 levels observed at USH during the comparison campaign. The large observed variability in CO_2 and CH_4 mole fractions clearly points out that continuous observation can gain considerable additional information which cannot be retrieved from periodical flask sampling followed by off-line analysis.

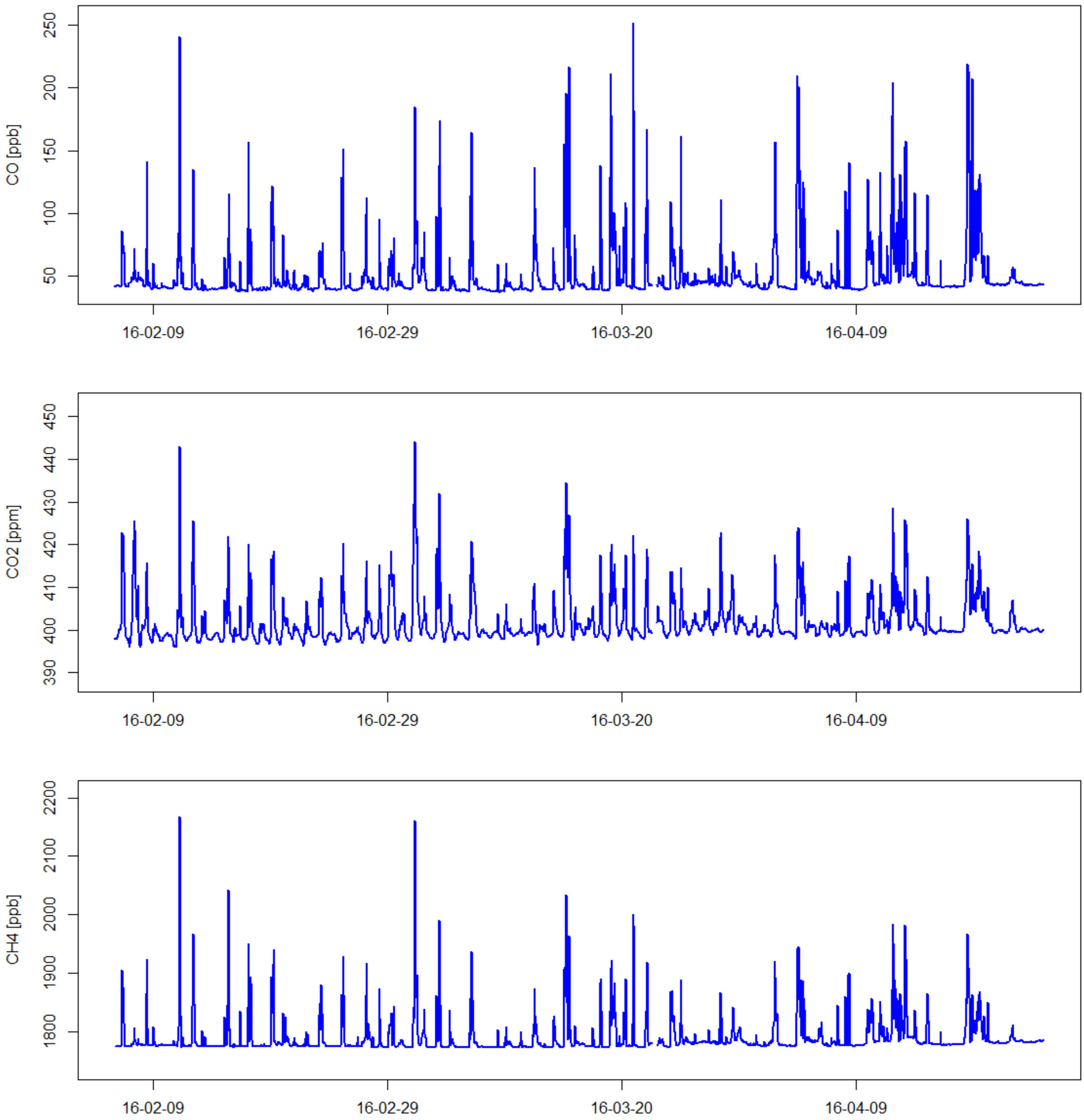

Figure 5. *CO (upper panel), CO_2 (middle panel) and CH_4 (lower panel) time series measured at USH with the Picarro G2401 during the comparison campaign.*

