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World Calibration Centre for Surface Ozone
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Laboratory Air Pollution / Environmental Technology

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World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, CARBON MONOXIDE, METHANE AND NITROUS OXIDE AT THE GLOBAL GAW STATION IZANA SPAIN, MARCH 2009

Submitted by
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CONTENTS

ASSESSMENT AND RECOMMENDATIONS

The fifth system and performance audit at the Global GAW station Izaña conducted by WCC-Empa[1] was carried out from 4 thru 10 March 2009 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007b]. The Izaña Atmospheric Research Centre (IZO) is operated by the Agencia Estatal de Meteorología (AEMET). The audit included comparisons at the Santa Cruz de Tenerife Station (SCO), which is a complementary facility of IZO.

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], and December 2004 [*Zellweger, et al.*, 2004].

The following people contributed to the audit:

Dr Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr Emilio Cuevas	AEMET, GAW country contact, station manager
Ms Yenny Gonzalez Ramos	AEMET, Surface Ozone programme
Mr Ramón Ramos	AEMET, Carbon monoxide programme
Mr Angel J. Gomez-Pelaez	AEMET, Greenhouse gas programme

Our assessment of the Izaña observatory in general, as well as the surface ozone, carbon monoxide, methane and nitrous oxide measurements in particular, is summarised below. The assessment criteria for the ozone comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003].

This report is distributed to the GAW country contact (Dr Emilio Cuevas) and the World Meteorological Organization in Geneva. The report including executive summaries will be posted on the internet.

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

Station Location and Access

The Izaña station (28.309°N 16.499°W) is located on the Island of Tenerife, Spain, roughly 300 km west of the African coast. The meteorological observatory is situated on a mountain plateau at an altitude of 2373 m a.s.l., approximately 15 km north-east of the volcano Teide. The local wind field at the site is dominated by north-westerly winds. A predominant meteorological attribute of the Canary Islands region is the presence of the trade wind inversion that persists through most of the year and is well below the altitude of the station. The ground in the vicinity around Izaña is loosely covered with light volcanic soil. The vegetation in the surrounding area is sparse, consisting mainly of broom. About 100 m south of the station a road leads to the meteorological observatory, and also serves the astrophysical institute of the Canaries and a nearby military camp. Because the road is closed to public traffic, only approximately 5 to 10 cars a day pass the vicinity. The complementary background urban pollution research Observatory at Santa Cruz de Tenerife (SCO, 28.473°N 16.247°W) is located on the roof of the IZO headquarters at 52 m a.s.l. in the city of Santa Cruz de Tenerife. This station is also part of GURME program.

Station Facilities

The IZO station consists of several buildings. The main building was completely renovated between 2000 and 2004. Large and modern laboratories as well as rooms for visiting scientists including kitchen and office facilities are available. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

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[1] WMO/GAW GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

Recommendation 1 (*, 2010)**
Several gas cylinders were not secured during the audit, which poses a serious safety issue. Wall brackets or other appropriate cylinders fixing need to be installed for all cylinders in use.

Station Management and Operation

The station is managed by AEMET and has its own budget and personnel. The station is visited daily by at least two (weekends) or more (weekdays) station operators and scientists.

Air Inlet System

Two state-of-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. Aerosol measurements are made in a dedicated building nearby, and all these systems are equipped with the corresponding inlet.

Surface Ozone Measurements

Instrumentation. Two TEI 49C ozone analyzers are currently used at the station for continuous surface ozone measurements. The instrumentation is 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.

Comparison (Performance Audit). The comparisons of the three TEI 49C analysers (IZO and SCO instruments) and the TEI 49C-PS ozone calibrator extended over a period of several hours for each instrument. The results are summarised below and the following equations characterise the instrument bias:

TEI 49C #63900-337 (IZO primary analyser): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.27 ppb) / 1.007 (1a)

TEI 49i #72491-371 (IZO secondary analyser): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] – 0.44 ppb) / 1.016 (1b)

TEI 49C-PS #56084-306 (IZO calibrator): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] - 0.00 ppb) / 1.001 (1c)

TEI 49C #032060000000731 (SCO analyser): 0 – 90 ppb good agreement

Unbiased O_3 mixing ratio (ppb) X_{O3} (ppb) = ([OA] + 0.15 ppb) / 1.025 (1d)

The results of these comparisons are presented in Figure 1.

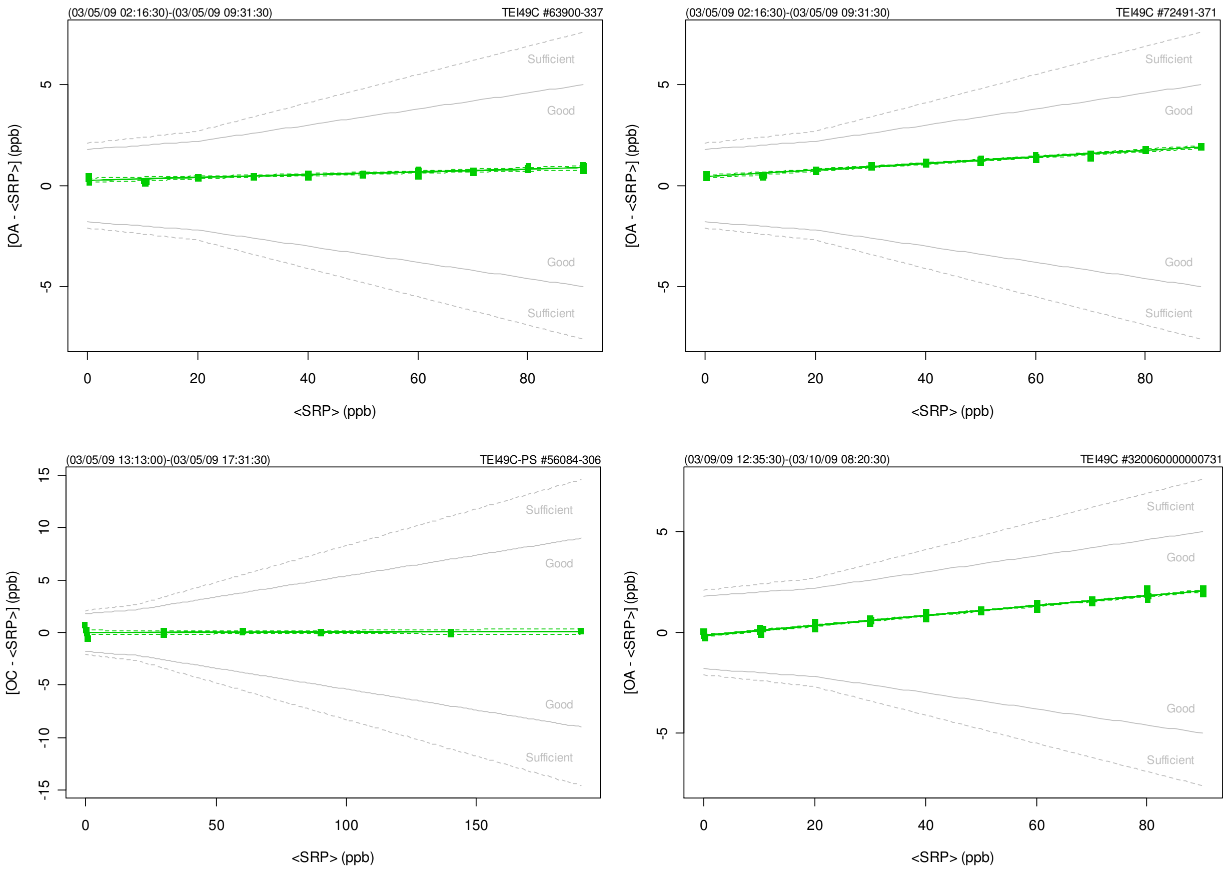

Figure 1. Bias of the IZO TEI 49C analysers (upper left/right), the IZO TEI 49C-PS calibrator (lower left) and the SCO TEI 49C analyser (lower right) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

All assessed instruments were in good calibration; however, the deviation of the IZO backup and the SCO analyzer was relatively large considering the excellent agreement between the WCC-Empa travelling standard and the station calibrator. It should be considered to adjust the instrument calibration factors rather than re-calculate the ozone levels based on the 3-monthly calibrations.

Recommendation 2 (*, ongoing)
It should be considered to adjust the analyser calibration factors based on a multiple point calibration with the station calibrator. Afterwards 3-monthly calibrations should be continued, but should not be used for further data correction unless significant differences are observed. In such a case the reason for the deviation needs to be identified.

Carbon Monoxide Measurements

Instrumentation. Izaña is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2. In addition, a TEI 48C-TL NDIR instrument was installed in 2004. The instrumentation is adequate for the intended purpose.

Standards. The station is equipped with nine laboratory standards obtained from NOAA/ESRL. The first set of standards (total four) was purchased in 1997 and 1999 (see Table 8 for details). In addition two of these standards were re-calibrated in 2003. A second set of five standards was purchased in 2006. The currently available IZO laboratory standards span the mole fraction range of 62 and 221 ppb. All standards have been certified by NOAA/ESRL based on the WMO-2000 (first set of standards) and WMO-2004 (second set) carbon monoxide calibration scales. According to the CCL (NOAA/ESRL), both scales are comparable and complementary, and standards on the two scales should be interchangeable to within 1-2 ppb. In addition, a 10-ppm standard from Air Liquide is available for the calibration of the NDIR instrument.

Comparison (Performance Audit). The comparison involved repeated challenges of the instrument with randomised carbon monoxide mole fractions from traveling standards (RGA-3) and a dilution system (TEI 48 C-TL, both IZO and SCO instruments). The following equations characterise the instrument bias, and the results are further illustrated in Figure 2:

RGA-3 #070188-008 (IZO):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 6.2 ppb) / 1.035 (2a)

TEI 48C-TL #75723-380 (IZO):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] + 5.2 ppb) / 0.916 (2b)

TEI 48C-TL #0531813062 (SCO):

Unbiased CO mixing ratio (ppb): X_{CO} (ppb) = ([CO] – 0.7 ppb) / 0.898 (2c)

The results of the RGA-3 system agreed within 3% compared to WCC-Empa, and for mole fractions above 150 ppb the agreement was better than 0.5%. The reason for the small difference at lower mole fractions could be the non-linearity of the RGA-3 system, or the uncertainty of the available laboratory standards.

Recommendation 3 (, ongoing)**
Measurements with the RGA-3 system should be continued.

Recommendation 4 (, 2010)**
Re-calibration of the NOAA/ESRL laboratory standards at NOAA is recommended.

The NDIR system proofed to be linear, but the IZO results were lower by approximately 10% when compared to WCC-Empa. This result was also confirmed with a direct measurement of the station standard.

The results presented for the IZO NDIR system were obtained after a replacement of the zero trap with the original Sofnocat 423 trap. A first check with the new zero trap (Sofnocat 514) showed that zero measurements were not reproducible.

A very similar result was found for the SCO TEI 48C-TL system; however, due to large disagreement between the WCC-Empa and the SCO zero readings, this comparison was only made using the WCC-Empa dilution system with interspersed zero checks (every 15 minutes) generated by the Empa dilution unit. Data of the comparison show that the instrument itself was working fine, but the issue with the SCO zero trap needs to be solved. A possible reason might be pressure changes when alternating between zero and ambient air.

Recommendation 5(*, 2010)**
Data obtained during the period when the Sofnocat 514 zero trap was in use (IZO instrument) should not be used. In addition, it is recommended to compare data obtained using the zero trap with external zero air.

Recommendation 6 (*, 2010)**
The zero trap of the SCO instrument needs to be re-designed or replaced. No difference should be observed between data acquired over the zero trap and external zero air sampled over the sample port.

Recommendation 7 (, 2010)**
It is recommended to calibrate the NDIR directly with a standard gas of 2 – 8 ppm CO. In addition, dilution experiments should be made to confirm the linearity of the system.

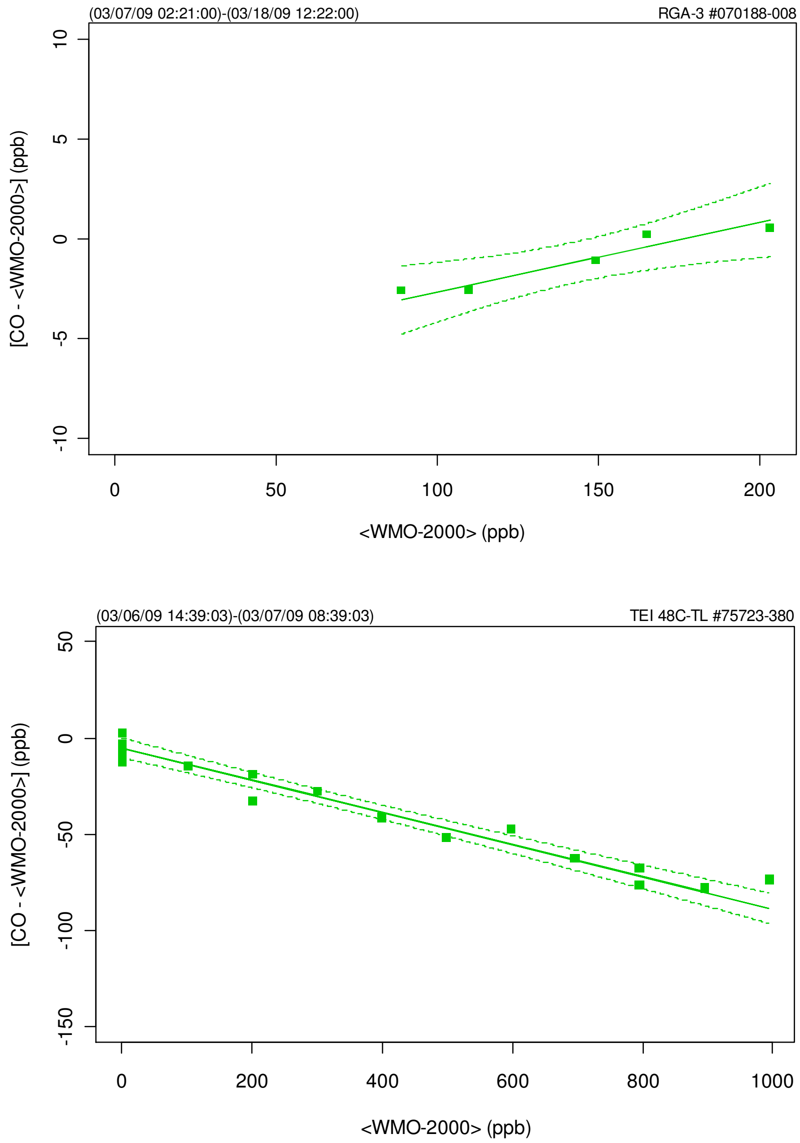

Figure 2. Bias of the Izaña carbon monoxide instrument (RGA-3, upper panel, and TEI 48C-TL, lower panel) with respect to the WMO-2000 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands.

