SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, METHANE, CARBON DIOXIDE, NITROUS OXIDE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION IZAÑA SEPTEMBER 2013

Submitted to the World Meteorological Organization by

C. Zellweger, M. Steinbacher and B. Buchmann

WMO World Calibration Centre WCC-Empa

Empa Dübendorf, Switzerland

R. Steinbrecher

WMO World Calibration Centre WCC-N_2O

Institute of Meteorology and Climate Research (IMK-IFU)

Garmisch-Partenkirchen, Germany

WCC-Empa Report 13/2

WCC-Empa Report 13/2

Contact Information:

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

CONTENTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The sixth system and performance audit by WCC-Empa[1] at the Global GAW station Izaña (IZO) was conducted from 26. September – 1. October 2013 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). The comparison included for the first time side-by-side measurements with a WCC-Empa travelling instrument over a period of approx. 4 months for carbon dioxide, methane and carbon monoxide The Izaña Atmospheric Observatory is operated by the Izaña Atmospheric Research Center (IARC), which is part of the Agencia Estatal de Meteorología (AEMET), and has the status of a WMO GAW 'global' station. The IZO research station hosts additional measurement programmes. It is part of the National Oceanic and Atmospheric Administration (NOAA) flask sampling programme, the Network for the Detection of Atmospheric Composition Change (NDACC) and the Aerosol robotic network (AERONET). A complete overview of the collaboration with other networks can be found on the station website (http://izana.aemet.es/).

Previous WCC-Empa audits at the Izaña GAW station were conducted in November 1996 (Herzog et al., 1996), February 1998 (Herzog et al., 1998), June 2000 (Zellweger et al., 2000), December 2004 (Zellweger et al., 2004) and March 2009 (Zellweger et al., 2009).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr Emilio Cuevas	AEMET, GAW country contact, station manager
Mr Angel J. Gomez-Pelaez	AEMET, Greenhouse gas programme
Ms Vanessa Gomez-Trueba	AEMET, Greenhouse gas programme
Mr Ramón Ramos	AEMET, Reactive gases programme
Mrs Marina Jover	AEMET, Reactive gases programme

This report summarises the assessment of the Izaña GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide measurements in particular. The ozone assessment was made according to the method developed by WCC-Empa and QA/SAC Switzerland (Klausen et al., 2003).

The report is distributed to all involved institutes and the World Meteorological Organization in Geneva. The report will be posted 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 Location and Access

The Izaña station is located on the Island of Tenerife, Spain, roughly 300 km west of the African coast. The meteorological observatory is situated on a mountain platform (2373 m a.s.l.), 15 km north-east of the volcano Teide (3718 m a.s.l.). The station is normally above the temperature inversion layer, which generally is well established over the island, and therefore mostly free of local anthropogenic influences. The location is adequate for the intended purpose. Year-round access to IZO is possible by car.

Further information is available from GAWSIS (http://gaw.empa.ch/gawsis) and the station web site (http://izana.aemet.es/).

[1] WMO/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 based on mutual agreement.

Station Facilities

The facilities at the site consist of a large building, which comprises spacious laboratories, a workshop, a residence with 7 double rooms with bath, kitchen, library, meeting rooms, and offices for visiting scientists and technicians. A complete overview of the facilities can be found on the station webpage. The IZO research station is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Station Management and Operation

The Izaña Atmospheric Research Center (IARC) is part of the Planning, Strategy and Business Development Direction from the Meteorological State Agency of Spain (AEMET). AEMET is an Agency of the Ministry of Agriculture, Food and Environment of Spain. The IARC manages the high mountain Izaña Atmospheric Observatory (IZO) and the complementary background urban air quality research Observatory at Santa Cruz de Tenerife (SCO). The IARC headquarter is located in Santa Cruz de Tenerife.

Air Inlet Systems

Two state-of-the-art central inlet systems are available for the measurement of gaseous species. Both air intakes are located at the top of the laboratory tower. Individual analytical systems are connected to one of these inlets.

Surface Ozone Measurements

Surface ozone measurements started in 1996 at the Izaña site, and continuous one-hourly time series are available since then. Two ozone analysers are running in parallel at IZO.

Instrumentation. The station is equipped with two ozone analysers (TEI 49C). The instrumentation is fully adequate for its intended purpose.

Standards. A TEI 49C-PS ozone standard is available at the site for instrument calibrations and checks. Calibrations are made every three months. With this equipment, adequate quality control of the IZO ozone measurements is possible.

Intercomparison (Performance Audit). The IZO ozone analysers and the IZO station calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The results of the comparisons are 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 (TS) and the IZO data acquisition (station analysers), and no further corrections were applied.

Following comparisons were made:

- Primary station analyser TEI 49C #63900-337 with current calibration settings (September 2013, COEF 1.053, BKG 0.0), including inlet filter.
- Primary station analyser TEI 49C #63900-337 with original calibration settings as of March 2009 (COEF 1.006, BKG 0.0), including new inlet filter.
- Secondary station analyser TEI 49C #72491-371 with current calibration settings (September 2013, COEF 1.042, BKG 0.0), including inlet filter.
- Station standard TEI 49C-PS #56084-306 with current calibration settings (September 2013, COEF 1.014, BKG -0.8). It was noticed that this instrument had software or electronic problems during this comparison, and the comparison was repeated with a new BKG setting of -0.1 afterwards.

- Since the problems with the station calibrator could not be solved during the audit, the instrument was shipped to Empa after the audit, repaired, and calibrated against the SRP in February 2014.

During the last WCC-Empa audit in 2009 it was recommended that the calibration settings of the IZO ozone analysers should be adjusted using a calibration with the IZO station calibrator. It was further recommended that after this initial calibration setting change, further adjustments should only be made after significant changes and identification of the reason for the changes. This recommendation was somehow unclear, and the IZO station staff frequently adjusted the calibration settings of both instruments after the calibrations which took place every three months. All changes of the calibration settings were well documented.

The calibration settings (COEF) of the ozone analysers that were encountered during the present audit clearly exceed the normal range for this type of instrument, which is usually between 1.005 and 1.035, depending on the individual instrument. Thus, it was expected that significant deviations will be observed, which was confirmed by the comparisons.

It was further noticed during the conditioning of the instruments with an ozone mole fraction of 500 ppb that a loss over the inlet filter cannot be excluded. A loss of approx. 10 ppb (corresponding to 2%) was observed with the filter in use for the primary instrument; the loss decreased to 3 ppb (0.6%) after exchange of the filter.

The following equations characterise the bias of the instruments:

TEI 49C #63900-337 (BKG 0.0 ppb, COEF 1.053):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.22 ppb) / 1.0177 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.52e-05 * X_{O3}^2) (1b)

TEI 49C #63900-337 (Settings of last audit in 2009, BKG 0.0 ppb, COEF 1.006):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.12 ppb) / 0.9819 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.80e-05 * X_{O3}^2) (1d)

TEI 49i #72491-371 (BKG 0.0 ppb, COEF 1.042):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.14 ppb) / 1.0221 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.52e-05 * X_{O3}^2) (1f)

TEI 49C-PS #56084-306 (BKG -0.8 ppb, COEF 1.014, A/B problem, see below):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] - 0.65 ppb) / 0.9903 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.61e-05 * X_{O3}^2) (1h)

TEI 49C-PS #56084-306 (BKG -0.1 ppb, COEF 1.014, without A/B problem):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] + 0.05 ppb) / 1.0090 (1i)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.52e-05 * X_{O3}^2) (1j)

The results of the comparison are further presented in the following figures.

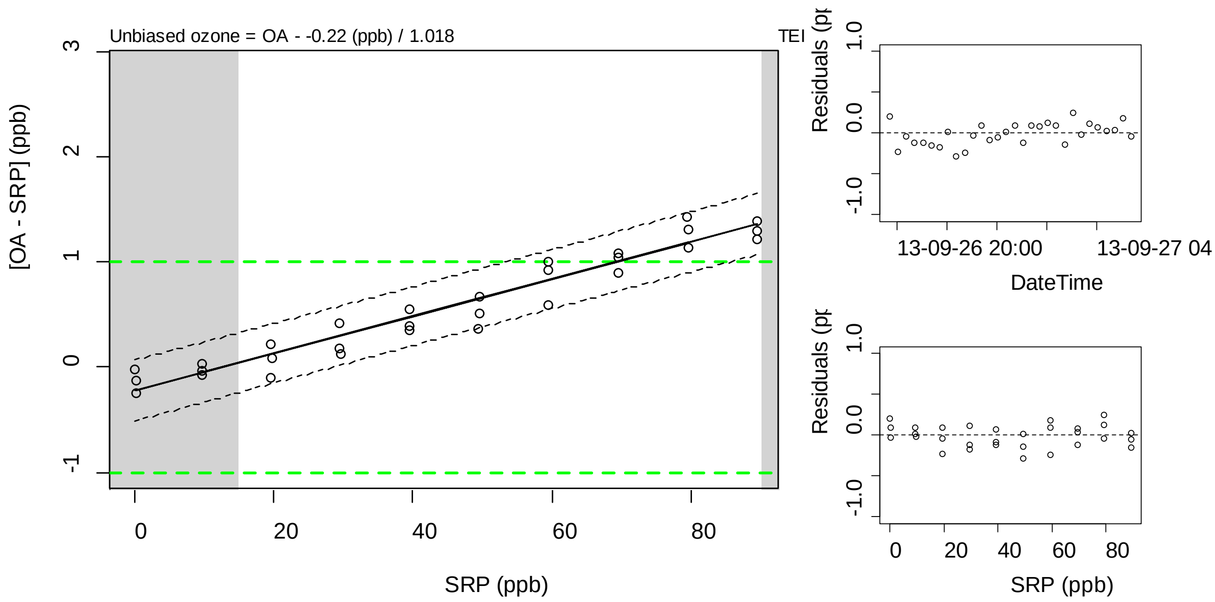

Figure 1. *Left: Bias of the primary IZO ozone analyser (TEI 49C #63900-337, BKG 0.0 ppb,* COEF *1.053) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The white area represents the mole fraction range relevant for IZO, whereas the green lines correspond to the DQOs. 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). The comparison was made including the inlet filter.*

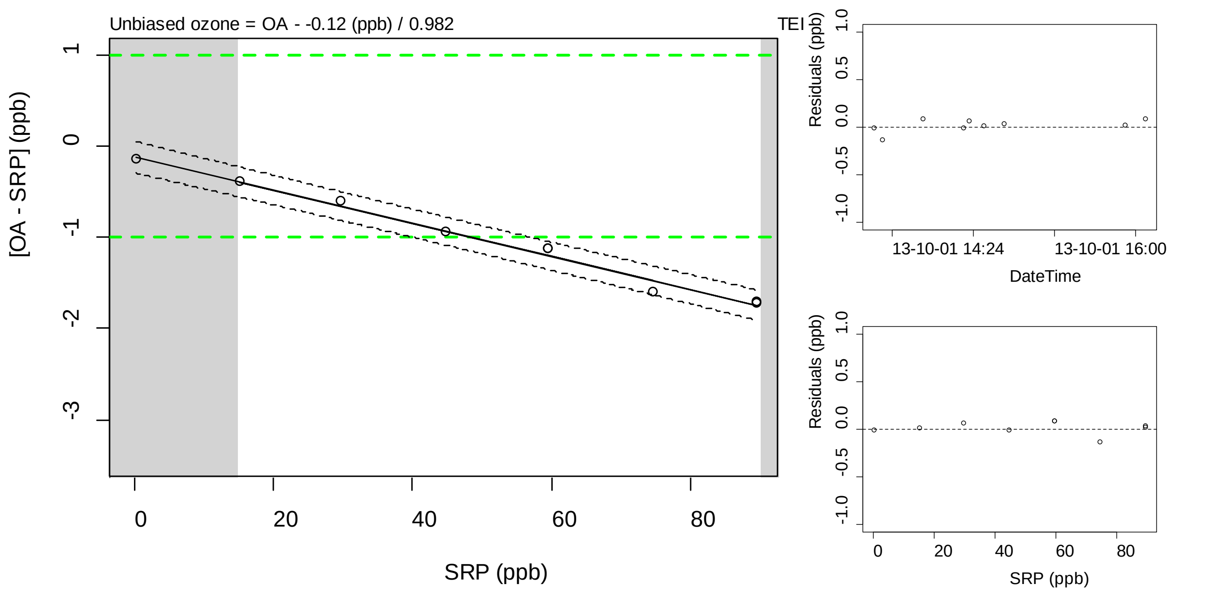

Figure 2. *Primary ozone analyser after setting the calibration back to the factors of the last audit (BKG 0.0 ppb,* COEF *1.006).*

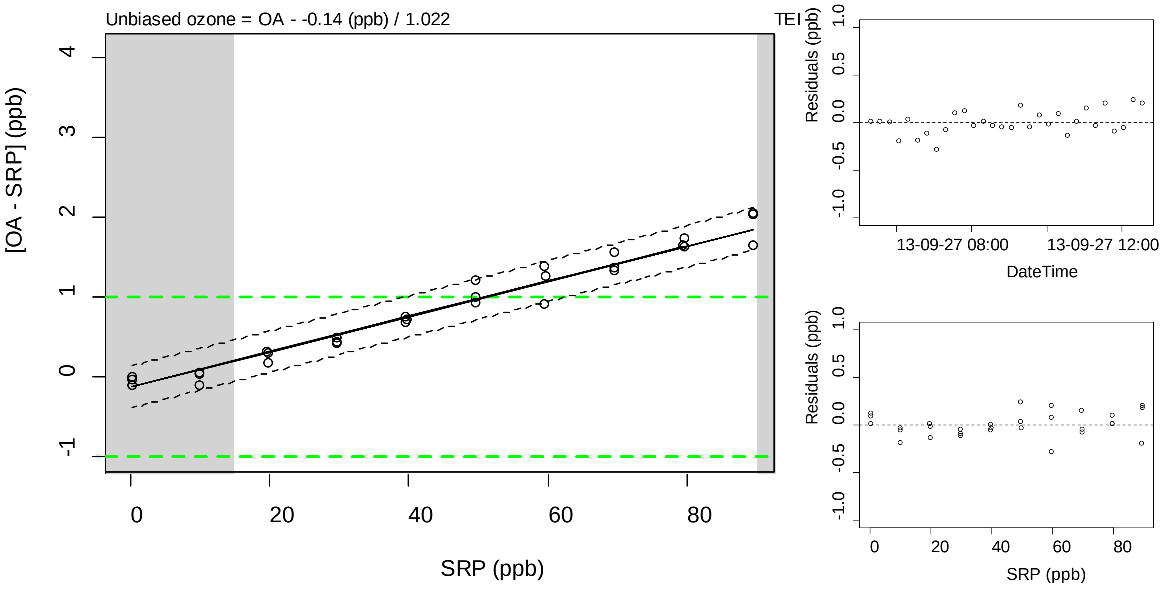

Figure 3. *Same as above for the secondary instrument (Settings: BKG 0.0 ppb, COEF 1.042).*

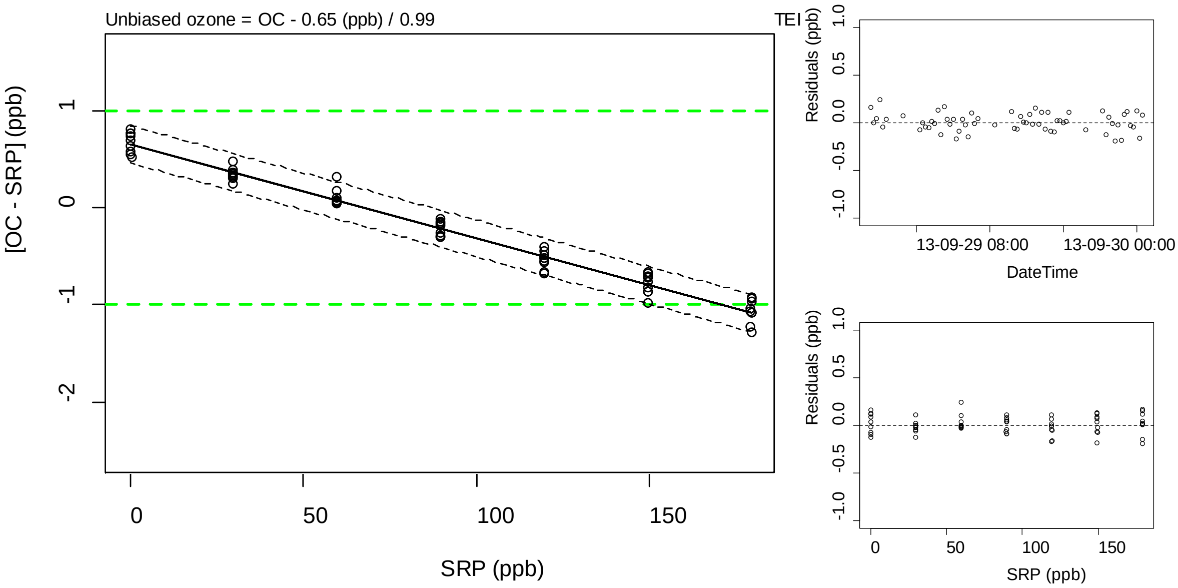

Figure 4. *Same as above for the station calibrator (BKG -0.8 ppb, COEF 1.014). During this comparison the instrument was in a wrong state (A/B problem, see further below).*

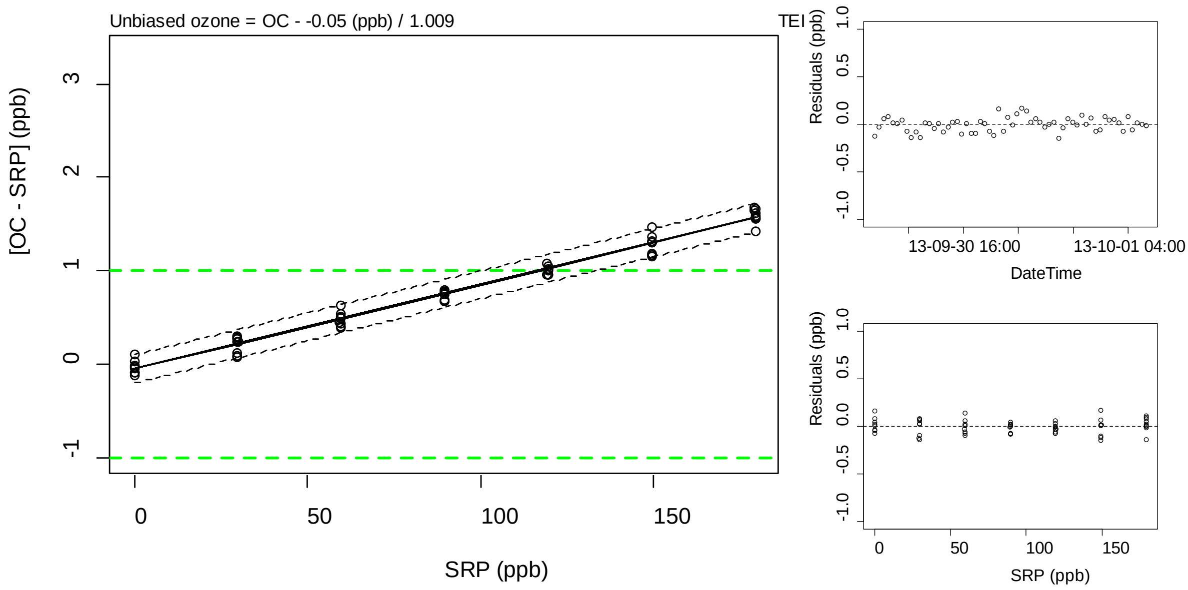

Figure 5. *Same as above for the station calibrator (BKG -0.1 ppb, COEF 1.014), without the A/B problem.*

The results of the comparisons can be summarised as follows:

Station calibrator TEI 49C-PS #56084-306:

It was noticed during the audit that the instrument had a problem with the electronics or the software. During the cell A/B diagnostics the instrument was sometimes showing only one of the two values instead of the mean value; furthermore, the values were updated very quickly, which potentially leads to insufficient flushing times during a measurement cycle. The instrument was reading significantly low (-1%) compared to the WCC-Empa reference in this state.