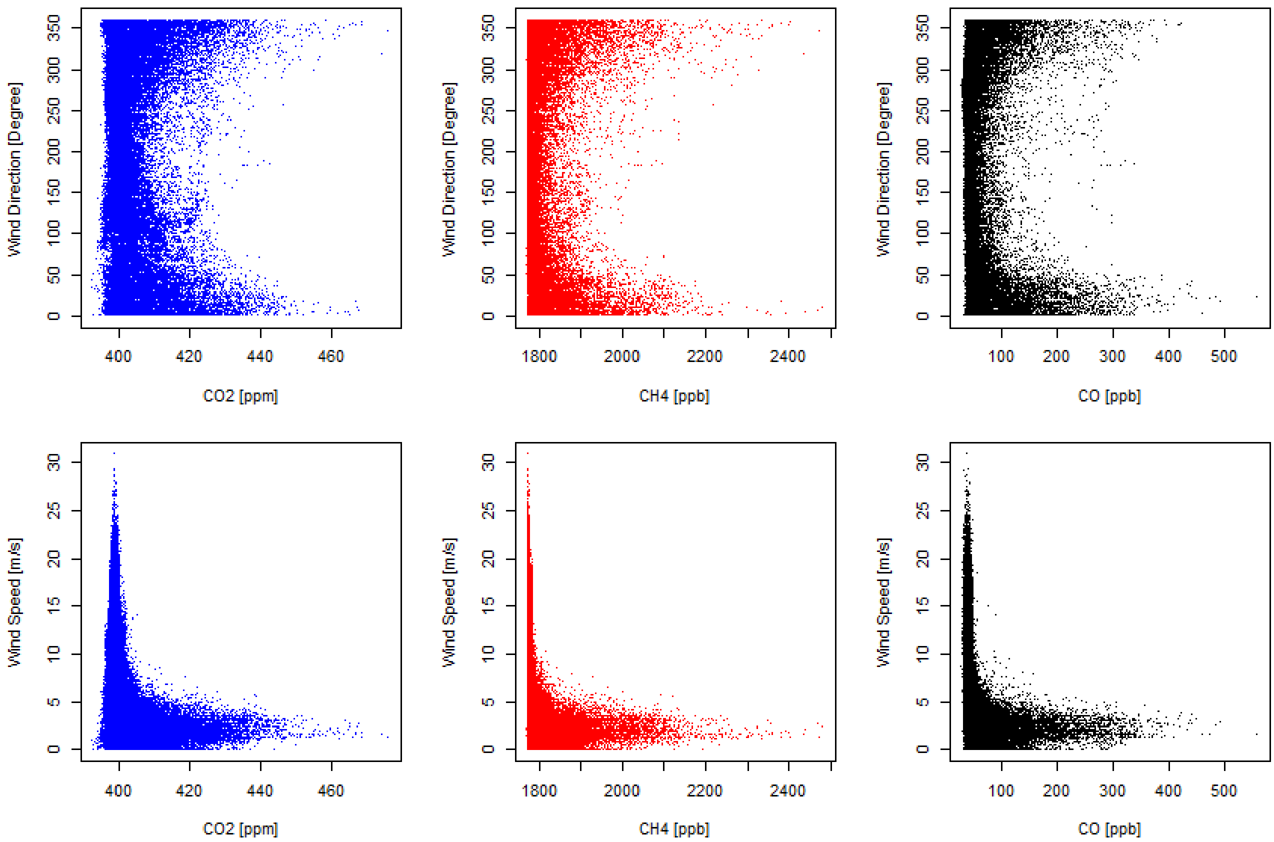

Figure 6. *Upper panel: Scatter plots of wind direction vs. CO_2 (left), CH_4 (middle) and CO (right). Lower panel: Same as above for wind speed. All data are 1 min averages.*

It can clearly be seen that there is a clean sector south of the USH station, whereas significant pollution is measured when the air is originating from the vicinity of the Ushuaia city. This is also the case during episodes with low wind speed, which allows accumulation of pollutants in the region. Further analysis of the data is beyond the scope of the current audit, but the results clearly show that the addition of more measurement parameters would be beneficial for the scientific value of the station.

Recommendation 9 (, important, ongoing)**

SMN is encouraged to enlarge the measurement programme at the USH station to strengthen the scientific value of the Argentinian contributions to GAW.

Data Acquisition and Management

USH is equipped with a centralised data acquisition system (GAWDAQ) for surface ozone and carbon monoxide. The system was programmed by QA/SAC-Switzerland and is based on LabView. Data used to be automatically transferred to an FTP server, which was located at Empa, in near-real time. This is now discontinued, and data are locally stored. Back-ups are available.

> **Recommendation 10 (**, important, ongoing)**
> *The GAWDAQ system can no longer be supported by QA/SAC Switzerland. It should be considered to replace the system, e.g. when the measurement programme is enlarged.*

Documentation

For each instrument, electronic log files are available. All relevant events and observations are recorded in these log files. The instrument manuals are available at the site. The reviewed information was comprehensive and up to date.

Data Submission

Surface O_3 (1994-2014) and CO (1994-2015 data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). USH usually submits data in yearly intervals. It is recommended that this procedure is continued. It was noted that CO data at WDCGG for the period 1994 – early 2008 (old TEI48 instrument) needs further quality control.

> **Recommendation 11 (***, critical, 2017)**
> *CO data of the TEI48 analyser (before May 2008) needs to be reviewed and further quality controlled. WDCGG needs to be contacted to make sure that invalid data is immediately removed from the data base. Re-submission of quality controlled data is strongly encouraged if possible.*

Conclusions

The Global GAW station Ushuaia is situated in a strategically important location for the GAW programme, which makes the available data a very significant contribution to GAW. The continuation of the USH measurement series is highly recommended and important for GAW.

The assessed parameters were mostly of high quality; however, ongoing investments in instrument replacement as well as in peripherals such as calibration gases and other consumables will be needed to sustain the measurements in future.

The measurement programme of the USH station is still very limited, especially when considering the global status of the station. The enlargement of the programme is highly recommended, e.g. by the addition of greenhouse gas measurements.

It was also recognized that the scientific use of the available data is now of high priority. The existing data is already regularly analysed, quality controlled and submitted to the corresponding data centres by the USH staff. Beyond this, more scientific use of the data by SMN should be envisaged. This requires ongoing education and training of the existing staff as well as collaboration with both national and international partners.

Summary Ranking of the Ushuaia GAW Station

System Audit Aspect	Adequacy#	Comment
Measurement programme	(2)	Relatively small number of parameters for a Global GAW station
Station access	(5)	Year round access by car
Facilities		
Laboratory and office space	(4)	Adequate but basic facilities.
Internet access	(3)	Limited bandwidth
Air Conditioning	(4)	Adequate for current measurements
Power supply	(5)	Reliable with few power cuts
General Management and Operation		
Organisation	(4)	Well-coordinated, limited resources available
Competence of staff	(4)	Skilled staff, more scientific collaboration needed
Air Inlet System	(4)	Simple but adequate system for current measurements
Instrumentation		
Ozone	(4)	Adequate but old instrumentation
CO	(3)	Low precision for Southern Hemisphere measurements
Standards		
Ozone	(3)	TEI 49C-PS available in Buenos Aires
CO	(3)	Working standards available, no local supplier
Data Management		
Data acquisition	(3)	Support by QA/SAC Switzerland discontinued
Data processing	(4)	Experienced staff
Data submission	(5)	Yearly submissions

#0: inadequate thru 5: adequate.

Dübendorf, August 2016

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APPENDIX

Ozone Measurements

Comparison of the Ozone Analyser and Ozone Calibrator

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

Setup and Connections

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 250 ppb. Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 1 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa data acquisition system.

Table 1. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
Settings	BKG -0.3, COEF 1.009
USH station analyser (OA)	
Model, S/N	TEI 49C #58546-318
Principle	UV absorption
Range	0-1 ppm
Settings	BKG +0.0 ppb, COEF 1.012
Pressure readings (mmHg)	Ambient 746.7; OA 742.9 (no adjustments were made)
RCC Buenos Aires Calibrator (OC)	
Model, S/N	TEI 49C-PS #56034-306
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.5 ppb, COEF 1.015
Pressure readings (mmHg)	Ambient 746.7; OC 745.1, adjusted to 746.8 before the comparison

Results

Each ozone level was applied for 15 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 1 above. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) and calibrator (OC) values.

The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary (Figure and Equations).