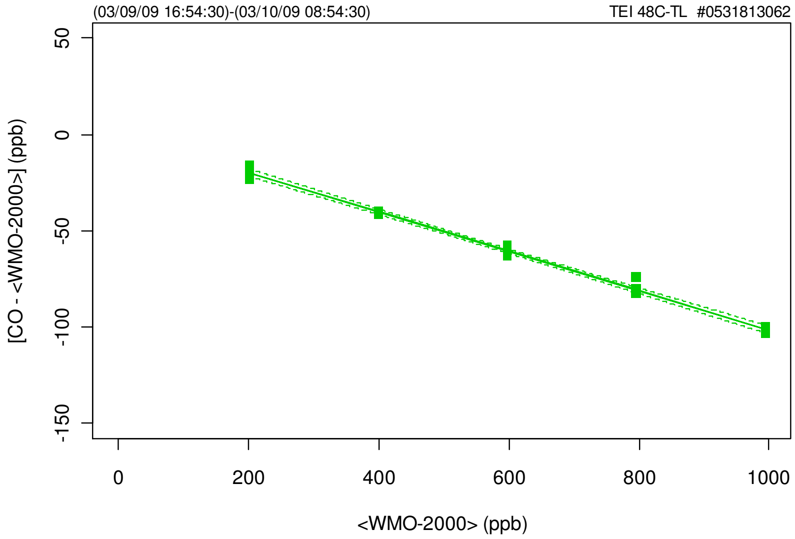

Figure 3. Bias of the SCO carbon monoxide instrument with respect to the WMO-2000 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands.

Methane Measurements

Instrumentation. At the time of the audit a Dani-3800 GC system was used for methane measurements. This system has been audited by WCC-Empa in 2004 [*Zellweger, et al.*, 2004]; a new Varian 3800 GC was already installed at IZO but was not working due to a defective FID.

Standards. A set of five laboratory standards spanning the mole fraction range of 1682 – 1948 ppb methane is available at IZO. The standards were purchased from NOAA/ESRL between 1997 and 2008, and all results are reported on the current NOAA04 methane calibration scale.

Comparison (Performance Audit). The comparison involved repeated measurements of WCC-Empa traveling standards with the IZO instrument. No significant deviations between the Izaña instrument and WCC-Empa were found. The following equation characterises the instrument bias (cf. Figure 4):

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = (CH_4) / 1.00007 (3)

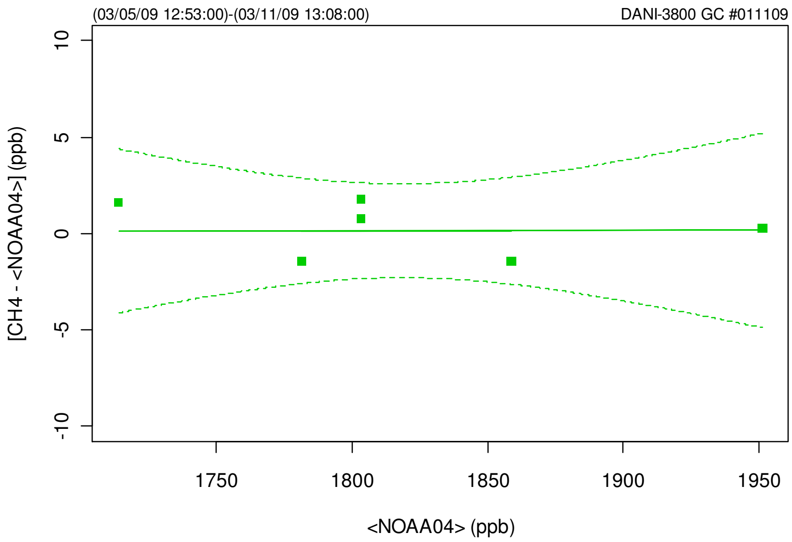

Figure 4. Bias of the Izaña methane GC with respect to the NOAA04 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Nitrous Oxide Measurements

Instrumentation. A VARIAN GC 3800 with an ECD is used for nitrous oxide monitoring at IZO. The GC and the ECD were purchased in 2002 and in 2005, respectively. Since June 2007 the GC-ECD has been in operation for regular N_2O monitoring. Since a comprehensive N_2O audit was made only shortly before this audit by the WCC-N_2O in November 2008, only a brief summary of the current results is presented here. More information including recommendations can be found in the audit report by WCC-N_2O [*Scheel*, 2009].

Standards. A set of five laboratory standards spanning the mole fraction range of 257 – 357 ppb nitrous oxide is available at IZO. The standards were purchased from NOAA/ESRL between 2006 and 2008, and all results are reported on the current NOAA-2006 N_2O calibration scale.

Comparison (Performance Audit). The comparison involved repeated measurements of WCC-Empa traveling standards with the IZO instrument. The N_2O mole fractions of the TS were assigned by the WCC-N_2O in 2007/2008, and have not been re-calibrated since then. The results of the comparison confirmed largely the findings by WCC- N_2O, although the deviations between IZO and WCC-Empa were slightly higher for the traveling standards with the lowest and highest mole fractions. The best agreement was found for the relevant mole fraction range between 315 and 325 ppb; the IZO N_2O measurements do therefore not significantly deviate from the GAW reference (NOAA-2006 mole fraction scale). The following equation characterises the instrument bias (cf. Figure 5):

Unbiased N_2O mixing ratio (ppb): X_{N2O} (ppb) = (N_2O) / 1.000097 (4)

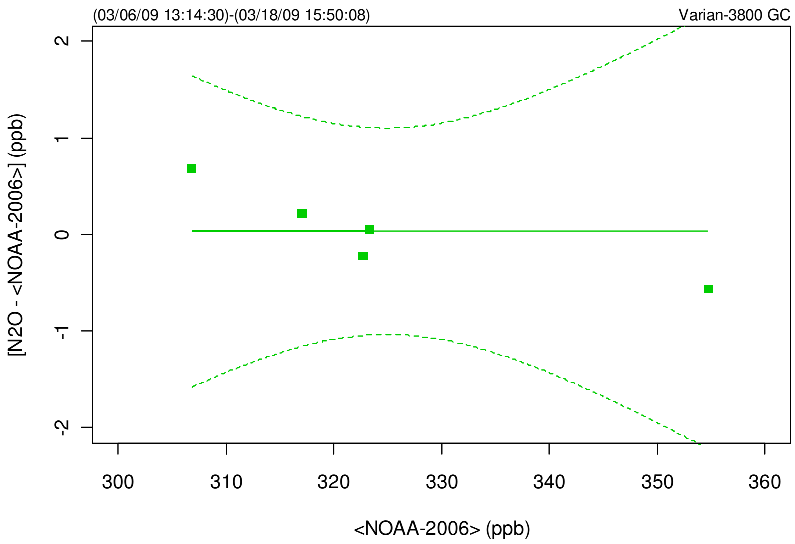

Figure 5. Bias of the Izaña N_2O GC with respect to the NOAA-2006 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. The regression was forced through zero.

Data Acquisition and Management

Data of all instruments is acquired with custom programmed software (Borland Delphi). Remote access to and control of several functions (instrument dependent) is possible via the internet.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone (1996 – April 2010), methane (1984 – July 2010) and carbon dioxide (1984 – May 2010) have been submitted by AEMET. No in-situ CO and N_2O data has been submitted yet.

Recommendation 8 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year, and first submission of CO and N_2O data is highly recommended.

Conclusions

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

Summary Ranking of Izaña Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access possible
Facilities		
Laboratory and office space	(5)	Spacious, state of the art
Air Conditioning	(5)	
Power supply	(5)	
Internet access	(5)	
General Management and Operation		
Organisation	(5)	
Competence of staff	(5)	
Air Inlet System	(5)	State-of-the-art inlet for gases
Instrumentation		
Ozone	(5)	TEI49C
Carbon monoxide	(4)	RGA-3 / TEI 48C-TL
Methane	(4)	Dani-3800
Nitrous Oxide	(5)	Varian-3800 GC/ECD
Other gases*	(5)	CO_2, SF_6, SO_2, nitrogen oxides
Aerosol parameters*	(5)	Comprehensive programme
Flask sampling	(5)	NOAA/ESRL
Meteo	(5)	
Standards		
Ozone	(5)	TEI 49C-PS
Carbon monoxide	(5)	NOAA/ESRL standards
Methane	(5)	NOAA/ESRL standards
Nitrous Oxide	(5)	NOAA/ESRL standards
Data Management		
Data acquisition	(5)	
Data processing	(5)	
Data submission	(2)	Only few data submitted

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

Dübendorf, October 2010

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

APPENDIX

Global GAW Station Izaña

Site description

The global GAW station Izaña is located on Tenerife, Spain, (28.300 N, 16.50° W) roughly 300 km west of the African coast. For more information, see the previous audit report [Zellweger, et al., 2004]. The station is also registered in GAWSIS (http://gaw.empa.ch/gawsis). Detailed information is available from the station web site (http://www.aemet.izana.org).

Measurement Programme

An overview of the measurement program and its status as of March 2009 is shown in Table 1. Refer to GAWSIS for more details.

Table 1. Measurement Programme at the IZO Station

Parameter*	**Current Instrument**
Aerosol	
Light absorption coefficient	MAAP (Thermo), PM10
Light scattering coefficient	TSI Nephelometer
Major chemical components (size fractionated)	Filter sampling, extraction
Mass concentration PM10	Filter sampling + gravimetry
Multiwavelength optical depth	4 Channel WORCC Filter Radiometer
Multiwavelength optical depth	Cimel and MFSR
Total number concentration	TSI UCPC 3010 and 3025A
Number size distribution	DMA
Vertical distribution of properties	Aerosol Micro Pulse Lidar
Ozone	
Surface ozone	UV absorption (TEI 49C)
Total column ozone	Brewer
Vertical ozone profile	ECC Sonde and Umkehr Method
Greenhouse Gas	
CO_2	NDIR
CH_4	Dani-3800 GC/FID
N_2O, SF_6	Varian-3800 GC/ECD
Reactive Gas	
CO	RGA-3 and TEI 48C-TL
NO, NO_2, NO_y, SO_2	TEI Series
Flask Sampling	
VOC, CFCs, HCFs, CO_2, CH_4, CO, H_2, SF_6, CO_2 isotopes	NOAA/ESRL flask sampling program
Radio Nuclide	
CO_2 isotopes	Flask Sampling
Solar radiation	
Diffuse and global solar radiation	Pyranometer (Kipp and Zonen)
Direct solar radiation	Pyrheliometer (Kipp and Zonen)
IR (direction unspecified)	Pyrgeometer (global, infrared)
UV Broadband	UV radiometry
UV Spectral	Brewer
Meteo	
PTU, wind speed + direction	

* Refer to GAWSIS or NOAA/ESRL website for more details

Ozone, Carbon Monoxide, Methane and Nitrous Oxide Distributions at Izaña

The monthly and yearly distributions of one hourly mean values for surface ozone, carbon monoxide, methane and nitrous oxide are shown in Figure 6.

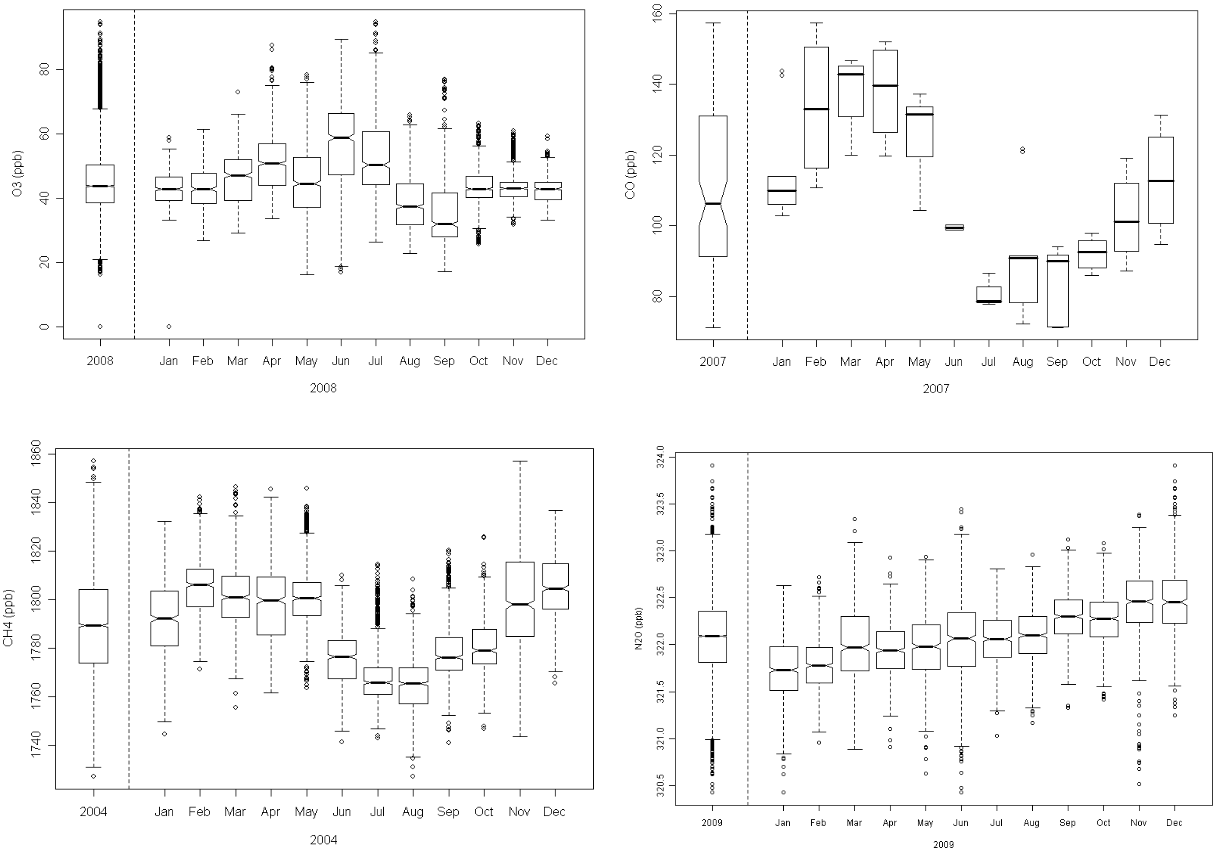

Figure 6. Yearly and monthly box plots of 1-hourly aggregates for surface ozone, carbon monoxide, methane and nitrous oxide. The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month. CO and N_2O data are preliminary.

Organisation and Contact Persons

The Izaña Atmospheric Research Centre (IZO) is operated by the Agencia Estatal de Meteorología (AEMET). Table 2 gives an overview of the current permanent and contracted staff and students of the IZO observatory.