The problem disappeared after a manual change of the ozone generator setting was made; the following comparison showed higher readings (+0.9%) compared to the WCC-Empa reference.

After this the instrument was operated with the IZO control software, and the A/B issue was partly observed during this period. In conclusion, the instrument was not reliable enough to be adequate as an ozone reference. Consequently, the instrument was shipped to Empa after the audit, and the following repair was made at Empa:

- Eprom on HC11 CLINK board 49L-PS Rev-0002-00 was exchanged with 49L-PS Rev-0004-95
- Eprom on HC11 PROCESSOR board 49-PS Rev-0003-00 was exchanged with 49-PS Rev-0004-95
- Both flow sensors were exchanged.
- Battery was exchanged
- Pump diaphragm was checked (was OK).

After the repair, the instrument was compared to the WCC-Empa ozone reference (SRP#15). The instrument was fully functional after repair and can be used as an ozone reference in its current condition.
The calibration certificate is attached at the end of the report.

Recommendation 1 (, important, 2015)**
The IZO ozone calibrator is reaching the end of its expected lifetime, and replacement should be planned.

Recommendation 2 (*, important, 2015 / ongoing)**
WCC-Empa recommends running a calibration of both ozone analysers with the ozone calibrator. The calibration settings can then be adjusted. After this initial adjustment, no further changes of the calibration settings should be made. The calibrator should then only be used for 3-monthly comparisons. If significant changes are observed during such comparisons, the reason needs to be identified.

Station analysers TEI 49C (both primary and secondary instruments):

During the initial comparisons, both analysers were reading significantly high compared to the WCC-Empa reference, which was expected due to the high calibration settings (COEF) of 1.053 and 1.042 of the primary and the secondary instrument. Furthermore, a potential ozone loss of 2% was observed during the conditioning period before the actual comparison.

For the primary instrument this would result in the following “correct” COEF setting:

Initial COEF	1.053
- bias to WCC-Empa	-0.018
- compensation of O_3 loss	-0.020
Expected correct COEF	1.015

A further comparison between the IZO primary ozone analyser and WCC-Empa with the COEF settings of 2009 (1.006) was made, which resulted in a lower finding of the IZO primary instrument of 1.8%. During the conditioning phase of this comparison, an ozone loss of 0.6% (new inlet filter) was observed. Based on this experiment, the correct COEF setting would be as follows:

Initial COEF	1.006
+ bias to WCC-Empa	+0.018
- compensation of O_3 loss	-0.006
Expected correct COEF	1.018

During the comparison of the 2009 audit, the following correct COEF would have been expected (assuming no loss at that time):

Initial COEF	1.006
+ bias to WCC-Empa	+0.007
- compensation of O_3 loss	-0.000
Expected correct COEF	1.013

Based on these comparisons, the COEF setting of the primary instrument is expected to be within the range of 1.013 to 1.018. This should now be confirmed with a further comparison against the station calibrator. To avoid any potential ozone loss over the inlet filter, the experiment should be done without the filter. However, the reason of the ozone loss over the filter needs also further attention.

Recommendation 3 (*, critical, 2015)**
The inlet filters / filter holders used at IZO need thoroughly be checked for ozone loss. A small ozone loss of 0.6% was observed with a new filter, which is indicating that the filter holders are either leaking or contaminated. This should be checked with further tests, and filter holders need to be replaced if results are confirmed.

Recommendation 4 (, minor, 2015-16)**
Replacement of the ozone analysers needs to be planned due to the age of the instruments (main analyser 14 years, back-up analyser 11 years).

Carbon Monoxide Measurements

On-going measurement of carbon monoxide at Izaña commenced in 1998, but validated data series are available only since 2008 due to calibration issues before that time. Carbon monoxide measurements at Izaña are made using GC with HgO reduction gas detector technique. The system has not significantly changed since the last audit by WCC-Empa in 2009.

Instrumentation. Izaña is equipped with a Trace Analytical RGA-3 GC-system for the measurement of CO. Instrumental details as well as a comprehensive uncertainty assessment are given in Gomez-Pelaez et al. (2013). In addition, a TEI48C-TL instrument is available at the station.

Standards. The station is equipped with laboratory standards from NOAA/ESRL. The first set of standards was purchased in 1997 and 1999. These standards are no longer in use and were replaced by a second set of five standards purchased in 2006. The currently available IZO laboratory standards span the mole fraction range of 63 to 221 ppb. These standards have been certified by NOAA/ESRL based on the WMO-X2004 CO calibration scale and are currently (September 2014) being re-calibrated at NOAA/ESRL. In addition, a 10-ppm standard from Air Liquide is available for the calibration of the NDIR instrument.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instruments with different carbon monoxide levels using WCC-Empa travelling standards. The TS were measured as if they were ambient air; i.e. TS injections alternated with injections from the single reference gas in use at the RGA-3. No direct comparisons of the TS against the IZO laboratory standards were performed. However, traceability of the single reference gas is maintained through calibration every two weeks using the laboratory standards. Note that the usual method in WMO Round Robins is to compare them directly with the laboratory standards –because this leads to a smaller uncertainty in the assignments. The following equations characterise the instrument bias, and the results are further illustrated in Figure 6 with respect to the WMO GAW DQOs (WMO, 2013, 2010):

RGA-3 #070188-008:

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 2.3) / 1.0097 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.7 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

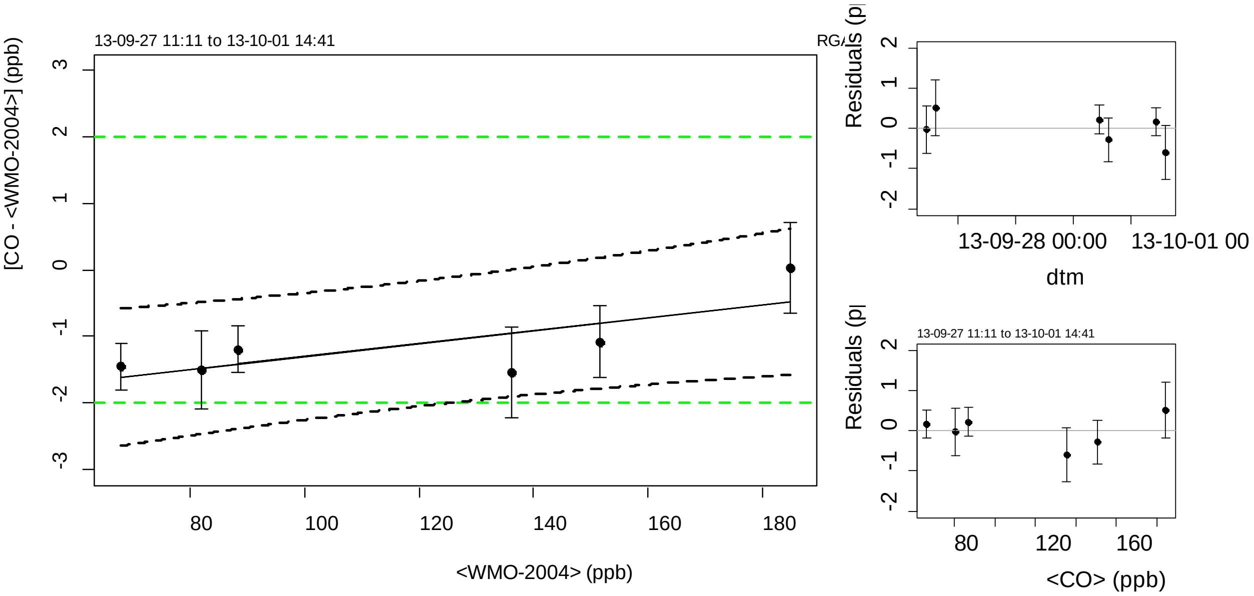

Figure 6. *Left: Bias of the IZO RGA-3 carbon monoxide instrument with respect to the WMO-X2004 CO scale as a function of mole fraction. The white area represents the mole fraction range relevant for IZO, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The TEI48C-TL instrument was also tested during the audit. It was noticed that the instrument responds to pressure changes. During zero air measurements through the Sofnocat cartridges, the pressure in the sample cell changes. This resulted in a change of the background compensation of the instrument (BKG setting). Furthermore, the instrument is very sensitive to temperature changes. Consequently, the data obtained with the TEI48C-TL instrument are of very limited use and should not be considered for further scientific use.

Recommendation 5 (*, minor, 2015)
The TEI48C-TL instrument is not reliable due to zero drift (temperature dependent), which cannot not be correctly compensated. Automatic zero measurements are biased due to sensitivity of the analyser to pressure changes. A possible solution would be the stabilisation of the sample pressure. However, WCC-Empa does not recommend to invest in this instrument, since more advanced analytical techniques are now available for the measurements of CO.

Recommendation 6 (, important, 2015/16)**
WCC-Empa encourages replacement of the TEI48C-TL instrument with an alternative technique (e.g. cavity enhanced absorption spectroscopy), and run the new instrument in parallel to the RGA-3 system.

The results of the CO comparisons can be summarised as follows:

For the RGA-3 system, good agreement with an offset of approx. -1 ppb was found between the IZO and WCC-Empa measurements of the TS. This is within the recommended compatibility goals for GAW measurements. The TEI 48C-TL instrument however was found to have several issues with temperature and pressure dependencies. In its current state, the instrument is not suitable for accurate CO measurements, and replacement with an alternative measurement technique should be considered.

Methane Measurements

On-going measurement of methane at Izaña commenced in July 1984, and continuous data series are available since then. Methane measurements at Izaña are made using GC with FID detector technique. Currently, two GC/FID systems are running in parallel.

Instrumentation. Dani-3800 GC/FID system (main instrument; used for data submission to WDCGG) and Varian 3800 GC/FID system (secondary instrument; still with issues to solve regarding the dedicated ambient air inlet/drying system).

Standards. The station is equipped with laboratory standards from NOAA/ESRL. The first set of standards was purchased in 1997 and 1999. These standards are no longer in use and were replaced by a second set of three standards purchased in 2006 (two of them) and 2008. The currently available IZO laboratory standards span the mole fraction range of 1682 to 1948 ppb. One of three standards is currently (September 2014) being re-calibrated at NOAA/ESRL; the remaining two will be re-calibrated after the return of this cylinder.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instruments with different methane levels from travelling standards. The TS were measured as if they were ambient air; i.e. TS injections alternated with injections from the single reference gas in use for the GC/FID, No direct comparisons of the TS against the IZO laboratory standards were performed. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 7 and Figure 8 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (green lines) (WMO, 2014, 2009).

DANI 3800 GC/FID:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 + 11.0) / 1.00638 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (2.1 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

Varian 3800 GC/FID:

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 + 8.1) / 1.00430 (3c)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (2.1 ppb^2 + 1.30e-07 * X_{CH4}^2) (3d)

The results of the comparisons can be summarised as follows:

Agreement within the WMO/GAW DQOs of ±2 ppb was found in the relevant mole fraction range of methane for both GC/FID instruments with a relatively large measurement uncertainty, which is typical for GC/FID measurements.

Recommendation 7 (*, minor, 2015/16)
It should be considered to replace one of the GC instruments with an alternative technique for CH_4 measurements (e.g. cavity enhanced absorption spectroscopy). These newer technologies have clearly advantages concerning precision, stability and temporal coverage compared to GC measurements.

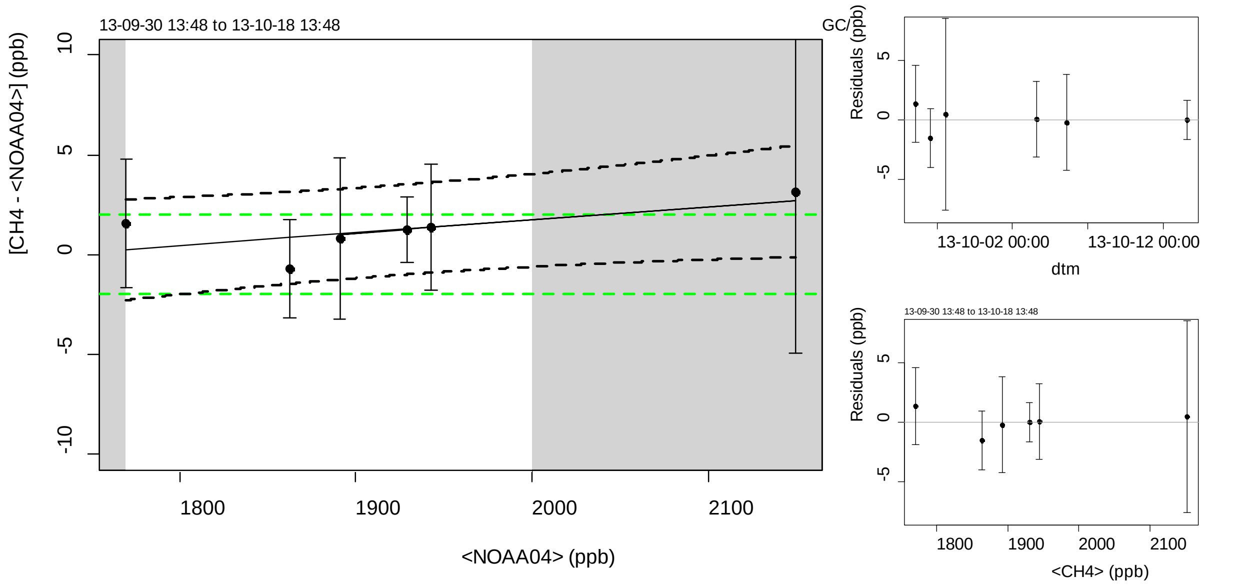

Figure 7. *Left: Bias of the DANI 3800 GC/FID methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for IZO, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

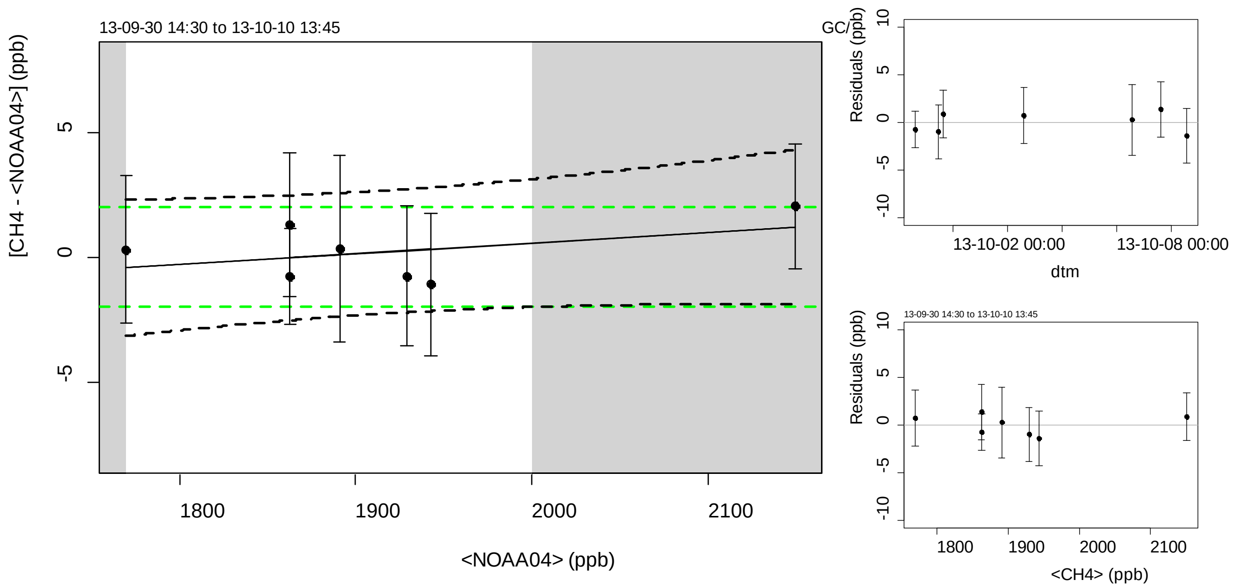

Figure 8. *Same as above for the Varian3800 GC/FID.*

Carbon Dioxide Measurements

Continuous measurements of CO_2 at IZO commenced in 1984, and continuous data is available since then.

Instrumentation. Initial measurements starting in 1984 were made using NDIR technique (Siemens Ultramat). In 2007, this instrument was replaced by a LI-COR LI-7000. In 2008, a back-up system (LI-COR LI-6252) was added. The instrumentation is adequate for the measurement of CO_2. A detailed description of the system can be found in the proceedings of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Gomez-Pelaez and Ramos, 2011).

Standards. A set of six NOAA laboratory standards is available at the station. In addition, working standards are available.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the IZO instruments with different CO_2 levels from travelling standards. The TS were measured as if they were ambient air; i.e. TS measurements alternated with the measurement –once per hour- of 3 working standards in the range 381-407 ppm. No direct comparisons of the TS against the IZO laboratory standards were made, but indirect, because the working standards were calibrated every two weeks using the laboratory standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equations characterise the instrument bias for the two LI-COR instruments. The results are further illustrated in Figure 9 and Figure 10 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (green lines) (WMO, 2014).

LI-COR LI-7000 #IRGA-0524:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 1.90) / 0.99521 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.005 ppm^2 + 3.276e-08 * $X_{CO2}{}^2$) (4b)

LI-COR LI- 6252 #IRG2-513:

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 + 4.02) / 1.01038 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.006 ppm^2 + 3.276e-08 * $X_{CO2}{}^2$) (4d)

The results of the comparison can be summarised as follows:

The results of the TS comparison agreed well within the WMO/GAW DQOs in the relevant mole fraction range above 380 ppm CO_2. The TS with a mole fraction of 373 ppm is outside the range of the working standards of the IZO station. The good agreement was also confirmed by the parallel measurements of ambient air between IZO and WCC-Empa. This is indicating that the whole measurement set-up including the inlet system and data processing is fully appropriate.