Table 2. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the USH ozone analyser (OA) TEI 49C #58546-318 with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-02-03 18:49	1	0	0.07	0.11	0.09	0.10	0.04	NA
2016-02-03 19:04	1	100	99.88	99.47	0.05	0.11	-0.41	-0.4
2016-02-03 19:19	1	200	199.65	199.15	0.06	0.28	-0.50	-0.3
2016-02-03 19:34	1	50	50.05	50.00	0.06	0.05	-0.05	-0.1
2016-02-03 19:49	1	250	249.40	248.86	0.14	0.22	-0.54	-0.2
2016-02-03 20:04	1	150	149.94	149.65	0.06	0.08	-0.29	-0.2
2016-02-03 20:19	2	0	-0.01	0.00	0.07	0.11	0.01	NA
2016-02-03 20:34	2	40	40.03	39.83	0.12	0.10	-0.20	-0.5
2016-02-03 20:49	2	20	20.05	19.82	0.07	0.10	-0.23	-1.1
2016-02-03 21:04	2	80	79.84	79.67	0.06	0.07	-0.17	-0.2
2016-02-03 21:34	2	10	10.34	10.15	0.16	0.21	-0.19	-1.8
2016-02-03 21:49	2	30	29.88	29.87	0.03	0.14	-0.01	0.0
2016-02-03 21:49	2	60	59.94	59.96	0.11	0.15	0.02	0.0
2016-02-03 22:04	2	90	89.84	89.73	0.07	0.14	-0.11	-0.1
2016-02-03 22:34	2	50	49.93	49.80	0.11	0.10	-0.13	-0.3
2016-02-03 22:49	2	70	69.95	69.89	0.06	0.15	-0.06	-0.1
2016-02-03 23:04	3	0	0.02	-0.07	0.10	0.16	-0.09	NA
2016-02-03 23:19	3	75	74.88	74.67	0.07	0.14	-0.21	-0.3
2016-02-03 23:34	3	225	224.59	224.26	0.15	0.17	-0.33	-0.1
2016-02-03 23:49	3	125	124.90	124.82	0.07	0.16	-0.08	-0.1
2016-02-04 00:04	3	175	174.81	174.74	0.14	0.22	-0.07	0.0
2016-02-04 00:26	3	25	25.15	25.07	0.13	0.22	-0.08	-0.3
2016-02-04 00:49	4	0	0.09	0.18	0.08	0.16	0.09	NA
2016-02-04 01:04	4	90	89.86	89.74	0.14	0.19	-0.12	-0.1
2016-02-04 01:19	4	30	30.00	30.02	0.05	0.15	0.02	0.1
2016-02-04 01:34	4	60	59.86	59.84	0.06	0.08	-0.02	0.0
2016-02-04 01:49	4	70	69.85	69.87	0.09	0.16	0.02	0.0
2016-02-04 02:04	4	40	40.04	39.90	0.12	0.08	-0.14	-0.3
2016-02-04 02:19	4	10	10.25	10.17	0.15	0.12	-0.08	-0.8
2016-02-04 02:34	4	20	19.97	19.82	0.07	0.12	-0.15	-0.8
2016-02-04 02:49	4	50	49.89	49.71	0.09	0.10	-0.18	-0.4
2016-02-04 03:04	4	80	79.91	79.85	0.07	0.17	-0.06	-0.1
2016-02-04 03:19	5	0	0.14	0.08	0.06	0.09	-0.06	NA
2016-02-04 03:34	5	100	99.86	99.70	0.11	0.08	-0.16	-0.2
2016-02-04 03:49	5	200	199.53	199.34	0.09	0.23	-0.19	-0.1
2016-02-04 04:04	5	50	50.06	49.76	0.10	0.12	-0.30	-0.6
2016-02-04 04:19	5	250	249.44	249.00	0.17	0.31	-0.44	-0.2
2016-02-04 04:34	5	150	149.91	149.64	0.07	0.13	-0.27	-0.2
2016-02-04 04:49	6	0	0.06	0.04	0.07	0.19	-0.02	NA
2016-02-04 05:04	6	40	40.02	39.60	0.07	0.21	-0.42	-1.0
2016-02-04 05:19	6	20	20.11	20.03	0.07	0.16	-0.08	-0.4
2016-02-04 05:34	6	80	79.84	79.54	0.10	0.09	-0.30	-0.4
2016-02-04 06:04	6	10	10.43	10.14	0.04	0.25	-0.29	-2.8
2016-02-04 06:19	6	30	29.91	29.85	0.12	0.19	-0.06	-0.2
2016-02-04 06:19	6	60	59.95	59.69	0.07	0.13	-0.26	-0.4

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-02-04 06:34	6	90	89.78	89.41	0.09	0.04	-0.37	-0.4
2016-02-04 07:04	6	50	50.05	50.00	0.08	0.15	-0.05	-0.1
2016-02-04 07:19	6	70	69.92	69.74	0.07	0.18	-0.18	-0.3
2016-02-04 07:34	7	0	0.14	-0.10	0.10	0.11	-0.24	NA
2016-02-04 07:49	7	75	74.84	74.73	0.10	0.14	-0.11	-0.1
2016-02-04 08:04	7	225	224.61	224.54	0.10	0.22	-0.07	0.0
2016-02-04 08:19	7	125	124.98	124.74	0.12	0.14	-0.24	-0.2
2016-02-04 08:34	7	175	174.66	174.54	0.08	0.09	-0.12	-0.1
2016-02-04 08:56	7	25	25.18	25.14	0.12	0.19	-0.04	-0.2
2016-02-04 09:19	8	0	0.06	0.13	0.10	0.20	0.07	NA
2016-02-04 09:34	8	90	89.82	89.94	0.09	0.12	0.12	0.1
2016-02-04 09:49	8	30	29.92	29.71	0.15	0.12	-0.21	-0.7
2016-02-04 10:04	8	60	59.85	59.63	0.08	0.12	-0.22	-0.4
2016-02-04 10:19	8	70	69.78	69.81	0.09	0.12	0.03	0.0
2016-02-04 10:34	8	40	39.90	39.74	0.10	0.21	-0.16	-0.4
2016-02-04 10:49	8	10	10.21	10.05	0.07	0.21	-0.16	-1.6
2016-02-04 11:04	8	20	19.96	19.75	0.06	0.06	-0.21	-1.1
2016-02-04 11:19	8	50	49.81	49.81	0.07	0.20	0.00	0.0
2016-02-04 11:34	8	80	79.83	79.72	0.04	0.10	-0.11	-0.1
2016-02-04 11:49	9	0	0.05	-0.05	0.06	0.15	-0.10	NA
2016-02-04 12:04	9	100	99.78	99.69	0.08	0.12	-0.09	-0.1
2016-02-04 12:19	9	200	199.49	199.47	0.16	0.23	-0.02	0.0
2016-02-04 12:34	9	50	50.05	50.03	0.09	0.06	-0.02	0.0
2016-02-04 12:49	9	250	249.34	249.21	0.13	0.22	-0.13	-0.1
2016-02-04 13:04	9	150	149.87	149.59	0.06	0.14	-0.28	-0.2