Table 2. IZO staff as of March 2009.

Director Dr Emilio Cuevas, Director of Izaña Atmospheric Observatory (Physics PhD)
Technical staff: Instrument operators and specialists Mr. Ramón Ramos, Field Manager (Physics graduate) Mr. César López, Instrument maintenance (Electronic Engineer) Mr. Marco Antonio Hernández (Electronic Technician) Ms. Sara Álvarez Díaz (Air Liquide's Security and quality control technician) Mr. Sergio Afonso, Ozonesonde specialist Ms. Cándida Hernández, Observer (Biology graduate) Mr. Virgilio Carreño, Observer (Physics graduate) Mr. Carlos Torres, Observer (Physics graduate)
Permanent research staff Mr. Alberto Redondas, Total column ozone, ozonesonde and UV radiation programs, Principal Investigator of the WMO Regional Brewer Calibration Centre for Europe (RBCC-E) (Physics graduate, PhD in course) Mr. Pedro Romero, Radiation and Water Vapour Program (Physics graduate) Mr. Carlos Marrero, Air quality program (Physics graduate, PhD in course) Mr. Juanjo Bustos, Meteorological support, McIdas Forecasting and analysis system (Physics graduate) Mr. Ángel Gómez-Peláez, Greenhouse and Carbon Cycle Gases Program (Physics graduate, PhD in course)
Contracted research staff Dr. Sergio Rodríguez, Physical and Chemical Aerosol Program (Physics PhD) Dr. Celia Milford, Air quality program (Physics PhD) Dr. Matthias Schneider, NDACC-FTIR program (Physics PhD) Dr. Silvia Alonso, Dust forecasting system (Physics PhD)
Students Ms. Carmen Guirado, UV and Radiation Program (Physics graduate, PhD in course) Ms. Yballa Hernández Pérez, Lidar instrument specialist (Physics graduate) Ms. Vanessa Gómez Trueba, Greenhouse and Carbon Cycle Gases Program (Physics graduate) Ms. Yenny González Ramos, Reactive Gases Program (Physics graduate, PhD in Course) Ms. Cristina Martin Bascuas, Air quality forecasting program (Physics graduate) Mr. Fernando Almansa Rodríguez, Total column ozone, ozonesonde and UV radiation programs, (Physics graduate) Mr. Javier Abreu Afonso, Physical and Chemical Aerosol Program (Physics graduate, PhD in Course) Ms. Rosa García Cabrera, Radiation Program (Physics graduate, PhD in Course) Mr. Juan José Rodríguez Franco, Total column ozone, ozonesonde and UV radiation programs (Physics graduate, PhD in Course) Mr. Eliezer Sepúlveda, Greenhouse and Carbon Cycle Gases Program (Physics graduate, PhD in Course)
Administrative staff Ms. Julieta Bethencourt, Administrative Section Chief Ms. Caridad M. Fernández de Mesa, Financial Unit Chief Ms. Pilar Salamo, Secretary Ms. Concha Sálamo, Secretary Mr. Marcos Damas, Driver

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 analyzers are running in parallel at the IZO site. The audit included all ozone instruments of the IZO station as well as the ozone analyzer of the Santa Cruz de Tenerife (SCO) regional GAW station.

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

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

Unchanged since the last WCC-Empa audit [*Zellweger, et al.*, 2004].

Instrumentation

The station is equipped with two ozone analyzers (TEI 49C). Instrumental details for the ozone analyzers (OA) are summarised in Table 3 below. The instrumentation has not changed since the last WCC-Empa audit.

Standards

One ozone standard (TEI 49C-PS) is available at the site. It is used every three months for comparisons with the station analyzers. Instrumental details for the ozone calibrator (OC) are summarised in Table 3 below.

Operation and Maintenance

The station is visited daily from Monday to Sunday, and the instruments are checked for general operation. An automatic zero check is made daily at 16:00 UTC. In addition, the station calibrator is used weekly for span checks, and every 3-4 months a full comparison between the OC and the station instruments is made. All other maintenance including inlet filter exchange (depending on the frequency of Sahara dust events) is performed on a case by case basis.

Data Acquisition and Data Transfer

The ozone data is acquired with custom programmed software (Borland Delphi). Remote access to and control of several functions (instrument dependent) is possible via the internet. 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. All data is re-calculated using the last calibration of the instrument. Currently the following corrections are applied:

TEI 49C #63900-337: O_3 final [pbb] = 0.32 + 1.0325 * (TEI 49C)
TEI 49C #72491-371: O_3 final [pbb] = 0.47 + 0.9851 * (TEI 49C)

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

Data Submission

Data of the surface ozone measurements have been submitted to the GAW World Data Centre for Methane at JMA (World Data Centre for Greenhouse Gases, WDCGG). Currently the complete time series covering the period from 1996 to April 2010 is available at WDCGG.

Documentation

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

Comparison of Ozone Analyzer

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

Table 3. Experimental details of the ozone comparison.

Transfer standard (TS)	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.008
IZO main ozone analyzer (OA)	Model, S/N	TEI 49C #63900-337
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.006
IZO backup ozone analyzer (OA)	Model, S/N	TEI 49C #72491-371
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.048
IZO ozone calibrator (OC)	Model, S/N	TEI 49C-PS #56085-306
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = -0.8; COEFF = 1.014
SCO ozone analyzer (OA)	Model, S/N	TEI 49C #032060000000731
	Principle	UV absorption
	Range	1 ppm
	Settings	BKG = 0.0; COEFF = 1.030
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm (WCC-Empa)
Connection between instruments		Ca. 1.5 meter of 1/4" PFA tubing between TS manifold and inlet filter of OA
Data acquisition	TS and OA	One minute aggregates from digital output (custom designed LabView programme of WCC-Empa)
Pressure readings at beginning of comparison (hPa)	Ambient	771.8 (Station reference)
	TS	775.4, adjusted to 771.8
	TEI 49C	772.2 (#63900-337), 772.2 (#72491-371) no adjustments were made
	TEI 49C-PS	762.2, adjusted to 771.8
Levels (ppb)		0, 10, 20, 30, 40, 50, 60, 70, 80, 90 (OA) 0, 30, 60, 90, 140, 190 (OC)
Duration per level (min)		15
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		3 runs (2009-03-05, IZO analyzer) 8 runs (2009-03-09 thru 10, SCO instrument)

Setup and Connections

Table 3 details the experimental setup during the comparison of the transfer standard with the station analyzers. The data used for the evaluation was recorded by the WCC-Empa data acquisition system as indicated. Raw data was corrected using the data of the last calibration (see above), which is the usual treatment for all data.

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 as described elsewhere [Klausen, et al., 2003]. The results are shown in Table 4 (TEI 49C #63900-337), Table 5 (TEI 49C #72491-371), Table 6 (TEI 49C-PS #56085-306) and Table 7 (TEI 49C #032060000000731). All results refer to the calibration factors as given in Table 3 above and were corrected using the formulas described under “data treatment”. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyzer (OA) values.

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the IZO ozone analyzer (OA) TEI 49C #63900-337 with the WCC-Empa transfer standard (TS).

DateTime (UTC-9)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2009-03-05 02:16	1	0	0.06	0.61	0	0.13	0.05
2009-03-05 02:31	1	10	10.17	10.49	0	0.38	0.13
2009-03-05 02:46	1	30	30.03	30.53	0	0.22	0.11
2009-03-05 03:01	1	90	90.01	90.83	0	0.12	0.16
2009-03-05 03:16	1	50	50.03	50.76	0	0.11	0.07
2009-03-05 03:31	1	60	59.99	60.82	0	0.17	0.10
2009-03-05 03:46	1	20	19.98	20.52	0	0.15	0.07
2009-03-05 04:01	1	80	79.99	80.88	0	0.11	0.12
2009-03-05 04:16	1	70	70.02	70.80	0	0.09	0.08
2009-03-05 04:31	1	40	40.02	40.52	0	0.12	0.10
2009-03-05 04:46	2	0	0.17	0.43	0	0.20	0.05
2009-03-05 05:01	2	50	49.97	50.65	0	0.18	0.12
2009-03-05 05:16	2	60	59.97	60.86	0	0.06	0.12
2009-03-05 05:31	2	10	10.33	10.52	0	0.40	0.14
2009-03-05 05:46	2	40	40.01	40.74	0	0.11	0.06
2009-03-05 06:01	2	80	79.98	80.94	0	0.14	0.12
2009-03-05 06:16	2	90	89.95	91.07	0	0.14	0.09
2009-03-05 06:31	2	30	30.02	30.61	0	0.16	0.07
2009-03-05 06:46	2	20	19.97	20.51	0	0.16	0.07
2009-03-05 07:01	2	70	70.02	70.87	0	0.11	0.10
2009-03-05 07:16	3	0	0.04	0.45	0	0.23	0.05
2009-03-05 07:31	3	70	70.01	70.76	0	0.12	0.13
2009-03-05 07:46	3	90	89.99	91.05	0	0.08	0.10
2009-03-05 08:01	3	20	19.98	20.44	0	0.12	0.09
2009-03-05 08:16	3	50	50.00	50.61	0	0.11	0.09
2009-03-05 08:31	3	10	10.49	10.76	0	0.49	0.13
2009-03-05 08:46	3	40	39.98	40.54	0	0.14	0.11
2009-03-05 09:01	3	80	80.03	81.09	0	0.09	0.14
2009-03-05 09:16	3	30	29.99	30.54	0	0.10	0.09
2009-03-05 09:31	3	60	60.03	60.60	0	0.20	0.11

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

Table 5. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the IZO back-up ozone analyzer (OA) TEI 49C #072491-371 with the WCC-Empa transfer standard (TS).

DateTime (UTC-9)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2009-03-05 02:16	1	0	0.06	0.71	0	0.13	0.04
2009-03-05 02:31	1	10	10.17	10.78	0	0.38	0.10
2009-03-05 02:46	1	30	30.03	31.03	0	0.22	0.09
2009-03-05 03:01	1	90	90.01	92.07	0	0.12	0.11
2009-03-05 03:16	1	50	50.03	51.44	0	0.11	0.08
2009-03-05 03:31	1	60	59.99	61.51	0	0.17	0.08
2009-03-05 03:46	1	20	19.98	20.87	0	0.15	0.05
2009-03-05 04:01	1	80	79.99	81.82	0	0.11	0.11
2009-03-05 04:16	1	70	70.02	71.63	0	0.09	0.06
2009-03-05 04:31	1	40	40.02	41.15	0	0.12	0.09
2009-03-05 04:46	2	0	0.17	0.66	0	0.20	0.04
2009-03-05 05:01	2	50	49.97	51.33	0	0.18	0.10
2009-03-05 05:16	2	60	59.97	61.60	0	0.06	0.07
2009-03-05 05:31	2	10	10.33	10.84	0	0.40	0.13
2009-03-05 05:46	2	40	40.01	41.31	0	0.11	0.07
2009-03-05 06:01	2	80	79.98	81.92	0	0.14	0.12
2009-03-05 06:16	2	90	89.95	92.02	0	0.14	0.11
2009-03-05 06:31	2	30	30.02	31.15	0	0.16	0.07
2009-03-05 06:46	2	20	19.97	20.84	0	0.16	0.06
2009-03-05 07:01	2	70	70.02	71.70	0	0.11	0.09
2009-03-05 07:16	3	0	0.04	0.50	0	0.23	0.04
2009-03-05 07:31	3	70	70.01	71.49	0	0.12	0.12
2009-03-05 07:46	3	90	89.99	92.01	0	0.08	0.15
2009-03-05 08:01	3	20	19.98	20.76	0	0.12	0.05
2009-03-05 08:16	3	50	50.00	51.24	0	0.11	0.10
2009-03-05 08:31	3	10	10.49	11.09	0	0.49	0.10
2009-03-05 08:46	3	40	39.98	41.15	0	0.14	0.06
2009-03-05 09:01	3	80	80.03	81.94	0	0.09	0.12
2009-03-05 09:16	3	30	29.99	31.04	0	0.10	0.05
2009-03-05 09:31	3	60	60.03	61.40	0	0.20	0.10

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

Table 6. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the IZO ozone calibrator (OC) TEI 49C-PS #56085-306 with the WCC-Empa transfer standard (TS).

DateTime (UTC-9)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2009-03-08 13:16	1	0	0.18	0.23	0	0.26	0.04
2009-03-08 13:31	1	30	29.98	29.87	0	0.16	0.06
2009-03-08 13:46	1	90	90.00	90.16	0	0.13	0.10
2009-03-08 14:01	1	140	140.00	139.99	0	0.09	0.11
2009-03-08 14:16	1	190	189.99	190.29	0	0.09	0.06
2009-03-08 14:31	1	60	59.99	60.27	0	0.12	0.07
2009-03-08 14:46	2	0	0.07	0.16	0	0.31	0.03
2009-03-08 15:01	2	190	190.00	190.30	0	0.10	0.08
2009-03-08 15:16	2	30	29.93	30.12	0	0.12	0.05
2009-03-08 15:31	2	60	60.02	60.22	0	0.12	0.04
2009-03-08 15:46	2	140	140.00	140.21	0	0.16	0.07
2009-03-08 16:01	2	90	90.02	90.03	0	0.10	0.08
2009-03-08 16:16	3	0	0.03	0.28	0	0.25	0.03
2009-03-08 16:31	3	90	90.02	90.10	0	0.11	0.12

DateTime (UTC-9)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2009-03-08 16:46	3	140	140.01	140.05	0	0.11	0.08
2009-03-08 17:01	3	60	60.01	60.16	0	0.10	0.08
2009-03-08 17:16	3	190	190.01	190.27	0	0.15	0.12
2009-03-08 17:31	3	30	30.01	30.13	0	0.17	0.09

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

Table 7. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the SCO ozone analyzer (OA) TEI 49C #032060000000731 with the WCC-Empa transfer standard (TS).