Recommendation 8 (*, minor, 2015/16)
Since a few years, spectroscopic measurement techniques are becoming more widely used. These instruments show clearly superior performance concerning water vapour interference, linearity and the use of calibration standards compared to NDIR. It should be considered to purchase such an instrument in the near future to ensure continuation of the long CO_2 time series at IZO.

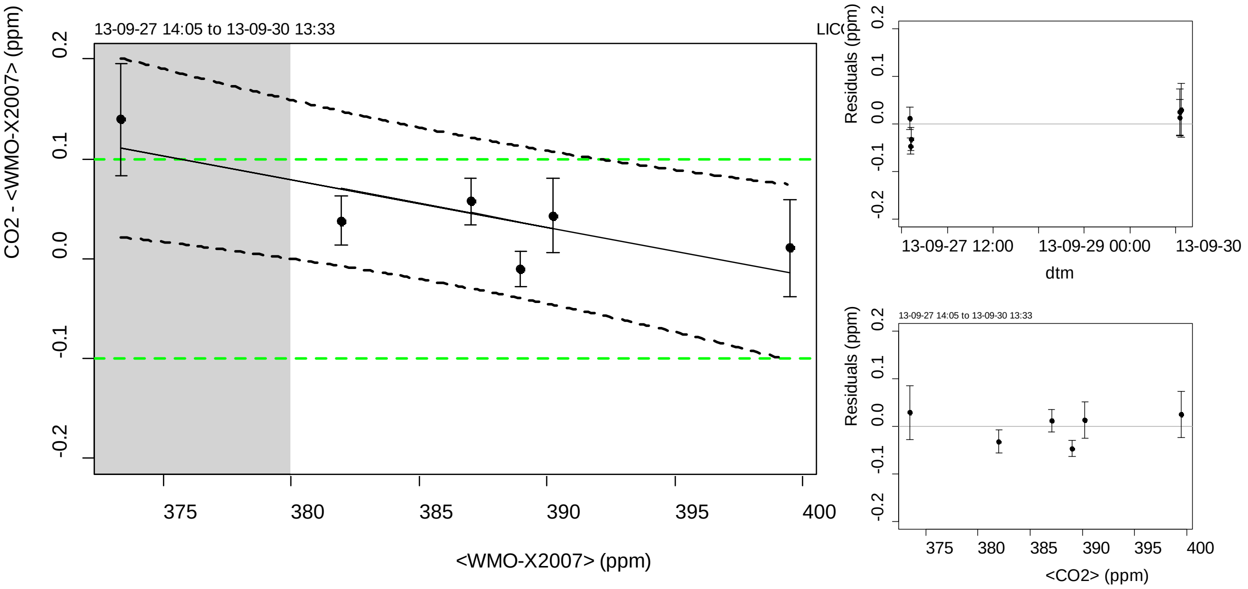

Figure 9. *Left: Bias of the IZO LICOR LI-7000 analyser with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for IZO, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

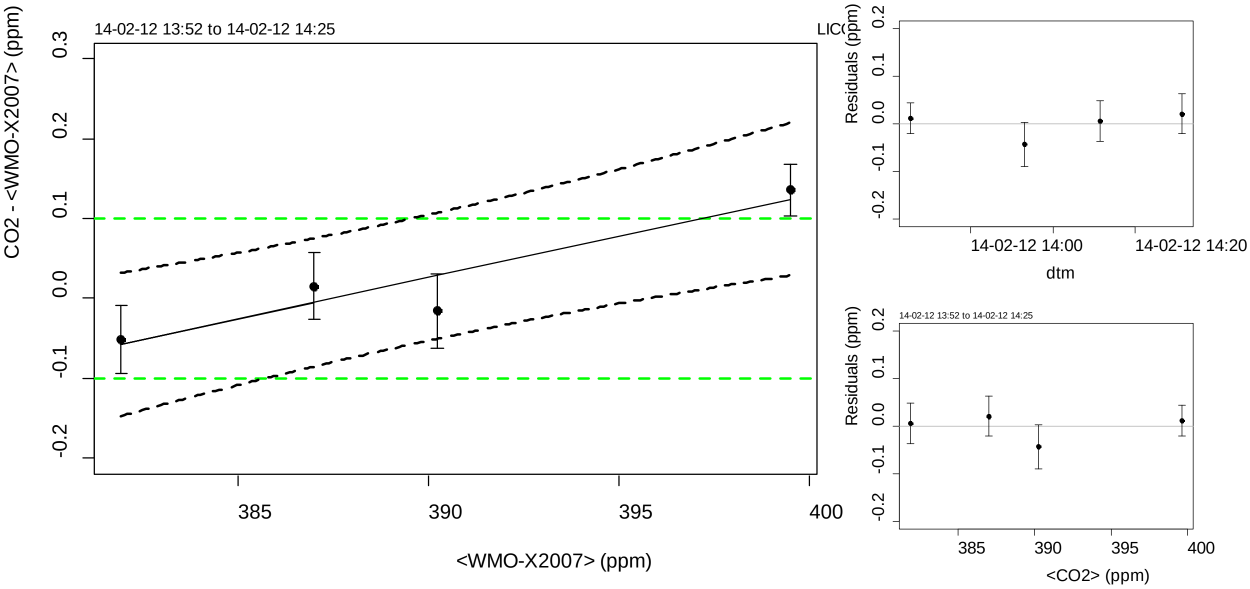

Figure 10. *Same as above for the IZO LICOR LI-6252 analyser.*

Nitrous Oxide Measurements

Continuous nitrous oxide measurements started at IZO in June 2007, and a complete time series is available since then.

Instrumentation. A Varian 3800 GC with an ECD detector is used for the measurements of N_2O. Detailed description of the instrumental set-up has been described elsewhere (Gomez-Pelaez and Ramos, 2009; Gomez-Pelaez et al., 2012; Scheel, 2009). The instrumentation is adequate for the measurement of N_2O.

Standards. The station is equipped with five laboratory standards that cover the relevant mole fraction range. All standards have been certified by NOAA/ESRL based on the WMO-X2006 N_2O calibration scale, and updated values referring to the WMO-X2006A N_2O scale were obtained from the NOAA web page; however, N_2O values are still reported on the WMO-X2006 scale.

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the IZO instrument with different nitrous oxide levels using WCC-Empa travelling standards. The TS were measured as if they were ambient air. TS injections alternated with injections from the single reference gas in use at the GC/ECD. No direct comparisons of the TS against the IZO laboratory standards were made. The following equations characterise the instrument bias, and the results are further illustrated in Figure 11 with respect to the WMO GAW DQOs (WMO, 2014, 2009):

Varian 3800:

Unbiased N_2O mixing ratio:	X_{N2O} (ppb) = (N_2O – 3.35) / 0.98890	(5a)
Remaining standard uncertainty:	u_{N2O} (ppb) = sqrt (0.07 ppb^2 + 1.01e-07 * $X_{N2O}{}^2$)	(5b)

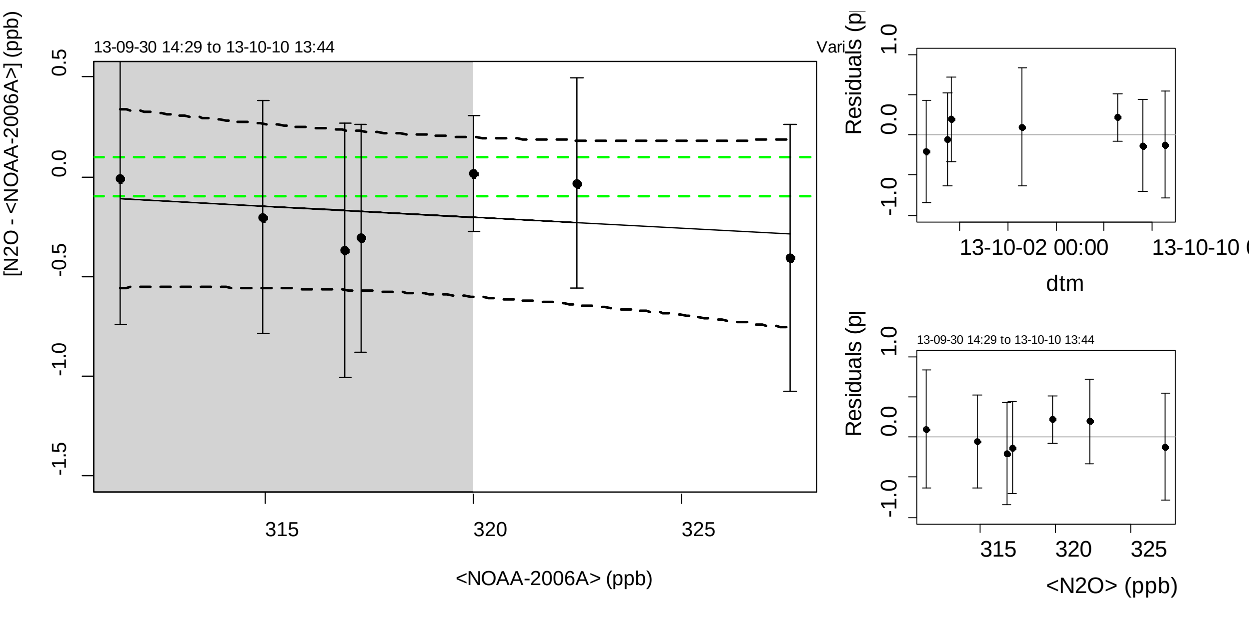

Figure 11. *Left: Bias of the IZO Varian 3800 GC/ECD nitrous oxide instrument with respect to the WMO-2006A reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for IZO, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The 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:

The IZO N_2O measurements still refer to the WMO-X2006 calibration scale, whereas the WCC-Empa travelling standards are traceable to the WMO-X2006A N_2O calibration scale. On average, the IZO measurements were slightly lower compared to WCC-Empa, which can be explained by the different calibration scales. The repeatability of the IZO measurements was relatively poor, which is typical for N_2O measurements with GC/ECD systems, resulting in rather large uncertainties associated with the comparison results. Within these uncertainties, no significant deviation between the WCC-Empa assigned values and the IZO results were observed, which is indicating that the whole measurement set-up is appropriate. The IZO N_2O standards are currently being re-certified at NOAA. It is recommended to convert the IZO N_2O values to the new scale once the re-certified values will become available.

Recommendation 9 (, important, 2015)**
IZO N_2O values need to be converted to the latest NOAA scale once revised values of the IZO standards will become available.

Recommendation 10 (, important, 2015)**
It should be explored if the repeatability of the IZO GC/ECD system can be improved. However, this is a challenging task using GC/ECD systems, and alternatively, the addition of an alternative measurement technique (e.g. Quantum Cascade Laser (QCL) spectroscopy) might be considered.

Parallel Measurements of Ambient Air

The audit included ambient air parallel measurements of CO, CH_4 and CO_2 with a WCC-Empa travelling instrument (TI) (Picarro G2401 SN # 617-CFKADS2001). The TI was running from 27 September 2013 through 11 February 2014. Measurements with the TI were alternating between an independent inlet system and the two IZO inlet systems. The air of the WCC TI was not dried. To account for the effect of water vapour, a correction function as described by Rella et al. (2013) was applied to the WCC-Empa CRDS data. Details of the calibration of the TI are given in the Appendix. The following figures show the results of the ambient air comparisons.

Carbon monoxide:

Figure 12 shows the comparison of the RGA-3 instrument (IZO) with the WCC-Empa Picarro G2401. One hourly average values are shown. The data coverage of the two methods is different; with the exception of calibrations, which were made every 40 h. , The CRDS instrument has a maximum data coverage of 100%, whereas only three instantaneous measurements per hour are available for the RGA-3. The scatter of the bias can to large extent be explained by the different data coverage. The average bias of approx. 2.8 ppb between the RGA-3 and the TI measurements is slightly larger than expected from the performance audit. Nevertheless, both systems captured the temporal variation very well. Furthermore, no dependency between the bias and the humidity was found, which is indicating that the water vapour correction of the TI worked well (not shown).

No influence of the inlet system was observed. This is indicating that the IZO inlet set-up is appropriate for CO measurements.

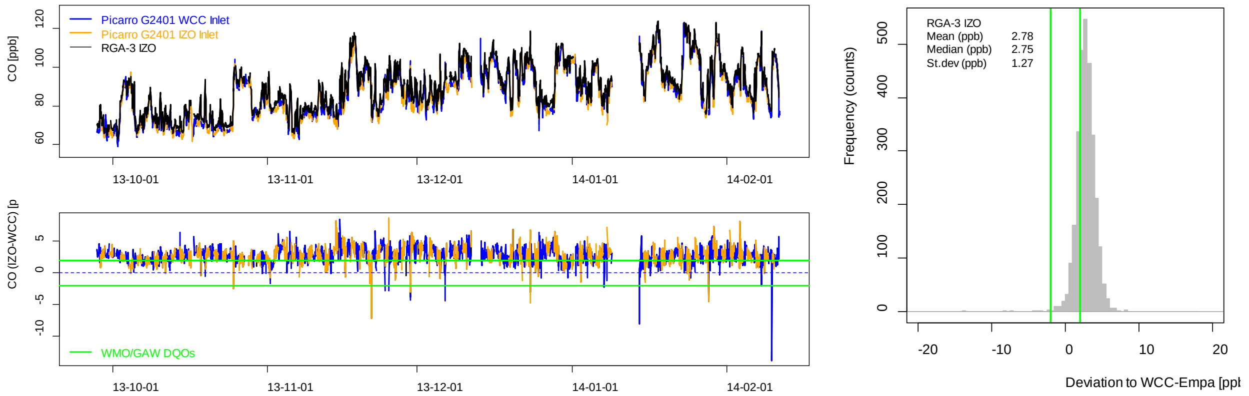

Figure 12. *Upper left panel: CO time series measured at IZO with the Picarro G2401 travelling instrument and the RGA-3 analyser (1-h averages) of IZO. Lower left panel: Deviations of the IZO system compared to the travelling instrument for the two inlet systems. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

Methane:

The following figures show the comparison of the IZO methane instruments with the WCC-Empa TI.

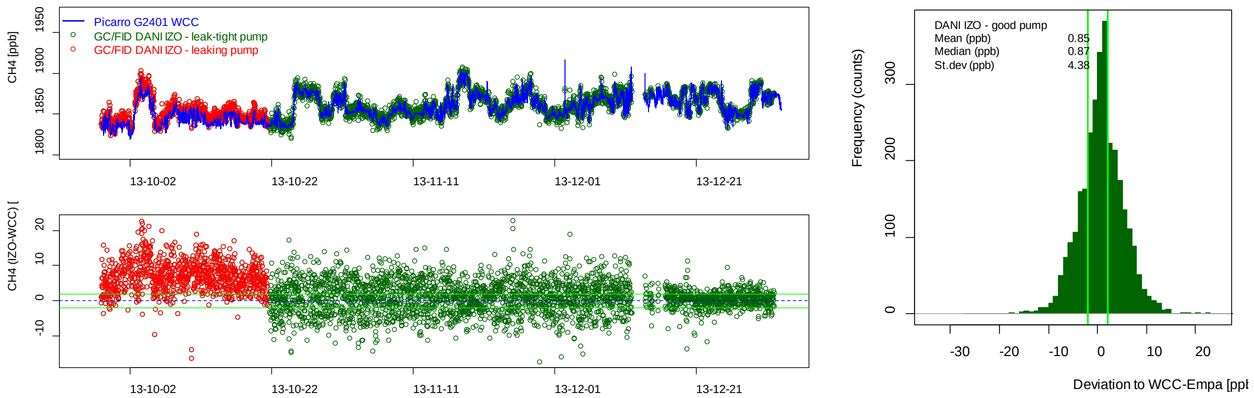

Figure 13. *Upper left panel: CH_4 time series measured at IZO with the Picarro G2401 travelling instrument (1-min averages) and the DANI 3800 GC/FID system (individual injections). Lower left panel: Deviation of the IZO system compared to the travelling instrument. Right panel: Frequency distribution of the deviations for the period with the leak-tight pump. The green lines refer to the WMO/GAW DQOs.*

The results of the DANI 3800 GC/FID can be summarised as follows:

A check of the pump performed by Izaña staff showed that the pump used to draw air to the DANI GC/FID system was leaking at the beginning of the campaign. Due to the high methane mole fraction inside the laboratory (GC/ECD carrier gas emissions), the ambient air measurements were contaminated, which resulted in significantly higher values of IZO compared to WCC-Empa. This problem was fixed by the exchange of the pump. The deviations after the exchange were not significant, but a high scatter was found due to the relatively poor repeatability of the DANI GC. Furthermore, small time lags will also lead to increased scatter, which however is expected to be small, since no obvious difference was observed when only night time data is compared.

The GC was then damaged by lightning at the end of December 2013, before the end of the comparison campaign. It could not be fixed before the end of the campaign in February 2014.