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the ozone calibrator (OC) TEI 49C-PS #56034-306 with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sd OC (ppb)	OC -TS (ppb)	OC -TS (%)
2016-02-03 18:49	1	0	0.07	0.21	0.09	0.05	0.14	NA
2016-02-03 19:04	1	100	99.88	99.66	0.05	0.09	-0.22	-0.2
2016-02-03 19:19	1	200	199.65	199.07	0.06	0.10	-0.58	-0.3
2016-02-03 19:34	1	50	50.05	50.07	0.06	0.03	0.02	0.0
2016-02-03 19:49	1	250	249.40	248.77	0.14	0.14	-0.63	-0.3
2016-02-03 20:04	1	150	149.94	149.62	0.06	0.09	-0.32	-0.2
2016-02-03 20:19	2	0	-0.01	0.35	0.07	0.08	0.36	NA
2016-02-03 20:34	2	40	40.03	40.09	0.12	0.06	0.06	0.1
2016-02-03 20:49	2	20	20.05	20.30	0.07	0.04	0.25	1.2
2016-02-03 21:04	2	80	79.84	79.96	0.06	0.02	0.12	0.2
2016-02-03 21:34	2	10	10.34	10.56	0.16	0.09	0.22	2.1
2016-02-03 21:49	2	30	29.88	30.09	0.03	0.10	0.21	0.7
2016-02-03 21:49	2	60	59.94	60.17	0.11	0.07	0.23	0.4
2016-02-03 22:04	2	90	89.84	89.96	0.07	0.13	0.12	0.1
2016-02-03 22:34	2	50	49.93	50.07	0.11	0.12	0.14	0.3
2016-02-03 22:49	2	70	69.95	70.08	0.06	0.07	0.13	0.2
2016-02-03 23:04	3	0	0.02	0.39	0.10	0.11	0.37	NA
2016-02-03 23:19	3	75	74.88	75.04	0.07	0.13	0.16	0.2
2016-02-03 23:34	3	225	224.59	224.24	0.15	0.22	-0.35	-0.2
2016-02-03 23:49	3	125	124.90	125.01	0.07	0.08	0.11	0.1
2016-02-04 00:04	3	175	174.81	174.75	0.14	0.15	-0.06	0.0
2016-02-04 00:26	3	25	25.15	25.33	0.13	0.16	0.18	0.7
2016-02-04 00:49	4	0	0.09	0.53	0.08	0.16	0.44	NA
2016-02-04 01:04	4	90	89.86	89.95	0.14	0.10	0.09	0.1
2016-02-04 01:19	4	30	30.00	30.29	0.05	0.07	0.29	1.0
2016-02-04 01:34	4	60	59.86	59.93	0.06	0.06	0.07	0.1
2016-02-04 01:49	4	70	69.85	70.03	0.09	0.27	0.18	0.3
2016-02-04 02:04	4	40	40.04	40.24	0.12	0.11	0.20	0.5
2016-02-04 02:19	4	10	10.25	10.57	0.15	0.18	0.32	3.1
2016-02-04 02:34	4	20	19.97	20.15	0.07	0.09	0.18	0.9
2016-02-04 02:49	4	50	49.89	50.00	0.09	0.10	0.11	0.2
2016-02-04 03:04	4	80	79.91	80.13	0.07	0.07	0.22	0.3
2016-02-04 03:19	5	0	0.14	0.49	0.06	0.13	0.35	NA
2016-02-04 03:34	5	100	99.87	99.88	0.12	0.11	0.01	0.0
2016-02-04 03:49	5	200	199.53	199.40	0.09	0.11	-0.13	-0.1
2016-02-04 04:04	5	50	50.06	50.19	0.10	0.07	0.13	0.3
2016-02-04 04:19	5	250	249.44	249.26	0.17	0.17	-0.18	-0.1
2016-02-04 04:34	5	150	149.91	149.81	0.07	0.13	-0.10	-0.1
2016-02-04 04:49	6	0	0.06	0.47	0.07	0.09	0.41	NA
2016-02-04 05:04	6	40	40.02	39.95	0.07	0.12	-0.07	-0.2
2016-02-04 05:19	6	20	20.11	20.38	0.07	0.09	0.27	1.3
2016-02-04 05:34	6	80	79.84	79.95	0.10	0.08	0.11	0.1
2016-02-04 06:04	6	10	10.43	10.65	0.04	0.18	0.22	2.1
2016-02-04 06:19	6	30	29.91	30.20	0.12	0.13	0.29	1.0
2016-02-04 06:19	6	60	59.95	60.09	0.07	0.11	0.14	0.2

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sd OC (ppb)	OC -TS (ppb)	OC -TS (%)
2016-02-04 06:34	6	90	89.78	89.80	0.09	0.05	0.02	0.0
2016-02-04 07:04	6	50	50.05	50.11	0.08	0.19	0.06	0.1
2016-02-04 07:19	6	70	69.92	69.98	0.07	0.03	0.06	0.1
2016-02-04 07:34	7	0	0.14	0.48	0.10	0.05	0.34	NA
2016-02-04 07:49	7	75	74.84	75.04	0.10	0.20	0.20	0.3
2016-02-04 08:04	7	225	224.61	224.66	0.10	0.11	0.05	0.0
2016-02-04 08:19	7	125	124.98	125.04	0.12	0.09	0.06	0.0
2016-02-04 08:34	7	175	174.66	174.70	0.08	0.12	0.04	0.0
2016-02-04 08:56	7	25	25.18	25.36	0.12	0.20	0.18	0.7
2016-02-04 09:19	8	0	0.06	0.39	0.10	0.04	0.33	NA
2016-02-04 09:34	8	90	89.82	90.04	0.09	0.12	0.22	0.2
2016-02-04 09:49	8	30	29.92	30.15	0.15	0.07	0.23	0.8
2016-02-04 10:04	8	60	59.85	59.88	0.08	0.15	0.03	0.1
2016-02-04 10:19	8	70	69.78	70.03	0.09	0.17	0.25	0.4
2016-02-04 10:34	8	40	39.90	40.08	0.10	0.08	0.18	0.5
2016-02-04 10:49	8	10	10.21	10.46	0.07	0.11	0.25	2.4
2016-02-04 11:04	8	20	19.96	20.18	0.06	0.08	0.22	1.1
2016-02-04 11:19	8	50	49.81	50.12	0.07	0.06	0.31	0.6
2016-02-04 11:34	8	80	79.83	80.09	0.04	0.05	0.26	0.3
2016-02-04 11:49	9	0	0.05	0.38	0.06	0.10	0.33	NA
2016-02-04 12:04	9	100	99.78	99.89	0.08	0.14	0.11	0.1
2016-02-04 12:19	9	200	199.49	199.71	0.16	0.11	0.22	0.1
2016-02-04 12:34	9	50	50.05	50.18	0.09	0.14	0.13	0.3
2016-02-04 12:49	9	250	249.34	249.36	0.13	0.12	0.02	0.0
2016-02-04 13:04	9	150	149.87	149.97	0.06	0.12	0.10	0.1

CO Measurements

Monitoring Set-up and Procedures

Standards

The following Table gives an overview of the current and past standards for the calibration of the CO instrument. Automatic zero and span checks are made daily at 11:00 local time using a dilution system. In addition, regular manual span checks (1-monthly) should be made.