DateTime (UTC-9)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2009-03-09 12:35	1	0	-0.10	0.02	0	0.11	0.04
2009-03-09 12:50	1	70	69.99	71.71	0	0.13	0.11
2009-03-09 13:05	1	90	90.00	92.28	0	0.12	0.05
2009-03-09 13:20	1	20	20.00	20.51	0	0.23	0.05
2009-03-09 13:35	1	50	50.02	51.13	0	0.12	0.05
2009-03-09 13:50	1	10	10.51	10.75	0	0.46	0.17
2009-03-09 14:05	1	40	40.00	41.10	0	0.12	0.08
2009-03-09 14:20	1	80	79.98	81.98	0	0.10	0.06
2009-03-09 14:35	1	30	29.97	30.75	0	0.18	0.08
2009-03-09 14:50	1	60	60.03	61.57	0	0.13	0.08
2009-03-09 15:05	2	0	-0.19	-0.06	0	0.15	0.03
2009-03-09 15:20	2	10	10.00	10.22	0	0.16	0.06
2009-03-09 15:35	2	30	29.98	30.73	0	0.13	0.06
2009-03-09 15:50	2	90	90.02	92.29	0	0.04	0.04
2009-03-09 16:05	2	50	49.96	51.09	0	0.13	0.07
2009-03-09 16:20	2	60	60.01	61.32	0	0.14	0.11
2009-03-09 16:35	2	20	20.02	20.62	0	0.13	0.05
2009-03-09 16:50	2	80	80.01	82.07	0	0.12	0.07
2009-03-09 17:05	2	70	70.03	71.61	0	0.07	0.05
2009-03-09 17:20	2	40	40.01	40.91	0	0.15	0.07
2009-03-09 17:35	3	0	0.02	-0.05	0	0.19	0.03
2009-03-09 17:50	3	50	50.01	51.23	0	0.10	0.05
2009-03-09 18:05	3	60	59.98	61.48	0	0.10	0.08
2009-03-09 18:20	3	10	10.16	10.27	0	0.28	0.12
2009-03-09 18:35	3	40	40.01	40.96	0	0.11	0.08
2009-03-09 18:50	3	80	79.98	82.26	0	0.16	0.10
2009-03-09 19:05	3	90	89.98	92.08	0	0.04	0.06
2009-03-09 19:20	3	30	29.97	30.62	0	0.12	0.05
2009-03-09 19:35	3	20	20.02	20.53	0	0.23	0.08
2009-03-09 19:50	3	70	70.01	71.74	0	0.08	0.13
2009-03-09 20:05	4	0	0.09	-0.10	0	0.24	0.04
2009-03-09 20:20	4	70	70.01	71.65	0	0.19	0.08
2009-03-09 20:35	4	90	89.98	92.11	0	0.12	0.12
2009-03-09 20:50	4	20	19.97	20.41	0	0.15	0.05
2009-03-09 21:05	4	50	49.99	51.10	0	0.08	0.07
2009-03-09 21:20	4	10	10.21	10.17	0	0.37	0.13
2009-03-09 21:35	4	40	40.01	40.77	0	0.13	0.06
2009-03-09 21:50	4	80	79.96	81.96	0	0.09	0.06
2009-03-09 22:05	4	30	29.97	30.51	0	0.13	0.08
2009-03-09 22:20	4	60	60.00	61.44	0	0.09	0.04
2009-03-09 22:35	5	0	0.12	-0.06	0	0.25	0.04
2009-03-09 22:50	5	10	9.99	10.30	0	0.19	0.07
2009-03-09 23:05	5	30	29.99	30.60	0	0.16	0.08

DateTime (UTC-9)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
2009-03-09 23:20	5	90	90.02	92.00	0	0.16	0.08
2009-03-09 23:35	5	50	50.01	51.14	0	0.13	0.06
2009-03-09 23:50	5	60	60.01	61.55	0	0.11	0.07
2009-03-10 00:05	5	20	19.98	20.30	0	0.16	0.05
2009-03-10 00:20	5	80	80.05	81.96	0	0.13	0.09
2009-03-10 00:35	5	70	70.02	71.76	0	0.11	0.07
2009-03-10 00:50	5	40	40.02	40.94	0	0.12	0.06
2009-03-10 01:05	6	0	0.09	-0.10	0	0.17	0.03
2009-03-10 01:20	6	50	49.99	51.19	0	0.11	0.06
2009-03-10 01:35	6	60	59.99	61.36	0	0.05	0.05
2009-03-10 01:50	6	10	10.03	10.14	0	0.11	0.07
2009-03-10 02:05	6	40	40.01	40.93	0	0.12	0.04
2009-03-10 02:20	6	80	80.00	81.96	0	0.10	0.08
2009-03-10 02:35	6	90	90.01	92.06	0	0.08	0.05
2009-03-10 02:50	6	30	29.96	30.49	0	0.12	0.06
2009-03-10 03:05	6	20	20.02	20.40	0	0.21	0.10
2009-03-10 03:20	6	70	69.98	71.66	0	0.10	0.07
2009-03-10 03:35	7	0	-0.10	-0.03	0	0.10	0.03
2009-03-10 03:50	7	70	69.97	71.50	0	0.10	0.09
2009-03-10 04:05	7	90	90.01	92.24	0	0.10	0.11
2009-03-10 04:20	7	20	19.94	20.17	0	0.18	0.04
2009-03-10 04:35	7	50	50.00	51.12	0	0.12	0.07
2009-03-10 04:50	7	10	10.01	10.25	0	0.11	0.06
2009-03-10 05:05	7	40	39.98	40.88	0	0.15	0.07
2009-03-10 05:20	7	80	80.01	81.75	0	0.09	0.10
2009-03-10 05:35	7	30	30.02	30.66	0	0.15	0.07
2009-03-10 05:50	7	60	60.00	61.26	0	0.13	0.08
2009-03-10 06:05	8	0	-0.02	-0.09	0	0.12	0.03
2009-03-10 06:20	8	10	10.06	10.36	0	0.19	0.09
2009-03-10 06:35	8	30	30.02	30.71	0	0.10	0.08
2009-03-10 06:50	8	90	89.98	92.18	0	0.09	0.09
2009-03-10 07:05	8	50	49.99	51.09	0	0.10	0.09
2009-03-10 07:20	8	60	60.02	61.45	0	0.08	0.08
2009-03-10 07:35	8	20	20.01	20.31	0	0.14	0.06
2009-03-10 07:50	8	80	80.01	81.91	0	0.08	0.07
2009-03-10 08:05	8	70	70.01	71.66	0	0.16	0.11
2009-03-10 08:20	8	40	39.98	40.86	0	0.10	0.07

#0: valid data; 1: invalid data.

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

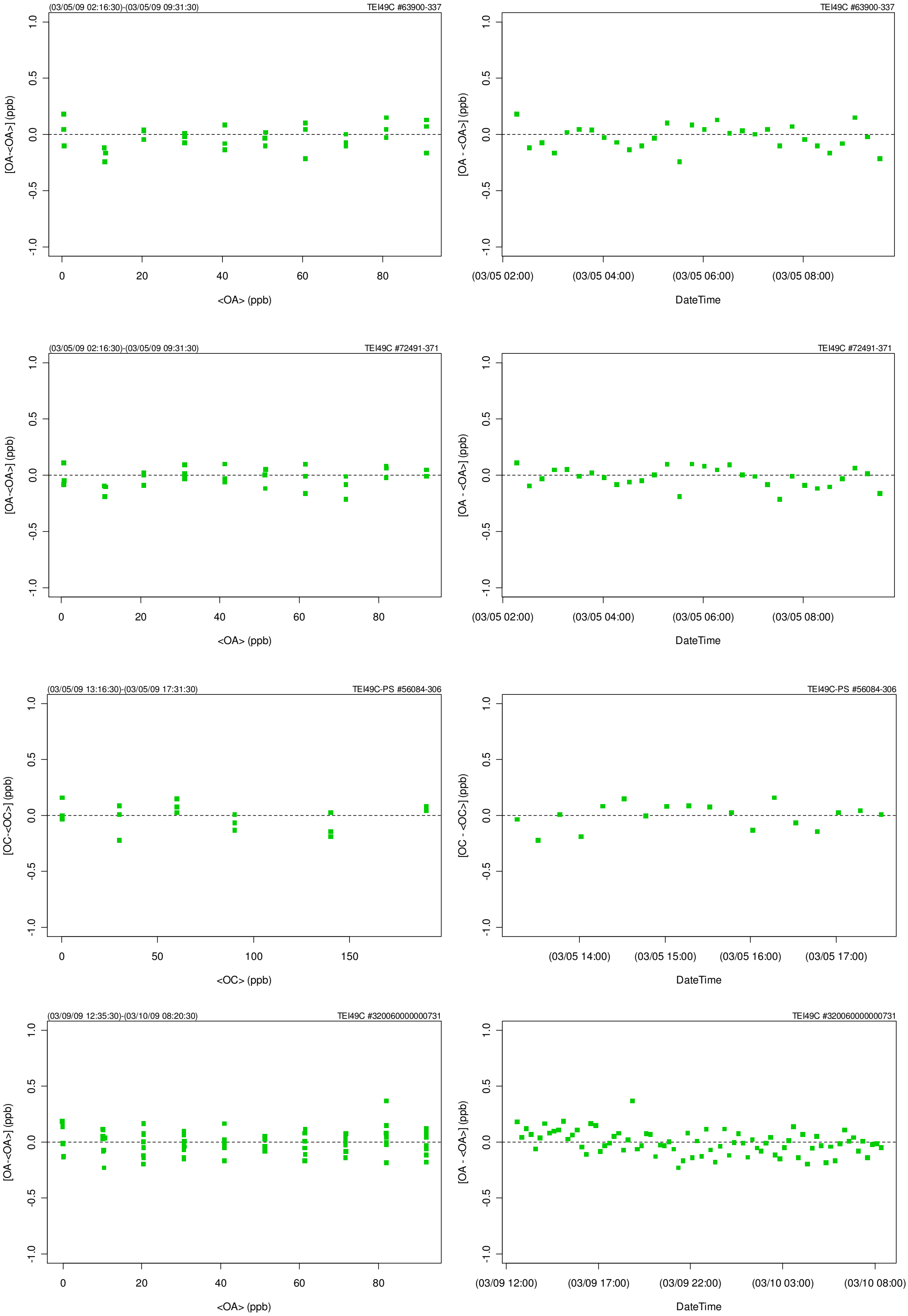

Figure 7. Regression residuals of the ozone comparisons (instrument see upper right corner of each graph) as a function of mole fraction (left panel) and time (right panel).

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

TEI 49C #63900-337 (IZO):

X_{O3} (ppb) = ([OA] - 0.27 ppb) / 1.007

u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.67e-05 * X_{O3}^2) (1a)

TEI 49C # 72491-371 (IZO):

X_{O3} (ppb) = ([OA] – 0.44 ppb) / 1.016

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

TEI 49C-PS # 56084-306 (IZO):

X_{O3} (ppb) = ([OA] - 0.00 ppb) / 1.001

u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.60e-05 * X_{O3}^2) (1c)

TEI 49C #032060000000731 (SCO):

X_{O3} (ppb) = ([OA] + 0.15 ppb) / 1.025

u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.48e-05 * X_{O3}^2) (1d)

Conclusions

The ozone measurements at IZO are performed on a very high level concerning quality assurance and control. The surface ozone standard of IZO has been calibrated at WCC-Empa in July 2008 and was found to agree perfectly with the traveling standard of WCC-Empa. In addition, the findings of this audit demonstrated good agreement between the main IZO ozone analyzer and WCC-Empa. Slightly higher readings but still good agreement was observed with the IZO backup and the SCO ozone analyzers.

Carbon Monoxide Measurements

Carbon monoxide measurements started in February 1998 at Izaña using a gas chromatograph with a mercuric oxide detector, and a complete time series is available since then. In 2004, an additional NDIR system was installed. However, CO data has not yet been submitted to WDCGG due to remaining uncertainties of the calibration scale. The audit comprised comparison of five traveling standards covering the mole fraction range from approx. 90 to 200 ppb carbon monoxide in air for the GC system. In addition, the NDIR system was compared using a dilution system in the mole fraction range of 0 1000 ppb CO. The audit included also an assessment of the NDIR CO analyzer of the Santa Cruz de Tenerife (SCO) regional GAW station. All comparisons were done according to Standard Operating Procedures [*WMO*, 2007a].

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

During the WCC-Empa audit in 2004 [*Zellweger, et al.*, 2004] the RGA-3 system was operating in a provisional measurement site, which became the aerosol lab in the meantime. The RGA-3 system was moved to the main laboratory building and is now installed in the same lab as the NDIR system. The inlet consists of a stainless steel inlet running from the tower terrace through the central service channel. The upper part is heated. A pump flushes the inlet with 2180 l/min. Inner diameter approx. 10 cm. The Inlet is protected against rain by an upside-down stainless steel bucket. The NDIR and RGA-3 CO instruments are installed in the 3rd floor of the building (11.5 m above ground). From the manifold, the instruments are connected using 1/4" PTFE tubing with a total length of approximately 11 m and a flow rate of 2 l/min. Total residence time is estimated to be approx. 10 seconds. The inlet system is adequate for analyzing CO concerning materials and residence time.

Instrumentation

Izaña is equipped with a Trace Analytical RGA-3 GC-system for the measurement of CO [*Zellweger, et al.*, 2004]. In addition, a TEI 48C-TL NDIR was installed at the station in 2004. Instrumental details are summarized in Table 9.

Standards and Calibration

NOAA/ESRL laboratory standards are available for non-linearity characterization of the RGA-3 system and for the calibration of working standards. Injections are made every 10 minutes and are alternating between ambient air and working standard. The working standard injections are used to calculate the ambient data. Every 2 weeks the working standard is calibrated against the IZO laboratory standards, and the parameters of the RGA-3 potential response curve

$$r = r_w \left(h / h_w \right)^b$$

are determined; where *r* is mixing ratio, *h* is the height of the measured CO peak, h_w is the mean CO peak height of the two bracketing working standard injections, and r_w and *b* are the parameters (determined through least squares fitting). Working standards (WS) are exchanged every 3 months. These WS are also filled at the site every 3 months and are used one year later. The reason for this seasonal filling is to have the same level of CO in the WS as in the ambient air. The NDIR system is calibrated every 3 months using a 10-ppm CO in N_2 standard from Air Liquide, and frequent zero checks (every 15 min) are made to account for short-term drift. Table 8 gives details of the cylinders currently available at the station.

Table 8. Carbon monoxide laboratory standards available at the IZO station

Manufacturer / # / Use	CO (ppb) (uncert.)	Matrix	Calibration		Scale	In service	
			Date	By		From	To
NOAA / CA03037 / LS	69.0 (1.4)	Natural air	1997	NOAA	WMO-2000	1997	Today
NOAA / CA03083 / LS	169.1 (2.3)	Natural air	1997	NOAA	WMO-2000	1997	Today
	168.0 (3.2)	Natural air	2003	NOAA	WMO-2000		
NOAA / CC115003 / LS	151.6 (2.2)	Natural air	1999	NOAA	WMO-2000	1999	Today
NOAA / CA2635 / LS	81.2 (1.8)	Natural air	1999	NOAA	WMO-2000	1999	Today
	83.9 (1.6)	Natural air	2003	NOAA	WMO-2000		
NOAA / CA6768 / LS	62.2 (0.6)	Natural air	2006	NOAA	WMO-2004	2006	Today
NOAA / CA6946 / LS	91.2 (0.6)	Natural air	2006	NOAA	WMO-2004	2006	Today
NOAA / CA6988 / LS	119.6 (0.8)	Natural air	2006	NOAA	WMO-2004	2006	Today
NOAA / CA6968 / LS	164.5 (1.1)	Natural air	2006	NOAA	WMO-2004	2006	Today
NOAA / CA6978 / LS	221.2 (1.5)	Natural air	2006	NOAA	WMO-2004	2006	Today
AL / 29076601 / LS (NDIR)	10000 (200)	Nitrogen			NIST		

Operation and Maintenance

RGA-3: unchanged since last audit [*Zellweger, et al.*, 2004].