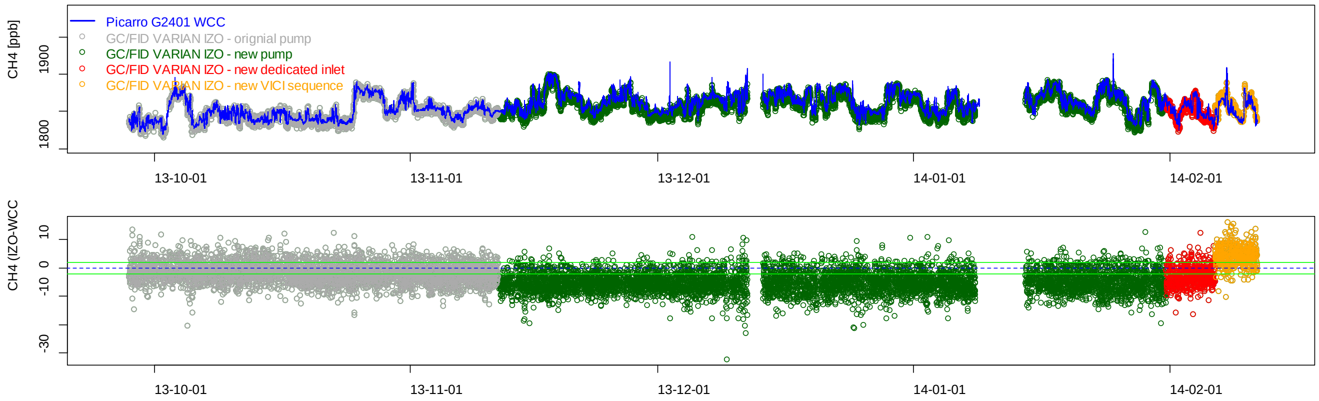

Figure 14. *Upper panel: CH_4 time series measured at IZO with the Picarro G2401 travelling instrument (1-min averages) and the Varian 3800 GC/FID system (individual injections). Lower panel: Deviation of the IZO system compared to the travelling instrument. The green lines refer to the WMO/GAW DQOs.*

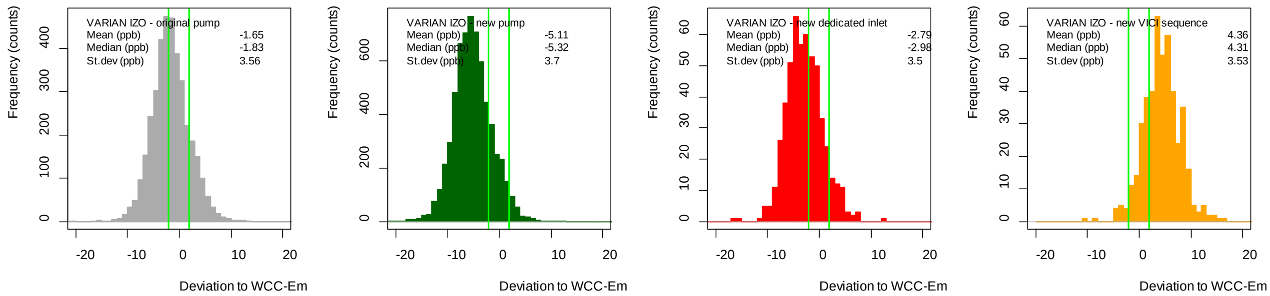

Figure 15. *Frequency distribution of the deviations for the different period shown in the above Figure.*

The results of the Varian 3800 GC/FID can be summarised as follows:

Initially, the agreement between the Varian GC/FID and the WCC-Empa TI was relatively good, but slightly degrading over time (grey points in above Figure). The pump (analogue to the DANI instrument) was then changed, which resulted in a significantly larger bias compared to WCC-Empa. The insertion of a vent after the cryo-cooled water trap and the removal of a 3-way-2-position solenoid valve after the pump, to get continuous flow through the water trap (red points) slightly improved the situation but IZO readings were still low. The VICI sequence of the Varian 3800 was then changed to flush the sample loop with ambient air during the same time than with standard gases (before this change the flushing time for ambient air was longer than for standard gases, but the equilibration time has been always the same). This resulted in a significantly positive bias; a potential reason could be diffusion of a small amount of the ECD carrier gas (Ar 95% / CH4 5%) into the valve that selects the sample loop to be flushed (one corresponds to the ECD and the other one to the FID).

Recommendation 11 (, important, 2015)**

The comparison campaign showed that the Varian 3800 GC/FID currently suffers from a number of issues when measuring ambient air that need to be solved. Alternatively, the replacement of one GC/FID system by a spectroscopic instrument could be considered, as recommended above.

Carbon dioxide:

Figure 16 shows the comparison of the LI-COR LI-7000 analyser with the WCC-Empa TI. The data coverage of the two methods is slightly different; with the exception of calibrations, which were made every 40 h. The CRDS instrument has a maximum data coverage of 100%, whereas the Li-7000 measures ambient air only 50 minutes per hour (the same applies for the Li-6252). At the beginning of the comparison campaign, no significant deviation was found on average between the LI-COR LI-7000 and the WCC-Empa TI; however, during the following short periods, larger deviations were observed (UTC):

2013-10-17 11:00 till 2013-10-21 11:00: negative bias
2013-10-24 10:00 till 2013-10-25 10:00: negative bias
2013-12-01 14:00 till 2013-12-03 12:00: positive bias
2014-01-16 18:00 till 2014-01-17 11:00: positive bias
2014-01-22 12:00 till 2014-01-24 12:00: negative bias
2014-01-29 17:00 till the breakdown of the LI-7000: negative bias

These periods always occurred between changes of the water trap, indicating either a CO_2 loss over the trap (negative bias) or a leak over the trap (positive bias).

Recommendation 12 (, important, 2015)**
It needs to be identified which of the water traps are resulting in CO_2 loss. Furthermore, it must be made sure that no leaks are present after the exchange of the traps.

A further long period with an initially growing and then constant negative bias occurred between 2013-12-13 20:00 and 2014-01-08 22:00. This period occurred after a long power outage caused by a severe thunderstorm. The calibration of the TI was also not working after 2013-12-18 till the end of the period; however, calibrations made on 16. and 18. December did not indicate problems with the TI system, although the first calibration of the TI after this period was approx. 0.1 ppm lower than usual. The final reason for the bias during this period could not be identified. Maybe a problem in the cryo-cooled water trap or damage in the LI-7000 during the thunderstorm that could have affected the performance of the instrument before the final breakdown at the beginning of February 2014 (the instrument was repaired later in Germany).

During all other periods, the bias between the LI-COR LI-7000 and the WCC-Empa TI was not significant, which is in line with the results found during the performance audit.

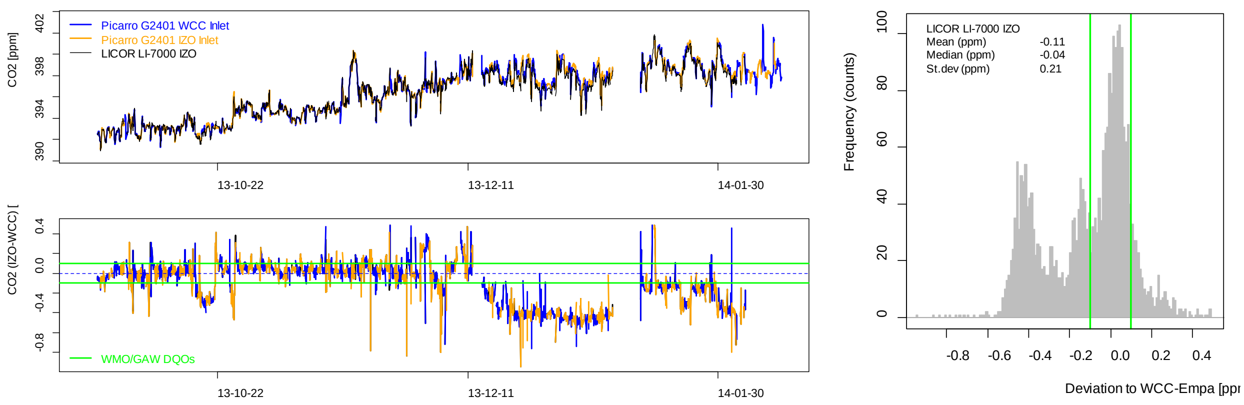

Figure 16. *Upper left panel: CO_2 time series (hourly averages) measured at IZO with the Picarro G2401 travelling instrument and the LI-COR LI-7000 analyser. Lower left panel: Deviations of the IZO system compared to the travelling instrument for the two inlet systems. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

The comparison between the LI-COR LI-6252 and the WCC-Empa TI is shown in Figure 17. On average, no significant bias was observed. However, several short periods with a positive bias of the LI-COR LI-6252 were observed. It should also be noted that the negative bias that was observed with the LI-COR LI-7000 was not found for this instrument.

No influence of the inlet system was observed for both IZO LI-COR instruments. This is indicating that the IZO inlet set-up is appropriate for CO_2 measurements.

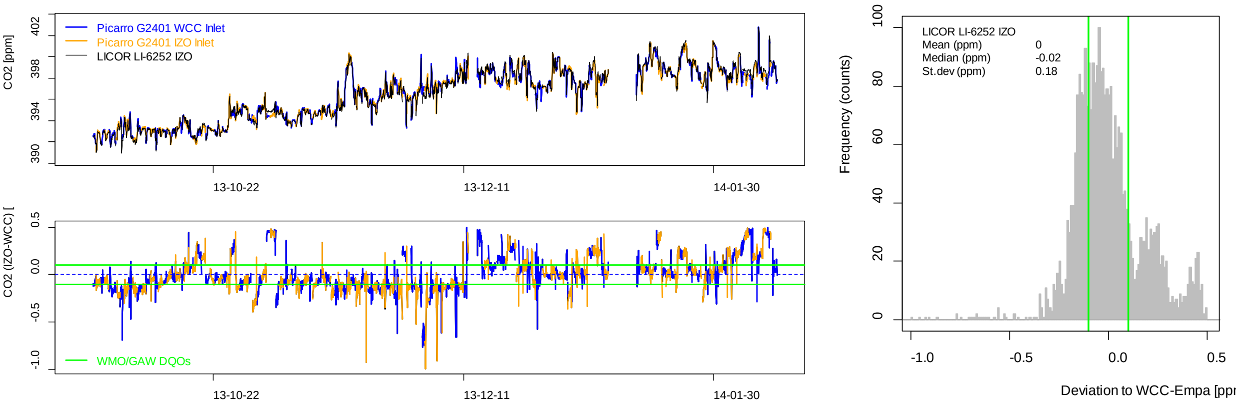

Figure 17. *Same as above for the LI-COR LI-6252 analyser.*

Recommendation 13 (*, minor, 2015/16)
The results of the comparison campaign showed that an accurate CO_2 measurement with the IZO NDIR system is possible but challenging. It should be considered to replace one of the two NDIR instruments by an alternative technique (e.g. CRDS) to ensure the continuation of the long-term CO_2 measurements at IZO.

Data Acquisition and Management

All instruments at IZO are equipped with custom made data acquisition software. Remote access is possible through the internet. All data acquisition systems are appropriate, and no further action is required.

Data Submission

For the parameters of the audit scope, in-situ data for O_3 (1987-2013), CO (2008-2014), CO_2 (1984-2014), CH_4 (1984-2013) and N_2O (2007-2013) was submitted to WDCGG by AEMET. All data has been timely submitted, which is exemplary.

Conclusions

The Global GAW station Izaña has a very comprehensive measurement programme and participates in different international monitoring and research programmes. The combination of long-term measurements of many GAW parameters and the location of the station make the Izaña Observatory a very important contribution to the GAW programme. The audit showed that most assessed parameters were of high quality; however, some of the instrumentation is becoming old, and future investment is needed to maintain the high level standard of the station.

Continuation of the Izaña measurement series and the scientific collaboration with external partners is highly recommended.

Summary Ranking of the Izaña GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	All year access possible
Facilities		
Laboratory and office space	(5)	Spacious laboratories, excellent infrastructure
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully functional
Power supply	(4)	Mostly reliable power supply, lightning protection needs improvement
General Management and Operation		
Organisation	(5)	Well established cooperation among different partners
Competence of staff	(5)	Mostly highly experienced staff
Air Inlet System	(5)	Fully adequate inlet systems
Instrumentation		
Ozone (IZO)	(5)	Adequate instrumentation
CO (RGA-3)	(4)	Potential calibration issues
CO (TEI48C-TL)	(1)	Issues with stability
CH_4 (GC/FID, Dani)	(3)	Relatively poor repeatability
CH_4 (GC/FID, Varian)	(2)	Poor repeatability, issues with ambient air measurements
N_2O	(4)	Adequate instrumentation
CO_2 (LICOR LI-6252 and 7000)	(4)	Issues with stability, addition of alternative technique recommended
Standards		
Ozone	(4)	Adequate instrumentation, more operator training needed
CO, CH_4, CO_2, N_2O	(5)	Full set of NOAA standards
Data Management		
Data acquisition	(5)	Adequate systems
Data processing	(5)	Experienced staff
Data submission (all audited parameters)	(5)	Very timely submission

#0: inadequate thru 5: adequate.

Dübendorf, May 2015

Dr. C. Zellweger
WCC-Empa

Dr. M. Steinbacher
QA/SAC Switzerland

Dr. B. Buchmann
Head of Department

APPENDIX

Global GAW Station Izaña

Site description and measurement programme

Information about the Izaña GAW station is available on the internet and the station is also registered in GAWSIS.

http://izana.aemet.es/
http://gaw.empa.ch/gawsis/reports.asp?StationID=7

Organisation and Contact Persons

An overview of the organisation as well as contact persons is available from the IZO web site (http://izana.aemet.es/).

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The ozone laboratory at IZO is air conditioned to approx. 20°C.

Air Inlet System

No change since the WCC-Empa audit in 2009 (Zellweger et al., 2009).

Instrumentation

Two ozone analysers (TEI 49C). Instrumental details are summarised in Table 1.

Standards

One ozone standard (TEI 49C-PS) is available at IZO. Instrumental details for the ozone calibrator (OC) are summarised in Table 1.

Operation and Maintenance

Check for general operation:	Daily (Mon – Sun) by the station operator.
Zero / Span check:	Zero: Daily automatic check, Span: Manual in weekly intervals.
Calibration/checks with standard:	Usually every 3-4 months.
Inlet filter exchange:	Regular exchange, frequency depending on Sahara dust events.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

Unchanged since the WCC-Empa audit in 2009 (Zellweger et al., 2009). One-minute averages including additional instrument status information are stored. Remote access to the data is possible through internet.

Data Treatment

Data validation is carried out at AEMET in St. Cruz. Time series are visualised and data is flagged as invalid in case of unexplainable values or based upon log book entries.

Documentation

Electronic station and instrument logbooks were available at the site. The information was comprehensive and up-to-date. The instrument manuals were available at the site.

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 90 ppb (analyser) and 0 to 175 ppb (calibrator). Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser including its inlet filter 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 (TS) and the station data acquisition system (OA).

Table 1. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
Settings	BKG = -0.4; COEFF = 1.007
Station Analyser (OA)	
Model, S/N	TEI 49C #63900-337
Principle	UV absorption
Range	0-1 ppm
Pressure readings (mmHg)	Ambient 576.0, OA 576.3, no adjustments were made
Station Analyser (OA)	
Model, S/N	TEI 49C #72491-371
Principle	UV absorption
Range	0-1 ppm
Pressure readings (mmHg)	Ambient 577.0, OA 577.0, no adjustments were made
Station Calibrator (OC)	
Model, S/N	TEI 49C-PS #56084-306
Principle	UV absorption
Range	0-1 ppm
Pressure readings (mmHg)	Ambient 577.0, OC 575.8, no adjustments were made

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. 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) value.

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 main IZO ozone analyser (OA) TEI 49C #63900-337 with the WCC-Empa travelling standard (TS) with initial calibration factors (COEF 1.053, BKG 0.0).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-09-26 19:43	1	0	-0.14	-0.01	0.14	0.03	0.13	NA
2013-09-26 20:03	1	20	19.45	19.51	0.09	0.06	0.06	0.3
2013-09-26 20:23	1	80	79.32	80.64	0.11	0.02	1.32	1.7
2013-09-26 20:43	1	70	69.39	70.45	0.05	0.05	1.06	1.5
2013-09-26 21:03	1	40	39.32	39.84	0.11	0.07	0.52	1.3
2013-09-26 21:23	1	90	89.32	90.71	0.07	0.09	1.39	1.6
2013-09-26 21:43	1	30	29.39	29.68	0.07	0.03	0.29	1.0
2013-09-26 22:03	1	10	9.43	9.55	0.04	0.05	0.12	1.3
2013-09-26 22:23	1	50	49.24	49.77	0.07	0.08	0.53	1.1
2013-09-26 22:43	1	60	59.28	60.04	0.17	0.10	0.76	1.3
2013-09-26 23:03	2	0	0.07	-0.02	0.15	0.08	-0.09	NA
2013-09-26 23:23	2	20	19.31	19.69	0.05	0.05	0.38	2.0
2013-09-26 23:43	2	40	39.27	39.82	0.07	0.14	0.55	1.4
2013-09-27 00:03	2	90	89.27	90.75	0.09	0.11	1.48	1.7
2013-09-27 00:23	2	50	49.34	50.17	0.10	0.06	0.83	1.7
2013-09-27 00:43	2	10	9.44	9.63	0.08	0.02	0.19	2.0
2013-09-27 01:03	2	30	29.30	29.65	0.11	0.08	0.35	1.2
2013-09-27 01:23	2	60	59.33	60.42	0.11	0.07	1.09	1.8
2013-09-27 01:43	2	70	69.33	70.59	0.07	0.06	1.26	1.8
2013-09-27 02:03	2	80	79.32	80.81	0.09	0.07	1.49	1.9
2013-09-27 02:23	3	0	0.07	0.09	0.04	0.09	0.02	NA
2013-09-27 02:43	3	50	49.35	50.03	0.17	0.04	0.68	1.4
2013-09-27 03:03	3	80	79.19	80.80	0.07	0.03	1.61	2.0
2013-09-27 03:23	3	10	9.61	9.69	0.11	0.06	0.08	0.8
2013-09-27 03:43	3	30	29.35	29.93	0.16	0.06	0.58	2.0
2013-09-27 04:03	3	40	39.29	40.01	0.08	0.10	0.72	1.8
2013-09-27 04:23	3	90	89.26	90.83	0.09	0.03	1.57	1.8
2013-09-27 04:43	3	70	69.37	70.58	0.06	0.03	1.21	1.7
2013-09-27 05:03	3	60	59.37	60.55	0.11	0.06	1.18	2.0
2013-09-27 05:23	3	20	19.53	19.77	0.19	0.10	0.24	1.2

Table 3. Same as above with the calibration factors as of the audit in 2009 (COEF 1.006, BKG 0.0).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-10-01 14:13	1	0	0.00	0.02	0.08	0.04	0.02	NA
2013-10-01 14:18	1	75	74.32	72.90	0.08	0.07	-1.42	-1.9
2013-10-01 14:42	1	60	59.30	58.36	0.10	0.06	-0.94	-1.6
2013-10-01 15:06	1	45	44.52	43.74	0.10	0.05	-0.78	-1.8
2013-10-01 15:09	1	30	29.54	29.11	0.29	0.09	-0.43	-1.5
2013-10-01 15:18	1	15	14.91	14.69	0.13	0.06	-0.22	-1.5
2013-10-01 15:30	1	90	89.34	87.81	0.09	0.04	-1.53	-1.7
2013-10-01 16:42	2	90	89.28	87.73	0.10	0.05	-1.55	-1.7
2013-10-01 16:54	2	60	59.37	58.43	0.17	0.12	-0.94	-1.6

Table 4. Same as above for the secondary instrument TEI 49i #72491-371 (Offset 0.0 ppb, Slope 1.042).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-09-27 07:18	1	0	0.02	0.06	0.16	0.08	0.04	NA
2013-09-27 07:33	1	20	19.43	19.90	0.15	0.02	0.47	2.4
2013-09-27 07:48	1	40	39.28	40.19	0.08	0.08	0.91	2.3
2013-09-27 08:03	1	90	89.20	91.03	0.07	0.04	1.83	2.1
2013-09-27 08:18	1	50	49.34	50.51	0.08	0.07	1.17	2.4
2013-09-27 08:33	1	10	9.68	9.74	0.21	0.09	0.06	0.6
2013-09-27 08:48	1	30	29.46	30.03	0.09	0.10	0.57	1.9
2013-09-27 09:03	1	60	59.34	60.42	0.11	0.03	1.08	1.8
2013-09-27 09:18	1	70	69.43	70.93	0.06	0.05	1.50	2.2
2013-09-27 09:33	1	80	79.36	81.26	0.08	0.05	1.90	2.4
2013-09-27 09:48	2	0	0.01	0.15	0.08	0.05	0.14	NA
2013-09-27 10:03	2	50	49.46	50.56	0.13	0.07	1.10	2.2
2013-09-27 10:18	2	80	79.35	81.17	0.09	0.02	1.82	2.3
2013-09-27 10:33	2	10	9.72	9.93	0.12	0.04	0.21	2.2
2013-09-27 10:48	2	30	29.45	30.09	0.05	0.05	0.64	2.2
2013-09-27 11:03	2	40	39.43	40.28	0.06	0.05	0.85	2.2
2013-09-27 11:18	2	90	89.37	91.57	0.14	0.06	2.20	2.5
2013-09-27 11:33	2	70	69.43	70.96	0.13	0.06	1.53	2.2
2013-09-27 11:48	2	60	59.40	60.83	0.12	0.07	1.43	2.4
2013-09-27 12:03	2	20	19.63	20.08	0.12	0.03	0.45	2.3
2013-09-27 12:18	3	0	-0.02	0.09	0.11	0.05	0.11	NA
2013-09-27 12:33	3	20	19.53	19.86	0.09	0.05	0.33	1.7
2013-09-27 12:48	3	80	79.31	81.12	0.08	0.09	1.81	2.3
2013-09-27 13:03	3	70	69.39	71.12	0.11	0.06	1.73	2.5
2013-09-27 13:18	3	40	39.50	40.38	0.07	0.10	0.88	2.2
2013-09-27 13:33	3	90	89.24	91.46	0.09	0.14	2.22	2.5
2013-09-27 13:48	3	30	29.53	30.12	0.13	0.04	0.59	2.0
2013-09-27 14:03	3	10	9.67	9.86	0.15	0.06	0.19	2.0
2013-09-27 14:18	3	50	49.34	50.70	0.08	0.04	1.36	2.8
2013-09-27 14:33	3	60	59.37	60.93	0.10	0.05	1.56	2.6

Table 5. Results for the ozone calibrator TEI 49C-PS #56084-306 (Offset -0.8 ppb, Slope 1.014). The instrument was in a wrong state (A/B ozone problem).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-09-29 02:59	1	0	-0.07	0.89	0.12	0.08	0.96	NA
2013-09-29 03:19	1	30	29.45	29.97	0.09	0.06	0.52	1.8
2013-09-29 03:39	1	180	179.01	178.18	0.10	0.11	-0.83	-0.5
2013-09-29 03:59	1	60	59.44	59.93	0.12	0.05	0.49	0.8
2013-09-29 04:19	1	120	119.22	118.86	0.07	0.07	-0.36	-0.3
2013-09-29 04:39	1	90	89.41	89.41	0.11	0.09	0.00	0.0
2013-09-29 06:29	1	150	149.32	148.79	0.12	0.02	-0.53	-0.4
2013-09-29 08:19	2	0	0.05	0.78	0.12	0.08	0.73	NA
2013-09-29 08:39	2	30	29.52	30.05	0.10	0.09	0.53	1.8
2013-09-29 08:59	2	90	89.45	89.37	0.06	0.06	-0.08	-0.1
2013-09-29 09:19	2	120	119.34	118.97	0.10	0.06	-0.37	-0.3
2013-09-29 09:39	2	180	179.18	178.32	0.12	0.06	-0.86	-0.5
2013-09-29 09:59	2	60	59.55	59.78	0.10	0.06	0.23	0.4
2013-09-29 10:19	2	150	149.31	148.84	0.07	0.04	-0.47	-0.3
2013-09-29 10:39	3	0	0.13	0.81	0.06	0.06	0.68	NA
2013-09-29 10:59	3	180	179.15	178.43	0.11	0.09	-0.72	-0.4
2013-09-29 11:19	3	60	59.50	59.78	0.16	0.08	0.28	0.5
2013-09-29 11:39	3	30	29.55	30.06	0.10	0.06	0.51	1.7
2013-09-29 11:59	3	150	149.20	148.64	0.09	0.06	-0.56	-0.4
2013-09-29 12:19	3	120	119.32	118.83	0.15	0.07	-0.49	-0.4
2013-09-29 12:39	3	90	89.43	89.30	0.07	0.06	-0.13	-0.1
2013-09-29 12:59	4	0	-0.03	0.81	0.09	0.09	0.84	NA
2013-09-29 13:19	4	30	29.46	29.97	0.14	0.07	0.51	1.7
2013-09-29 13:39	4	180	179.04	178.01	0.10	0.05	-1.03	-0.6
2013-09-29 13:59	4	60	59.46	59.80	0.10	0.07	0.34	0.6
2013-09-29 14:19	4	120	119.22	118.90	0.10	0.10	-0.32	-0.3
2013-09-29 14:39	4	90	89.40	89.41	0.08	0.08	0.01	0.0
2013-09-29 16:29	4	150	149.32	148.70	0.11	0.02	-0.62	-0.4
2013-09-29 18:19	5	0	-0.04	0.89	0.14	0.06	0.93	NA
2013-09-29 18:39	5	30	29.52	29.99	0.09	0.05	0.47	1.6
2013-09-29 18:59	5	90	89.30	89.20	0.09	0.05	-0.10	-0.1
2013-09-29 19:19	5	120	119.21	118.96	0.12	0.05	-0.25	-0.2
2013-09-29 19:39	5	180	179.14	178.26	0.09	0.07	-0.88	-0.5
2013-09-29 19:59	5	60	59.58	59.83	0.06	0.07	0.25	0.4
2013-09-29 20:19	5	150	149.31	148.80	0.13	0.13	-0.51	-0.3
2013-09-29 20:39	6	0	-0.01	0.78	0.14	0.06	0.79	NA
2013-09-29 20:59	6	180	179.12	178.39	0.08	0.06	-0.73	-0.4
2013-09-29 21:19	6	60	59.51	59.74	0.13	0.06	0.23	0.4
2013-09-29 21:39	6	30	29.53	30.17	0.17	0.07	0.64	2.2
2013-09-29 21:59	6	150	149.15	148.49	0.07	0.05	-0.66	-0.4
2013-09-29 22:19	6	120	119.31	119.09	0.11	0.07	-0.22	-0.2
2013-09-29 22:39	6	90	89.48	89.35	0.10	0.08	-0.13	-0.1
2013-09-29 22:59	7	0	0.04	0.75	0.09	0.07	0.71	NA
2013-09-29 23:19	7	30	29.48	30.03	0.12	0.04	0.55	1.9
2013-09-29 23:39	7	180	179.09	178.23	0.11	0.07	-0.86	-0.5

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-09-29 23:59	7	60	59.51	59.76	0.06	0.07	0.25	0.4
2013-09-30 00:19	7	120	119.21	118.91	0.12	0.07	-0.30	-0.3
2013-09-30 00:39	7	90	89.45	89.52	0.08	0.08	0.07	0.1
2013-09-30 02:29	7	150	149.33	148.65	0.11	0.02	-0.68	-0.5
2013-09-30 04:19	8	0	-0.04	0.89	0.07	0.05	0.93	NA
2013-09-30 04:39	8	30	29.48	29.89	0.09	0.09	0.41	1.4
2013-09-30 04:59	8	90	89.38	89.40	0.09	0.04	0.02	0.0
2013-09-30 05:19	8	120	119.22	118.89	0.12	0.05	-0.33	-0.3
2013-09-30 05:39	8	180	179.19	178.12	0.08	0.06	-1.07	-0.6
2013-09-30 05:59	8	60	59.55	59.77	0.07	0.04	0.22	0.4
2013-09-30 06:19	8	150	149.25	148.47	0.08	0.06	-0.78	-0.5
2013-09-30 06:39	9	0	-0.03	0.86	0.12	0.05	0.89	NA
2013-09-30 06:59	9	180	179.16	178.40	0.08	0.08	-0.76	-0.4
2013-09-30 07:19	9	60	59.54	59.75	0.13	0.08	0.21	0.4
2013-09-30 07:39	9	30	29.51	29.99	0.11	0.04	0.48	1.6
2013-09-30 07:59	9	150	149.17	148.69	0.08	0.06	-0.48	-0.3
2013-09-30 08:19	9	120	119.36	118.89	0.07	0.07	-0.47	-0.4
2013-09-30 08:39	9	90	89.42	89.46	0.08	0.05	0.04	0.0

Table 6. Results for the ozone calibrator TEI 49C-PS #56084-306 (Offset -0.8 ppb, Slope 1.014) without A/B ozone problem.

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-09-30 13:32	1	30	29.31	29.56	0.15	0.04	0.25	0.9
2013-09-30 13:52	1	60	59.14	59.77	0.12	0.04	0.63	1.1
2013-09-30 14:12	1	120	119.09	120.36	0.11	0.03	1.27	1.1
2013-09-30 14:32	1	180	179.11	180.95	0.10	0.05	1.84	1.0
2013-09-30 14:52	1	90	89.40	90.34	0.10	0.03	0.94	1.1
2013-09-30 15:12	1	150	149.23	150.73	0.08	0.04	1.50	1.0
2013-09-30 15:32	2	0	-0.01	0.14	0.10	0.04	0.15	NA
2013-09-30 15:52	2	120	119.18	120.32	0.10	0.04	1.14	1.0
2013-09-30 16:12	2	30	29.49	29.73	0.11	0.04	0.24	0.8
2013-09-30 16:32	2	90	89.34	90.20	0.07	0.03	0.86	1.0
2013-09-30 16:52	2	180	179.12	180.75	0.08	0.04	1.63	0.9
2013-09-30 17:12	2	150	149.28	150.79	0.09	0.04	1.51	1.0
2013-09-30 17:32	2	60	59.52	60.18	0.12	0.04	0.66	1.1
2013-09-30 17:52	3	0	0.04	0.10	0.11	0.04	0.06	NA
2013-09-30 18:12	3	60	59.38	60.04	0.11	0.04	0.66	1.1
2013-09-30 18:32	3	90	89.34	90.20	0.07	0.02	0.86	1.0
2013-09-30 18:53	3	120	119.28	120.46	0.10	0.05	1.18	1.0
2013-09-30 19:12	3	180	179.16	180.95	0.08	0.06	1.79	1.0
2013-09-30 19:32	3	30	29.54	29.95	0.10	0.03	0.41	1.4
2013-09-30 19:52	3	150	149.22	150.60	0.12	0.08	1.38	0.9
2013-09-30 20:12	4	0	0.02	0.14	0.06	0.02	0.12	NA
2013-09-30 20:33	4	30	29.43	29.72	0.13	0.04	0.29	1.0
2013-09-30 20:53	4	60	59.42	59.98	0.11	0.04	0.56	0.9

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-09-30 21:13	4	120	119.29	120.53	0.09	0.04	1.24	1.0
2013-09-30 21:33	4	180	179.15	180.92	0.07	0.04	1.77	1.0
2013-09-30 21:53	4	90	89.51	90.37	0.08	0.04	0.86	1.0
2013-09-30 22:13	4	150	149.30	150.67	0.08	0.05	1.37	0.9
2013-09-30 22:34	5	0	-0.09	0.17	0.14	0.02	0.26	NA
2013-09-30 22:54	5	120	119.12	120.26	0.13	0.05	1.14	1.0
2013-09-30 23:14	5	30	29.38	29.84	0.06	0.04	0.46	1.6
2013-09-30 23:34	5	90	89.27	90.20	0.14	0.05	0.93	1.0
2013-09-30 23:54	5	180	179.08	180.96	0.09	0.04	1.88	1.0
2013-10-01 00:14	5	150	149.23	150.89	0.07	0.04	1.66	1.1
2013-10-01 00:35	5	60	59.48	60.27	0.09	0.03	0.79	1.3
2013-10-01 00:55	6	0	0.01	0.13	0.13	0.04	0.12	NA
2013-10-01 01:15	6	60	59.45	60.16	0.15	0.04	0.71	1.2
2013-10-01 01:35	6	90	89.39	90.35	0.08	0.03	0.96	1.1
2013-10-01 01:55	6	120	119.35	120.54	0.12	0.05	1.19	1.0
2013-10-01 02:15	6	180	179.21	180.98	0.09	0.03	1.77	1.0
2013-10-01 02:35	6	30	29.66	30.06	0.13	0.03	0.40	1.3
2013-10-01 02:56	6	150	149.22	150.57	0.10	0.07	1.35	0.9
2013-10-01 03:16	7	0	0.01	0.08	0.09	0.03	0.07	NA
2013-10-01 03:36	7	30	29.42	29.86	0.07	0.03	0.44	1.5
2013-10-01 03:56	7	60	59.40	60.07	0.05	0.02	0.67	1.1
2013-10-01 04:16	7	120	119.20	120.41	0.10	0.04	1.21	1.0
2013-10-01 04:36	7	180	179.21	181.07	0.07	0.03	1.86	1.0
2013-10-01 04:57	7	90	89.47	90.40	0.11	0.05	0.93	1.0
2013-10-01 05:17	7	150	149.23	150.79	0.11	0.05	1.56	1.0
2013-10-01 05:37	8	0	0.05	0.08	0.10	0.03	0.03	NA
2013-10-01 05:57	8	120	119.27	120.42	0.08	0.05	1.15	1.0
2013-10-01 06:17	8	30	29.52	29.99	0.12	0.03	0.47	1.6
2013-10-01 06:37	8	90	89.36	90.34	0.11	0.05	0.98	1.1
2013-10-01 06:58	8	180	179.19	181.01	0.12	0.05	1.82	1.0
2013-10-01 07:18	8	150	149.36	150.87	0.13	0.06	1.51	1.0
2013-10-01 07:38	8	60	59.49	60.07	0.10	0.04	0.58	1.0
2013-10-01 07:58	9	0	-0.03	0.16	0.09	0.02	0.19	NA
2013-10-01 08:18	9	60	59.35	59.95	0.13	0.05	0.60	1.0
2013-10-01 08:38	9	90	89.33	90.28	0.08	0.04	0.95	1.1
2013-10-01 08:59	9	120	119.30	120.51	0.14	0.05	1.21	1.0
2013-10-01 09:19	9	180	179.21	180.96	0.09	0.04	1.75	1.0

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

All laboratories at IZO are air-conditioned to approx. 20°C.

Air Inlet System

Unchanged since the WCC-Empa audit in 2009 (Zellweger et al., 2009).

Instrumentation

Izaña is equipped with a Trace Analytical RGA-3 GC-system for the measurement of CO. Instrumental details are listed in Table 8. In addition, a TEI 48C-TL NDIR system is available. However, this instrument is currently not used because of stability issues.

Standards

The station is equipped with laboratory standards from NOAA. Old NOAA standards from 1999 are now used as working standards. Furthermore, WS are filled at IZO every 4-5 months using a RIX pump. The calibration scheme remained unchanged since the last WCC-Empa audit in 2009.

Table 7. Carbon monoxide standards available at IZO as of September 2013.

Manufacturer / # / Use	CO (ppb) (uncert.)	Matrix	Calibration		Scale	In service	
			Date	By		From	To
NOAA / CA6768 / LS	62.6 (0.6)	Natural air	2006	NOAA	WMO-2004	2009	Today
NOAA / CA6946 / LS	91.2 (0.6)	Natural air	2006	NOAA	WMO-2004	2009	Today
NOAA / CA6988 / LS	119.6 (0.8)	Natural air	2006	NOAA	WMO-2004	2009	Today
NOAA / CA6968 / LS	164.5 (1.1)	Natural air	2006	NOAA	WMO-2004	2009	Today
NOAA / CA6978 / LS	221.2 (1.5)	Natural air	2006	NOAA	WMO-2004	2009	Today

In addition, ppm level standards (in synthetic air) are available for the NDIR instrument. A recalibration of the CO standards listed in the above Table in September 2014 at NOAA indicated that all standards remained stable with the exception of CA6946, which showed a significant upward drift of approx. 4.7 ppb, which might explain some of the differences observed during the audit.

Operation and Maintenance (RGA-3)

Sequence:	6 injections per hour, ambient air alternating with WS injections.
Check for general operation:	Daily (Mon – Fri) by the station operator. Frequent checks of, chromatogram, peak width, CO-retention times, and cylinder pressures are made.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

Unchanged since the WCC-Empa audit in 2009 (Zellweger et al., 2009).

Data Treatment

See Gomez-Pelaez et al. (2013) for a comprehensive description of the current data treatment procedures.

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.

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 Table 23 below.

Setup and Connections

Table 8 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 IZO data acquisition system.

Table 8. Experimental details of IZO CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air). For assigned values and standard uncertainties see Table 23.	
Station Analyser IZO (AL)	
Model, S/N	RGA-3 #070188-008
Principle	HgO reduction gas detector
Drying system	-65°C (cooling trap)
Comparison procedures	
Connection	The TS were connected to spare calibration gas ports and measured as if they were ambient air (i.e., alternating TS and WS injections).

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 Table 9.

Table 9. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the RGA-3 instrument (AL) with the WCC-Empa TS (WMO-2004 CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(13-09-27 11:11:00)	130905_FB03383	81.9	0.2	80.4	0.6	9.0	-1.5	-1.8
(13-09-27 14:41:00)	070927_FF21167	185.0	0.5	185.0	0.7	8.0	0.0	0.0
(13-09-30 11:01:00)	130905_FA02493	88.3	0.0	87.1	0.4	12.0	-1.2	-1.4
(13-09-30 14:41:00)	130819_FB03865	151.6	0.5	150.5	0.6	8.0	-1.1	-0.7
(13-10-01 10:31:00)	130905_FB03358	67.9	0.6	66.4	0.4	9.0	-1.5	-2.1
(13-10-01 14:41:00)	130819_FB03860	136.2	0.8	134.7	0.7	14.0	-1.5	-1.1

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

Same as for carbon monoxide.

Instrumentation

Dani-3800 GC/FID (main instrument; used for data submission to WDCGG) system and Varian 3800 GC/FID system (secondary instrument; still with issues to solve in its dedicated ambient air inlet/drying system). Instrumental details are listed in Table 11.

Standards

The station is equipped with laboratory standards from NOAA. Older NOAA standards are now used as working standards and are not listed in the table below. Furthermore, WS are filled at IZO whenever necessary using a RIX pump. The calibration scheme remained unchanged since the last WCC-Empa audit in 2009.

Table 10. Methane standards available at IZO as of September 2013.

Manufacturer / # / Use	CH_4 (ppb) (uncert.)	Matrix	Calibration		Scale	In service	
			Date	By		From	To
NOAA / CA06930 / LS	1682.14 (0.10)	Natural air	2006	NOAA	NOAA2004	2006	Today
NOAA / CA06932 / LS	1826.04 (0.11)	Natural air	2006	NOAA	NOAA2004	2006	Today
NOAA / CA08201 / LS	1947.87 (0.47)	Natural air	2008	NOAA	NOAA2004	2008	Today

Operation and Maintenance

Sequence:	Ambient air injections every 30 min for the Dani GC-FID and every 15 min for the Varian GC-FID, with WS injections in-between.
Check for general operation:	Daily (Mon – Fri) by the station operator.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

Unchanged for the DANI GC/FID since the WCC-Empa audit in 2009 (Zellweger et al., 2009). The data treatment for the Varian GC-FID is similar to that for the DANI GC-FID.

Data Treatment

Unchanged since the WCC-Empa audit in 2009 (Zellweger et al., 2009).

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 23 below.

Setup and Connections

Table 11 shows details of the experimental setup during the comparison of the transfer standards and the station analyser. The data used for the evaluation was recorded by the station data acquisition system.

Table 11. Experimental details of the comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air). For assigned values and standard uncertainties see Table 23.	
Station Analysers (OA)	
Model, S/N	DANI 3800 GC/FID #011109
Principle	GC/FID
Model	Varian 3800 GC/FID
Principle	GC/FID
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port (GC/FID) and measured as if they were ambient air (i.e., alternating TS and WS injections).

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 Tables.

Table 12. CH_4 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the DANI 3800 GC/FID (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(13-09-30 13:48:00)	110511_FB03382	1769.78	0.03	1771.34	3.23	10	1.56	0.09
(13-10-01 13:48:00)	130905_FB03383	1862.57	0.06	1861.86	2.49	14	-0.71	-0.04
(13-10-02 13:33:00)	110808_FA02505	2149.66	0.09	2152.77	8.05	11	3.11	0.14
(13-10-08 14:03:00)	130819_FB03860	1942.79	0.08	1944.18	3.17	11	1.39	0.07
(13-10-10 13:48:00)	130819_FB03865	1890.94	0.10	1891.73	4.03	12	0.79	0.04
(13-10-18 13:48:00)	130905_FA02493	1928.99	0.08	1930.23	1.64	12	1.24	0.06

Table 13. Same as above for the Varian 3800 GC/FID.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(13-09-30 14:30:51)	130905_FB03358	1862.78	0.05	1862.01	1.92	14	-0.77	-0.04
(13-10-01 11:15:50)	130905_FA02493	1928.99	0.08	1928.24	2.82	12	-0.75	-0.04
(13-10-01 15:26:30)	110808_FA02505	2149.66	0.09	2151.71	2.50	14	2.05	0.10
(13-10-04 14:23:20)	110511_FB03382	1769.78	0.03	1770.09	2.94	15	0.31	0.02
(13-10-08 13:30:47)	130819_FB03865	1890.94	0.10	1891.28	3.73	14	0.34	0.02
(13-10-09 14:53:20)	130905_FB03383	1862.57	0.06	1863.88	2.89	12	1.31	0.07
(13-10-10 13:45:51)	130819_FB03860	1942.79	0.09	1941.80	2.87	14	-0.99	-0.05

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

Same as for carbon monoxide.

Instrumentation

LI-COR LI-7000 and LI-COR LI-6252. Instrumental details are listed in Table 15, and further details can be found in the proceedings of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Gomez-Pelaez and Ramos, 2011).

Standards

The station is equipped with laboratory standards from NOAA. Older NOAA standards are now used as working standards and are not listed in the table below. Furthermore, WS are filled at IZO whenever necessary using a RIX pump and a system similar to that of NOAA/GMD to slightly modify (increase or decrease) the CO_2 mole fraction of the ambient air is used to fill the WS. Three WS are used simultaneously for each analyser, covering at present the mole fraction range 381-407 ppm (approximate range, it depends of the actual exact mole fractions of the WS filled), which exceeds the CO_2 mole fraction range observed at Izaña.

Table 14. NOAA carbon dioxide standards available at IZO as of September 2013.

Cylinder #	CO_2 (ppm) (uncert.)	Matrix	Calibration		Scale	In service	
			Date	By		From	To
CA02839	398.97 (0.01)	Natural air	2008	NOAA	WMO-X2007	2008	Today
CA06800	368.49 (0.01)	Natural air	2006	NOAA	WMO-X2007	2006	Today
CA06817	356.88 (0.01)	Natural air	2005	NOAA	WMO-X2007	2006	Today
CA06905	378.94 (0.01)	Natural air	2006	NOAA	WMO-X2007	2006	Today
CA07421	391.26 (0.01)	Natural air	2008	NOAA	WMO-X2007	2008	Today
CA07969	410.14 (0.04)	Natural air	2008	NOAA	WMO-X2007	2008	Today

Operation and Maintenance

Sequence:	Three WS measurements per hour (3 min per WS).
Check for general operation:	Daily (Mon – Fri) by the station operator.
Other (cleaning, leak check etc.):	As required.

Data Acquisition, Data Transfer and Data Treatment

Custom made software. For details refer to the proceedings of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Gomez-Pelaez and Ramos, 2011).

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 23 below.

Setup and Connections

Table 15 shows details of the experimental setup during the comparison of the transfer standards and the station analysers. The data used for the evaluation was recorded by the station data acquisition system.

Table 15. Experimental details of the comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air). For assigned values and standard uncertainties see Table 23.	
Station Analysers (OA)	
Model, S/N	LICOR LI-7000 #IRGA-0524
Principle	NDIR
Model, S/N	LICOR LI-6252 #IRG2-513
Principle	NDIR
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port and measured as if they were ambient air (i.e., alternating the measurements of several TS and the usual WS measurements - 3 WS, each one measured during 3 minutes every hour-).

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 Tables.

Table 16. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the LICOR LI-7000 analyser (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(13-09-27 14:05:44)	130819_FB03865	387.01	0.01	387.07	0.02	45	0.06	0.02
(13-09-27 14:17:13)	130905_FB03358	388.97	0.04	388.96	0.02	27	-0.01	0.00
(13-09-27 14:25:44)	130905_FA02493	381.95	0.04	381.99	0.02	45	0.04	0.01
(13-09-30 13:05:44)	130905_FB03383	390.23	0.04	390.27	0.04	75	0.04	0.01
(13-09-30 13:33:18)	110808_FA02505	373.36	0.02	373.50	0.06	63	0.14	0.04
(13-09-30 13:06:36)	130819_FB03860	399.50	0.03	399.51	0.05	84	0.01	0.00

Table 17. Same as above for the LICOR LI-6252 analyser (OA).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(14-02-12 14:25:44)	130819_FB03865	387.01	0.01	387.03	0.04	75	0.02	0.01
(14-02-12 14:15:44)	130905_FA02493	381.95	0.04	381.90	0.04	75	-0.05	-0.01
(14-02-12 14:06:33)	130905_FB03383	390.23	0.04	390.21	0.05	57	-0.02	-0.01
(14-02-12 13:52:39)	130819_FB03860	399.50	0.03	399.64	0.03	71	0.14	0.04

Nitrous Oxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide.

Air Inlet System

Same as for carbon monoxide.

Instrumentation

Varian 3800 GC with an ECD detector; details are published in the proceedings of the GGMT meetings and a WCC-N_2O audit report (Gomez-Pelaez and Ramos, 2009; Gomez-Pelaez et al., 2012; Scheel, 2009). The instrumentation is adequate for the measurement of N_2O. Instrumental details are listed in Table 19.

Standards

The station is equipped with laboratory standards from NOAA. Furthermore, WS are filled at IZO whenever necessary using a RIX pump.

Table 18. NOAA nitrous oxide standards available at IZO as of September 2013.

Manufacturer / # / Use	CH_4 (ppb) (uncert.)	Matrix	Calibration		Scale	In service	
			Date	By		From	To
NOAA / CA06739 / LS	257.31 (0.16)	Natural air	2006	NOAA	NOAA2006	2006	present
NOAA / CA06996 / LS	305.89 (0.12)	Natural air	2006	NOAA	NOAA2006	2006	present
NOAA / CA06970 / LS	330.14 (0.16)	Natural air	2006	NOAA	NOAA2006	2006	present
NOAA / CA06964 / LS	356.81 (0.15)	Natural air	2006	NOAA	NOAA2006	2006	present
NOAA / CA08203 / LS	321.58 (0.07)	Natural air	2008	NOAA	NOAA2006	2008	present

Operation and Maintenance

Check for general operation: Daily (Mon – Fri) by the station operator.

Other (cleaning, leak check etc.): As required.

Data Acquisition and Data Transfer

DANI GC: Varian Star software with a 16-bit A/D board operating at 40 Hz is used for data acquisition. Varian GC: Data is acquired on internal computer of the GC system, and digitally transferred to an external computer where it is further processed using the Varian Star software.

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 23 below.

Setup and Connections

Table 19 shows details of the experimental setup during the comparison of the transfer standards and the station analyser. The data used for the evaluation was recorded by the station data acquisition system.

Table 19. Experimental details of the comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air). For assigned values and standard uncertainties see Table 23.	
Station Analysers (OA)	
Model, S/N	Varian 3800 with ECD detector
Principle	GC/ECD
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port and measured as if they were ambient air (i.e., alternating TS and WS injections).

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 Table 20.

Table 20. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Varian 3800 GC/ECD (AL) (WMO-2006 N_2O scale) with the WCC-Empa TS (WMO-2006A N_2O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(13-09-30 14:29:30)	130905_FB03358	316.92	0.16	316.55	0.64	14	-0.37	-0.12
(13-10-01 11:14:30)	130905_FA02493	314.95	0.11	314.75	0.58	12	-0.20	-0.06
(13-10-01 15:14:30)	110808_FA02505	322.48	0.02	322.45	0.53	16	-0.03	-0.01
(13-10-04 14:22:00)	110511_FB03382	311.53	0.09	311.52	0.73	15	-0.01	0.00
(13-10-08 13:37:00)	130819_FB03865	320.01	0.07	320.03	0.29	13	0.02	0.01
(13-10-09 14:52:00)	130905_FB03383	317.29	0.07	316.98	0.57	12	-0.31	-0.10
(13-10-10 13:44:30)	130819_FB03860	327.60	0.08	327.19	0.67	14	-0.41	-0.13

WCC-Empa Travelling 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 -0.4, COEF 1.007

Zero air source: Pressurized air – Breitfuss 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 21. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 18). 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)).

$$X_{TS} \text{ (ppb)} = ([TS] + 0.16 \text{ ppb}) / 0.9997 \qquad (6a)$$

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

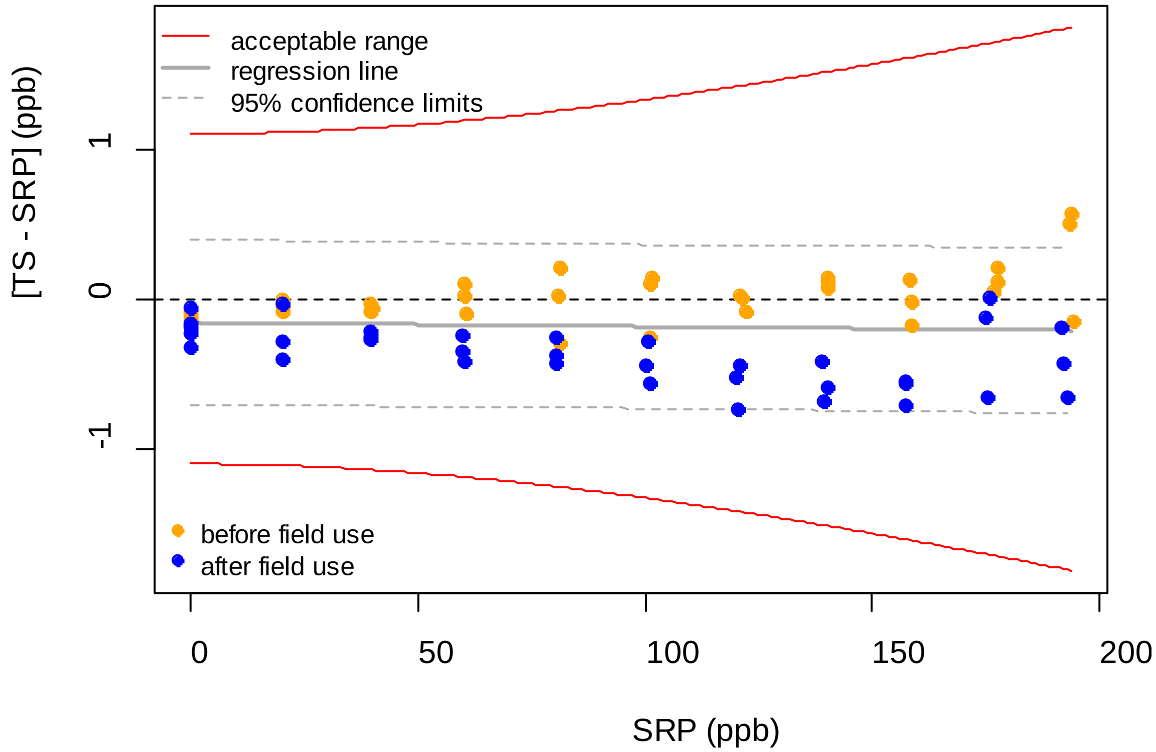

Figure 18. *Deviations between travelling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 21. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa travelling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2013-09-09	1	0	-0.15	0.21	-0.24	0.07
2013-09-09	1	120	122.08	0.11	122.00	0.05
2013-09-09	1	40	39.84	0.34	39.79	0.12
2013-09-09	1	180	177.35	0.39	177.47	0.21
2013-09-09	1	60	60.07	0.26	60.10	0.06
2013-09-09	1	20	20.17	0.19	20.13	0.08
2013-09-09	1	140	140.34	0.29	140.46	0.19
2013-09-09	1	160	158.66	0.13	158.48	0.07
2013-09-09	1	190	193.49	0.28	194.00	0.14
2013-09-09	1	80	80.68	0.28	80.70	0.07
2013-09-09	1	100	101.03	0.27	101.13	0.08
2013-09-09	1	0	0.04	0.16	-0.20	0.06
2013-09-09	2	0	0.01	0.21	-0.11	0.06
2013-09-09	2	60	60.44	0.18	60.34	0.07
2013-09-09	2	180	177.53	0.55	177.75	0.18
2013-09-09	2	190	194.16	0.29	194.00	0.20
2013-09-09	2	120	121.10	0.16	121.11	0.06
2013-09-09	2	40	39.68	0.25	39.60	0.03
2013-09-09	2	20	20.19	0.20	20.11	0.06
2013-09-09	2	80	81.13	0.09	80.83	0.09
2013-09-09	2	140	140.25	0.28	140.33	0.08
2013-09-09	2	160	158.44	0.16	158.42	0.11
2013-09-09	2	100	101.25	0.36	101.00	0.07
2013-09-09	2	0	-0.05	0.25	-0.12	0.06
2013-09-09	3	0	-0.02	0.23	-0.16	0.10
2013-09-09	3	80	81.17	0.14	81.38	0.09
2013-09-09	3	100	101.57	0.24	101.71	0.08
2013-09-09	3	20	20.21	0.18	20.20	0.08
2013-09-09	3	60	60.18	0.22	60.29	0.09
2013-09-09	3	140	140.39	0.16	140.54	0.09
2013-09-09	3	190	193.68	0.53	194.25	0.13
2013-09-09	3	160	158.36	0.24	158.49	0.13
2013-09-09	3	40	39.63	0.14	39.60	0.11
2013-09-09	3	180	176.64	0.23	176.69	0.15
2013-09-09	3	120	121.00	0.30	121.02	0.05
2013-09-09	3	0	-0.04	0.13	-0.14	0.09
2014-03-05	4	0	0.03	0.29	-0.20	0.14
2014-03-05	4	140	140.01	0.23	139.43	0.12
2014-03-05	4	80	80.28	0.22	80.02	0.11
2014-03-05	4	20	20.25	0.31	19.85	0.08
2014-03-05	4	190	192.27	0.33	191.84	0.29
2014-03-05	4	60	59.78	0.30	59.42	0.10
2014-03-05	4	120	120.16	0.21	119.64	0.05
2014-03-05	4	40	39.32	0.35	39.04	0.09
2014-03-05	4	180	175.47	0.29	174.81	0.15
2014-03-05	4	160	157.48	0.51	156.93	0.08
2014-03-05	4	100	100.32	0.43	99.88	0.03
2014-03-05	4	0	-0.01	0.21	-0.19	0.10

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2014-03-05	5	0	-0.13	0.23	-0.19	0.11
2014-03-05	5	40	39.49	0.23	39.28	0.12
2014-03-05	5	100	101.27	0.15	100.71	0.11
2014-03-05	5	180	175.59	0.37	175.60	0.15
2014-03-05	5	20	19.99	0.18	19.96	0.07
2014-03-05	5	60	59.96	0.24	59.54	0.12
2014-03-05	5	80	80.38	0.36	80.00	0.10
2014-03-05	5	120	120.55	0.26	119.82	0.10
2014-03-05	5	140	138.98	0.36	138.56	0.13
2014-03-05	5	160	157.35	0.32	156.65	0.04
2014-03-05	5	190	191.67	0.47	191.47	0.14
2014-03-05	5	0	0.05	0.16	-0.12	0.10
2014-03-05	6	0	0.06	0.42	-0.13	0.05
2014-03-05	6	120	120.80	0.24	120.35	0.11
2014-03-05	6	190	192.91	0.31	192.26	0.23
2014-03-05	6	80	80.26	0.35	79.84	0.08
2014-03-05	6	140	139.18	0.18	138.49	0.10
2014-03-05	6	160	157.24	0.36	156.68	0.07
2014-03-05	6	20	20.06	0.19	19.78	0.14
2014-03-05	6	60	59.64	0.26	59.39	0.06
2014-03-05	6	180	175.07	0.49	174.95	0.09
2014-03-05	6	40	39.30	0.26	39.04	0.10
2014-03-05	6	100	100.47	0.39	100.19	0.07
2014-03-05	6	0	0.12	0.29	-0.21	0.09

[#]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, Methane and Nitrous Oxide. 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 travelling 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-X2004 scale (Novelli et al., 2003)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004 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 mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).
CO_2 and CH_4: Picarro G1301 (Cavity Ring Down Spectroscopy).

Table 22 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 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 23, and Figure 19 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 22. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO	sd	CH_4	sd	N_2O	sd	CO_2	sd	CO	sd	CH_4	sd	N_2O	sd	CO_2	sd
	NOAA assigned values								WCC-Empa assigned values							
	(ppb)		(ppb)		(ppb)		(ppm)		(ppb)		(ppb)		(ppb)		(ppm)	
CC339523	347.9	0.3	1854.60	0.13	322.52	0.12	396.88	0.06	350.9	0.3	1854.76	0.03	322.52	0.02	396.94	0.02
CC339524	390.7	0.2	1980.28	0.30	355.42	0.16	795.42	0.06	394.1	0.4	1981.18	0.04	355.42	0.02	796.36	0.04
CC311846	166.4	0.1	1805.24	0.12	338.27	0.11	377.86	0.04	167.2	0.3	1805.07	0.11	338.27	0.01	377.84	0.02

Table 23. 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)
070927_FF21167	185.27	0.54	1663.55	0.08	352.36	0.01	402.54	0.24
110511_FB03382	60.00	0.37	1769.78	0.03	315.19	0.02	311.66	0.10
110808_FA02505	189.81	0.19	2149.66	0.09	373.36	0.02	322.57	0.02
120719_FA02770	194.08	0.05	1869.64	0.03	333.61	0.03	335.58	0.04
130819_FB03853	135.58	1.01	1942.90	0.09	399.48	0.02	327.67	0.09
130819_FB03855	151.27	0.62	1890.77	0.08	386.97	0.02	319.87	0.07
130819_FB03860	135.53	0.86	1942.79	0.08	399.50	0.03	327.68	0.08
130819_FB03865	151.14	0.52	1890.94	0.10	387.01	0.01	320.13	0.06
130905_FA02493	87.09	0.04	1928.99	0.08	381.95	0.04	315.08	0.08
130905_FB03358	66.25	0.63	1862.78	0.05	388.97	0.04	317.02	0.16
130905_FB03383	80.64	0.21	1862.57	0.06	390.23	0.04	317.37	0.09

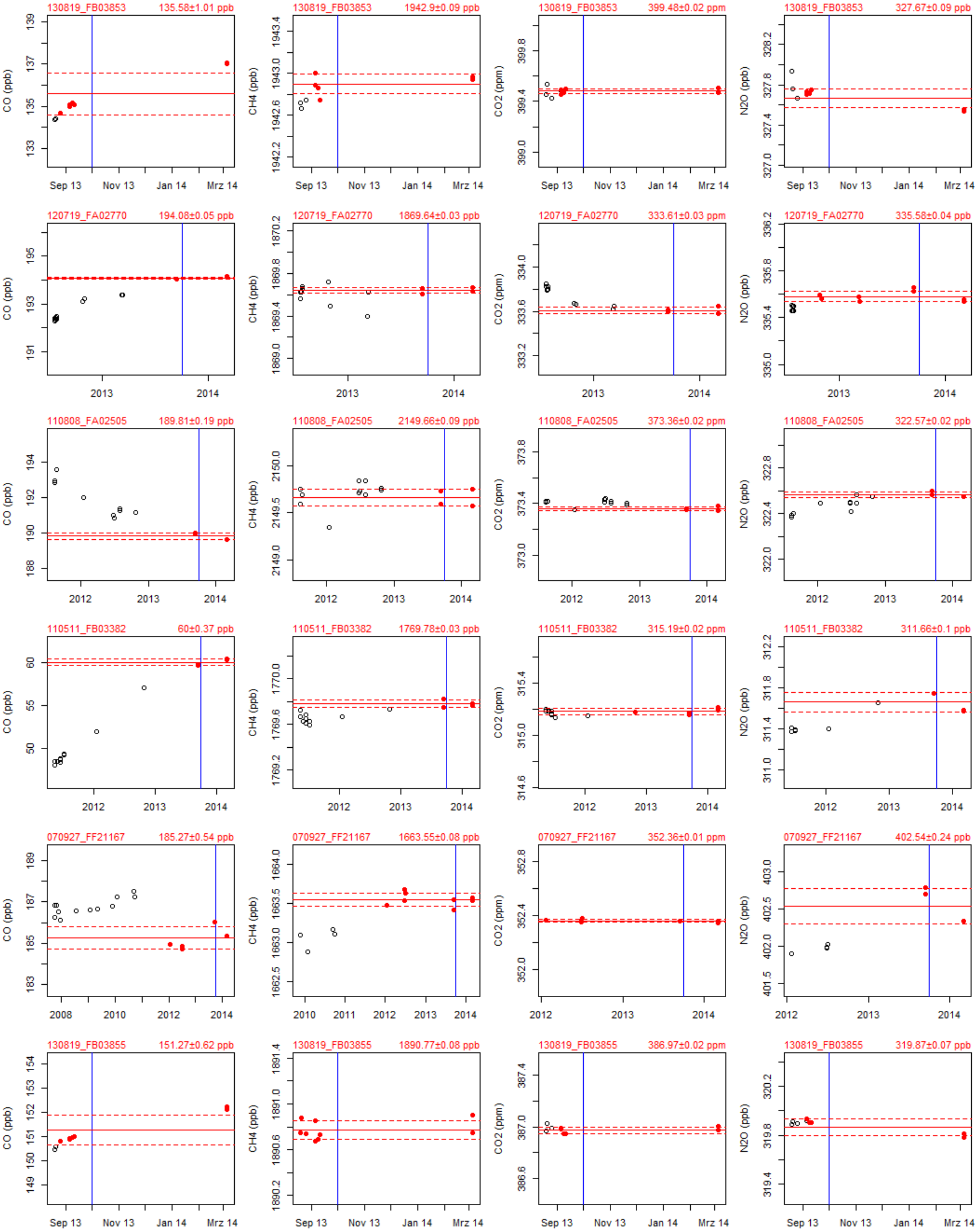

Figure 19. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue horizontal line refers to the date of the audit.*

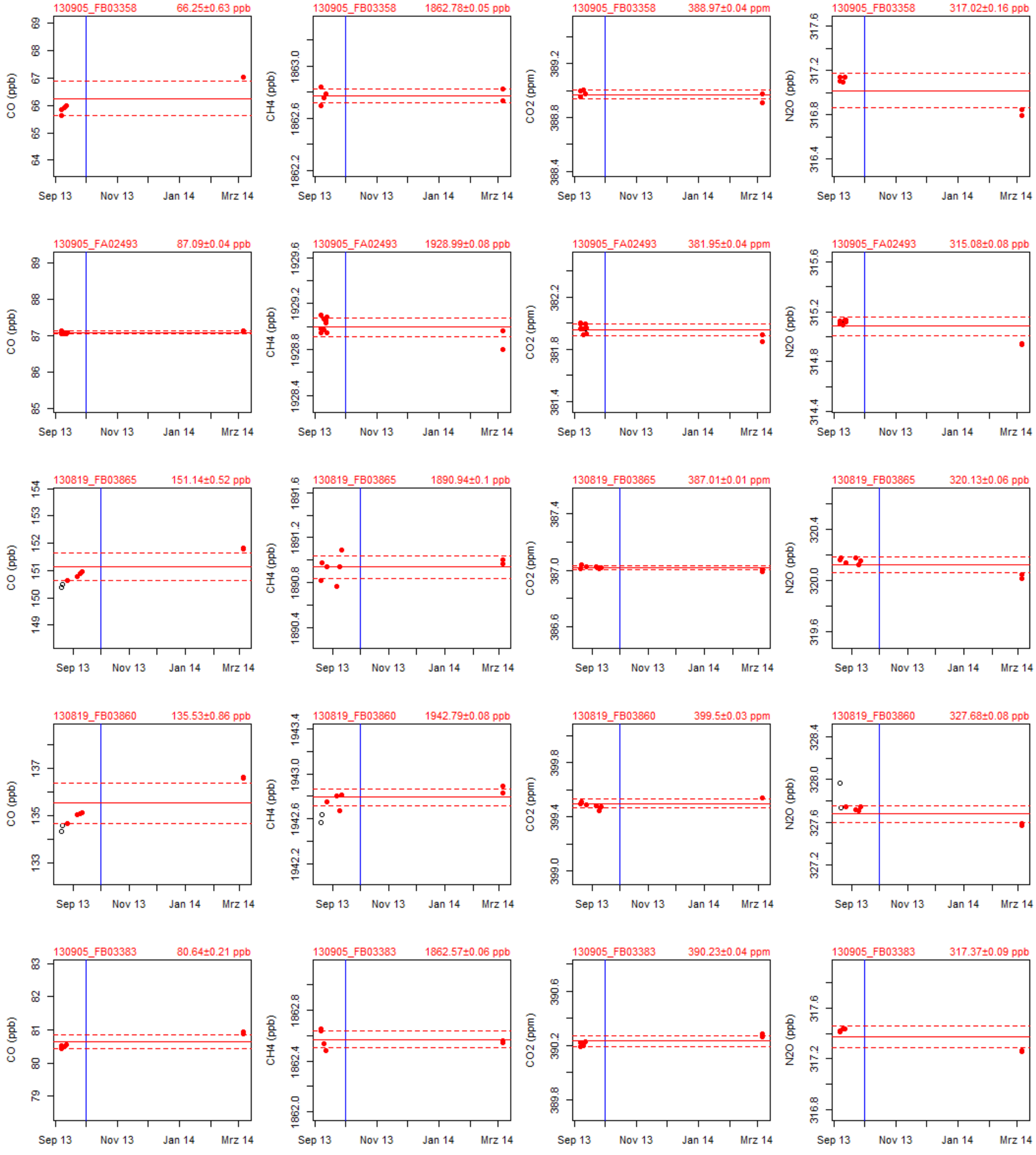

Figure 20. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue horizontal line refers to the date of the audit.*

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 40 h using one of the TS as a working standard (130819_FB03853), and two additional TS (070927_FF21167, 130905_FB03358) were used as target cylinders. 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 below figure. The maximum drift between two WS measurements was approx. 2 ppb for CH_4 and <0.1 ppm for CO_2. The two target standards were within half of the WMO GAW compatibility goals except for one measurement.

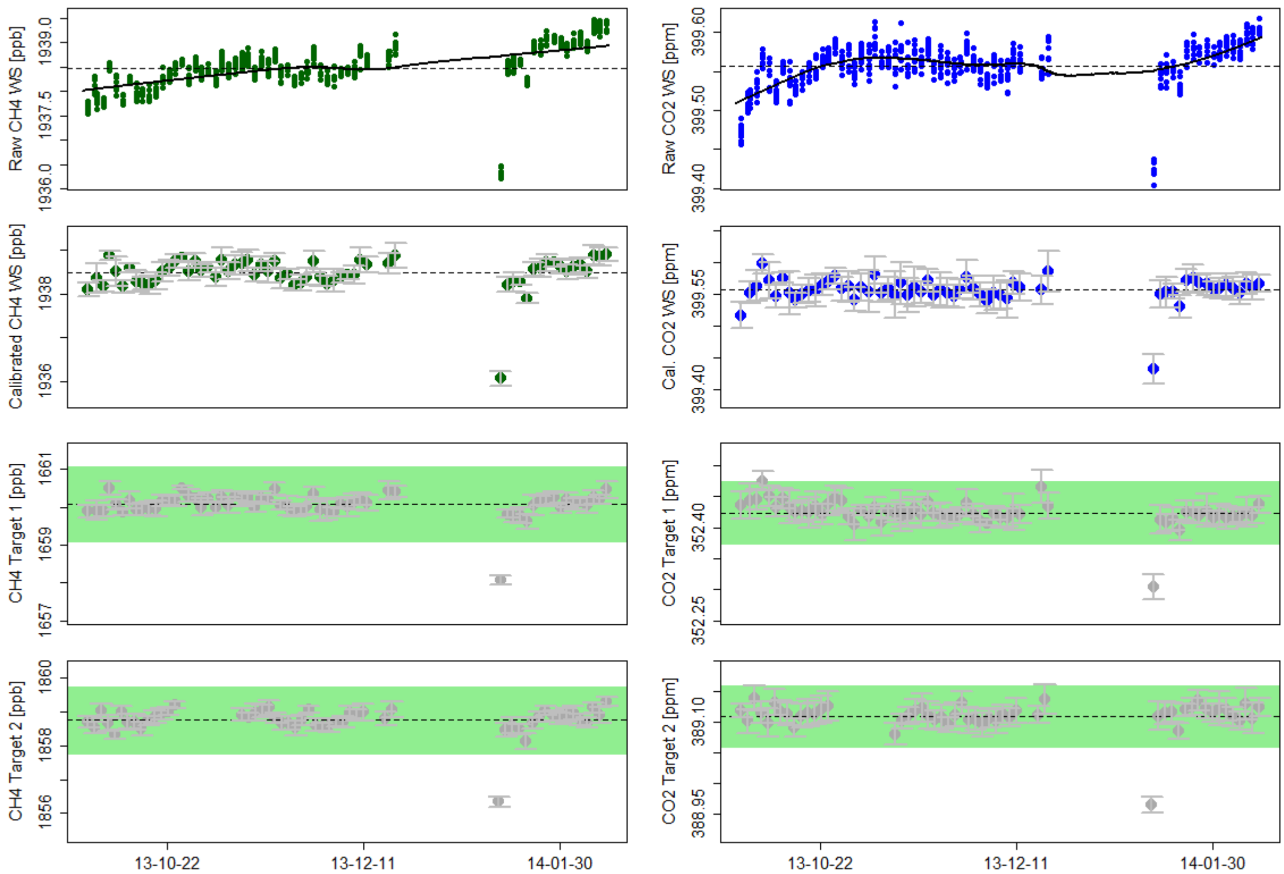

Figure 21. *CH_4 (left panel) and CO_2 (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1-min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target standards. 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.*

The two target standards were within half of the WMO GAW compatibility goals except for one measurement.

For CO, all three standards were used to apply a correction to the data. The average of the loess fits were used to account for instrumental drift. After applying the drift correction the variability of the CO WS was not significantly different from half of the WMO/GAW compatibility goals, as shown in the figure below.

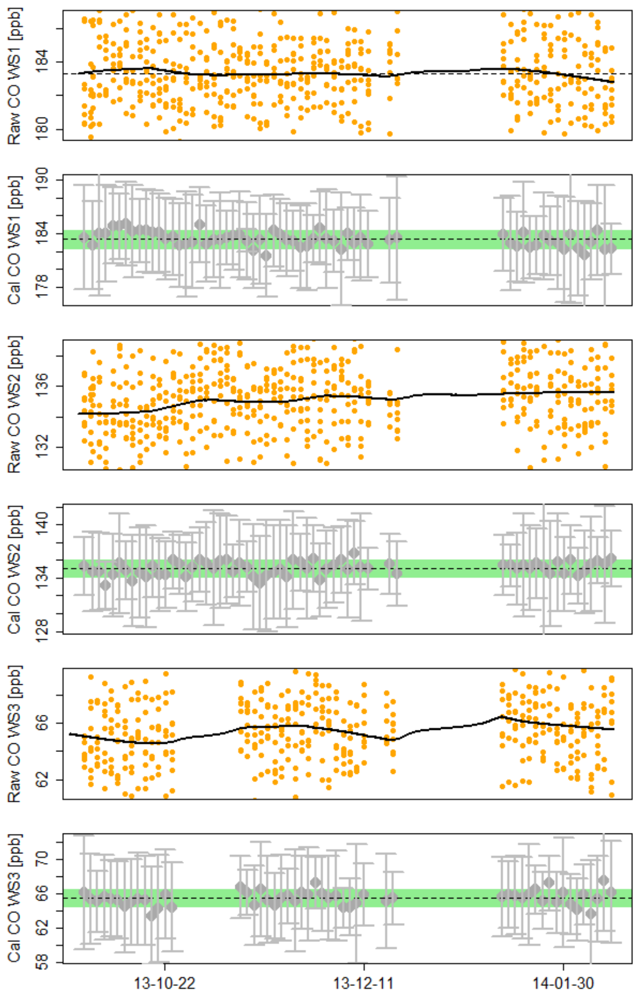

Figure 22. *CO calibrations of the WCC-Empa-TI. The panel with the orange dots show raw 1-min values of the working standards and the corresponding loess fits (black lines) used to account for drift. The other panels show the variation of the WS (10 min averages with standard deviation) after applying the drift correction. The green area represents half of the WMO/GAW compatibility goals.*

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

Ozone Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2013-09-26 through 2013-09-27
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Ramon Ramos, Marina Jover
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 -0.4, COEF 1.007
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9997±0.0008) □ [SRP] - (0.16±0.07)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #63900-337
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset = 0.0; Span = 1.053
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0177±0.0006) □ [SRP] - (0.22±0.03)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.22 ppb) /1.0177
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.52e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	Offset = 0.0; Span = 1.006
1.6.8	Calibration after audit (ppb):	[OA] = (0.9819±0.0012) □ [SRP] - (0.12±0.07)
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	X_{O3} (ppb) = ([OA] + 0.12 ppb) /0.9819
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.80e-05 * X_{O3}^2)
1.7	Comments:	Second comparison: Settings were changed to values of the audit in 2009. Main instrument.
1.8	Reference:	WCC-Empa Report 13/2

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

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

Ozone Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2013-09-27
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Ramon Ramos, Marina Jover
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 -0.4, COEF 1.007
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9997±0.0008) □ [SRP] - (0.16±0.07)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C #72491-371
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset = 0.0; Span = 1.042
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0221±0.0008) □ [SRP] - (0.14±0.04)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.14 ppb) /1.0221
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.52e-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 13/2

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

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

Ozone Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2013-09-27
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Ramon Ramos, Marina Jover
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 -0.4, COEF 1.007
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9997±0.0008) □ [SRP] - (0.16±0.07)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49C-PS #56084-306
1.6.2	Range of calibration:	0 – 200 ppb
1.6.3	Coefficients at start of audit	Offset = -0.8; Span = 1.014
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9903±0.0002) □ [SRP] + (0.65±0.03)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.65 ppb) /0.9903
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.62e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	Offset = -0.8; Span = 1.014
1.6.8	Calibration after audit (ppb):	OA] = (1.0090 ±0.0002) □ [SRP] - (0.05±0.03)
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	X_{O3} (ppb) = ([OA] + 0.05 ppb) /1.0090
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.53e-05 * X_{O3}^2)
1.7	Comments:	First comparison: Instrument was in wrong condition (A/B problem), second comparison with correct A/B averaging.
1.8	Reference:	WCC-Empa Report 13/2

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

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

Carbon Monoxide Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2013-09-27 through 2013-10-01
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Angel Gomez-Pelaez
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	RGA-3 #070188-008
1.6.2	Range of calibration:	68 – 185 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.0097±0.0042) □ X_{CO} - (2.2±0.5)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 2.3) / 1.0097
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (0.7 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 13/2

[CO]: Instrument readings; X: mixing ratios on the WMO-2004 CO scale.

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

Methane Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2013-09-30 through 2013-10-18
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Angel Gomez-Pelaez, Vanessa Gomez-Trueba
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	DANI 3800 GC/FID
1.6.2	Range of calibration:	1770 – 2150 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CH_4 = (1.00638±0.00370) $\times$ X_{CH4} - (11.0±7.1)
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 + 11.0) / 1.00638
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (2.1 ppb^2 + 1.30e-07 * X_{CH4}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 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 13/2

[CH_4]: Instrument readings; X: mixing ratios on the NOAA04 CH_4 scale.

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

Methane Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2013-09-30 through 2013-10-10
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Angel Gomez-Pelaez, Vanessa Gomez-Trueba
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS] standards	TS calibrated against the WCC-Empa laboratory
1.6	Station Analyser:	
1.6.1	Analyser Model:	Varian 3800 GC/FID
1.6.2	Range of calibration:	1770 – 2150 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (1.00430 \pm 0.00401) \times X_{CH4} - (8.0 \pm 7.7)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 + 8.1) / 1.00430$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt $(2.1\ \text{ppb}^2 + 1.30\text{e-}07 * X_{CH4}^2)$
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 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 13/2

[CH_4]: Instrument readings; X: mixing ratios on the NOAA04 CH_4 scale.

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

Carbon Dioxide Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2013-09-27 through 2013-09-30
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Angel Gomez-Pelaez
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	LICOR LI-7000 #IRGA-0524
1.6.2	Range of calibration:	373 – 400 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.99521 \pm 0.00176) \cdot X_{CO2} + (1.90 \pm 0.68)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 - 1.90) / 0.99521$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.005 ppm^2 + 3.28e-08 * X_{CO2}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 13/2

[CO_2]: Instrument readings; X: mixing ratios on the WMO-X2007 CO_2 scale.

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

Carbon Dioxide Audit Executive Summary (IZO)

0.4	Station Name:	Izaña
0.5	GAW ID:	IZO
0.6	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Carbon Dioxide

1.9	Date of Audit:	2014-02-12
1.10	Auditor:	Christoph Zellweger
1.11	Station staff involved in audit:	Angel Gomez-Pelaez, Vanessa Gomez-Trueba
1.12	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.13	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.14	Station Analyser:	
1.14.1	Analyser Model:	LICOR LI-6252 #IRG2-513
1.14.2	Range of calibration:	382 – 400 ppm
1.14.3	Coefficients at start of audit	NA
1.14.4	Calibration at start of audit (ppm):	CO_2 = (1.01038±0.00316) □ X_{CO2} - (4.02±1.23)
1.14.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 + 4.02) / 1.01038
1.14.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.006 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$)
1.14.7	Coefficients after audit	NA
1.14.8	Calibration after audit (ppm):	NA
1.14.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.14.10	Standard uncertainty after compensation of calibration bias after audit(ppm):	NA
1.15	Comments:	NA
1.16	Reference:	WCC-Empa Report 13/2

[CO_2]: Instrument readings; X: mixing ratios on the WMO-X2007 CO_2 scale.

Nitrous Oxide Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.30900°N 16.49940°W (2373 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2013-09-30 through 2013-10-10
1.2	Auditor:	Christoph Zellweger
1.3	Station staff involved in audit:	Angel Gomez-Pelaez, Vanessa Gomez-Trueba
1.4	WCC-Empa N_2O Reference:	NOAA laboratory standards (WMO-2006A scale)
1.5	N_2O Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	Varian 3800 GC with ECD detector
1.6.2	Range of calibration:	311 – 328 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$N_2O = (0.98890 \pm 0.01461) \cdot X_{N2O} + (3.35 \pm 4.46)$
1.6.5	Unbiased N_2O mixing ratio (ppb) at start of audit:	X_{N2O} (ppb) = (N_2O – 3.35) / 0.98890
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{N2O} (ppb) = sqrt (0.07 ppb^2 + 1.01e-07 * X_{N2O}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased N_2O mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	IZO values were on WMO-X2006 N_2O calibration scale
1.8	Reference:	WCC-Empa Report 13/2

[N_2O]: Instrument readings; X: mixing ratios on the WMO-2006A N_2O scale.

REFERENCES

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, Journal Of Geophysical Research-Atmospheres, 110, Article D18306, 2005.

Gomez-Pelaez, A. J. and Ramos, R.: Improvements in the Carbon Dioxide and Methane Continuous Measurement Programs at Izaña Global GAW Station (Spain) during 2007-2009, GAW report (No. 194) of the “15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques (Jena, Germany; September 7-10, 2009, World Meteorological Organization (TD No. 1553), 133-138, 2011, 2011.

Gomez-Pelaez, A. J. and Ramos, R.: Installation of a new gas chromatograph at Izaña GAW station (Spain) to measure CH4, N2O, and SF6, GAW Report (No. 186) of the "14th WMO/IAEA meeting of experts on Carbon dioxide, other greenhouse gases, and related tracers measurement techniques (Helsinki, Finland, 10-13 September 2007)", edited by Tuomas Laurila, World Meteorological Organization (TD No. 1487), 55-59, 2009, 2009.

Gomez-Pelaez, A. J., Ramos, R., Gomez-Trueba, V., Campo-Hernandez, R., Dlugokencky, E. J., and Conway, T. J.: New improvements in the Izaña (Tenerife, Spain) global GAW station in-situ greenhouse gases measurement program, GAW report (No. 206) of the "16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2011) (Wellington, New Zealand, 25-28 October 2011)", edited by Gordon Brailsford, World Meteorological Organization, 76-81, 2012, 2012.

Gomez-Pelaez, A. J., Ramos, R., Gomez-Trueba, V., Novelli, P. C., and Campo-Hernandez, R.: A statistical approach to quantify uncertainty in carbon monoxide measurements at the Izaña global GAW station: 2008-2011, Atmos. Meas. Tech., 6, 787-799, 2013.

Herzog, A., Buchmann, B., and Hofer, P.: System and Performance Audit for Surface Ozone , Global GAW Station Izana, Tenerife, February 1998, WCC-Empa Report 98/2, Empa Dübendorf, Switzerland, 30 pp., 1998.

Herzog, A., Buchmann, B., and Hofer, P.: System and Performance Audit for Surface Ozone, Global GAW Station Izana, Tenerife, November 1996, WCC-Empa Report, Empa Dübendorf, Switzerland, 25 pp., 1996.

Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, Journal of Geophysical Research-Atmospheres, 108, 4622, doi:4610.1029/2003JD003710, 2003.

Novelli, P. C., Masarie, K. A., Lang, P. M., Hall, B. D., Myers, R. C., and Elkins, J. W.: Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, Journal of Geophysical Research-Atmospheres, 108, 4464, doi:4410.1029/2002JD003031, 2003.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech., 6, 837-860, 2013.

Scheel, H. E.: System and Performance Audit for Nitrous Oxide at the Global GAW Station Izaña, Tenerife, Spain, November 2008, WCC-N2O Report 2008/11, WCC-N2O, c/o Forschungszentrum Karlsruhe, IMK-IFU, Germany, 2009.

WMO: 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013), Beijing, China, 10-13 June 2013, GAW Report No. 213, World Meteorological Organization, Geneva, Switzerland, 2014.

WMO: Guidelines for Continuous Measurements of Ozone in the Troposphere, WMO TD No. 1110, GAW Report No. 209, World Meteorological Organization, Geneva, Switzerland, 2013.

WMO: Guidelines for the Measurement of Atmospheric Carbon Monoxide, GAW Report No. 192, World Meteorological Organization, Geneva, Switzerland, 2010.

WMO: Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance, GAW Report No. 185, World Meteorological Organization, Geneva, Switzerland, 2009.

WMO: Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland, 2007a.

WMO: WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, GAW Report #172, World Meteorological Organization, Geneva, Switzerland, 2007b.

Zellweger, C., Herzog, A., Buchmann, B., and Hofer, P.: System and Performance Audit of Surface Ozone and Carbon Monoxide at the Global GAW Izana and for Surface Ozone at Punta del Hidalgo, Tenerife, June 2000, WCC-Empa Report 00/2, Dübendorf, Switzerland, 53 pp., 2000.

Zellweger, C., Klausen, J., and Buchmann, B.: System and Performance Audit of Surface Ozone Carbon Monoxide and Methane at the Global GAW Station Izana, Spain, December 2004, WCC-Empa Report 04/4, Empa, Dübendorf, Switzerland, 59 pp., 2004.

Zellweger, C., Klausen, J., Buchmann, B., and Scheel, H. E.: System and Performance Audit of Surface Ozone,Carbon Monoxide, Methane and Nitrous Oxide at the Global GAW Station Izaña, Spain, March 2009, WCC-Empa Report 09/1, Dübendorf, Switzerland, 53 pp., 2009.

Zhao, C. L. and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, Journal of Geophysical Research-Atmospheres, 111, 2006.

LIST OF ABBREVIATIONS

AEMET	Agencia Estatal de Meteorología
AERONET	Aerosol robotic network
AL	Analyser
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
dtm	Date/Time
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
IARC	Izaña Atmospheric Research Center
IZO	Izaña Global GAW station
LS	Laboratory Standard
NOAA	National Oceanic and Atmospheric Administration
NDACC	Network for the Detection of Atmospheric Composition Change
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Travelling Standard
UV	Ultra Violet
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard

CALIBRATION CERTIFICATE OF IZO OZONE CALIBRATOR

Eidgenössische Materialprüfungs- und Forschungsanstalt
Laboratoire fédéral d'essai des matériaux et de recherche
Laboratorio federale di prova dei materiali e di ricerca
Institut federal da controlla da material e da retschertgas
Swiss Federal Laboratories for Materials Testing and Research

Empa
Überlandstrasse 129
CH-8600 Dübendorf
Tel. +41-44-765 11 11
Fax +41-44-765 11 12

EMPA

Laboratory Air Pollution / Environmental Technology

Calibration Laboratory accredited by the Swiss Accreditation Service
The Swiss Accreditation Service is one of the signatories to the EA Multilateral Agreement for the recognition of calibration certificates

Certificate-No.	**2013-5214004135**
Date:	**2014-01-17**
Pages:	**4**

Client: AGENCIA ESTATAL DE METEOROLOGÍA (AEMET)
C/ La Marina, 20, Planta 6
38001 Santa Cruz de Tenerife
SPAIN

Order-No. 5214004135
Contact person: Ramón Ramos

Calibration Certificate

Test object:	Ozone analyzer	Type: TEI 49C-PS S/N 56085-306 (COEF 1.014, BKG -0.6)
Primary standard:	Ozone primary standard NIST, Gaithersburg	type SRP S/N 15
Measurement Conditions:	Date of the calibration: Location:	2014-01-16 Empa Dübendorf Air-conditioned laboratory (LA 028)
	Environmental conditions:	Temperature: 23 ± 1 °C Pressure: 957.4 – 959.6 hPa
	Absorption coefficient (α):	308.32 $cm^{-1}atm^{-1}$ (Base e, 1013hPa, 273.15K, 253.7nm)
	Warm-up time: Conditioning:	>48 hours 1 hour at 350 $nmolmol^{-1}$ ozone
	Zero air / ozone generator:	The zero air unit and the ozone generator of the SRP were used.
Measurement program:	A measurement cycle consisted of ozone measurements at 11 mole fractions, ranging between 0 – 250 $nmolmol^{-1}$. Three measurement cycles were made.	
Measurement uncertainty:	The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approx. 95%.	

This certificate documents the traceability to national standards, which realize the physical unit of measurements (SI).
The measurements, the uncertainty with confidence probability and calibration methods are given on the following pages and are part of the certificate.

S SCHWEIZERISCHER KALIBRIERDIENSTDIENST
C SERVICE SUISSE D'ETALONAGE
SERVIZIO SVIZZERA DI TARURA
S SWISS CALIBRATION SERVICE

SCS Accreditation No. **SCS 089**

SWISS CALIBRATION

Results:

No.	Reference		TEI 49C-PS #56085-306			
	SRP#15	s_d		s_d	deviation to reference	
	nmolmol^{-1}	nmolmol^{-1}	nmolmol^{-1}	nmolmol^{-1}	nmolmol^{-1}	%
1	0.01	0.20	-0.12	0.07	-0.13	NA
2	126.89	0.34	127.11	0.13	0.22	0.17
3	151.59	0.25	152.07	0.11	0.48	0.32
4	202.78	0.38	203.56	0.07	0.77	0.38
5	249.36	0.26	250.21	0.11	0.85	0.34
6	226.55	0.21	227.45	0.14	0.91	0.40
7	75.20	0.31	75.24	0.10	0.04	0.06
8	50.63	0.21	50.83	0.20	0.19	0.38
9	176.60	0.31	177.20	0.08	0.61	0.34
10	26.32	0.34	26.30	0.11	-0.02	-0.08
11	100.72	0.15	101.04	0.10	0.32	0.32
12	-0.04	0.30	-0.08	0.10	-0.04	NA
13	-0.08	0.23	-0.10	0.11	-0.02	NA
14	126.89	0.22	127.19	0.11	0.30	0.24
15	50.94	0.44	51.20	0.13	0.26	0.50
16	151.54	0.32	152.00	0.10	0.46	0.31
17	202.58	0.30	203.52	0.11	0.94	0.46
18	176.32	0.19	177.16	0.12	0.84	0.48
19	249.03	0.31	249.94	0.12	0.90	0.36
20	75.35	0.16	75.26	0.13	-0.09	-0.12
21	226.46	0.16	227.76	0.10	1.29	0.57
22	100.09	0.29	100.36	0.21	0.27	0.27
23	26.23	0.23	26.31	0.10	0.08	0.30
24	-0.24	0.29	-0.14	0.10	0.10	NA
25	0.06	0.18	-0.05	0.15	-0.10	NA
26	249.90	0.61	250.94	0.26	1.03	0.41
27	202.11	0.45	203.07	0.13	0.96	0.47
28	176.33	0.26	177.12	0.11	0.79	0.45
29	125.48	0.26	125.87	0.09	0.39	0.31
30	226.43	0.19	227.44	0.16	1.01	0.45
31	26.54	0.47	26.16	0.10	-0.39	-1.46
32	150.69	0.27	151.52	0.16	0.83	0.55
33	50.60	0.20	50.76	0.10	0.17	0.33
34	74.99	0.25	75.64	0.15	0.65	0.86
35	99.95	0.40	100.44	0.11	0.49	0.49
36	-0.03	0.19	-0.01	0.20	0.02	NA

s_d: standard deviation (n = 10 measurement values)
NA: not applicable

Pressure sensor: The pressure sensor of the TEI 49C-PS #56085-306 was compared to the reference barometer (GB-1, meteolabor AG) at ambient pressure. The initial reading of the TEI 49C-PS (952.8 hPa) was adjusted to the reference pressure (958.2 hPa).

Calibration function: The following calibration function for the range between 0-250 $nmol mol^{-1}$ was determined from the comparison on 2013-11-26/27 at a temperature of 23±1°C and a pressure of 957.4 – 959.6 hPa.

Reference value (SRP#15) = (0.9955 x TEI 49C-PS #56085-306 + 0.10) $nmol mol^{-1}$

Measurement uncertainty: of the calibration

reference value (SRP#15)	value (TEI 49C-PS)	± uncertainty
0 $nmol mol^{-1}$	-0.1	± 1.0 $nmol mol^{-1}$
25 $nmol mol^{-1}$	25.1	± 1.2 $nmol mol^{-1}$
50 $nmol mol^{-1}$	50.1	± 1.5 $nmol mol^{-1}$
75 $nmol mol^{-1}$	75.2	± 2.0 $nmol mol^{-1}$
100 $nmol mol^{-1}$	100.4	± 2.5 $nmol mol^{-1}$
125 $nmol mol^{-1}$	125.5	± 3.0 $nmol mol^{-1}$
150 $nmol mol^{-1}$	150.6	± 3.6 $nmol mol^{-1}$
175 $nmol mol^{-1}$	175.7	± 4.1 $nmol mol^{-1}$
200 $nmol mol^{-1}$	200.8	± 4.7 $nmol mol^{-1}$
225 $nmol mol^{-1}$	225.9	± 5.3 $nmol mol^{-1}$
250 $nmol mol^{-1}$	251.0	± 5.8 $nmol mol^{-1}$

The measurement uncertainty given in the above table was determined in the Empa calibration laboratory under well known, ideal conditions. It reflects the minimal uncertainty, which can be guaranteed for the actual state of the tested instrument. To estimate the maximum uncertainty of a specific instrument, additional parameters such as long-term drift, temperature and pressure variability, maintenance and competence of the staff have to be considered. Thus, a careful evaluation of the uncertainty budget is indicated considering customer specific circumstances.

Figure 1 shows the linear regression of the difference (TEI 49C-PS #56085-306 - SRP#15) versus SRP#15, including the prediction interval (95%). The measurement values of the inter-comparison are within the range of the prediction interval with a probability of 95%. The prediction interval is a measure of the uncertainty of the calibration function.

Figure 2 shows the regression residuals versus the run index (time dependence) and the mole fraction. The absence of a temporal trend indicates stable instrument conditions. The absence of mole fraction dependence in the residuals indicates linearity of the instrument.

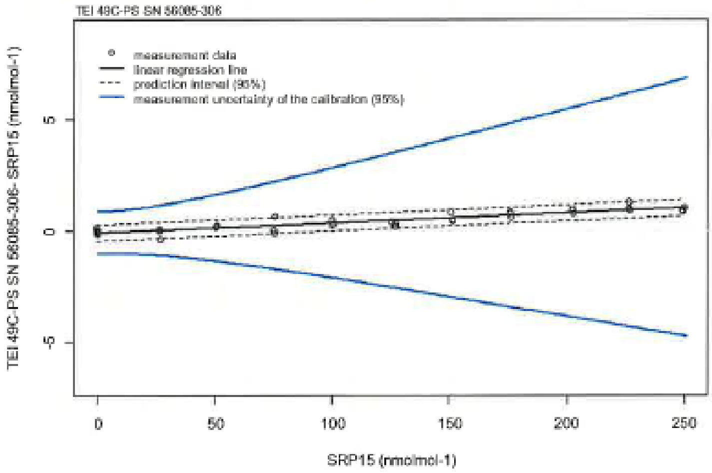

Figure 1: Linear regression of the difference (TEI 49C-PS #56085-306- SRP#15) vs. SRP#15.

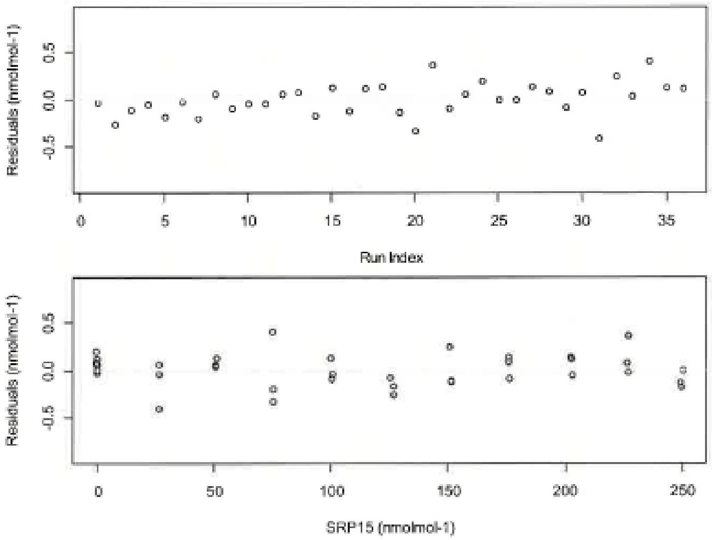

Figure 2: Regression residuals of the ozone inter-comparison as a function of run index (upper panel) and mole fraction (lower panel).

Dübendorf, 17.Januar 2014

Empa Dübendorf,
Laboratory Air Pollution/Environmental Technology

Head of the calibration service

Head of the Laboratory

Dr. C. Zellweger

Dr. L. Emmenegger