Table 4. CO Standards available at USH.

Cylinder ID	Manufacturer	Use	CO (ppb)	U_{CO} (ppb)	Start of use	End of use
080808_CA08263	Empa	Dilution	38390.0	760.0	Stock	
CA05308	Scott Marrin	Dilution	98800.0	990.0	Nov 08	cont.
CA05309	Scott Marrin	Dilution	98800.0	990.0	Stock	.
080808_CA08220	Empa	Direct calibration	2582.0	52.0	Nov 08	cont.

In addition to the above standards, WCC-Empa left two cylinders that were used for the performance audit and the parallel measurements with the Picarro G2401 at the USH station. These cylinders are intended to be used as calibration standards for the planned GHG measurements. Details of these tanks can be found below in the chapter WCC-Empa Traveling Standards.

Comparison of the Carbon Monoxide Analyser

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix.

Setup and Connections

Table 5 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the USH data acquisition system.

Table 5. Experimental details the CO comparison.

Travelling standard (TS)	
A CO in air standard (080808_CA08263, 38.39 ppm CO, 1900 psi) prepared by WCC-Empa and calibrated against the WMO- X2000 carbon monoxide scale at WCC-Empa has been used in combination with a dilution system. Levels ranging from 0 to 800 ppb (steps of 50 ppb) were generated in random order and were simultaneously measured by the USH instrument and the WCC-Empa Picarro G2401, which was calibrated using two calibration standards. The calibrated Picarro readings were taken as the reference value. Details of the standards used for the calibration of the Picarro are given in Table 9.	
USH analyser	
Model, S/N	HORIBA APMA-360 SN 712020
Principle	Non-Dispersive Infrared (NDIR) Absorption Spectroscopy
Drying system	PERMAPURE Nafion drier
Comparison procedures	
Connection	The output of the dilution system was connected to the sample inlet of the Horiba APMA360

Results

The results of the assessment are shown in the Executive Summary (figures and equations), and the individual measurements of the TS are presented in the following Table.

Table 6. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the HORIBA APMA-360 SN 712020 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	CO Level	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-02-05 03:56:30)	0	-0.4	1.9	6.9	13.2	4	7.3	NA
(16-02-05 04:26:30)	800	804.8	1.9	797.7	5.2	4	-7.2	-0.9
(16-02-05 04:56:30)	50	53.2	1.1	39.6	9.6	4	-13.6	-25.6
(16-02-05 05:26:30)	0	0.2	1.5	3.1	5.7	4	3.0	NA
(16-02-05 05:56:30)	760	755.4	1.5	754.3	1.5	4	-1.1	-0.1
(16-02-05 06:26:30)	100	102.9	1.3	105.7	7.7	4	2.8	2.7
(16-02-05 06:56:30)	0	-0.2	1.8	0.2	1.0	4	0.4	NA
(16-02-05 07:26:30)	700	704.8	1.3	711.1	5.0	4	6.4	0.9
(16-02-05 07:56:30)	150	153.9	1.6	152.8	7.1	4	-1.1	-0.7
(16-02-05 08:26:30)	0	0.2	1.0	-4.2	6.6	4	-4.3	NA
(16-02-05 08:56:30)	650	654.9	2.1	653.0	2.1	4	-1.9	-0.3
(16-02-05 09:26:30)	200	203.9	1.5	204.4	5.9	4	0.5	0.3
(16-02-05 09:56:30)	0	-0.4	1.3	-2.1	10.0	4	-1.7	NA
(16-02-05 10:26:30)	610	605.1	1.5	603.8	3.0	4	-1.4	-0.2
(16-02-05 10:56:30)	250	254.2	1.7	247.8	6.2	4	-6.4	-2.5
(16-02-05 11:26:30)	0	0.1	1.1	-1.0	5.0	4	-1.2	NA
(16-02-05 11:56:30)	550	554.6	1.3	554.7	2.3	4	0.1	0.0
(16-02-05 12:26:30)	300	304.0	1.4	301.6	2.2	4	-2.4	-0.8
(16-02-05 12:56:30)	0	0.4	1.5	0.7	3.5	4	0.3	NA
(16-02-05 13:26:30)	500	503.9	1.5	504.2	7.7	4	0.3	0.1
(16-02-05 13:56:30)	350	354.1	2.0	350.4	4.0	4	-3.7	-1.0
(16-02-05 14:26:30)	0	0.1	1.7	-3.6	3.5	4	-3.7	NA
(16-02-05 14:56:30)	450	454.2	2.0	455.0	9.9	4	0.9	0.2
(16-02-05 15:26:30)	400	404.3	1.3	411.4	8.0	4	7.1	1.8

WCC-Empa Traveling Standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the Standard Reference Photometer before and after the audit. The following instruments were used:

WCC-Empa ozone reference: NIST Standard Reference Photometer SRP #15 (Master)

WCC-Empa TS: TEI 49C-PS #54509-300, BKG -0.3, COEF 1.009

Zero air source: Pressurized air –zero air generator – Purafil – charcoal – outlet filter

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 7. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 7). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

X_{TS} (ppb) = ([TS] - 0.14 ppb) / 1.0017 (6a)

u_{TS} (ppb) = sqrt((0.43 ppb)^2 + (0.0034 * X)^2) (6b)