TEI 48C-TL: Automatic zero checks and ambient air measurements are alternating in 15 minute intervals. A Sofnocat 423 CO scrubber is used for the zero checks. The inlet filter is exchanged every 3 months, and the instrument is cleaned every 6 months.

Both systems are checked for general operation each working day. Remote access is possible, and instrument parameters and chromatograms (RGA-3) are frequently checked. The cooling trap is changed whenever necessary.

Data Acquisition and Data Transfer

RGA-3: unchanged since last audit [*Zellweger, et al.*, 2004]. Peak integration is carried out both for area and height but peak height is used for the final data set.

TEI 48C-TL: Data is acquired with custom programmed software (Borland Delphi). Remote access to and control of several functions is possible via the internet. One-minute averages including additional instrument status information are stored. Remote access to the data is possible through internet.

Data Treatment

The station operator plots the data and examines the chromatograms (RGA-3). Comments and notes are made in electronic log files. The final data evaluation is done at the headquarters in SCO and includes again plausibility checks and the application of the appropriate calibration factors based on the working and laboratory standard results (e.g. for RGA-3, the potential response curve, tied to the working standard, is used)..

Data Submission

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

Documentation

All information is entered in hand written log books (also the information previously stored in electronic log files, which is printed and pasted in the physical log books). The log book entries were comprehensive and up-to-date. Instrument manuals are available at the site.

Comparison of the Carbon Monoxide Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included comparisons of the traveling standards at Empa before and after the comparison of the analyzer. Details of the traveling standards are given in Table 9 (cylinders) and Table 10 (dilution system) below.

Setup and Connections

The RGA-3 instrument was compared by direct measurements of traveling standards. Details of this experiment are shown in Table 9. The data used for the evaluation was recorded by the IZO data acquisition system. The TEI 48C instrument was compared using a dilution system; details are summarized in Table 10.

Table 9. Experimental details of the carbon monoxide comparison (RGA-3 instrument).

Traveling standard (TS)		WCC-Empa Traveling standards (6 l aluminium cylinder containing natural air with H_2 mole fractions above ambient levels)
Levels (ppb) (WMO2004 CO scale)		Level / Cylinder / Reference / St. Uncert. 1 / 070808_FA02769 / 88.66 / 1.12 2 / 071122_FA30491 / 109.56 / 0.55 3 / 070807_FA02770 / 148.88 / 0.87 4 / 071122_FA01477 / 164.67 / 0.90 5 / 070927_FA02493 / 203.00 / 1.11
Field instrument	Model, S/N	RGA3, S/N 070188-006
	Principle	GC with HgO Reduction Detector Pre-column: Unibeads 1S 60/80 Analytical column: Mole sieve 5Å 60/80 Carrier: Synthetic air – Sofnocat - Mole sieve, 20 ml/min Column temp. 105℃, Detector temp. 264℃ Sample loop 1 ml Sample air dried to dew point -49℃ (cooling trap)
Connection of TS to field instrument		Spare reference gas port
Data Acquisition		Station data acquisition
Duration per level (min)		Injections every 20 min; total 4-18 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (2009-03-07 to 2009-03-18)

Table 10. Experimental details of the carbon monoxide comparison (NDIR instruments).

Travelling standard (TS) (WMO2004 CO scale)		One cylinder (081001_FA02474, 49.34±0.49 ppm CO in a mixture of synthetic and natural air) and a zero-air generator (silica gel - inlet filter 5 µm - metal bellow pump - Sofnocat - outlet filter 5 µm) custom-built by WCC-Empa, in combination with a dilution system (Redy MFCs)
Levels (ppb)		11 levels ranging from 0-1000 ppb
IZO NDIR analyzer	Model, S/N	TEI 48C-TL #75723-380
	Principle	NDIR, gas filter correlation
	Modification	Nafion PD50 24'' (split flow mode)
	Range	1 ppm
	Settings	Zero -0.204 ppm / Span 1.000
SCO NDIR analyzer	Model, S/N	TEI 48C-TL # 0531813062
	Principle	NDIR, gas filter correlation
	Modification	Nafion PD50 24'' (split flow mode), zero checks every 15 min using Sofnocat 423
	Range	1 ppm
	Settings	Zero 9.188 ppm (frequent changes) / Span 0.967
Connection of TS to field instrument		Sample inlet
Data Acquisition		1-minute averages from station data acquisition system
Duration per level (min)		60 min, inclusive of interspersed automatic zero (15') checks every 30 minutes
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		TEI 48C IZO: 1 run (2009-03-06 thru 07) TEI 48C SCO: 1 run (2009-03-09 thru 10)

Results - IZO RGA-3 system

The GC system was compared using WCC-Empa traveling standards. Each level was injected between 4 and 18 times. This resulted in a maximum of 18 useable single injections per level. These were further aggregated by level before use in the assessment (cf. Table 11).

Table 11. CO aggregates computed from single injections for each level and repetition during the comparison of the IZO RGA-3 analyser (AL) with WCC-Empa traveling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(03/07/09 02:21:00)	071122_FA01477	164.67	0.90	164.91	0.66	4	0.24	0.15
(03/12/09 12:21:00)	070927_FA02493	203.00	1.11	203.57	0.69	6	0.57	0.28
(03/13/09 12:29:40)	070808_FA02769	88.66	1.12	86.07	0.27	18	-2.59	-2.92
(03/16/09 12:34:00)	071122_FA30491	109.56	0.55	107.02	0.37	10	-2.55	-2.33
(03/18/09 12:22:00)	070807_FA02770	148.88	0.87	147.82	0.43	12	-1.06	-0.71

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

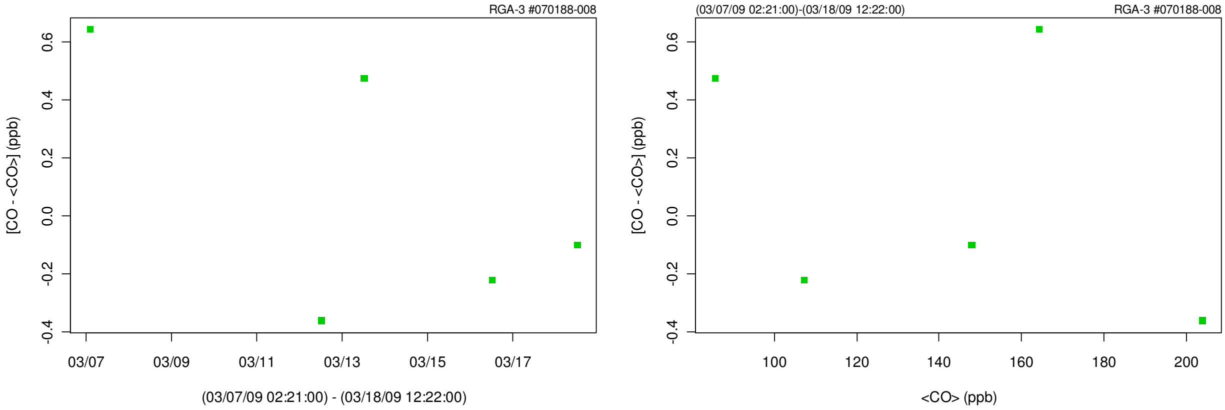

Figure 8. Regression residuals of the IZO RGA-3 based on the comparison with traveling standards. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

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

X_{CO} (ppb) = ([CO] + 6.2 ppb) / 1.035

u_{CO} (ppb) = sqrt (2.2 ppb^2 + 1.40e-04 * X_{CO}^2) (2a)

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

Results - IZO TEI 48C-TL Instrument

The TEI 48C-TL NDIR instrument system was compared using a dilution system and one CO standard with a high mixing ratio (details see Table 10). Each carbon monoxide level was applied for 60 minutes, which resulted in a maximum of 21 useable 1-min averages per level and run. These were corrected for zero-drift and further aggregated by level before use in the assessment (cf. Table 12).

Table 12. CO aggregates computed from single injections for each level and repetition during the comparison of the IZO TEI 48C-TL CO analyser (AL) with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL(ppb)	No. 1' av.	AL-TS(ppb)	AL-TS(%)
(03/06/09 14:39:03)	200.1	2.0	167.5	3.4	21	-31.4	-16.3
(03/06/09 15:39:03)	0.0	1.0	-12.6	3.6	21	-12.6	NA
(03/06/09 16:39:03)	795.3	8.0	719.2	7.9	21	-76.2	-9.6
(03/06/09 17:39:03)	0.0	1.0	-6.7	6.6	21	-6.7	NA
(03/06/09 18:39:03)	498.5	5.0	446.7	2.8	21	-51.7	-10.4
(03/06/09 19:39:03)	0.0	1.0	-3.4	4.4	21	-3.4	NA
(03/06/09 20:39:03)	994.2	10.0	920.6	5.0	21	-73.6	-7.4
(03/06/09 21:39:03)	399.3	4.0	358.0	5.5	21	-41.3	-10.3
(03/06/09 22:39:03)	0.0	1.0	-2.9	3.7	21	-2.9	NA
(03/06/09 23:39:03)	597.0	6.0	549.4	3.8	21	-47.6	-8.0
(03/07/09 00:39:03)	696.0	7.0	633.3	3.8	21	-62.7	-9.0
(03/07/09 01:39:03)	0.0	1.0	2.5	3.8	21	2.5	NA
(03/07/09 02:39:03)	100.9	1.0	86.6	5.0	21	-14.3	-14.1
(03/07/09 03:39:03)	895.0	9.0	817.1	4.1	21	-77.9	-8.7

Date Time (UTC)	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL(ppb)	No. 1' av.	AL-TS(ppb)	AL-TS(%)
(03/07/09 04:39:03)	0.0	1.0	-3.1	3.6	21	-3.1	NA
(03/07/09 05:39:03)	299.6	3.0	271.7	3.3	21	-27.9	-9.3
(03/07/09 06:39:03)	200.1	2.0	181.1	3.4	21	-17.7	-9.5
(03/07/09 07:39:03)	0.0	1.0	-7.8	4.8	21	-7.8	NA
(03/07/09 08:39:03)	795.3	8.0	727.7	4.5	21	-67.6	-8.5

Figure 9 shows the regression residuals of the IZO TEI48C-TL instrument plotted against time and mole fraction. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of mole fraction dependence (right panel) in the residuals indicates linearity of the instrument.

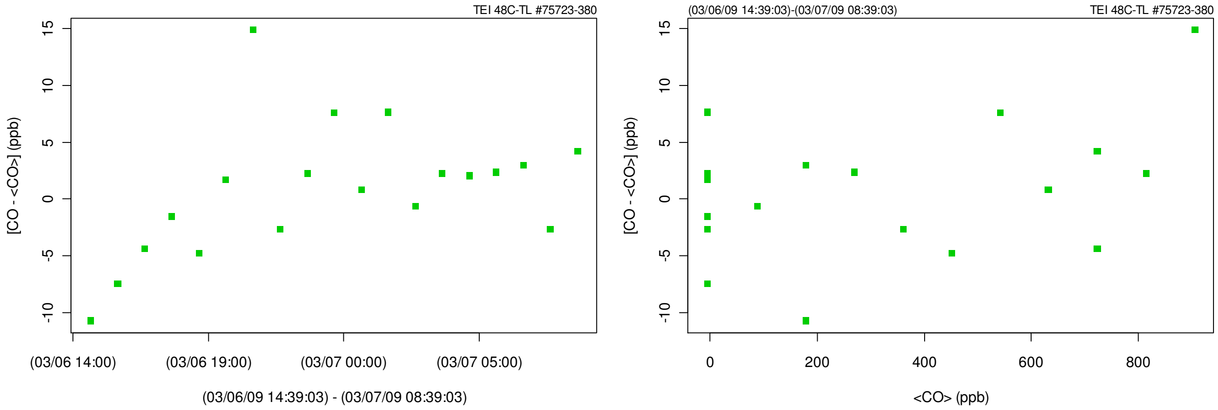

Figure 9. Regression residuals of the IZO TEI 48C-TL analyser based on the comparison with the WCC-Empa dilution system. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

Based on these comparison results, unbiased carbon monoxide volume mole fractions X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed using equation (2b) for the IZO TEI 48C-TL system.

$$X_{CO} \text{ (ppb)} = ([CO] + 5.2 \text{ ppb}) / 0.916$$

$$u_{CO} \text{ (ppb)} = \text{sqrt} (51.1 \text{ ppb}^2 + 4.14\text{e-}05 * X_{CO}^2) \qquad (2b)$$

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

Results - SCO TEI 48C-TL Instrument

The SCO TEI 48C-TL NDIR instrument system was also compared using a dilution system and one CO standard with a high mixing ratio (details see Table 10). However, the automatic zero checks of the SCO system was not working during the comparison; large deviations were observed between the SCO automatic zero checks and the zero air produced with the WCC-Empa dilution unit. Therefore, the comparison was run using the WCC-Empa dilution system only. Each carbon monoxide level was applied for 30 minutes, which resulted in a maximum of 11 useable 1-min averages per level and run. These were corrected for zero-drift using zero data of the dilution system. The data was further aggregated by level before use in the assessment (cf. Table 13).

Table 13. CO aggregates computed from single injections for each level and repetition during the comparison of the SCO TEI 48C-TL CO analyser (AL) with WCC-Empa travelling standards (TS).

Date Time (UTC)	TS (ppb)	uTS (ppb)	AL (ppb)	sdAL(ppb)	No. 1' av.	AL-TS(ppb)	AL-TS(%)
(03/09/09 16:54:30)	795.3	8.0	721.2	2.3	10	-74.2	-9.3
(03/09/09 17:25:00)	200.1	2.0	184.3	1.9	11	-15.8	-7.9
(03/09/09 17:54:30)	597.0	6.0	539.7	2.7	10	-57.3	-9.6
(03/09/09 18:54:30)	399.3	4.0	359.5	3.7	10	-39.8	-10.0
(03/09/09 19:25:00)	795.3	8.0	714.0	1.9	11	-81.3	-10.2
(03/09/09 19:54:30)	200.1	2.0	181.2	3.1	10	-19.0	-9.5
(03/09/09 20:54:30)	994.2	10.0	893.0	2.9	10	-101.2	-10.2
(03/09/09 21:25:00)	399.3	4.0	357.4	2.8	11	-41.9	-10.5
(03/09/09 21:54:30)	795.3	8.0	713.7	2.4	10	-81.6	-10.3
(03/09/09 22:54:30)	597.0	6.0	537.3	3.2	10	-59.7	-10.0
(03/09/09 23:25:00)	994.2	10.0	891.6	2.1	11	-102.6	-10.3
(03/09/09 23:54:30)	399.3	4.0	359.8	1.6	10	-39.5	-9.9
(03/10/09 00:54:30)	200.1	2.0	177.0	2.2	10	-23.1	-11.5
(03/10/09 01:25:00)	597.0	6.0	536.3	3.9	11	-60.6	-10.2
(03/10/09 01:54:30)	994.2	10.0	890.7	3.0	10	-103.5	-10.4
(03/10/09 02:54:30)	795.3	8.0	712.4	2.4	10	-82.9	-10.4
(03/10/09 03:25:00)	200.1	2.0	180.5	2.9	11	-19.6	-9.8
(03/10/09 03:54:30)	597.0	6.0	535.9	2.5	10	-61.1	-10.2
(03/10/09 04:54:30)	399.3	4.0	359.1	3.5	10	-40.2	-10.1
(03/10/09 05:25:00)	795.3	8.0	714.0	3.7	11	-81.3	-10.2
(03/10/09 05:54:30)	200.1	2.0	178.8	2.3	10	-21.4	-10.7
(03/10/09 06:54:30)	994.2	10.0	894.3	3.1	10	-99.9	-10.0
(03/10/09 07:25:00)	399.3	4.0	358.6	1.7	11	-40.7	-10.2
(03/10/09 07:54:30)	795.3	8.0	715.0	2.9	10	-80.3	-10.1
(03/10/09 08:54:30)	597.0	6.0	533.8	3.2	10	-63.1	-10.6

Figure 10 shows the regression residuals of the SCO TEI 48C-TL instrument plotted against time and mole fraction. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of mole fraction dependence (right panel) in the residuals indicates linearity of the instrument.

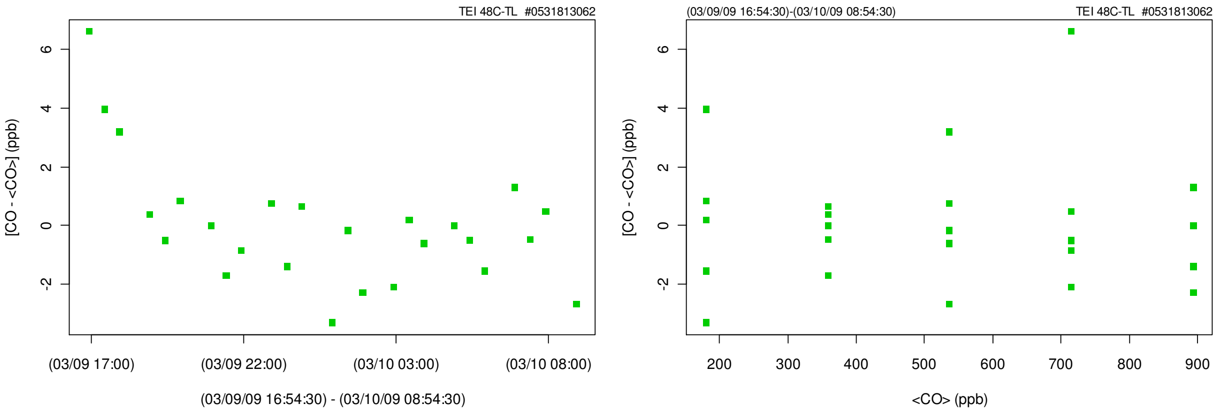

Figure 10. Regression residuals of the SCO TEI 48C-TL analyser based on the comparison with the WCC-Empa dilution system. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

Based on these comparison results, unbiased carbon monoxide volume mole fractions X_{CO} and an estimate for the remaining combined standard uncertainty u_{CO} can be computed using equation (2c) for the SCO TEI 48C-TL system.

X_{CO} (ppb) = ([CO] – 0.7 ppb) / 0.898

u_{CO} (ppb) = sqrt (23.0 ppb^2 + 4.71e-05 * X_{CO}^2) (2c)

Note that the comparison of the SCO instrument was made without automatic zero checks.

Changes made to the instruments

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

Conclusions

Good agreement was found between WCC-Empa traveling standards and the Izaña CO gas chromatographic instrument (RGA-3), but larger deviations were found for the IZO NDIR instrument. This deviation can most likely be attributed to a calibration issue (cf. recommendation 5). In addition, verification of the automatic zero checks by an external zero air source is needed.

The results obtained with the SCO NDIR instrument showed a similar bias as the IZO NDIR system, most likely due to the same calibration issue. In addition, an issue with the automatic zero checks was identified during the audit; consequently, the audit result is valid for the instrument only and should not be used to apply a correction to previously acquired data unless the issue with the zero checks has been resolved.

Methane Measurements

Methane measurements started at IZO in July 1984, and a complete time series is available since then. The current comparison was made with the original instrument that has been in operation since 1984. An additional GC/FID system for methane measurements has recently been installed at IZO but was not yet available during the audit.

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

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

During the WCC-Empa audit in 2004 [*Zellweger, et al.*, 2004] the methane GC/FID system was operating in a provisional measurement site, which became the aerosol lab in the meantime. The GC/FID system was moved to the main laboratory building. The inlet consists of a stainless steel inlet running from the tower terrace through the central service channel. The upper part is heated. A pump flushes the inlet with 2180 l/min. Inner diameter approx. 10 cm. The Inlet is protected against rain by an upside-down stainless steel bucket. The methane GC/FID instrument is installed in the 3rd floor of the building (11.5 m above ground). From the manifold, the instrument is connected using 1/4" PTFE tubing with a total length of approximately 7 m and a flow rate of approx. 2 l/min. The air is dried using a glass trap / cryo cooler set to -33°C.Total residence time is estimated to be approx. 10 seconds. The inlet system is adequate for analyzing CH_4 concerning materials and residence time.

Instrumentation

Izaña is equipped with a Dani-3800 gas chromatograph with an FID detector for ambient methane. Instrument details are summarised in Table 15.

Standards and Calibration

The IZO methane scale is directly linked to the CCL at NOAA/ESRL. Table 14 shows details of the cylinders currently available at the station. In addition to the laboratory standards, working standards consisting of natural air from Izaña are available.

Table 14. Methane laboratory standards (LS) available at Izaña (NOAA-04 methane scale)

Manufacturer / # / Use	CH_4 (ppb) (uncert.)	Matrix	Calibration		Scale	In service	
			Date	By		From	To
NOAA / CA03075 / LS	1796.05 (0.80)	Natural air	1997	NOAA	NOAA2004	1997	Today
NOAA / CA03794 / LS	1839.60 (0.37)	Natural air	1999	NOAA	NOAA2004	1999	Today
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

Mostly unchanged since the last audit by WCC-Empa [*Zellweger, et al.*, 2004]. The calibration of the instrument is performed using the working standard. Injections are made every 15 minutes, alternating between sample and standard. Peak area is used for data evaluation.

Daily checks are made for tank pressures, temperatures, flow rates, and retention times. The humidity trap is exchanged when necessary. Further measures are taken when something unusual is observed.

Data Acquisition and Data Transfer

The original data acquisition system described in the last audit report [*Zellweger, et al.*, 2004] was still available during the audit. In addition, Varian Star software with a 16-bit A/D board operating at 40 Hz is used since January 2006 for data acquisition. Self-developed software is used to integrate the peaks of the chromatograms acquired with Varian star software (see Gomez-Pelaez & Ramos, [*WMO*, in preparation-a]). The evaluation of the audit results was made using the data of the new system.

Data Treatment

Peak integration is performed automatically, and two consecutive working tank signals are used to calculate the ambient air mole fraction. If one or both working standard injections are missing or invalid, the result of the injection of ambient air is rejected. For data previous to 2002, the difference of the two working tank injections must further be below a certain threshold to be considered as valid data, whereas for data after 2003, a more sophisticated criterion is used (see Gomez-Pelaez et al., [*WMO*, 2006]). The working tank is calibrated using the station standards every two weeks. Peak area is used for data evaluation, and a linear fit through zero is used as a calibration function.

Data Submission

Data of the in-situ methane measurements have been submitted to the GAW World Data Centre for Methane at JMA (World Data Centre for Greenhouse Gases, WDCGG). Currently the complete time series covering the period from 1984 to July 2010 is available at WDCGG.

Documentation

Information about calibrations is stored in electronic log books, and is also printed and pasted in a hand written log book, which contains all information. The log book entries were comprehensive and up-to-date. Instrument manuals are available at the site.

Comparison of Methane Analyzers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007a] and included comparisons of the traveling standards at Empa before and after the comparison of the analyzer. Details of the traveling standards are given in Table 15 below.

Setup and Connections

Table 15 shows details of the experimental setup during the comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the IZO data acquisition system, and no further corrections were applied.

Table 15. Experimental details of the methane comparison.

Traveling standard (TS)		WCC-Empa Traveling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 070808_FA02769 / 1713.73 / 0.91 2 / 071122_FA30491 / 1803.15 / 0.74 3 / 070807_FA02770 / 1858.60 / 0.58 4 / 071122_FA01477 / 1951.36 / 1.12 5 / 070927_FA02493 / 1781.23 / 0.24
Field instrument	Model, S/N	Dani-3800 #011109
Connection of TS to field instrument		TS were connected to the sample selection valve of the IZO system
Data Acquisition		Station data acquisition
Number of injections		Injections every 10 min; total 15-31 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (2009-03-05 to 09)

Results

Each TS was injected between 15 to 24 times, which resulted in a maximum of 24 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 16).

Table 16. CH_4 aggregates computed from single injections (mean and standard deviation) for each level during the comparison of the IZO methane analyzer with the WCC-Empa traveling standards (TS).

Date	TS Identification	TS (ppb)	uTS (ppb)	AL* (ppb)	sdAL (ppb)	AL** (ppb)	sdAL (ppb)	N	AL-TS (ppb)**	AL-TS (%)**
(03/05/09 12:53:00)	071122_FA30491	1803.15	0.74	1804.12	3.62	1803.94	1.65	15	0.79	0.04
(03/05/09 15:58:00)	071122_FA01477	1951.36	1.21	1952.65	5.72	1951.64	1.68	16	0.28	0.01
(03/06/09 12:43:00)	070808_FA02769	1713.73	0.91	1712.04	2.97	1715.34	3.06	17	1.62	0.09
(03/06/09 17:03:52)	070807_FA02770	1858.60	0.58	1858.01	5.00	1857.17	2.30	22	-1.44	-0.08
(03/07/09 12:29:55)	070927_FA02493	1781.23	0.24	1780.80	4.05	1779.79	3.40	14	-1.44	-0.08
(03/11/09 13:08:00)	071122_FA30491	1803.15	0.74	1803.86	3.02	1804.92	2.02	24	1.77	0.10

* old integrator.
** new integrator; these values were used for the calculation of the audit results.

Figure 11 shows the regression residuals of the Dani-3800 GC plotted against time and mole fraction. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of mole fraction dependence (right panel) in the residuals indicates linearity of the instrument.

Based on the comparison results, unbiased methane volume mixing ratios of the Dani-3800 analyzer X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed from the single injection comparison data using equation (3).

$$X_{CH4}\ (ppb) = (CH_4) / 1.00007$$
$$u_{CH4}\ (ppb) = \sqrt{5.4\ ppb^2 + 1.49e\text{-}07 * X_{CH4}^2} \qquad (3)$$

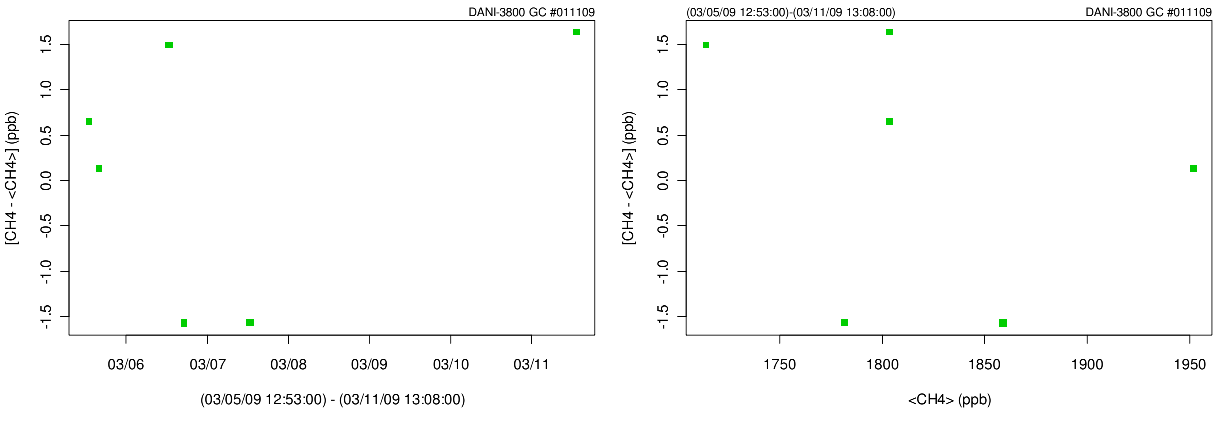

Figure 11. Regression residuals of the IZO methane GC. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

Conclusions

No significant deviations between Izaña and WCC-Empa were found. The good result of the comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. Therefore no further technical recommendations are made by WCC-Empa. The repeatability of the Izaña GC was acceptable, with an average standard deviation of 0.22% (old integrator) and 0.13% (new integrator, 15-24 injections). The best GC-FID systems at GAW stations reach average standard deviations below 0.1%. The current system will be replaced in the near future by a new GC/FID system.

Nitrous Oxide Measurements

Nitrous oxide measurements of Izaña were audited by the World Calibration Centre for N_2O (http://imk-ifu.fzk.de/wcc-n2o) in November 2008. An audit report [*Scheel*, 2009] describing the whole measurement set-up is downloadable from the GAWSIS station report [*GAWSIS*, 2010]; therefore, only a brief description of technical details is presented here.

Continuous nitrous oxide measurements started at IZO in June 2007, and a complete time series is available since then. However, due to the relative recent start of the measurements, data have not yet been submitted to WDCGG.

Monitoring Set-up and Procedures

Air Conditioning

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

Air Inlet System

The N_2O system is installed in the same laboratory as the CH_4 instrument. It is also connected to the stainless steel manifold (see CH_4). The air inlet system is adequate for analyzing N_2O concerning materials and residence time.

Instrumentation

A Varian 3800 GC with an ECD detector is used for the measurements of N_2O. A detailed description of the instrumental set-up is given in the GAW WMO Report 186 [*WMO*, 2009]

Standards and Calibration

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 NOAA-2006 N_2O scale calibration scale. Table 17 shows details of the cylinders currently available at the station. In addition to the laboratory standards, working standards consisting of natural air from Izaña are available.

Table 17. N_2O laboratory standards (LS) available at Izaña (NOAA-2006 N_2O scale)

Manufacturer / # / Use	N_2O (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

A detailed SOP is available, and a daily check list with engineering parameters and chromatogram status is filled in. The carrier and calibration gas consumption is routinely checked.

Data Acquisition and Data Transfer

Varian Star software with a 16-bit A/D board operating at 40 Hz is used for data acquisition.

Data Submission

Data of the in-situ N_2O measurements have not yet been submitted to the GAW World Data Centre for Greenhouse Gases (WDCGG).

Documentation

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

Comparison of Nitrous Oxide Measurements

The travelling standards used for the comparison were calibrated by WCC-N_2O in April 2008. Since then, no re-calibrations have been made. Details of the traveling standards are given in Table 18 below.

Setup and Connections

Table 18 shows details of the experimental setup during the comparison of the transfer standard and the station GC. The data used for the evaluation was recorded by the IZO data acquisition system, and no further corrections were applied.

Table 18. Experimental details of the N_2O comparison.

Traveling standard (TS)		WCC-Empa* Traveling standards (aluminium cylinder containing natural air)
Levels (ppb)		Level / Cylinder / Reference* / std dev 1 / 070808_FA02769 / 306.79 / 0.28 2 / 071122_FA30491 / 317.03 / 0.22 3 / 070807_FA02770 / 322.68 / 0.17 4 / 071122_FA01477 / 323.34 / 0.19 5 / 070927_FA02493 / 354.71 / 0.31
Field instrument	Model, S/N	Varian 3800 #3405
Connection of TS to field instrument		TS were connected to the sample selection valve of the IZO system
Data Acquisition		Station data acquisition
Number of injections		Injections every 15 min; total 16-32 injections per level
Sequence of levels		Randomised sequence
Runs		1 run (2009-03-06 to 18)

* Mixing ratios were assigned by the WCC-N_2O

Results

Each TS was injected between 16 to 32 times, which resulted in a maximum of 32 useable injections per level. These were further aggregated by level before use in the assessment (cf. Table 19).

Table 19. N_2O aggregates computed from single injections (mean and standard deviation) for each level during the comparison of the IZO nitrous oxide GC with the WCC-Empa traveling standards (TS).

Date	TS Identification	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(03/06/09 13:14:30)	070927_FA02493	354.71	0.31	354.15	0.38	16	-0.56	-0.16
(03/06/09 17:59:30)	071122_FA30491	317.03	0.22	317.25	0.47	16	0.22	0.07
(03/18/09 15:50:08)	070808_FA02769	306.79	0.28	307.48	0.45	32	0.69	0.22
(03/16/09 13:29:30)	071122_FA01477	323.34	0.19	323.39	0.54	16	0.05	0.02
(03/17/09 13:14:30)	070807_FA02770	322.68	0.17	322.45	0.50	16	-0.23	-0.07

The deviations between WCC-Empa and IZO were not significant for the TS in the ambient mole fraction range (average 0.01 ppb, standard deviation 0.23 ppb, min -0.23 ppb, max 0.22 ppb). The average deviation in the relevant mixing ratio range meets the recommendations (comparability of ±0.1 ppb) made by WMO [*WMO*, 2009]; however, individual measurements slightly exceed these recommendations. Slightly larger deviations were found for the lowest and highest

TS. The results are generally in agreement with the audit by WCC- N_2O, although slightly higher deviations were observed for mole fractions different from ambient levels.

Figure 12 shows the regression residuals of the Varian-3800 GC plotted against time and mole fraction. The absence of a temporal trend (left panel) indicates stable instrument conditions. The absence of mole fraction dependence (right panel) in the residuals indicates linearity of the instrument.

Based on the comparison results, unbiased N_2O volume mixing ratios of the Varian-3800 GC X_{N2O} and an estimate for the remaining combined standard uncertainty u_{N2O} can be computed from the single injection comparison data using equation (4).

$$X_{N2O} \text{ (ppb)} = (N_2O) / 1.000097$$

$$U_{N2O} \text{ (ppb)} = \text{sqrt} (0.22 \text{ ppb}^2 + 1.04\text{e-}06 * X_{N2O}^2) \quad (4)$$

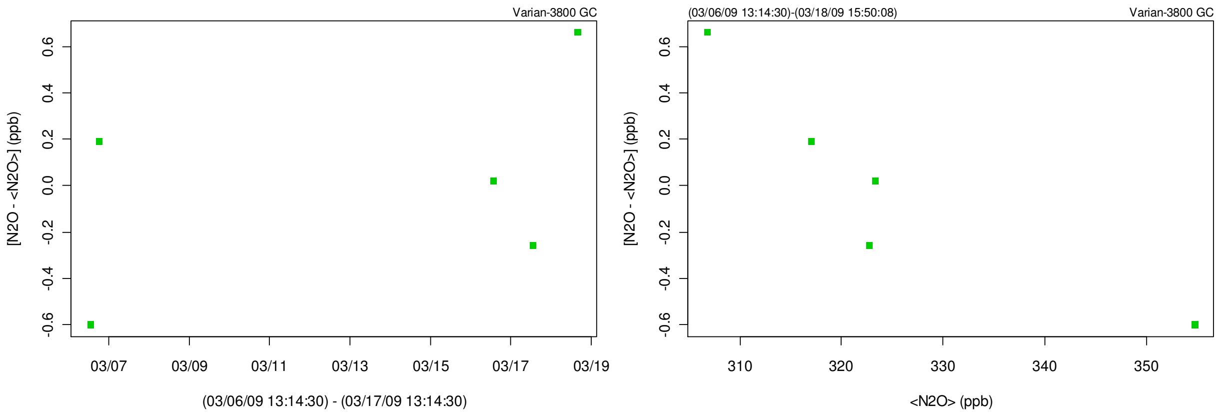

Figure 12. Regression residuals of the IZO N_2O GC. Points represent averages of valid single injections. Left panel: time dependence; Right panel: mole fraction dependence.

Conclusions

No significant deviations between the Izaña measurements and WCC-Empa traveling standard were found in the relevant mixing ration range of 315 to 325 ppb N_2O. The good result of the comparison shows that the whole analytical system is appropriate for the measurement of N_2O. Therefore no further technical recommendations are made by WCC-Empa. A more detailed assessment was made was made by the WCC-N_2O in November 2008.

WCC-Empa Traveling Standards

Ozone

The WCC-Empa traveling standard (TS) was compared with the Standard Reference Photometer before and after use during the field audit. Details of these comparisons at the Empa calibration laboratory are summarised in Table 20, the comparison data is given in Table 21.

Table 20. Experimental details of the comparison of traveling standard (TS) and Standard Reference Photometer (SRP).

Standard Reference Photometer		NIST SRP#15 (WCC-Empa)
Traveling standard (TS)	Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
	Settings	BKG = -0.2; COEFF = 1.009
Ozone source		Internal generator of SRP
Zero air supply		Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa)
Connection between instruments		Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet
Data acquisition		SRP data acquisition system, 1-minute averages with standard deviations
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		Variable based on standard deviation criterion, the last 10 30-second readings are aggregated
Sequence of Levels		Repeated runs of randomised sequence
Runs		3 runs before shipment of TS (2009-01-27) 3 runs after return of TS (31 2009-05-12)

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 traveling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2009-01-27	1	0	0.09	0.22	-0.10	0.24
2009-01-27	1	30	31.99	0.29	32.04	0.32
2009-01-27	1	140	138.61	0.26	138.54	0.21
2009-01-27	1	190	186.70	0.29	186.60	0.19
2009-01-27	1	90	89.98	0.22	89.97	0.19
2009-01-27	1	60	60.61	0.20	60.53	0.21
2009-01-27	1	0	-0.20	0.32	0.11	0.13
2009-01-27	2	0	0.08	0.29	-0.08	0.18
2009-01-27	2	60	60.54	0.23	60.79	0.33
2009-01-27	2	30	32.09	0.21	32.04	0.32
2009-01-27	2	140	138.22	0.32	138.42	0.25
2009-01-27	2	190	185.52	0.27	185.85	0.34
2009-01-27	2	90	89.59	0.31	89.85	0.45
2009-01-27	2	0	-0.06	0.30	0.04	0.10
2009-01-27	3	0	0.17	0.23	-0.14	0.21
2009-01-27	3	90	89.92	0.24	89.93	0.18
2009-01-27	3	30	31.84	0.24	31.76	0.12
2009-01-27	3	190	185.68	0.22	185.85	0.34
2009-01-27	3	60	60.25	0.30	60.26	0.26
2009-01-27	3	140	137.35	0.16	137.02	0.28
2009-01-27	3	0	-0.08	0.25	-0.02	0.22
2009-05-12	4	0	-0.06	0.25	-0.36	0.17
2009-05-12	4	30	31.48	0.44	31.35	0.19
2009-05-12	4	140	137.92	0.23	137.81	0.21
2009-05-12	4	190	185.47	0.35	185.26	0.27
2009-05-12	4	60	60.03	0.21	59.70	0.24
2009-05-12	4	90	89.28	0.31	89.11	0.31
2009-05-12	4	0	-0.06	0.23	-0.05	0.35
2009-05-12	5	0	0.04	0.14	-0.09	0.17
2009-05-12	5	60	60.22	0.36	59.86	0.26
2009-05-12	5	140	137.65	0.33	137.41	0.21
2009-05-12	5	30	31.40	0.19	31.50	0.18
2009-05-12	5	190	185.13	0.31	184.98	0.14
2009-05-12	5	90	89.27	0.37	89.15	0.16
2009-05-12	5	0	0.08	0.44	-0.29	0.17
2009-05-12	6	0	-0.22	0.27	-0.33	0.31
2009-05-12	6	90	89.58	0.17	89.38	0.44
2009-05-12	6	60	60.05	0.26	59.66	0.27
2009-05-12	6	140	137.45	0.31	137.15	0.18
2009-05-12	6	190	185.04	0.24	184.52	0.21
2009-05-12	6	30	31.55	0.23	31.17	0.15
2009-05-12	6	0	-0.03	0.25	-0.04	0.17

#the level is only indicative.

The traveling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen, et al.*, 2003] (cf. Figure 13). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (equation 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [*Klausen, et al.*, 2003]).

X_{TS} (ppb) = ([TS] + 0.09 ppb) / 0.999

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

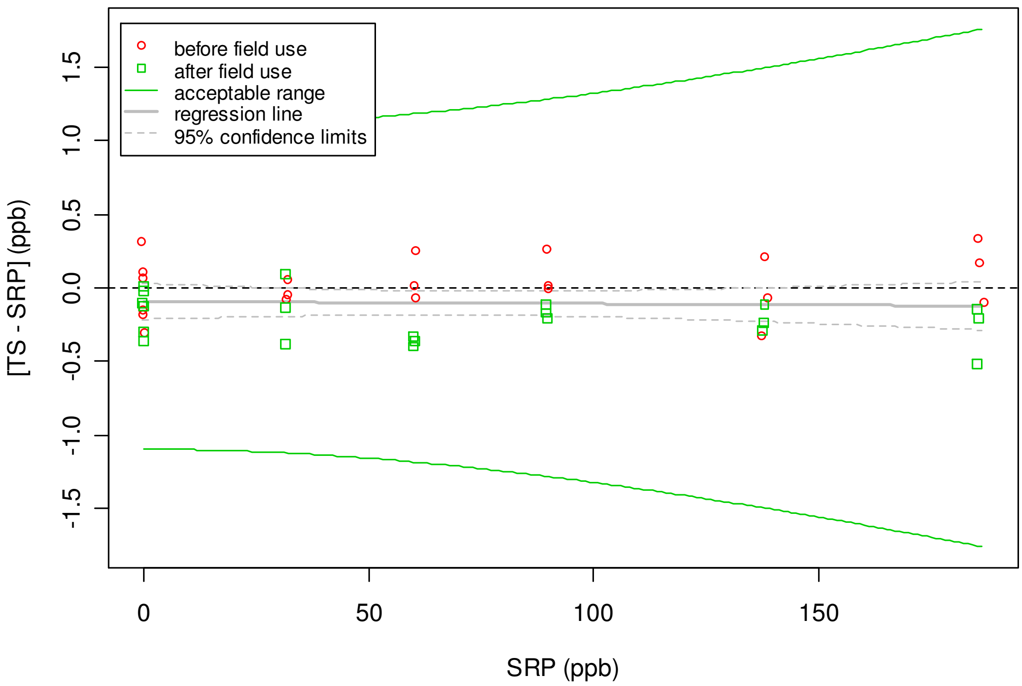

Figure 13. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Carbon Monoxide

WCC-Empa refers to the revised WMO/GAW carbon monoxide scale (hereafter: WMO-2000 scale) [*Novelli, et al.*, 2003] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL by way of traveling standards. The scale was transferred to the traveling standard using an Aerolaser AL5001 vacuum-fluorescence analyzer, an instrument with high precision and proven linearity. Details are given in Table 22 and Table 23.

Table 22. Experimental details of the transfer of the WMO-2000 carbon monoxide scale to the traveling standard (TS) used during the field comparison.

Reference scale		Laboratory standards (30L aluminium cylinders) obtained directly from the Central Calibration Laboratory. The transfer of the scale is based on one specific cylinders, CA02854 (295.5±3.0 ppb) WMO-2000 CO scale
Transfer instrument	Model, S/N	Aerolaser AL5001, S/N 117 (WCC-Empa)
Traveling standard - cylinders		Carbon monoxide cylinders for direct comparisons. (cf. Table 23)
Traveling standard - dilution unit		zero air (1) and a high mole fraction carbon monoxide cylinder (2), in combination with a dilution unit (3)
(1) Zero air supply		Ambient air – Silicagel PS drying cartridge – zero air generator (Purafil, Sofnocat, filter) (WCC-Empa)
(2) Carbon monoxide cylinder		081001_FA02474, 49.34±0.49 ppm CO (α=0.05).
(3) Dilution unit		WCC-Empa dilution system with Red-y MFCs. The levels used were calibrated before and after the field comparison against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851).
Connection between instruments		Ca. 2 meter 1/8" stainless steel tubing (cylinders). Ca. 5 meter 6 mm Sertoflex tubing (dilution unit).
Range (ppb)		90 – 200 ppb cf. Table 23
Duration per level (min)		Three 4-minute averages alternating with calibrations
Sequence of Levels		Repeated runs of randomised sequence

Table 23. Calibration of the carbon monoxide traveling standards with the WCC-Empa reference before and after the audit.

dte	070807_FA02770	sd	070808_FA02769	sd	070927_FA02493	sd	071122_FA01477	sd	071122_FA30491	sd
2009-01-23			**87.94**	0.52						
2009-01-26	**148.56**	0.68			**202.68**	0.80	**164.41**	0.72	**109.51**	0.43
2009-05-11	**149.19**	0.74	**89.39**	0.57	**203.32**	0.81	**164.93**	0.61	**109.62**	0.64

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

Table 24. Calibration of the WCC-Empa dilution system and carbon monoxide mole fractions measured with the transfer instrument.

	Mass Flow Controller MFC 1 (mL min^{-1})			Mass Flow Controller MFC 2 (mL min-1)			Carbon Monoxide Mixing Ratio (ppb)		
Date	Setpoint	Measured#	sd	Setpoint	Measured	sd	Expected	Measured#	sd
2009-02-11	2987.9	2999.9	0.6	12.11	12.16	0.01	199.3	199.0	0.7
2009-02-11	3000.0	3011.8	0.8	0.00	0.02	0.01	0.0	0.1	0.5
2009-02-11	2951.6	2963.9	0.7	48.43	48.49	0.01	794.3	795.6	1.3
2009-02-11	2969.7	2981.7	0.8	30.27	30.37	0.01	497.5	497.9	1.1
2009-02-11	2939.5	2951.8	0.7	60.54	60.63	0.01	993.1	992.0	1.8
2009-02-11	2975.8	2987.6	0.7	24.22	24.32	0.01	398.4	399.2	1.6
2009-02-11	2963.7	2975.6	0.7	36.33	36.38	0.01	596.0	596.3	1.5
2009-02-11	2957.6	2969.7	0.8	42.38	42.42	0.01	694.9	695.7	1.1
2009-02-11	2993.9	3005.7	0.8	6.05	6.11	0.01	100.0	100.2	0.7
2009-02-11	2945.5	2957.7	0.7	54.49	54.57	0.01	893.9	892.4	2.1
2009-02-11	2981.8	2993.6	0.8	18.16	18.23	0.01	298.7	299.0	1.0
2009-05-12	2987.9	2996.3	0.6	12.11	12.25	0.01	201.0	198.8	0.7
2009-05-12	3000.0	3008.9	0.7	0.00	0.11	0.01	0.0	0.3	0.2
2009-05-12	2951.6	2960.9	0.7	48.43	48.58	0.01	796.4	796.5	1.1
2009-05-12	2969.7	2978.7	0.6	30.27	30.46	0.01	499.4	498.1	1.4
2009-05-12	2939.5	2948.9	0.8	60.54	60.70	0.01	995.2	993.2	1.2
2009-05-12	2975.8	2984.6	0.7	24.22	24.41	0.01	400.2	399.3	0.7
2009-05-12	2963.7	2972.7	0.6	36.33	36.47	0.01	598.0	596.9	0.9
2009-05-12	2957.6	2966.6	0.8	42.38	42.51	0.01	697.1	695.8	1.5
2009-05-12	2993.9	3002.5	0.7	6.05	6.21	0.01	101.8	100.2	0.5
2009-05-12	2945.5	2954.5	1.3	54.49	54.65	0.01	896.1	893.4	0.7
2009-05-12	2981.8	2990.4	0.7	18.16	18.32	0.01	300.5	299.3	0.9

Methane

WCC-Empa refers to the WMO/GAW methane scale (hereafter: NOAA04 scale) [*Dlugokencky, et al.*, 2005] hosted and maintained by the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) who act as the GAW Central Calibration Laboratory (CCL). WCC-Empa maintains a set of laboratory standards obtained from the CCL (cf. Table 25). The scale was transferred to the traveling standards using a Varian 3400 gas chromatograph with an FID detector. Details of the traveling standards are given in Table 26.

Table *25*. NOAA/ESRL CH_4 laboratory standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Cylinder#	Methane [ppb]* (NOAA04)
CA05373	1608.57 ± 0.08 ppb
CA05316	1712.54 ± 0.16 ppb
CA04462	1817.39 ± 0.19 ppb
CA04580	1905.36 ± 0.25 ppb

*Certificates (CMDL83) from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316 and CA05373). Values were converted to NOAA04 scale by applying a factor of 1.0124.

Table 26. Calibration of the methane traveling standards with the WCC-Empa reference (Average mole fraction in ppb ± sd (n = 10)).

Date	070807_FA02770	sd	070808_FA02769	sd	070927_FA02493	sd	071122_FA01477	sd	071122_FA30491	sd
2008-07-23	**1858.26**	0.89								
2008-10-28			**1712.42**	1.08					**1802.86**	1.16
2008-11-03	**1857.87**	0.84					**1950.18**	2.18		
2009-01-22			**1713.88**	1.31	**1781.35**	1.26			**1802.29**	1.81
2009-01-26	**1858.71**	1.07					**1952.72**	0.89		
2009-05-11	**1859.26**	0.80	**1714.26**	1.89	**1781.09**	0.79	**1950.55**	1.02	**1803.62**	1.32
2009-05-12	**1858.91**	0.99	**1714.34**	2.45	**1781.24**	1.45	**1951.97**	1.06	**1803.83**	1.44
AVG / **su**	**1858.60**	0.58	**1713.73**	0.91	**1781.23**	0.24	**1951.36**	1.21	**1803.15**	0.74

Nitrous Oxide

WCC-Empa refers to the WMO/GAW nitrous oxide scale (hereafter: NOAA-2006 scale) [*Hall, et al.*, 2007]. The TS used during this audit have been calibrated by the WCC-N_2O in April 2008. The standards have not been recalibrated after the audit.

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Ozone Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-03-05
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Yenny González Ramos, Ramón Ramos
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(0.9998±0.0010) × [SRP] - (0.09±0.14)
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C #63900-337
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.0 ppb, SPAN 1.006
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.007±0.001) × [SRP] + (0.27±0.11)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] - 0.27) / 1.007
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.29\ ppb^2 + 2.66e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	Main station analyzer
1.7	Reference:	WCC-Empa Report 09/1

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

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Ozone Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-03-05
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Yenny González Ramos, Ramón Ramos
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(0.9998±0.0010) × [SRP] - (0.09±0.14)
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C #72491-371
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.0 ppb, SPAN 1.048
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.016±0.001) × [SRP] + (0.44±0.10)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] - 0.44) / 1.016
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.62e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	Backup analyzer
1.7	Reference:	WCC-Empa Report 09/1

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

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Ozone Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-03-05
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Yenny González Ramos, Ramón Ramos
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(0.9998±0.0010) × [SRP] - (0.09±0.14)
1.5	Ozone Calibrator [OC]	
1.5.1	Model:	TEI 49C-PS # 56084-306
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Coefficients at start of audit	BKG -0.8 ppb, SPAN 1.014
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.001±0.000) × [SRP] - (0.00±0.11)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OC] + 0.00) / 1.001
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.29\ ppb^2 + 2.60e\text{-}5 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	Station calibrator
1.7	Reference:	WCC-Empa Report 09/1

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

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Carbon Monoxide Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2009-03-07 to 2009-03-18	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Ramón Ramos	
1.3	CO Reference:	WMO-2000	
1.4	CO Transfer Standard [TS]		
1.4.1	CO Cylinders:	070808_FA02769	88.66±1.12 ppb
		071122_FA30491	109.55±0.55 ppb
		070807_FA02770	148.88±0.87 ppb
		071122_FA01477	164.67±0.90 ppb
		070927_FA02493	203.00±1.11 ppb
1.5	CO analyzer:		
1.5.1	Model:	RGA-3, S/N 070188-006	
1.5.2	Range of calibration:	87 – 203 ppb	
1.5.3	Coefficients at start of audit	NA	
1.5.4	Calibration at start of audit (ppb):	CO = (1.035±0.011) × X – (6.2±1.5)	
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 6.2) / 1.035	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (2.2\ ppb^2 + 1.40e\text{-}04 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	NA	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged	
1.6	Comments:	Gas chromatograph, main instrument	
1.7	Reference:	WCC-Empa Report 09/1	

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

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Carbon Monoxide Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2009-03-06 to 2009-03-07
1.2	Auditor:	Dr. C. Zellweger
1.1.1	Station staff involved in audit:	Yenny González Ramos, Ramón Ramos
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	081001_FA02474, 49.34±0.49 ppm
1.4.2	Zero Air:	Ambient air, Sofnocat, Purafil, filter (WCC-Empa)
1.4.3	Dilution unit:	WCC-Empa dilutions system (Redy MFCs)
1.4.4	Range of calibration:	0 – 1000 ppb
1.5	CO analyzer	
1.5.1	Model:	TEI 48C-TL #75723-3808
1.5.2	Range of calibration:	0 – 1000 ppb
1.5.3	Coefficients at start of audit	Zero -0.204 ppm, Span 1.000
1.5.4	Calibration at start of audit (ppb):	CO = (0.916±0.003) × X - (5.2±0.5)
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	X = (CO + 5.2) / 0.916
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (51.2 \text{ ppb}^2 + 4.14e\text{-}05 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 09/1

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

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Methane Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2009-03-05 to 2009-03-09	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Ángel Gómez-Peláez, Ramón Ramos	
1.3	CH_4 Reference:	NOAA04	
1.4	CH_4 Transfer Standard [TS]		
1.4.1	CH_4 Cylinders:	070808_FA02769	1713.73±0.91 ppb
		070927_FA02493	1781.23±0.24 ppb
		071122_FA30491	1803.15±0.74 ppb
		070807_FA02770	1858.60±0.58 ppb
		071122_FA01477	1951.36±1.12 ppb
1.5	CH_4 analyzer [CA]		
1.5.1	Model:	Dani-3800 #011109	
1.5.2	Range of calibration:	1713 –1952 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$CH_4 = (1.00007 \pm 0.00037) \times X$	
1.5.5	Unbiased CH_4 mole fraction (ppb) at start of audit:	$X = CH_4 / 1.00007$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (5.4 \text{ ppb}^2 + 1.49\text{e-}07 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased CH_4 mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/1	

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

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Nitrous Oxide Audit Executive Summary (IZO)

0.1	Station Name:	Izaña
0.2	GAW ID:	IZO
0.3	Coordinates/Elevation:	28.3090°N 16.4994°W (2373 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2009-03-05 to 2009-03-09	
1.2	Auditor:	Dr. C. Zellweger	
1.2.1	Station staff involved in audit:	Ángel Gómez-Peláez, Ramón Ramos	
1.3	N_2O Reference:	NOAA-2006	
1.4	N_2O Transfer Standard [TS]		
1.4.1	N_2O Cylinders:	070808_FA02769	306.79±0.28 ppb
		071122_FA30491	317.03±0.22 ppb
		070807_FA02770	322.68±0.17 ppb
		071122_FA01477	323.34±0.19 ppb
		070927_FA02493	354.71±0.31 ppb
1.5	N_2O analyzer [CA]		
1.5.1	Model:	Varian 3800 #3405	
1.5.2	Range of calibration:	306 –355 ppb	
1.5.3	Coefficients at start of audit	not applicable	
1.5.4	Calibration at start of audit (ppb):	$N_2O = (1.000097 \pm 0.000691) \times X$	
1.5.5	Unbiased N_2O mole fraction (ppb) at start of audit:	$X = N_2O / 1.000097$	
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	$u_X \approx (0.22\ ppb^2 + 1.04e\text{-}06 \times X^2)^{1/2}$	
1.5.7	Coefficients after audit	not applicable	
1.5.8	Calibration after audit (ppb):	unchanged	
1.5.9	Unbiased N_2O mole fraction (ppb) after audit:	unchanged	
1.5.10	Standard uncertainty after compensation of calibration bias after audit (ppb):	unchanged	
1.6	Comments:		
1.7	Reference:	WCC-Empa Report 09/1	

[N_2O]: Instrument readings; X: mole fractions on the NOAA-2006 N_2O scale.

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Ozone Audit Executive Summary (SCO)

0.1	Station Name:	Santa Cruz (Tenerife)
0.2	GAW ID:	SCO
0.3	Coordinates/Elevation:	28. 4725°N 16. 2473°W (52 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2009-03-09 to 2009-03-10
1.2	Auditor:	Dr. C. Zellweger
1.2.1	Station staff involved in audit:	Yenny González Ramos
1.3	Ozone Reference [SRP]:	NIST SRP#15
1.4	Ozone Transfer Standard [TS]	
1.4.1	Model and serial number:	TEI 49C PS #0810-153
1.4.2	Range of calibration:	0 – 200 ppb
1.4.3	Mean calibration (ppb):	(0.9998±0.0010) □ [SRP] - (0.09±0.14)
1.5	Ozone Analyzer [OA]	
1.5.1	Model:	TEI 49C #032060000000731
1.5.2	Range of calibration:	0 – 100 ppb
1.5.3	Coefficients at start of audit	BKG 0.0 ppb, SPAN 1.030
1.5.4	Calibration at start of audit (ppb):	[OA] = (1.025±0.000) □ [SRP] - (0.15±0.06)
1.5.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OA] + 0.15) / 1.025
1.5.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_X □ (0.27 ppb^2 + 2.48e-5 □ X^2)$^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 09/1

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

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Carbon Monoxide Audit Executive Summary (SCO)

0.1	Station Name:	Santa Cruz (Tenerife)
0.2	GAW ID:	SCO
0.3	Coordinates/Elevation:	28. 4725°N 16. 2473°W (52 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2009-03-09 to 2009-03-10
1.2	Auditor:	Dr. C. Zellweger
1.1.2	Station staff involved in audit:	Yenny González Ramos, Ramón Ramos
1.3	CO Reference:	WMO-2000
1.4	CO Transfer Standard [TS]	
1.4.1	CO Cylinder:	081001_FA02474, 48.84±0.49 ppm
1.4.2	Zero Air:	Ambient air, Sofnocat, Purafil, filter (WCC-Empa)
1.4.3	Dilution unit:	WCC-Empa dilutions system (Redy MFCs)
1.4.4	Range of calibration:	0 – 1000 ppb
1.5	CO analyzer	
1.5.1	Model:	TEI 48C-TL # 0531813062
1.5.2	Range of calibration:	0 – 1000 ppb
1.5.3	Coefficients at start of audit	Zero 9.188 ppm, Span 0.967
1.5.4	Calibration at start of audit (ppb):	$CO = (0.898 \pm 0.004) \times X + (0.7 \pm 1.4)$
1.5.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = (CO – 0.7) / 0.898$
1.5.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (23.0\ ppb^2 + 4.71e\text{-}05 \times X^2)^{1/2}$
1.5.7	Coefficients after audit	unchanged
1.5.8	Calibration after audit (ppb):	unchanged
1.5.9	Unbiased CO mixing ratio (ppb) after audit:	unchanged
1.5.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged
1.6	Comments:	
1.7	Reference:	WCC-Empa Report 09/1

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

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LIST OF ABBREVIATIONS

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