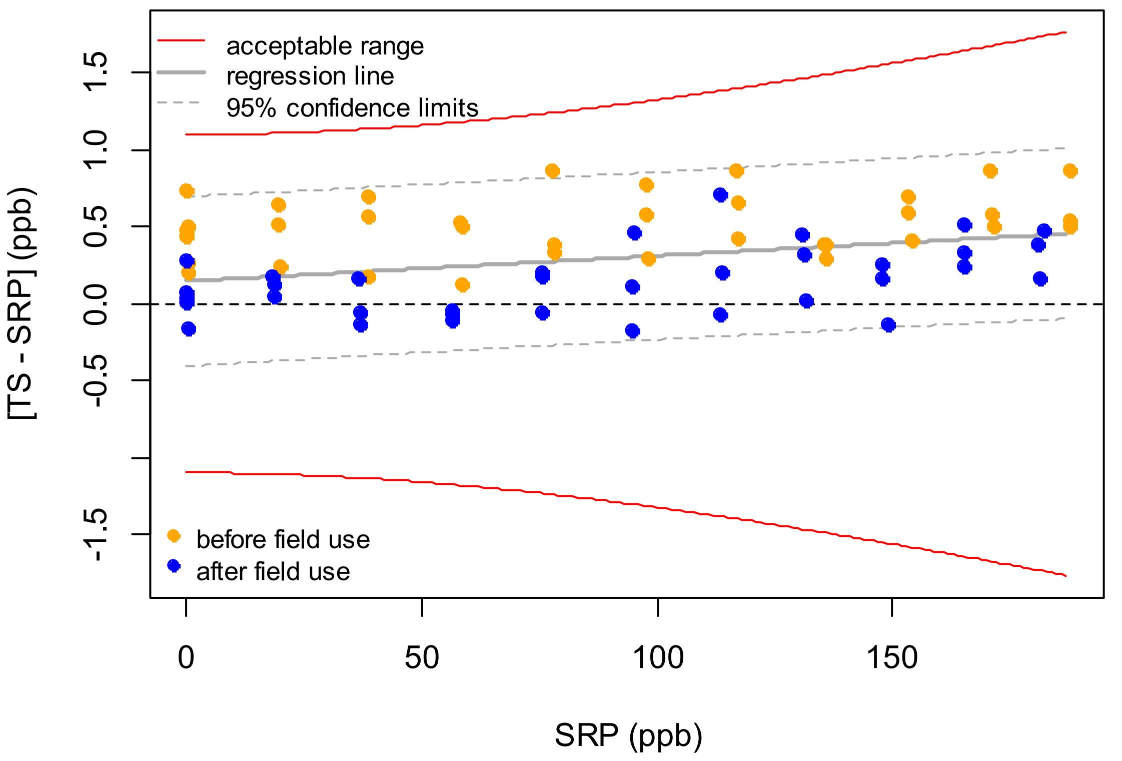

Figure 7. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 7. Five-minute aggregates computed from 10 valid 30-second values for the 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)
2015-09-07	1	0	0.08	0.18	0.34	0.29
2015-09-07	1	155	154.00	0.31	154.41	0.25
2015-09-07	1	170	171.42	0.26	171.92	0.24
2015-09-07	1	80	78.18	0.25	78.51	0.66
2015-09-07	1	100	97.99	0.25	98.28	0.23
2015-09-07	1	115	117.10	0.40	117.75	0.11
2015-09-07	1	135	135.68	0.24	136.07	0.21
2015-09-07	1	60	58.34	0.19	58.48	0.11
2015-09-07	1	190	187.65	0.24	188.19	0.17
2015-09-07	1	40	38.43	0.24	38.62	0.21
2015-09-07	1	20	19.39	0.15	19.90	0.38
2015-09-07	1	0	-0.02	0.27	0.41	0.26
2015-09-07	2	0	0.13	0.24	0.34	0.22
2015-09-07	2	60	58.35	0.23	58.85	0.17
2015-09-07	2	135	135.89	0.37	136.28	0.45
2015-09-07	2	190	187.58	0.18	188.45	0.19
2015-09-07	2	155	153.47	0.38	154.06	0.31
2015-09-07	2	20	19.67	0.24	19.91	0.39
2015-09-07	2	80	77.85	0.34	78.72	0.21
2015-09-07	2	40	38.34	0.32	38.91	0.16
2015-09-07	2	100	97.83	0.19	98.41	0.15
2015-09-07	2	115	116.96	0.15	117.83	0.20
2015-09-07	2	170	170.97	0.25	171.84	0.15
2015-09-07	2	0	0.00	0.22	0.49	0.21
2015-09-07	3	0	0.09	0.18	0.60	0.18
2015-09-07	3	40	38.35	0.13	39.05	0.26
2015-09-07	3	170	171.29	0.29	171.87	0.11
2015-09-07	3	60	58.14	0.25	58.67	0.23
2015-09-07	3	20	19.55	0.24	20.20	0.06
2015-09-07	3	115	117.03	0.24	117.45	0.12
2015-09-07	3	155	153.29	0.20	153.99	0.10
2015-09-07	3	80	78.11	0.20	78.50	0.29
2015-09-07	3	190	187.57	0.23	188.07	0.22
2015-09-07	3	100	97.84	0.34	98.61	0.13
2015-09-07	3	135	135.79	0.26	136.08	0.24
2015-09-07	3	0	-0.13	0.19	0.60	0.07
2016-07-26	4	0	0.12	0.18	-0.04	0.06
2016-07-26	4	130	131.63	0.28	131.65	0.10
2016-07-26	4	55	56.41	0.31	56.35	0.10
2016-07-26	4	115	113.48	0.31	113.42	0.11
2016-07-26	4	95	94.47	0.26	94.29	0.12
2016-07-26	4	35	36.36	0.27	36.54	0.06
2016-07-26	4	150	147.68	0.21	147.85	0.23
2016-07-26	4	180	181.19	0.25	181.35	0.16
2016-07-26	4	165	165.03	0.35	165.54	0.15
2016-07-26	4	20	18.30	0.23	18.48	0.09
2016-07-26	4	75	75.57	0.25	75.75	0.08
2016-07-26	4	0	-0.01	0.18	0.02	0.09
2016-07-26	5	0	-0.06	0.29	0.01	0.09
2016-07-26	5	95	94.96	0.35	95.42	0.08

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2016-07-26	5	20	18.56	0.21	18.60	0.04
2016-07-26	5	180	182.24	0.29	182.71	0.33
2016-07-26	5	115	113.72	0.30	113.93	0.12
2016-07-26	5	35	36.67	0.25	36.61	0.06
2016-07-26	5	55	56.47	0.16	56.37	0.06
2016-07-26	5	75	75.44	0.17	75.65	0.07
2016-07-26	5	165	165.10	0.22	165.44	0.13
2016-07-26	5	130	130.87	0.24	131.33	0.09
2016-07-26	5	150	147.89	0.28	148.15	0.09
2016-07-26	5	0	-0.21	0.34	0.07	0.08
2016-07-26	6	0	0.04	0.30	0.05	0.11
2016-07-26	6	35	36.69	0.27	36.56	0.06
2016-07-26	6	150	148.89	0.19	148.75	0.17
2016-07-26	6	55	56.40	0.11	56.36	0.07
2016-07-26	6	180	181.08	0.21	181.47	0.09
2016-07-26	6	165	165.15	0.34	165.40	0.08
2016-07-26	6	75	75.62	0.27	75.57	0.11
2016-07-26	6	95	94.50	0.25	94.61	0.09
2016-07-26	6	20	18.34	0.38	18.47	0.10
2016-07-26	6	130	131.25	0.31	131.57	0.22
2016-07-26	6	115	113.19	0.37	113.90	0.11
2016-07-26	6	0	-0.02	0.26	0.05	0.08

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide and Methane. NOAA/ESRL was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL by way of traveling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-X2014A scale (Novelli et al., 2003), (http://www.esrl.noaa.gov/gmd/ccl/co_scale.html)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004A scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

More information about the NOAA/ESRL calibration scales can be found on the GMD website (www.esrl.noaa.gov/gmd/ccl). The scales were transferred to the TS using the following instruments:

CO and N_2O: Aerodyne QC-TILDAS-CS analyser
CO_2 and CH_4: Picarro G1301 / Picarro G2401.

Table 8 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. For internal consistency among the available laboratory standards (LS) at WCC-Empa, new values have been assigned to the NOAA standards for some tanks. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 9, and Figure 8 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS.

Table 8. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	**CO (ppb)**	**sd**	**CH_4 (ppb)**	**sd**	**N_2O (ppb)**	**sd**	**CO_2 (ppm)**	**sd**
CB11485	110.88	0.88	1844.80	1.00	328.46	0.22	394.30	0.06
CB11499	141.03	0.80	1933.77	1.00	329.15	0.22	407.33	0.06
CC311846	463.76	1.40	2485.30	1.00	357.19	0.30	484.39	0.06

Table 9. Calibration summary of the WCC-Empa travelling standards.

TS	**CO (ppb)**	**sdCO (ppb)**	**CH_4 (ppb)**	**$sdCH_4$ (ppb)**	**CO_2 (ppm)**	**$sdCO_2$ (ppm)**	**N_2O (ppb)**	**sdN_2O (ppb)**
120614_CB09197	90.45	1.01	1778.03	0.08	329.53	0.02	321.66	0.09
130822_CB10205	278.47	0.19	2397.66	0.13	427.18	0.02	326.81	0.04

The standards listed in Table 9 were left at USH for the use as working standards of future GHG measurements.

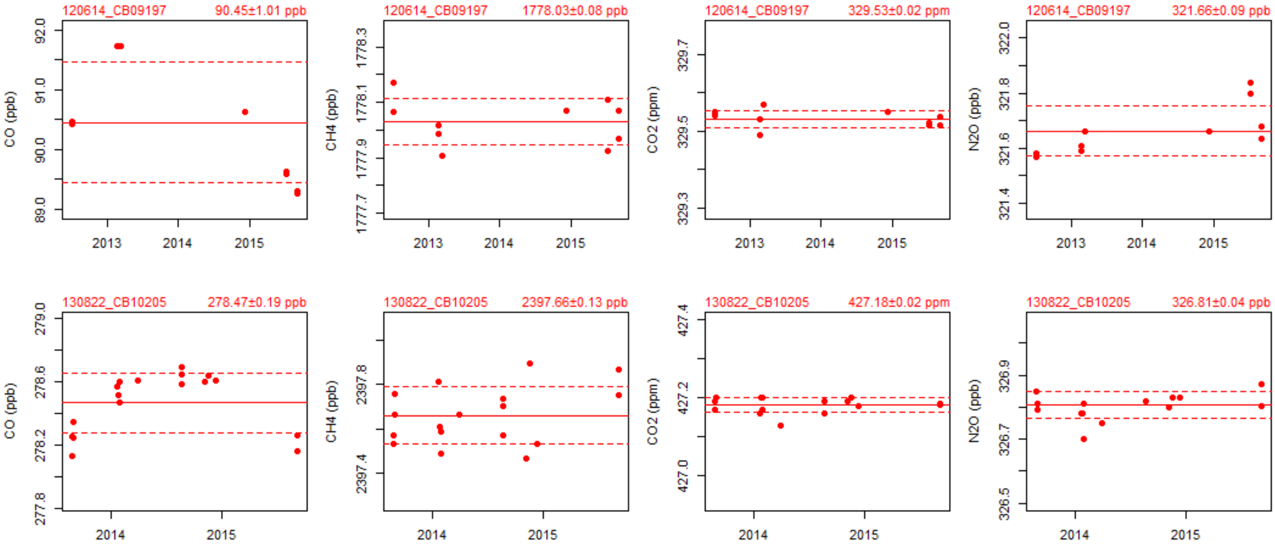

Figure 8. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.*

Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH_4 and CO_2, the Picarro G2401 was calibrated every 1810 min using one WCC-Empa TS as a working standard, and the other TS was used as a target. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 0.5 ppb for CH_4 and 0.05 ppm for CO_2. The two target cylinders were within half of the WMO GAW compatibility goals for all measurements.

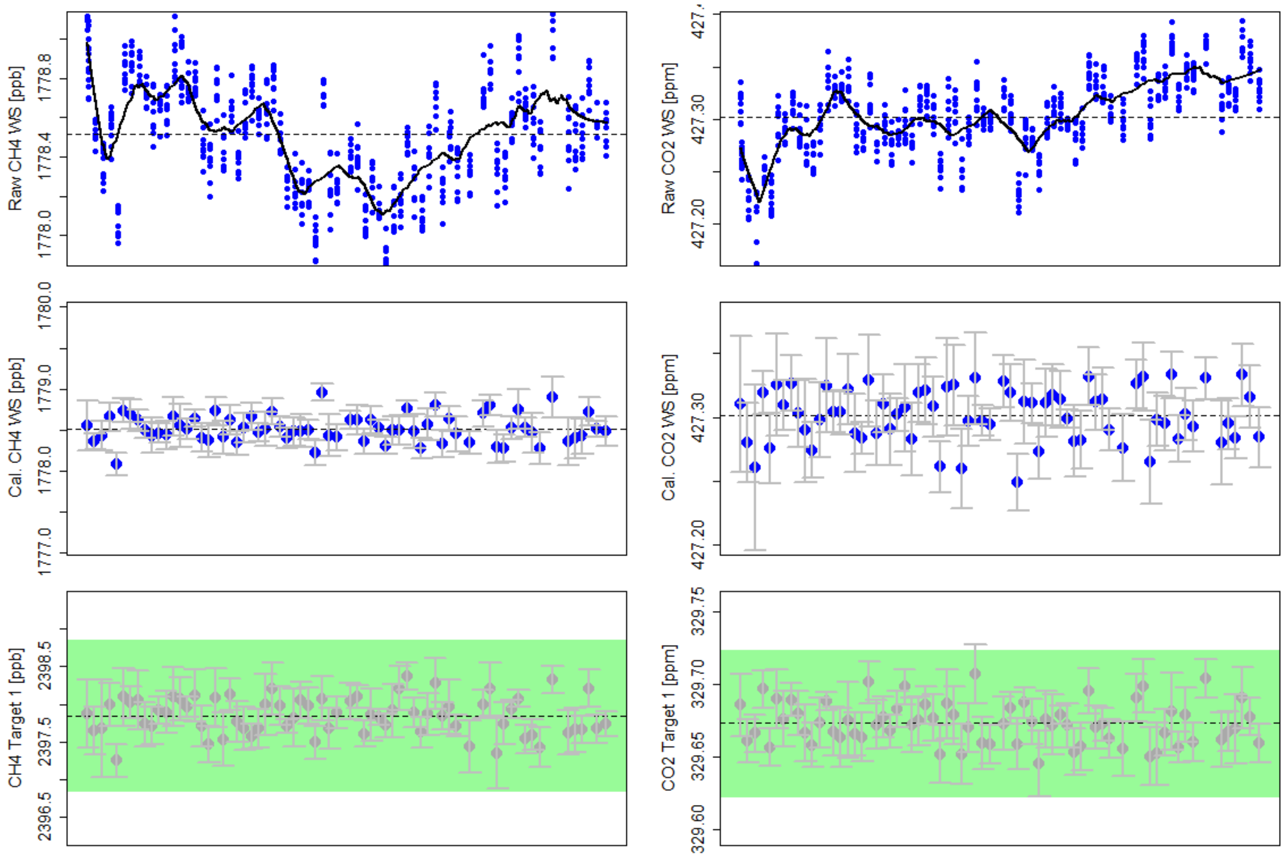

Figure 9. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1-min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target cylinders. Individual points in the three lower panels are 10 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

For CO, the Picarro G2401 was calibrated every 1810 min using two WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

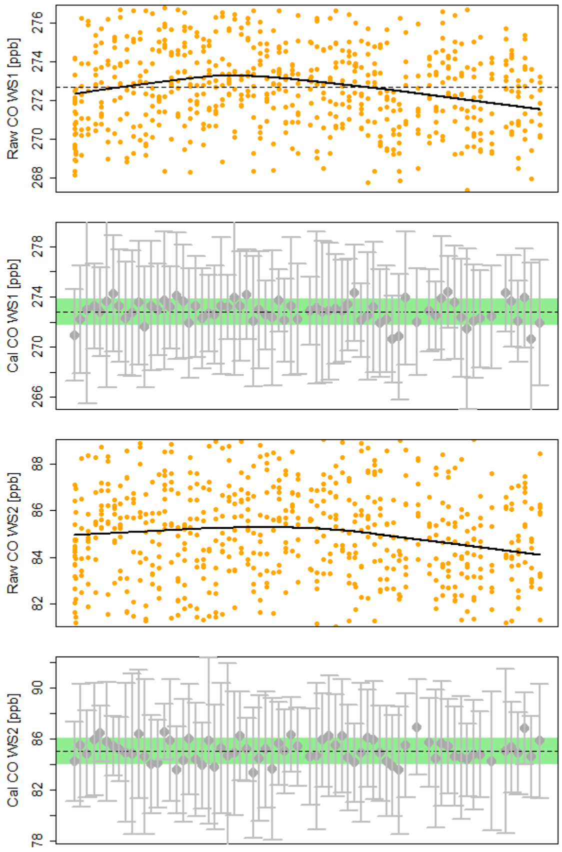

Figure 10. *CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1-min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 10 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.*

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Ozone Audit Executive Summary

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.8485°S 68.3107°W (18 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2016-02-03/04
1.2	Auditor:	Christoph Zellweger and Stefan Bugmann
1.3	Station staff involved in audit:	Manuel Cupeiro
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C-PS #54509-300, BKG -0.3, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	[TS] = (1.0017±0.0006) • [SRP] + (0.14±0.05)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #58546-318
1.6.2	Range of calibration:	0 – 250 ppb
1.6.3	Coefficients at start of audit	BKG = +0.0; COEF = 1.012
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0008±0.0003) • [SRP] + (0.06±0.03)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.06 ppb) / 1.0008
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.53e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 16/1

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Ozone Audit Executive Summary

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.8485°S 68.3107°W (18 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2016-02-03/04
1.2	Auditor:	Christoph Zellweger and Stefan Bugmann
1.3	Station staff involved in audit:	Manuel Cupeiro
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C-PS #54509-300, BKG -0.3, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	[TS] = (1.0017±0.0006) · [SRP] + (0.14±0.05)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C-PS #56034-306
1.6.2	Range of calibration:	0 – 250 ppb
1.6.3	Coefficients at start of audit	BKG -0.5 ppb, COEF 1.015
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9993±0.0003) · [SRP] + (0.43±0.02)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	XO3 (ppb) = ([OA] - 0.43 ppb) / 0.9993
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.54e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 16/1

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Carbon Monoxide Audit Executive Summary

0.1	Station Name:	Ushuaia
0.2	GAW ID:	USH
0.3	Coordinates/Elevation:	54.8485°S 68.3107°W (18 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2016-02-05
1.2	Auditor:	Christoph Zellweger and Stefan Bugmann
1.3	Station staff involved in audit:	Manuel Cupeiro
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-X2014A scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2014A scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	HORIBA APMA-360 SN 712020
1.6.2	Range of calibration:	0 – 804 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.0006±0.0035) $\cdot$ X_{CO} - (1.0±1.4)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 1.0) / 1.0006
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (10.1 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 16/1

[CO]: Instrument readings; X: mixing ratios on the WMO-X2014A CO scale.

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LIST OF ABBREVIATIONS

BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
LS	Laboratory Standard
NA	Not Applicable
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
RCC-BsAs	Regional Calibration Center Buenos Aires
SMN	Servicio Meteorológico Nacional
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
USH	Ushuaia GAW Station
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization