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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 00/2

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE AND CARBON MONOXIDE AT THE GLOBAL GAW STATION IZAÑA AND FOR SURFACE OZONE AT PUNTA DEL HIDALGO TENERIFE, JUNE 2000

Submitted by

C. Zellweger, A. Herzog, B. Buchmann, P. Hofer

WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

EMPA Dübendorf, Switzerland

Contents:

1. Abstract 5
2. Introduction 9
3. Global GAW Site Izaña 11
3.1. Site Characteristics 11
3.2. Operators 13
3.3. Ozone Level at Izaña....................14
3.4. Carbon Monoxide Level at Izaña 14
4. Measurement Technique at Izaña 17
4.1. Surface Ozone 17
4.1.1. Air Inlet System 17
4.1.2. Instrumentation....................17
4.1.3. Operation and Maintenance 18
4.1.4. Data Handling....................19
4.1.5. Documentation 19
4.1.6. Competence 19
4.2. Carbon Monoxide 20
4.2.1. Air Inlet System for CO....................20
4.2.2. CO Analyser at Izaña 20
4.2.3. Gas Standards 21
4.2.4. Operation and Maintenance, CO 21
4.2.5. Data Handling....................22
4.2.6. Documentation 22
5. Intercomparison of Ozone Instruments (Izaña)....................23
5.1. Experimental Procedure 23
5.2. Results 24
6. Intercomparison of in situ Carbon Monoxide Analyser....................31
6.1. Experimental Procedure 31
6.2. Results 33
7. Local Measurement Site Punta del Hidalgo 37
7.1. Site Characteristics 37
7.2. Operators 37
7.3. Ozone Level 37
8. Measurement Technique at Punta del Hidalgo 39
8.1. Air Inlet System 39
8.2. Instrumentation....................39
8.3. Operation and Maintenance 40
8.4. Data Handling....................40
8.5. Documentation 40
9. Intercomparison of Ozone Instruments (Hidalgo) 41
9.1. Experimental Procedure 41
9.2. Results 42
Appendix 47
I Calibrator TEI 49C-PS #306 of the Izaña Observatory 47
II EMPA Transfer Standard TEI 49C-PS 49
III Stability of the Transfer Standard TEI 49C-PS 50
IV WCC Carbon Monoxide Reference....................53

Figures:

Figure 1: Intercomparison of the TEI 49C with the WCC transfer standard 5
Figure 2: Intercomparison of the Dasibi 1008-RS (back-up instrument) with the WCC transfer standard 6
Figure 3: Intercomparison of the Izaña RGA-3 gas chromatograph with the transfer standards of the WCC (conventional true value) 7
Figure 4: Picture of the station Izaña (view from the provisional station) 11
Figure 5: The provisional station (left) with the nearby military camp in the background 12
Figure 6: Inside the provisional station 12
Figure 7: Map of the Canary Islands and African Continent 13
Figure 8: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Izaña of the year 1999. Availability of data: 93%. 15
Figure 9: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at Izaña of the period 10.12.98 to 22.11.99. Availability of data: 70%. 15
Figure 10: Experimental set up for the ozone intercomparison...24
Figure 11: Individual linear regressions of intercomparisons 1 and 2, TEI 49C 26
Figure 12: Mean linear regression of intercomparisons 1 and 2, TEI 49C 26
Figure 13: Individual linear regressions of intercomparisons 1 and 2, Dasibi 1008-RS.............27
Figure 14: Mean linear regression of intercomparisons 1 and 2, Dasibi 1008-RS 27
Figure 15: Intercomparison of instrument TEI 49C..28
Figure 16: Intercomparison of instrument Dasibi 1008-RS 29
Figure 17: Experimental set up for the carbon monoxide intercomparison 33
Figure 18: Deviations (ppb) between RGA-3 and CMDL transfer standards (conventional true value) 34
Figure 19: Differences (%) between the RGA-3 and the CMDL transfer standard (the red error bars show the given uncertainty of the CMDL gas cylinders)...........................35
Figure 20: Picture of the station Punta del Hidalgo...37
Figure 21: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Punta del Hidalgo of the year 1997. Availability of data: 86%......................38
Figure 22: Individual linear regressions of intercomparisons 1 and 2, Dasibi 1008-AH.............43
Figure 23: Mean linear regression of intercomparisons 1 and 2, Dasibi 1008-AH 43
Figure 24: Intercomparison of instrument Dasibi 1008-AH 44
Figure 25: Flow schematic of TEI 49C-PS...50
Figure 26: Instruments set up SRP -TEI 49C-PS 51
Figure 27: Transfer standard before audit..52
Figure 28: Transfer standard after audit...52

Tables:

Table 1: Staff of the Izaña Atmospheric Observatory 14
Table 2: Ozone analysers at Izaña 18
Table 3: Field CO analyser at Izaña 20
Table 4: Station CO cylinders 21
Table 5: Experimental details 23
Table 6: 1. Intercomparison of ozone field instruments 25
Table 7: 2. Intercomparison of ozone field instruments 25
Table 8: Summary of the recommendation of the 1998 audit and current state 31
Table 9: Experimental details of the carbon monoxide intercomparison 32
Table 10: Intercomparison measurement at Izaña for CO 34
Table 11: Intercomparison measurement at Izaña for CO based on the peak area 36
Table 12: Field instrument at Punta del Hidalgo 39
Table 13: Experimental details 41
Table 14: 1. Intercomparison, field instrument 42
Table 15: 2. Intercomparison, field instrument 42
Table 16: Experimental details 47
Table 17: Ozone calibrator at global GAW station Izaña 48
Table 18: 1. Intercomparison, TEI 49C-PS #306 48
Table 19: 2. Intercomparison, TEI 49C-PS #306 48
Table 20: 3. Intercomparison, TEI 49C-PS #306 49
Table 21: Intercomparison procedure SRP - TEI 49C-PS 50
Table 22: CO Standards at the WCC 53

1. Abstract

A system and performance audit was conducted by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane at the global GAW station Izaña and the local measurement site Punta del Hidalgo, Tenerife.

Global GAW station Izaña

The global GAW site Izaña was audited for the third time by the WCC. The reason for this is that regular system and performance audits should be conducted at global GAW sites, and that the carbon monoxide measurements became operational at Izaña shortly after the last audit in 1998. The biggest change of the station since then was the temporarily movement to a provisional site on 14 April 2000 nearby the old facilities due to ongoing renovation work.

The results of the audit at Izaña can be summarised as follows:

All the instruments were housed in a provisional building nearby the old station. The whole inlet system was moved to the new place, and everything was installed very functional. The intercomparison of the ozone measurements consisted of multipoint runs between the EMPA transfer standard and the ozone instruments of the station. They showed good agreement between the transfer standard and the on-site instruments. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range up to 100 ppb (Figures 1 and 2).

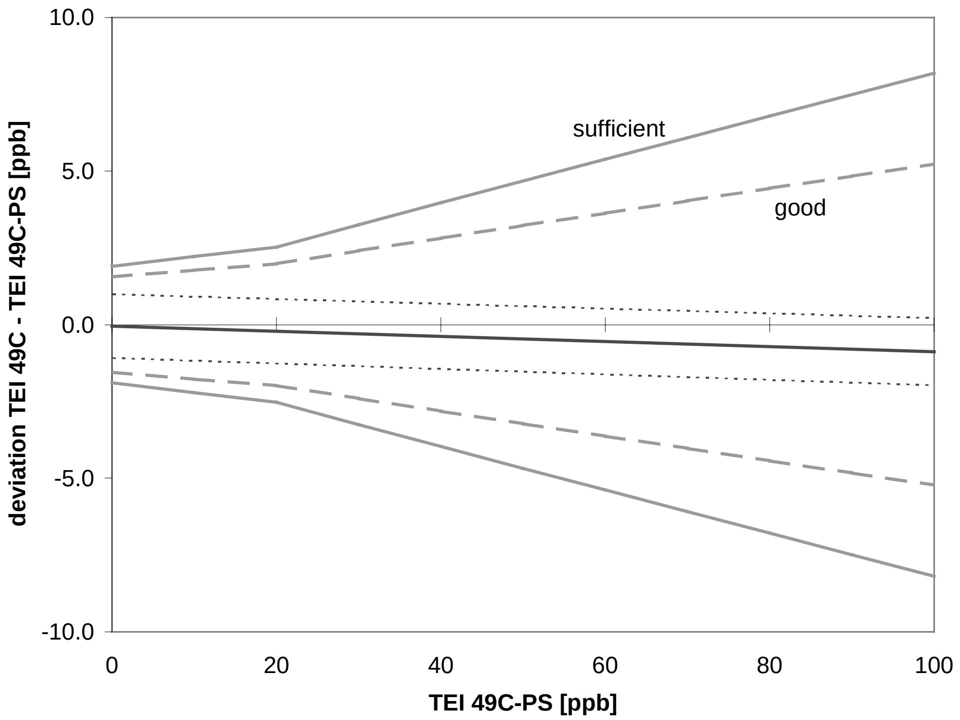

Figure 1: Intercomparison of the TEI 49C with the WCC transfer standard

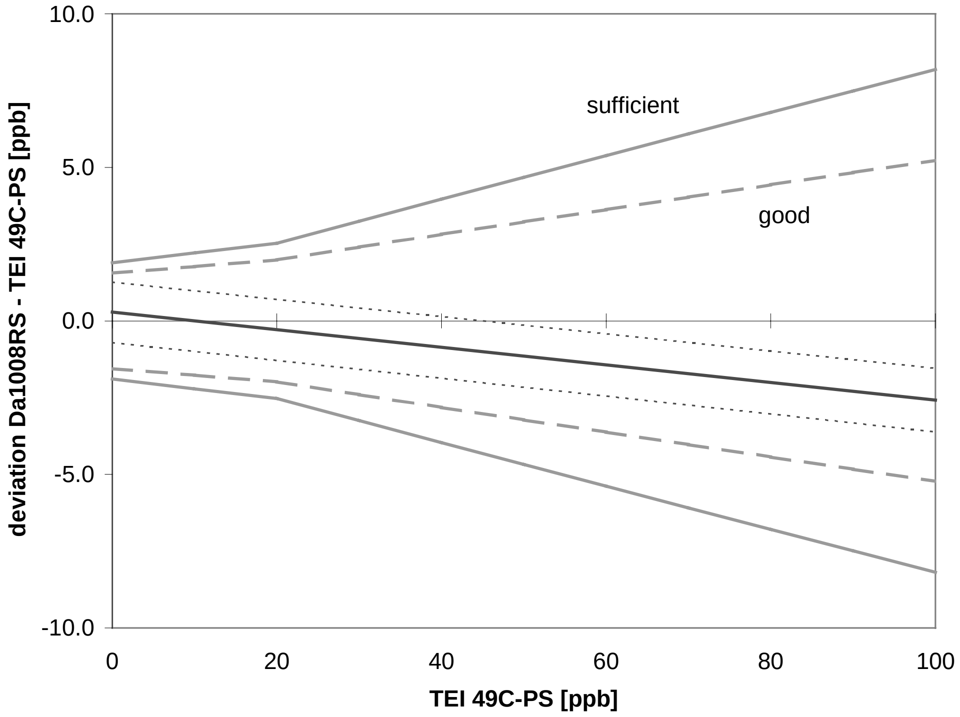

Figure 2: Intercomparison of the Dasibi 1008-RS (back-up instrument) with the WCC transfer standard

A first system audit for the carbon monoxide measurements at Izaña was performed by the WCC in 1998, and several recommendations were suggested for consideration. Shortly after the 1998 audit, all the suggested changes of the system were made, and the CO measurements became operational in late 1998. Due to the improvement of the system, a performance audit for carbon monoxide was conducted for the first time at Izaña during this audit.
The intercomparison of the carbon monoxide measurements consisted of multipoint analysis of the four transfer standards of the WCC (approx. 50, 100, 150 and 200 ppb CO) with the RGA-3 instrument at Izaña. The results of the CO intercomparison measurements (Figure 3) showed good agreement and deviate only up to 4% from the conventional true value with a certified uncertainty of the WCC transfer standards of approximately 1% until 200 ppb. The highest deviation of 4% was found for the 200 ppb transfer standard, whereas the other transfer standards showed a deviation of ≤ 2.3%. Regarding the relevant concentration range (61 and 149 ppb, 5-and 95-percentile respectively), this is an excellent result.

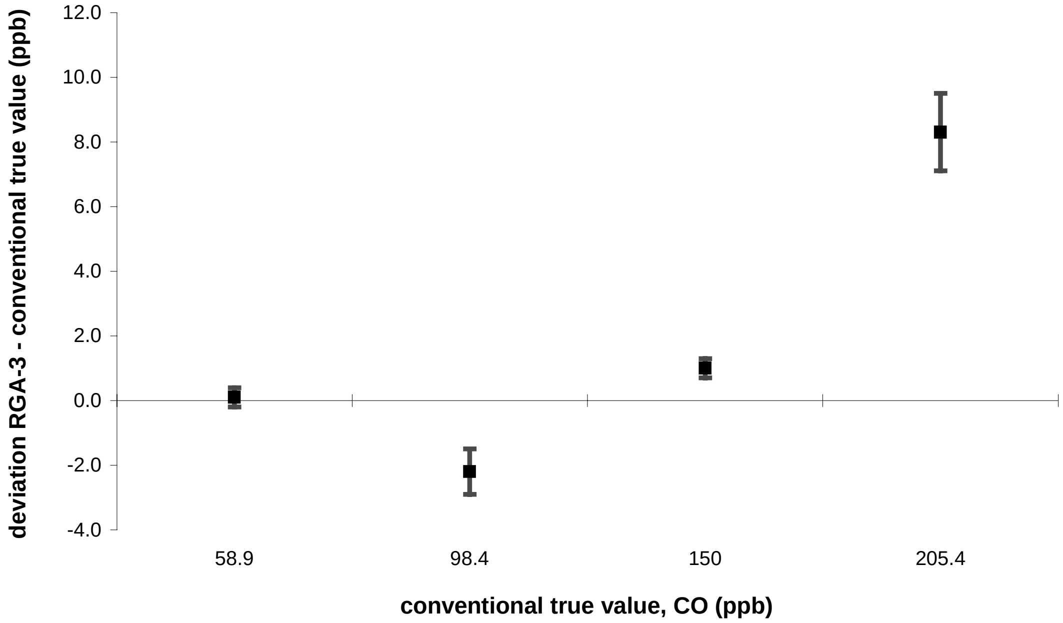

Figure 3: Intercomparison of the Izaña RGA-3 gas chromatograph with the transfer standards of the WCC (conventional true value)

Both the ozone and carbon monoxide measurements at Izaña were performed at a high level. The whole system from the air inlet to the instrumentation, including maintenance and data handling, is operated with great care. The staff involved in the measurements and the data evaluation is highly motivated and experienced. Therefore only minor recommendations were suggested by the WCC.

Punta del Hidalgo

In addition to the audit at Izaña, a system and performance audit for surface ozone was performed at the local measurement site Punta del Hidalgo at the north-west coast of Tenerife. The same staff as in Izaña is involved in the measurements. The instrument used for ozone measurements at Punta del Hidalgo is a Dasibi 1008-AH. The intercomparison of the ozone measurements consisted of multipoint runs between the EMPA transfer standard and the ozone instrument of the station. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range up to 100 ppb. The results of the intercomparison were also confirmed by previous calibration runs with the Dasibi 1008-AH performed by INM at Izaña.

Dübendorf, 21. November 2000 EMPA Dübendorf, WCC

Project engineer Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

In establishing a co-ordinated quality assurance programme for the WMO Global Atmosphere Watch programme, the air pollution and environmental technology section of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the WMO-GAW World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. At the beginning of 1996 our work started within the GAW programme with the parameter surface ozone. The activities were extended to carbon monoxide in the middle of 1997, and methane performance audits will be available by the end of the year 2000. The detailed goals and tasks of the WCC concerning surface ozone are described in the WMO-GAW report No. 104.

In agreement with the responsible persons in charge of O_3 and CO measurements at the Instituto National Meteorologia (INM), Tenerife, the third system and performance audit at the global GAW station Izaña was conducted. The station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters. With regard to the location in the Atlantic, in combination with its high altitude, it offers an excellent opportunity for monitoring of large scale distributed pollution in the free troposphere.

Additionally, a system and performance audit was performed at Punta del Hidalgo. Its location at the north-west shore of Tenerife with prevailing winds form the Atlantic ocean enables the observation of the of large scale distributed pollution in the marine boundary layer.

The scope of the audit, which took place from June 6 to 12, 2000, was confined to the surface ozone and carbon monoxide measurements. The entire process from the inlet system to the data processing and the quality assurance was gone through during the audit procedure. The ozone audit was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the ozone intercomparison have been developed by EMPA and are based on WMO-GAW Report No. 97 ("Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, June 1998, available on request from the authors at: EMPA, Section 134, Ueberlandstr. 129, CH-8600 Dübendorf, or downloadable from www.empa.ch/gaw).

In addition to the last audit in February 1998, the carbon monoxide measurement was audited since the instrumentation reached the state of routine operation, and the recommended changes from the last system audit are now implemented.

The present audit report is submitted to the station manager and the World Meteorological Organisation (WMO) in Geneva.

Previous audits at Izaña were performed by EMPA-WCC in February 1998 and in November 1996. System and performance audits at global GAW stations will be regularly conducted on mutual arrangement about every two years.

3. Global GAW Site Izaña

3.1. Site Characteristics

The station Izaña is located on the Island of Tenerife, Spain, (coordinates: 28°18' N, 16°30' W) roughly 300 km west of the African coast (Figures 4 to 6). The meteorological observatory is situated on a mountain platform at an altitude of 2367 m a.s.l., 15 km north-east of the volcano Teide (3718 m a.s.l.). 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 of 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 buildings of the measurement station are presently renovated, and all the instrumentation was moved to a provisional measurement site between April 10 and 14, 2000 (Figure 5) about 100 m south of the old location. All the instruments are installed inside the air conditioned building close to the air inlet. The inlet system was moved entirely from the former measurement site to the provisional building.

Over the past few years, the near environment of the site has not changed in a way that could have influenced the ozone measurements. However, there is currently some additional traffic (less than 10 vehicles per day) due to the construction work at the main building.

Figure 4: Picture of the station Izaña (view from the provisional station)

Figure 5: The provisional station (left) with the nearby military camp in the background

Figure 6: Inside the provisional station

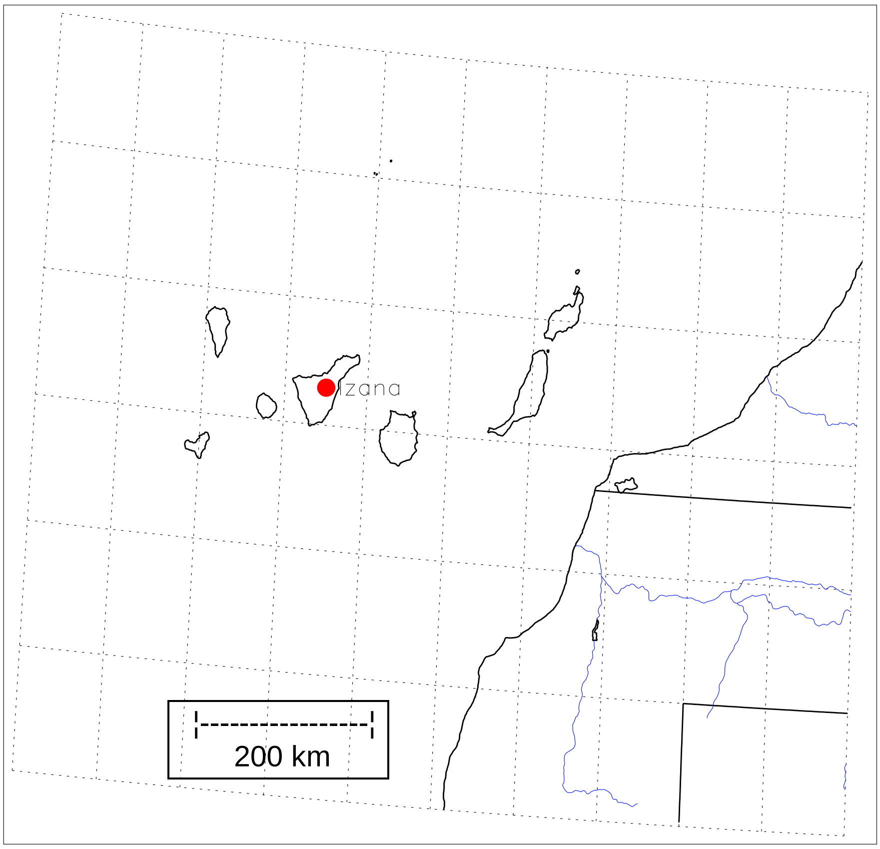

Figure 7: Map of the Canary Islands and African Continent

3.2. Operators

The meteorological observatory at Izaña (IZO) was set up in 1984 by the Instituto Nacional de Meteorologia (INM).

Dr Emilio Cuevas' team, who is in charge of the operation of the station at Izaña, consists of an interdisciplinary group of physicists, technicians and supporting staff. The structure of the station management at Izaña is shown in Table 1.

Table 1: Staff of the Izaña Atmospheric Observatory

Dr Emilio Cuevas, Director of Izaña Atmospheric Observatory (Physics PhD.), Head of the Ozone and UV Group
Operators and Specialists Mr Juanma Sancho, Ozone and UV Group, Responsible for the tropospheric ozone program (surface ozone and ozone profiles), (Physics graduate, PhD in course) Mr Alberto Redondas, Ozone and UV Group, Responsible for the stratospheric ozone and UV radiation program, (Physics graduate, PhD in course) Mr Sergio Afonso, Ozone and UV Group, Ozonesounding instrument specialist Mr Virgilio Carreño, Ozone and UV Group, PhD student, (Physics graduate) Mr Carlos Torres, Ozone and UV Group, PhD student, (Physics graduate) Mrs Dulce de la Cruz, Ozone and UV Group, PhD student, (Physics graduate) Dr Xavier Calbet, Head of the Aerosol and Radiation Group, (Physics PhD) Mrs Carmen Romero, Aerosol and Radiation Group, (Physics graduate, PhD in course) Mr Pedro Romero, Aerosol and Radiation Group, (Physics graduate) Mrs Pilar Ripodas, Head of the Carbon Cycle Group, (Physics graduate, PhD in course) Mr Ramon Ramos, Carbon Cycle Group, (Physics graduate) Mr Juanjo Bustos, Meteorological support, (Physics graduate) Mr Ramon Juega, Instrument specialist Mr Jaime Estevez, Instrument specialist Mr Victor Quintero, Instrument specialist Mr Carlos Marsal, Electronic Technician Mr Manuel Estevez, Maintenance Technician Mr Matthias Schneider, PhD student, operator of the FTIR instrument
Supporting staff Mrs Esther Calvo, Financial Section Chief Mrs Pilar Salamo, Secretary Mrs Concha Salamo, Secretary Mr Marcos Damas, Driver

3.3. Ozone Level at Izaña

The site characteristics and the relevant ozone concentration range can be well described by the frequency distribution. The frequency distribution of the hourly mean values from 1999 is shown in Figure 8. The relevant ozone concentrations range between 30 and 70 ppb according to the 5 and 95 percentile of the hourly mean values. Source of data: INM

3.4. Carbon Monoxide Level at Izaña

The relevant carbon monoxide concentration range can be well defined by the frequency distribution. In Figure 9, the frequency distribution of the hourly mean values from 10.12.1998 to 22.11.1999 is shown. The relevant CO concentrations were calculated, ranging between 61 and 149 ppb according the 5 and 95 percentile of the hourly mean values. Source of data: INM

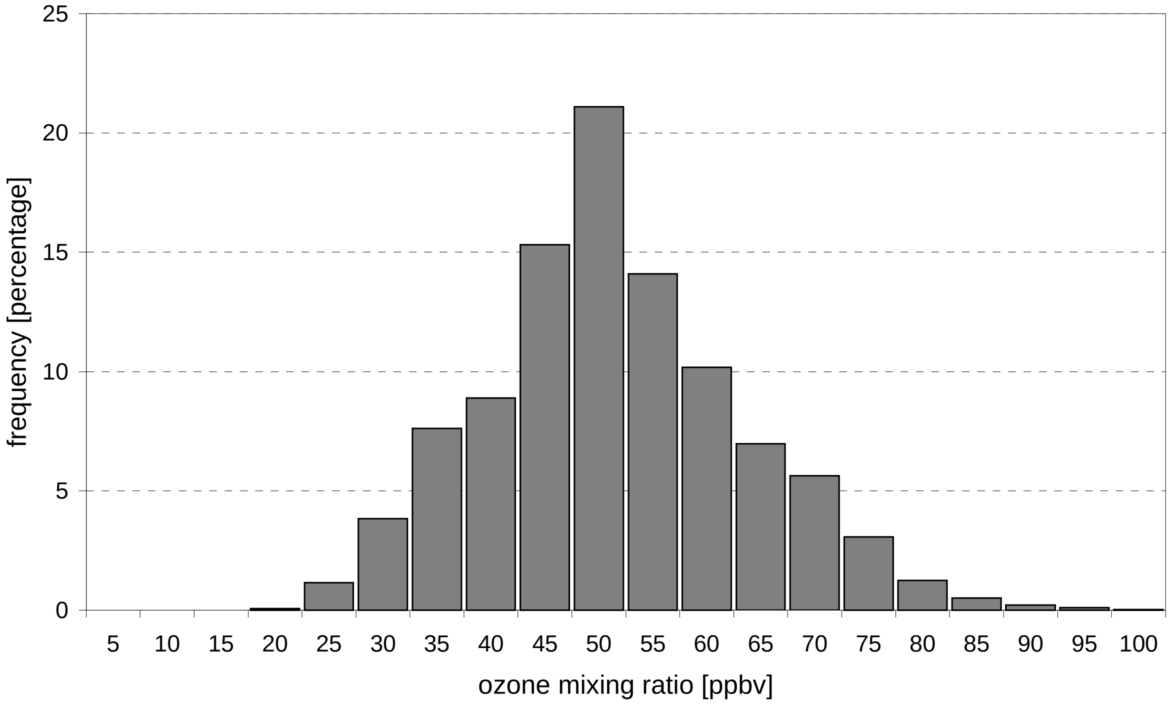

Figure 8: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Izaña of the year 1999. Availability of data: 93%.

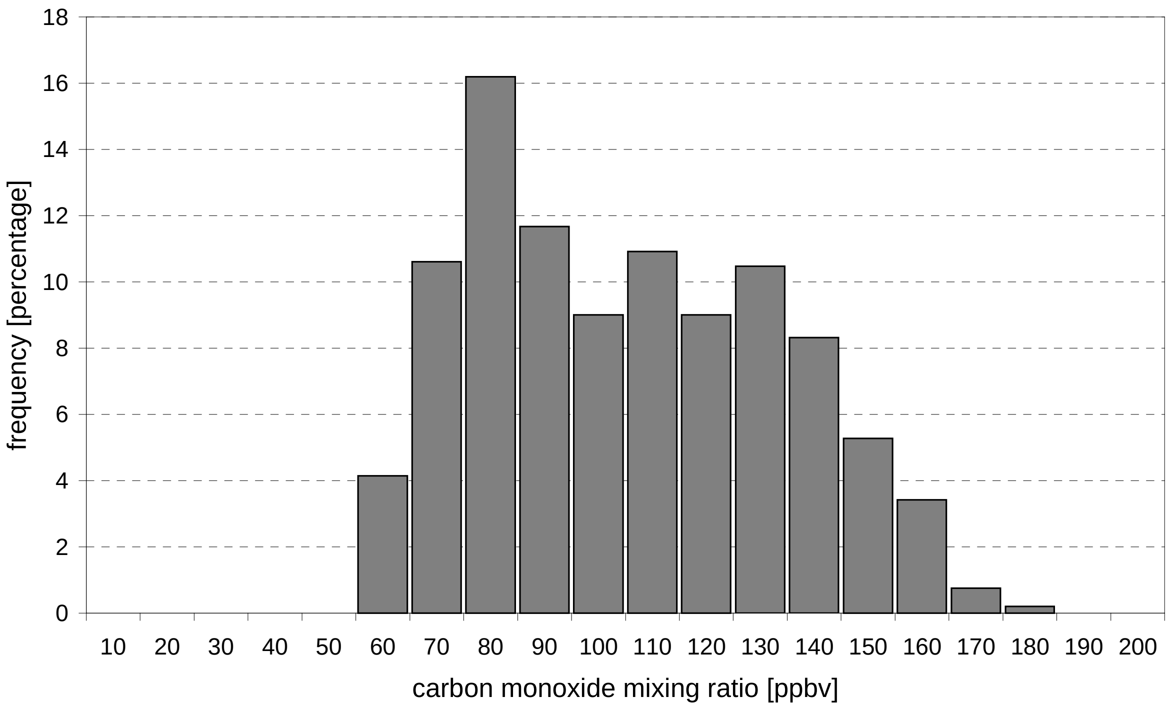

Figure 9: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at Izaña of the period 10.12.98 to 22.11.99. Availability of data: 70%.

4. Measurement Technique at Izaña

4.1. Surface Ozone

4.1.1. Air Inlet System

The air inlet system for the ozone measurements is mounted on the flat platform at the top of the provisional measurement station. The inlet part of the system on the flat roof is 2.5 m high and about 10 m above ground and consists of an inverse stainless steel bucket, stacked on a stainless steel tube (50 mm i.d., 4 m long), shielding the system from rain and snow. The sampling line is a combination of the 4 m long stainless steel tube leading directly through a hole in the side-wall near the ceiling of the station and a glass manifold indoors (50 mm i.d., 0.5 m long). It is continuously flushed at 1.5 m^3 per minute with ambient air. For the ozone measurements, a PFA teflon tube (4 mm i.d., 3 m long) branches off within the first 0.3 m from the glass manifold passing a teflon inlet filter (dust and particles) from where the air stream splits to the ozone analysers. The sample pumps of the analysers are being used to draw ambient air through these teflon tubes according to the instrument's specified internal flows. The total residence time of the ambient air through the inlet line to the instruments was calculated to be 2 seconds.

Since the last audit, the air inlet system has been only slightly modified. The major change is the lower height of the air intake of 10 m compared to 17 m at the old location.

Comment

The teflon tube and the rain protection at the inlet were clean and free of dust. The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. In investigations during the audit in 1996 no loss of ozone could be detected.

4.1.2. Instrumentation

The instruments are installed in an environmentally controlled room (between 20 to 25°C) in an instrument rack and are protected from direct sunlight.

The instrumentation used for measuring ozone at Izaña during the audit is shown in Table 2 (note the new basic instrument, backup is identical to the instrumentation of the audits in November 1996 and February 1998).

In April 1997, an ozone calibrator of the type TEI 49C-PS had been purchased (financed by WMO) for the Izaña Observatory and is used for regular calibration of the analysers on site as well as for conducting ozone audits within the SCO_3P Project and the GAW Programme in South America. This ozone calibrator was integrated into the inter-calibration procedure by EMPA and the results are shown in Appendix I.

The zero air unit consists of an activated charcoal cartridge (approx. 1 litre volume) and a particulate filter. It is used to determine the analyser's daily zero. This daily zero check at 16:00 GMT is automatically triggered by the data acquisition software. The data of twelve one minute means is stored in a separate file. The performance of daily span checks had been stopped since the station has its own photometer.

Table 2: Ozone analysers at Izaña

Type	TEI 49C #62900-337	Dasibi 1008-RS #5797
Method	UV absorption	UV absorption
Usage	basic instrument since 5.10.99	backup instrument
at Izaña	Since 1. February 1999	for several years
Range	0-200 ppb	0-1000 ppb (0-1 V)
Analog output	0-10 V	0-100 mV amplified to 0-10 V
Electronic offset	- 4.1 ppb	5 units (corresponding ppb)
Electronic coefficient	1.006	308 (absorption coeff.)

Comment

The measurement technique used is the UV-method which is the preferred method in the GAW programme.

The operation of two ozone analysers simultaneously at Izaña considerably increases data quality. A well maintained ozone analyser (TEI 49C) serves as the basic instrument.

4.1.3. Operation and Maintenance

Preventive maintenance of the instruments incorporates adjustment of the pressure transducers and cleaning of the instruments glass cell, and is performed on a case by case basis (every 2-6 month). The instruments are protected with a dust inlet filter. The filter is changed every one to three months, depending on the season or Sahara dust events.

Automatic zero checks are performed as a daily check of the ozone analysers at 16:00 GMT. This data is stored in a separate file and is used later for data reprocessing and correcting the ambient air measurement values. The station calibrator is used weekly for a manual span check (90 ppb). Every three weeks, the analysers are checked at three ozone levels (10, 45, 90 ppb for 10 min). However, this two tests are not considered as calibrations, and further actions are only taken if a considerable disagreement is noticed. Three times a year, a multipoint calibration using the TEI 49C-PS #56085-306 is performed and the applied ozone levels are 0 / 10 / 30 / 45 / 60 / 90 ppb. The photometer was certified with the NIST Standard Reference Photometer #12 of the AES in Canada in July 1996 and was inter-compared with the WCC transfer standard in February 1998 (TEI 49C-PS #54509-300) and during this audit (TEI 49C-PS #62026-333).

Comment

The appearance of the provisional station was very clean. Although the station was only in operation since one month, everything was already functionally arranged.

The maintenance is carried out on a case by case basis. This has its advantage over following a strict schedule due to the fact that there is no unnecessary interruption of the instruments. Since the required experience for such a practice is present we do not recommend any change to this procedure, even though it differs from the description in the SOP of GAW report No. 97. With the frequent use of the ozone calibrator for span checks and calibrations and running two analysers in parallel, a very well maintenance regime has been established.

4.1.4. Data Handling

The person who is responsible for the instrument operation is also in charge of data reviewing and processing.

The data acquisition facility is installed at the site next to the ozone analysers. It consists of an ADC circuit board and a data acquisition software. About once a month the data is reprocessed and recalculated. Two ozone data files are generated. One file contains the ten-minute mean values and the other one the daily zero readings (12 one-minute means) from the zero checks at 16:00 GMT. The invalid values (according to the logbook) or suspect data from each data file are then manually removed from the dataset. The validated data is averaged to the appropriate mean values; hourly means for the ozone data and 12 one-minute means for the zero readings. Suspect data is defined as hourly mean values with a standard deviation higher than 8 ppb. Based on the long term experience of the operators, such high standard deviation is generally due to instrument malfunction and does not reflect true ambient air concentrations. However, for cases of sharp changes in the 10 minute values, or extraordinarily high or low ozone concentrations the data is further investigated for plausibility. High ozone mixing ratios can usually be explained by stratospheric intrusions, while low ozone levels very often correspond with Sahara dust events or fogy conditions. Back trajectories are used for the investigation of such events. The final results are achieved by subtracting the daily zero mean value from the hourly mean values, using the two cleared data files. Diagrams for visual control are plotted from the final data.

From the final data, the daily mean and the highest hourly mean of each day are extracted and saved in a defined data format. At present surface ozone data is not reported to the database of the World Ozone Data Centre (WODC) at AES in Canada and also not yet submitted to the new World Data Centre for Surface Ozone (WDCSO) at NILU.

Comment

The procedure of data treatment for each instrument is well organised and clearly arranged.

4.1.5. Documentation

Within the GAW guidelines for documentation, transparency as well as access to the station documents is required. During the audit the documentation was reviewed for availability and usefulness. The station logbook (bound, copy with carbon paper) is found at the site or at the institute in Santa Cruz where it is needed for the purpose of data review. It contained all necessary information listed chronologically. A monitor logbook is attached to the instruments on site. It contains specific facts concerning the instrument, e.g. calibrations or failures. The instrument manuals were available at the site. A checklist for primary function controls, e.g. actual value and zero check results, is filled in daily by the observer in charge.

Comment

The documentation has improved considerably since the first audit in 1996, and all the necessary information was available.

4.1.6. Competence

All persons associated directly or indirectly with the operation of the station are highly motivated and experts in their fields. Due to long-term experience and adequate education, the operators were very familiar with the techniques and problems connected with ozone measurements.

4.2. Carbon Monoxide

4.2.1. Air Inlet System for CO

The same air inlet as for the ozone measurements is used for carbon monoxide (see section 4.1.1). Additionally, a cryo trap (-55 to –65°C) is used to freeze out water. From the manifold to the instrument a total length of 8 m teflon tubing (4 mm i.d.) is used with a flow rate of 700 ml min^{-1}. The total residence time is less than 10 s.

Comments

The used inlet system (same as for O_3) is adequate for analysing CO concerning construction materials as well as residence time.

4.2.2. CO Analyser at Izaña

A RGA-3 GC-system is used as an in situ CO analyser. It is installed in the environmentally controlled provisional measurement station. Instrumental details are listed in Table 3.

Table 3: Field CO analyser at Izaña

instrument	Trace Analytical GC
model, S/N	RGA3, S/N 070188-006
at Izaña	since 1998
configuration (model)	E-001 (Trace Analytical terminology) since December 1998
method	GC / HgO Detector
interval of sample injection	10 min (alternatingly working standard and ambient air)
loop	1 ml
columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5A 60/80
carrier gas	synthetic air – Sofnocat - Mole sieve - GC, 20 ml/min
operating temperatures	Detector: 265 °C, Column: 105 °C
analog output	0-1 V
calibration interval	every 20 min
instrument's specials	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equalise pressure

Comments

The gas chromatography technique followed by mercury reduction detection, as operated at Izaña, is a widely-used method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision (WMO-GAW report No. 98).

The RGA-3 analyser at the site was in a good condition.

4.2.3. Gas Standards

The following gas standard (Table 4) are used at the site for the verification the measurements. The working standard is calibrated against the CMDL scale every two weeks.

Table 4: Station CO cylinders

	Gas cylinders	filling	Conc.
1	Working standard filled with ambient air at Izaña. Two cylinders are filled every month during nighttime and are used as working tanks about one year later.	real air (dried)	164.6 ppb
2	CMDL CA03037	natural dry air	64.6 ppb
3	CMDL CA03083	natural dry air	162.7 ppb
4	CMDL CA02635	natural dry air	73.7 ppb
5	CMDL CC115003	natural dry air	146.0 ppb

Comments

The alternating calibration of the system with the working standard validates the measurements. Since the working tank contains ambient air of Izaña which was sampled about one year earlier, the concentration of the analysed ambient air and the working tank are comparable. This system provides a high level of quality assurance.

4.2.4. Operation and Maintenance, CO

Most of the maintenance works for the RGA-3 CO analyser are performed on a case by case basis, i.e. cleaning the optical filters every few month, exchanging the lamp (if test point is below 90 mV) and reset the electronic baseline.

The station observer inspects daily the CO measurements for a quick check of general operation of the analysers. This includes checking of the test points 1 and 2 of the RGA-3 and examination of chromatograms. As preventative maintenance, the Sofnocat® cartridge of the on-site zero air supply is replaced semi-annually to annually (the Sofnocat® is regenerated). Furthermore, the Hg-scrubber is replaced every six months.

The system is calibrated with a CO working standard (ambient air form Izaña, concentration varies with season) which is injected alternately with ambient air. This working tank is calibrated to the CMDL scale about every two weeks. The zero air is checked about once a year or on demand.

Comments

The appearance of the station is clean and functional.

Because of the operators experience with gas chromatography some of the maintenance is carried out according to a schedule and some on a case by case basis. Daily check of the analyser's test points and examining chromatograms gives the person in charge enough information about the state of the instrument.

4.2.5. Data Handling

The data acquisition facility consists of a Perkin Elmer Integrator 900 and Perkin Elmer Software. An additional software developed at INM is used to trigger the solenoid valves and the integrator. All the raw data and chromatograms are stored and transferred occasionally to INM for final data evaluation. Peak integration is carried out both for area and height but peak height. Data evaluation has been carried out using peak area, but in future peak height will be used for the final dataset.

The responsibility of data reviewing and data management is split between the station operator and the data reviewer at INM. In a first step, the station operator examines the chromatograms. Comments and notes are made in a logbook. These comments contain e.g. calibration notes or remarks on events that might influence the data. To get the final results, the raw data (every single chromatogram) is recalculated by applying the appropriate calibration factor. This parameter is evaluated from the pre- and post-analysis of the working standard.

To date none of the data has been reported to the GAW WDC for greenhouse gases in Tokyo.

Comment

Transparency is assured with the log files, which are carefully written and up-to-date. The review process of the data set is regarded as reliable.

The available data series should be submitted to the WDC for greenhouse gases as soon as possible.

4.2.6. Documentation

Within the GAW guidelines for documentation, transparency and access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness.

At the station a logbook for the daily performed checks was available. These daily observations include the temperature of the cooling trap, room temperature, temperatures of the column and the detector, checks of the valves and the tank pressure of the carrier gas and the working standard. The station observer also records additional information that might be of importance for data interpretation (mainly meteorological observations).

The instrument manuals as well as a maintenance logbook were available at the site. The instrument logbook consisted of single forms kept in a file. The information reported (malfunction, changes of the instrument, repair) was kept up to date.

Comments

The log files were kept up-to-date and were clearly structured. All the necessary information was available at the site.

5. Intercomparison of Ozone Instruments (Izaña)

5.1. Experimental Procedure

The WCC transfer standard TEI 49C PS (details see Appendix II) was hooked up to power at the site for warming up over night (in deviation from the GAW Report No. 97 which recommends only one hour of warm-up). During this stabilisation time the standard and the PFA tubing connections to the instruments were conditioned with 200 ppb ozone for 10 minutes. During the next day, two comparison runs between the field instruments (analysers) and the WCC transfer standard were performed. In the meantime the inlet system and the station documentation were inspected. Table 5 shows the experimental details and Figure 13 the experimental set up of the audit. In general, no modifications of the ozone analysers which could influence the measurements were made for the intercomparisons.

The EMPA acquisition system, which was used for the audit, consisted of a 16-channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instruments and of the transfer standard the data was collected by both data acquisition systems (EMPA and INM) and showed no discrepancy. For data interpretation the EMPA data was used. Finally, the observed results were discussed in an informal review with the person involved.

The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in the Appendix III.

Table 5: Experimental details

audit team:	C. Zellweger, A. Herzog
reference:	EMPA: TEI 49C-PS #62026-333 transfer standard
field instruments:	TEI 49C #62900-337 Dasibi 1008-RS #5797
ozone source:	EMPA: TEI 49C-PS, internal generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	EMPA: 16-channel ADC circuit board, software
pressure transducers reading:	TEI 49C-PS (EMPA): 770 hPa TEI 49C: 770 hPa (no adjustment necessary) Dasibi 1008-RS: 770 hPa (no adj. necessary)
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	10 / 30 / 45 / 60 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	2 x on June 7, 2000
connection between instruments:	about 1.5 meter of 1/4" PFA tubing

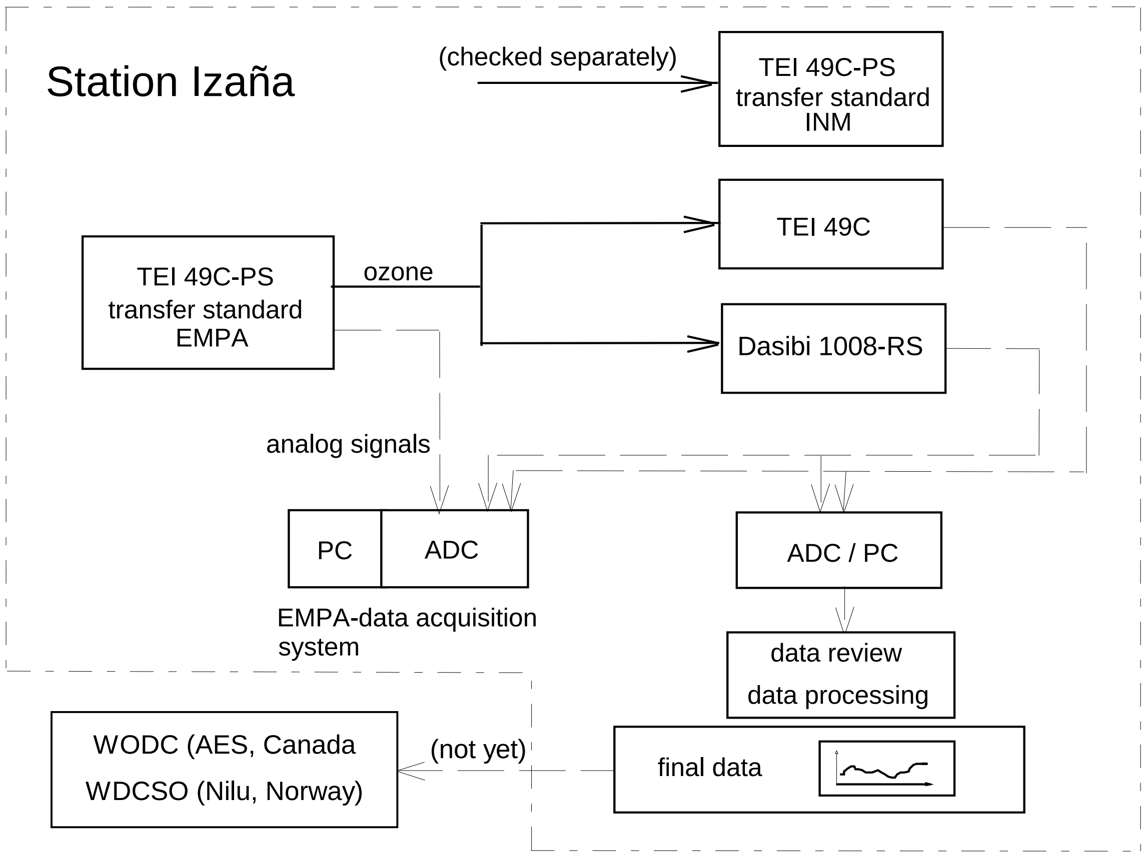

Figure 10: Experimental set up for the ozone intercomparison

5.2. Results

The results comprise the two runs of the intercomparison between the two field instruments TEI 49C and Dasibi 1008-RS and the WCC transfer standard TEI 49C-PS, carried out on June 7, 2000.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Tables 6 and 7. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 8 to 11 show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard. The results of the two runs are then summarised to the mean regression equation and presented in a graph with the assessment criteria for GAW field instruments (Figures 12 and 13).

The data used for the evaluation were recorded by the EMPA data acquisition system. This raw data was treated according the usual station method. Corresponding to this procedure the daily zero offset was determined by the zero check at 16:00 GMT. The individual resulting offsets were subtracted from the data of the intercomparison (see 4.4.). The offsets were: TEI 49C: 4.2 ppb; Dasibi 1008-RS: 4.6 ppb. In Tables 5 and 6 the recalculated data are listed.

Table 6: 1. Intercomparison of ozone field instruments

No.	transfer standard		TEI 49C				Dasibi 1008-RS			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.4	0.14	1.5	0.22	1.1		1.8	1.13	1.4	
2	44.9	0.11	45.1	0.27	0.2	0.4%	44.5	1.01	-0.4	-0.9%
3	90.1	0.13	89.8	0.35	-0.2	-0.3%	88.0	1.29	-2.0	-2.3%
4	10.1	0.17	10.2	0.44	0.1	0.8%	10.3	1.36	0.2	2.1%
5	60.1	0.16	59.5	0.33	-0.6	-1.1%	58.3	1.39	-1.8	-3.0%
6	29.9	0.19	29.6	0.43	-0.3	-1.0%	29.2	1.28	-0.7	-2.2%
7	0.2	0.12	0.2	0.27	-0.1		0.2	1.26	-0.1	

Table 7: 2. Intercomparison of ozone field instruments

No.	transfer standard		TEI 49C				Dasibi 1008-RS			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.4	0.15	0.1	0.27	-0.3		-0.2	1.00	-0.1	
2	59.9	0.15	58.9	0.21	-1.0	-1.7%	57.8	0.94	-1.5	-2.5%
3	10.0	0.14	9.5	0.19	-0.5	-4.5%	9.4	1.17	-0.1	-0.7%
4	90.0	0.18	89.0	0.21	-1.0	-1.1%	87.3	1.03	-2.3	-2.6%
5	29.9	0.11	29.4	0.28	-0.5	-1.8%	28.4	1.16	-1.2	-4.1%
6	45.0	0.13	44.1	0.27	-0.9	-1.9%	43.5	1.39	-1.1	-2.4%
7	0.4	0.14	-0.2	0.29	-0.6		-0.2	1.18	0.1	

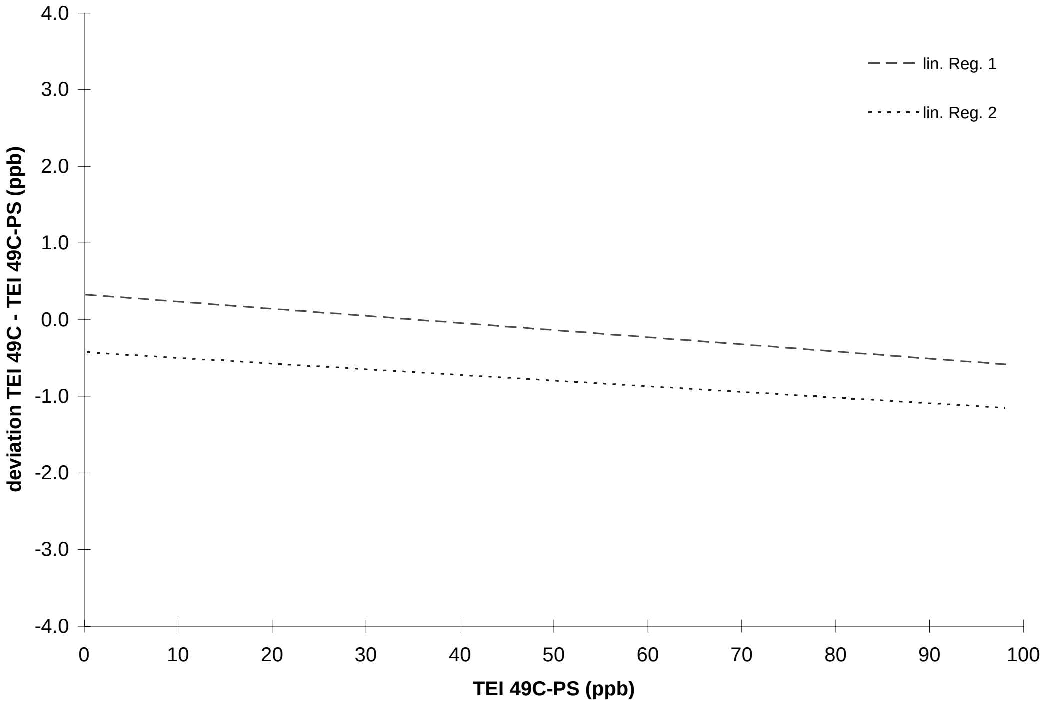

Figure 11: Individual linear regressions of intercomparisons 1 and 2, TEI 49C

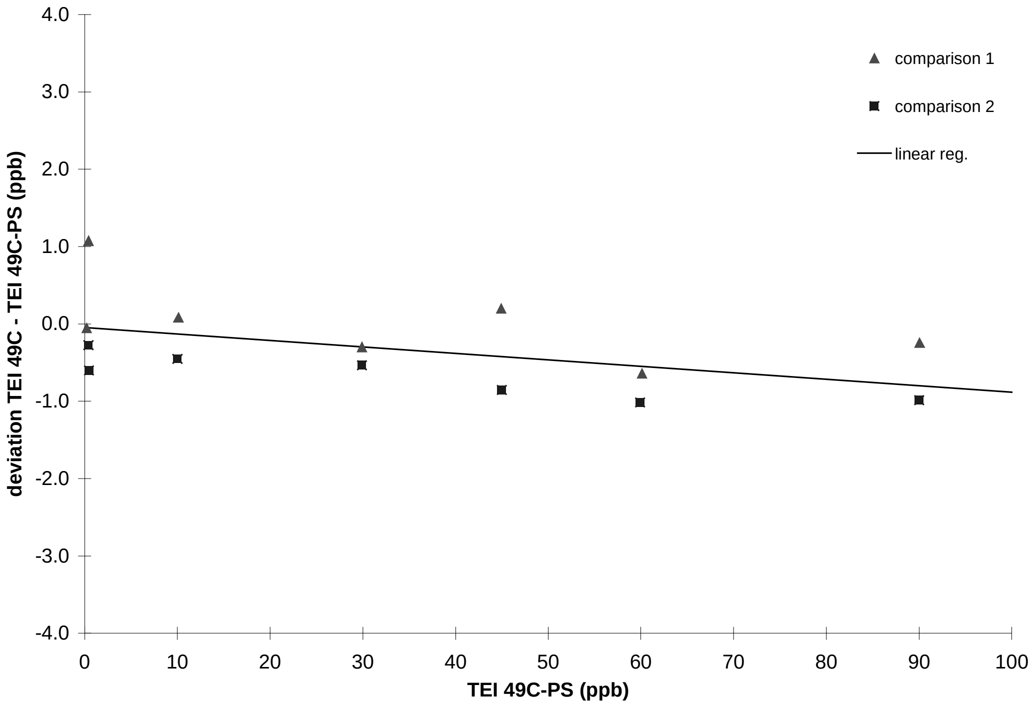

Figure 12: Mean linear regression of intercomparisons 1 and 2, TEI 49C

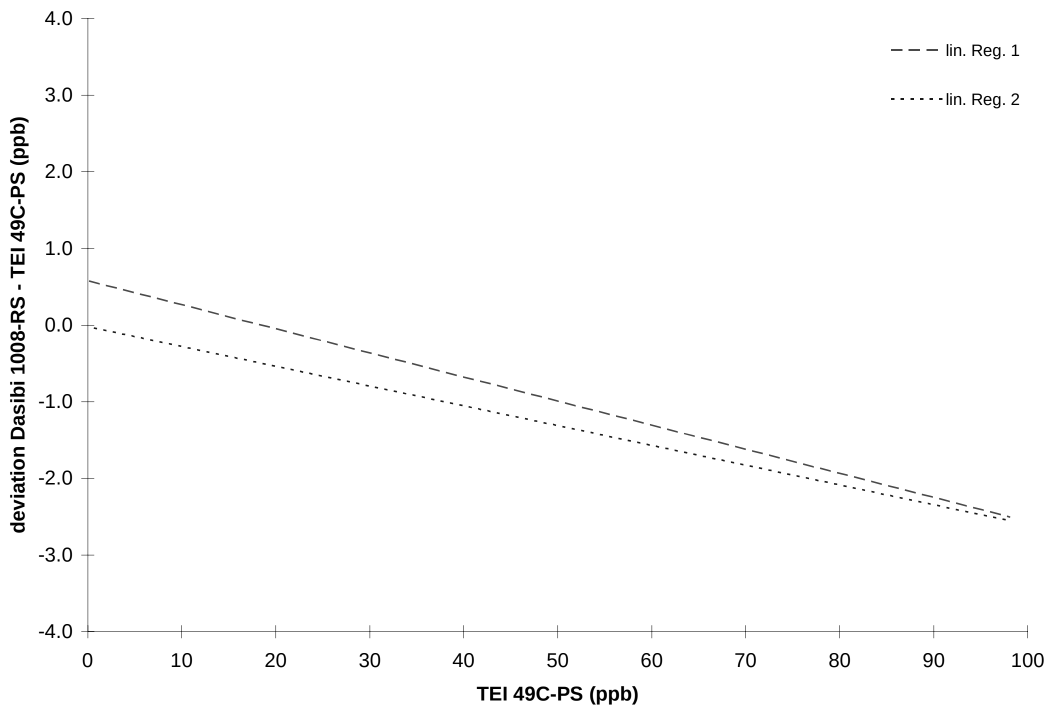

Figure 13: Individual linear regressions of intercomparisons 1 and 2, Dasibi 1008-RS

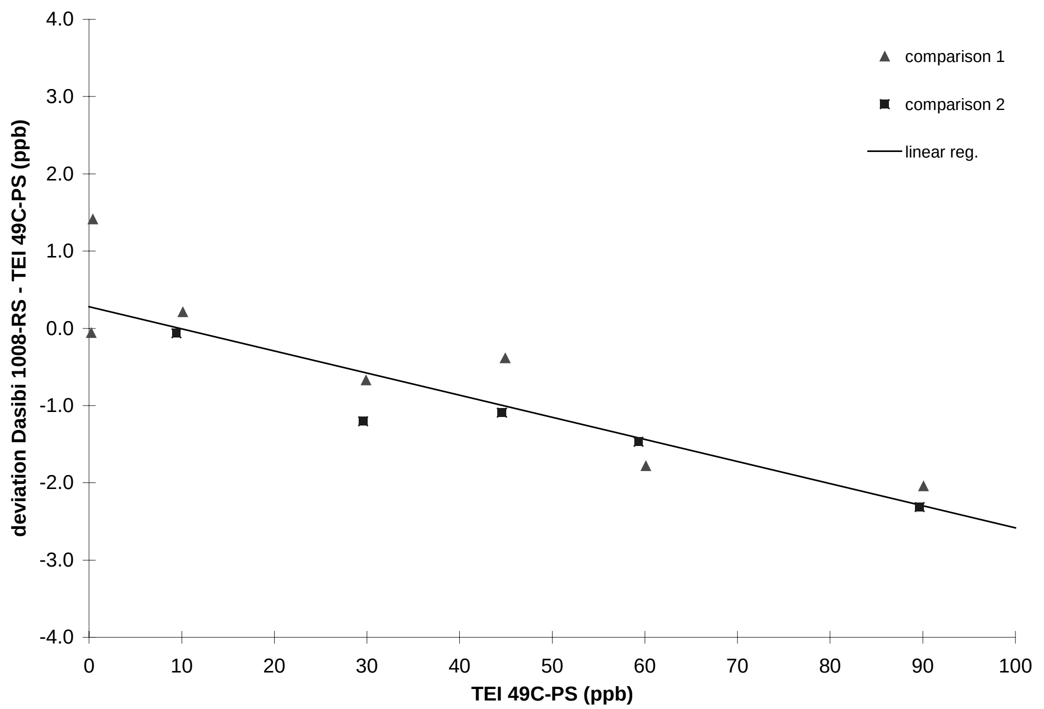

Figure 14: Mean linear regression of intercomparisons 1 and 2, Dasibi 1008-RS

From the intercomparisons of the TEI 49C #62900-337 and the Dasibi 1008-RS #5797 field instruments with the TEI 49C-PS transfer standard, from EMPA, the resulting linear regression (for the range of 0-100 ppb ozone) are:

TEI 49C:

TEI 49C = 0.992 x TEI 49C-PS - 0.05 ppb

TEI 49C = O_3 mixing ratio in ppb, determined for TEI 49C #62900-337

TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #62026-333

Standard deviation of:	- slope s_m	0.0043	(f = 2) f=degree of freedom
	- offset S_b in ppb	0.20	(f = 2)
	- residuals in ppb	0.37	(f = 12)

Dasibi 1008-RS:

Dasibi 1008-RS = 0.971 x TEI 49C-PS + 0.28 ppb

Dasibi 1008-RS = O_3 mixing ratio in ppb, determined for Dasibi 1008-RS #5797

TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #62026-333

Standard deviation of:	- slope s_m	0.0040	(f = 2) f=degree of freedom
	- offset S_b in ppb	0.18	(f = 2)
	- residuals in ppb	0.44	(f = 12)

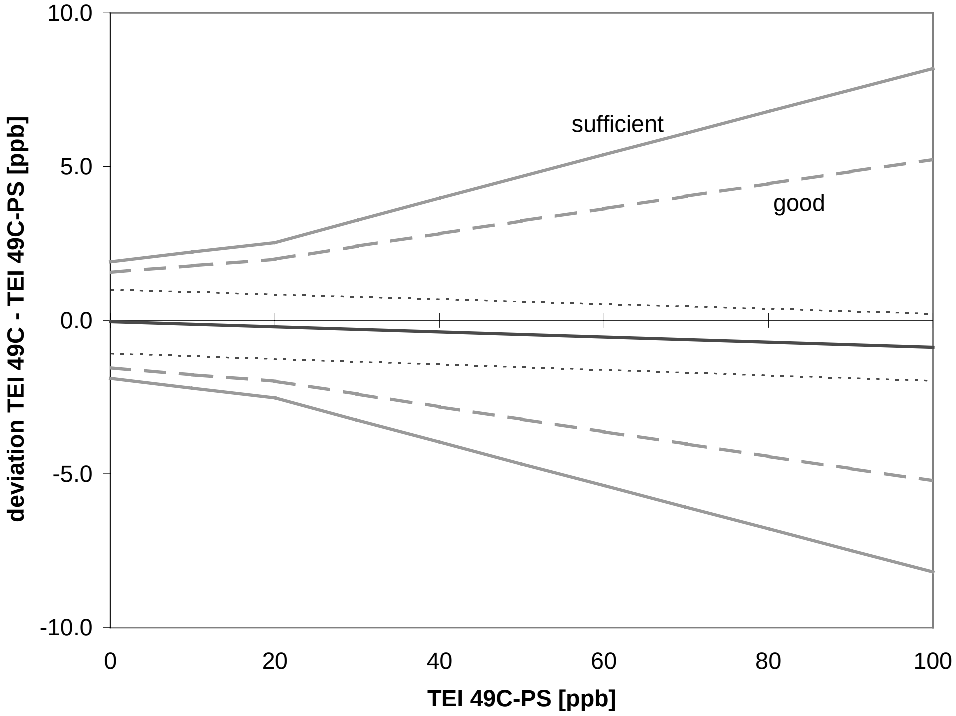

Figure 15: Intercomparison of instrument TEI 49C

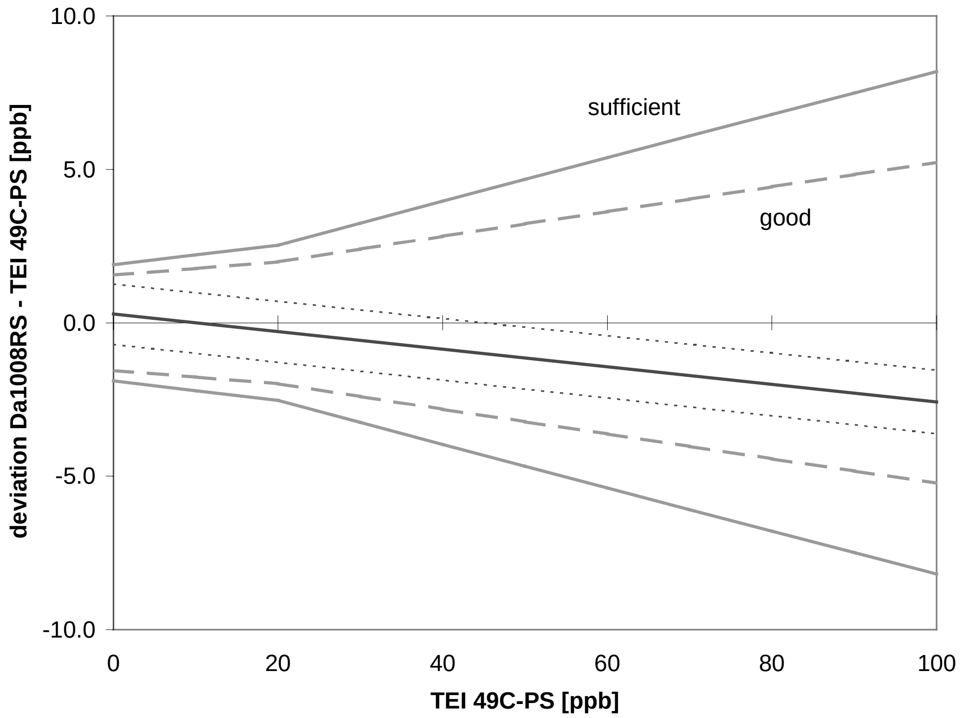

Figure 16: Intercomparison of instrument Dasibi 1008-RS

Comment

The ozone concentration observed at Izaña (1999) usually ranged between 30 and 70 ppb (5- and 95- percentile of hourly mean values).

The basic field instrument, TEI 49C, clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (see Figure 15). However, the deviation among the two intercomparisons was rather large for a TEI 49C. The reason for this could not be evaluated during the audit, but the signal of the EMPA data acquisition was not completely stable during the intercomparison. An influence of the nearby antenna of the military camp on the data acquisition can not be excluded.

The linear regression analysis from the intercomparisons in 1996 and 1998 and during this audit are very similar. In 1998, the stability of the Dasibi 1008-RS backup instrument has declined compared to 1998. Since then the instrument remained stable and fulfils the assessment criteria as "good".

It was noted during the intercomparison measurement that the zero air supply of the WCC transfer standard was not working properly when indoor air was used. This is also the reason that only two intercomparison runs were performed. Using indoor air for the zero air supply resulted in a offset of about 6 ppb.

Recommendation

All the ozone instruments at Izaña fulfilled the assessment criteria as "good" and are in a good condition. No further action is necessary for the ozone measurements. The rather large deviation between the intercomparisons is probably due to the poor stability of the EMPA data acquisition during the audit. However, it should be considered to use ambient air for the zero air supply during calibration runs. This can easily be achieved by connecting the zero air supply to the inlet system.

6. Intercomparison of in situ Carbon Monoxide Analyser

The carbon monoxide analysis was for the first time audited during February 1998 by the WCC. However, the system had not yet reached the state of routine operation at that time, and several recommendations were suggested for consideration by the WCC. Table 8 summarises the recommendation of the 1998 audit and the actual state of the measurement system.

Table 8: Summary of the recommendation of the 1998 audit and current state

Problems during the 1998 audit	State of the system in 1998	Recommendations of the 1998 audit	State of the system in June 2000
• cooling trap for ambient air:	none	pre-treatment of ambient air with a cooling trap (-55°C)	cooling trap (-55 to -65°C) for ambient air in use
• noisy signal	old HgO-bed	replace HgO-bed (check of linearity)	replaced, noise to signal ratio good
• column	one column system: mole sieve 13X 60/80	two column system: unibeads 1S 60/80 and mole sieve 5A 60/80	two column system operational since December 1998
• data acquisition	a basic software which does not have the possibility to reintegrate peaks	replace the actual software with a more sophisticated integration system	Perkin Elmer software used, reintegration of the peaks is possible
• calibration	procedure not fixed yet	hourly calibration with a working tank, working tank compared to CMDL cylinders	working tank calibrated against CMDL standards, automated calibration
• flow schematic	specific application S-001, according the "RGA-3 operating manual"	specific application E-001, according the "RGA-3 operating manual" (one loop, two columns)	application E-001 used
• documents	laboratory journal	additional instrument logbook	instrument logbook available at the site

It can be seen from Table 8 that all the suggested recommendations of the 1998 audit were done by the station operators, and the system has now reached the state of routine operation. Therefore, the whole audit procedure including intercomparison measurements with the WCC transfer standards was done during this audit.

6.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CO measurements by QA/SAC until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97), was adapted for CO accordingly.

The four transfer standards of the WCC (approx. 50, 100, 150 and 200 ppb CO) were stored in the same room as the CO measurement system to equilibrate for two days. The transfer standards were calibrated against CMDL laboratory standards (CA03209, CA02803, CA03295, CA02859) at EMPA. Figure 17 shows the connection of the transfer standards to the analyser at the station. Before the intercomparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected and analysed 5 times on June 8. The automated analysis procedure with an injection every 10 minutes was performed in the sequence station working standard – WCC transfer standard. No modifications of the RGA-3 carbon monoxide analyser were made for the intercomparison. The data was acquired by the station software, and the data (mean values and standard deviations) was reprocessed by the station operator and submitted to the WCC.

Additionally, the zero air supply (synthetic air / Sofnocat / Mol sieve) was tested after the audit by the station operator. No carbon monoxide could be detected.

The experimental details are summarised in Table 9.

Table 9: Experimental details of the carbon monoxide intercomparison

audit team, WCC	C. Zellweger, A. Herzog
reference:	WCC Transfer standards (ppb): FAO1467; FAO1469; FF30491, FF31496
field instrument:	RGA-3 #070188-009
zero air supply:	station: synthetic air – Sofnocat – Molecular sieve
data acquisition system:	Perkin Elmer chromatography software
number of concentrations:	4 + zero air of station
approx. concentration levels:	50 /100 / 150 / 200 ppb
number of injection per concentration:	5
Sequence	working standard – WCC transfer standard

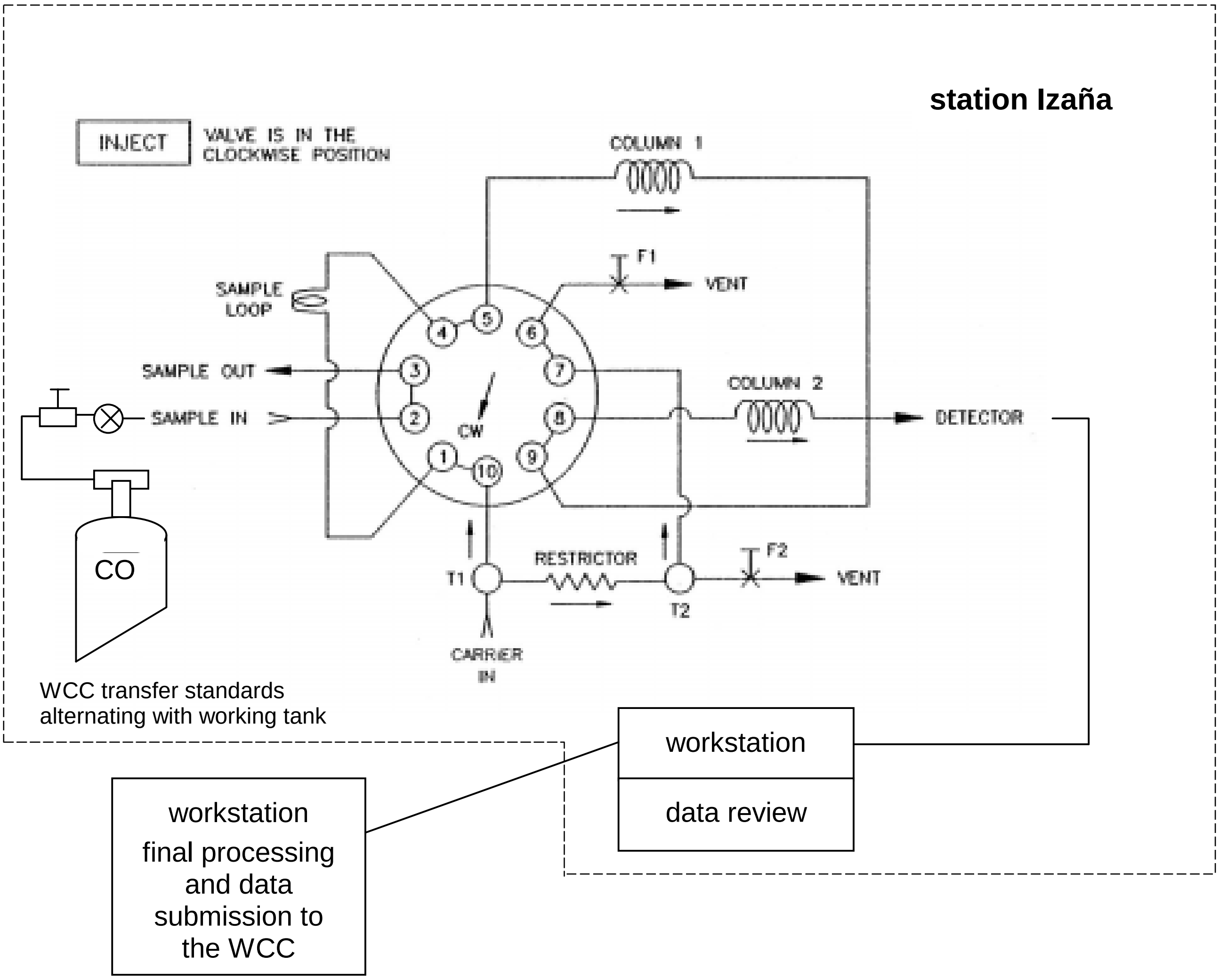

Figure 17: Experimental set up for the carbon monoxide intercomparison

6.2. Results

The results of the intercomparison between the RGA-3 field instrument and the four WCC transfer standards are shown in Table 10. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figures 15 and 16 show the results of the linear regression analysis of the field instrument compared to the WCC transfer standards. The data from the RGA-3 field instrument were submitted to the WCC by the station operator and are based on calibration of the instrument against the CMDL standards available at Izaña.

Table 10: Intercomparison measurement at Izaña for CO

No.	WCC standard	RGA-3 #070188-009 (Peak Height)				
	conc.	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	58.9 ± 1.5	59.0	0.3	5	0.1	0.2
2	98.4 ± 1.0	96.2	0.7	5	-2.2	-2.3
3	150.0 ± 1.5	151.0	0.3	5	1.0	0.7
4	205.4 ± 2.0	213.7	1.2	5	8.3	4.0

The summary of the CO comparisons (for the CO range 50 - 210 ppb) of the RGA-3 CO analyser with the WCC transfer standards (CMDL cylinders) is the following linear regression equation:

$$\text{RGA-3} = 1.059 \times \text{CMDL scale} - 5.8 \text{ ppb}$$

RGA-3 = CO mixing ratio in ppb, determined for RGA-3 #070188-009
CMDL scale = CO mixing ratio in ppb from the four CMDL transfer standards of the WCC

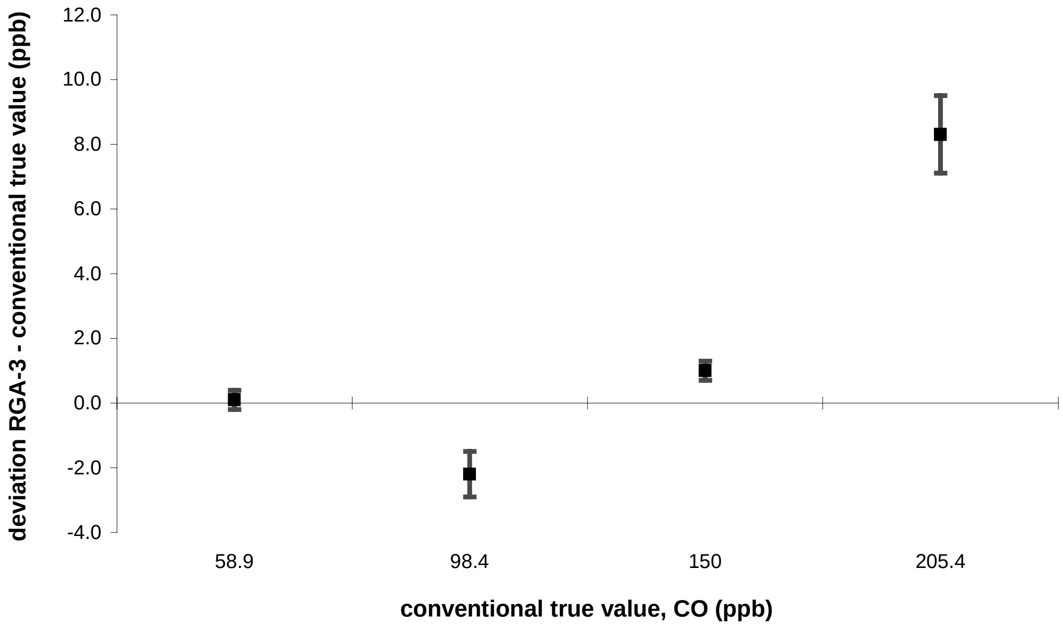

Figure 18: Deviations (ppb) between RGA-3 and CMDL transfer standards (conventional true value)

Figure 18 shows the absolute differences (ppb) between RGA-3 and the WCC transfer standards (conventional true value). The red error bars represent the standard deviation of five injections of the same cylinder. The relative deviation between the RGA-3 and the WCC transfer standards is shown in Figure 19.

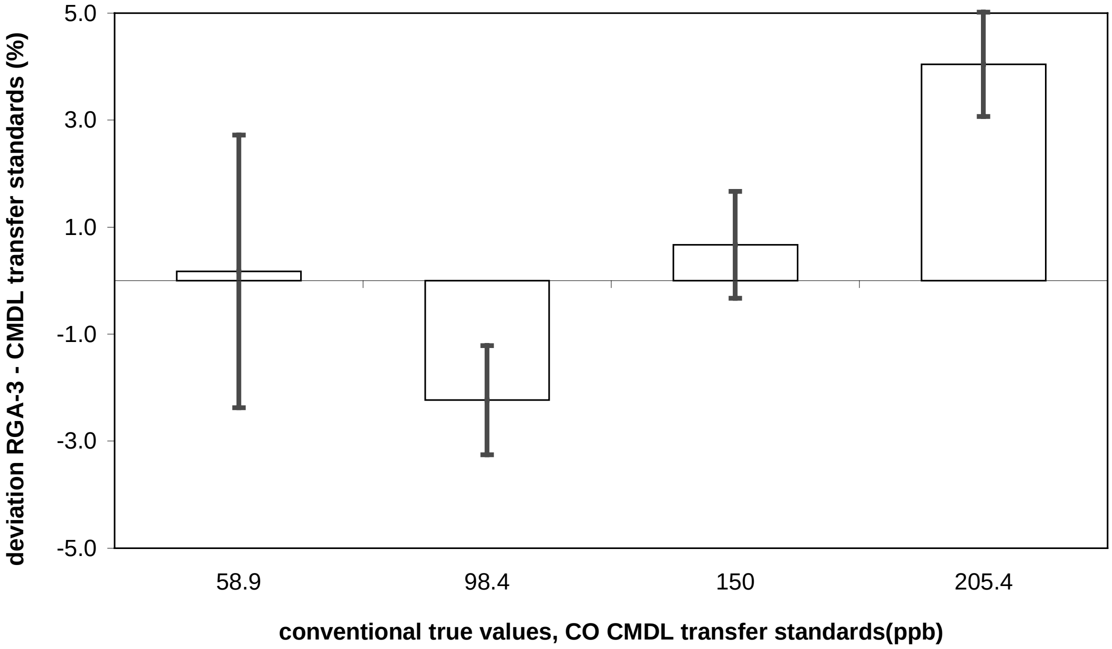

Figure 19: Differences (%) between the RGA-3 and the CMDL transfer standard (the red error bars show the given uncertainty of the CMDL gas cylinders)

Comment

All the CO measurements performed at Izaña were based on the CMDL scale for carbon monoxide. The WCC also used CMDL certified standards for the calibration of the transfer standards. However, the certified values from CMDL will be revised in the near future. As a consequence, the absolute value of the WCC and Izaña will slightly change. However, the influence on the results of the intercomparison is expected to be negligible.

The intercomparison of the CO measurement showed excellent results for the three lower concentrations (58.9, 98.4, and 150.0 ppb). Only a deviation of up to 2.3 % was found for these cylinders. Considering the certified uncertainty of the CMDL transfer of approx. 1% there is no significant deviation between the transfer standard concentration and the measurements at Izaña. A higher deviation of 4% was found for the cylinder with 205.4 ppb. However, regarding the relevant concentration range, this result can still be considered as good.

The peak height was used for the calculation of the intercomparison measurements at Izaña. However, the calculation based on the peak area was also submitted to the WCC by the station operator. The results are summarised in Table 11.

Table 11: Intercomparison measurement at Izaña for CO based on the peak area

No.	WCC standard	RGA-3 #070188-009 (Peak Area)				
	conc.	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	58.9 ± 1.5	63.6	0.5	5	4.7	8.0
2	98.4 ± 1.0	99.1	1.9	5	0.7	0.7
3	150.0 ± 1.5	150.6	1.3	5	0.6	0.4
4	205.4 ± 2.0	210.6	3.1	5	5.2	2.5

It can bee seen from Table 11 that the two cylinders with 98.4 and 150.0 ppb show also excellent agreement between the measurements of Izaña and the conventional true value from the WCC. A higher deviation was found for the lower concentration, which could be explained with integration difficulties due to peak tailing. Peak height is the preferred integration option for low concentrations. However, the deviation for the 205.4 ppb cylinder was lower (2.5% instead of 4.0%) with the peak area used as integration method.

Recommendation

Since the last audit in February 1998, the CO measurement system has considerably improved. A very sophisticated calibration procedure with the use of natural ambient air collected at Izaña was implemented. All the recommended changes of the 1998 audit were done, and the system became operational in late 1998. The station operators used both peak area and peak height for the data evaluation. For the calculation of the final data the peak height is preferable due to lower standard deviation between single injections. The improvement of the system is reflected in very good results of the intercomparison measurements. Therefore no further action is recommended by the WCC.

7. Local Measurement Site Punta del Hidalgo

7.1. Site Characteristics

The station Punta del Hidalgo is located on the Island of Tenerife, Spain, (coordinates: 28°34' N, 16°20' W) roughly 300 km west of the African coast. The site is located on top of a lighthouse directly at the north coast of Tenerife near the village of Bajamar, approximately 9 km north of San Cristobal de la Laguna. The prevailing wind direction is north-east throughout the year. This allows the study of the marine free troposphere. The site has road access from a small village nearby, and only few vehicles visit the lighthouse. Because of the strong north-easterly wind, local air pollution is unlikely.

Figure 20: Picture of the station Punta del Hidalgo

7.2. Operators

Mr. Juanma Sancho, Ozone and UV Group of the Izaña Observatory, is also responsible for the ozone measurements conducted at Punta del Hidalgo (other personnel involved see table 1, section 3.2).

7.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well described by the frequency distribution. Figure 21 shows the frequency distribution of the hourly mean values from the year 1997. The relevant ozone concentrations were calculated to range from 22 to 52 ppb according to the 5 and 95 percentile of the hourly mean values. Source of data: INM

Ozone measurements at Punta del Hidalgo were performed between late 1996 and early 1998, and started again in spring 2000. The site characteristics allow the observation of the undisturbed marine troposphere and accomplish the measurements of Izaña.

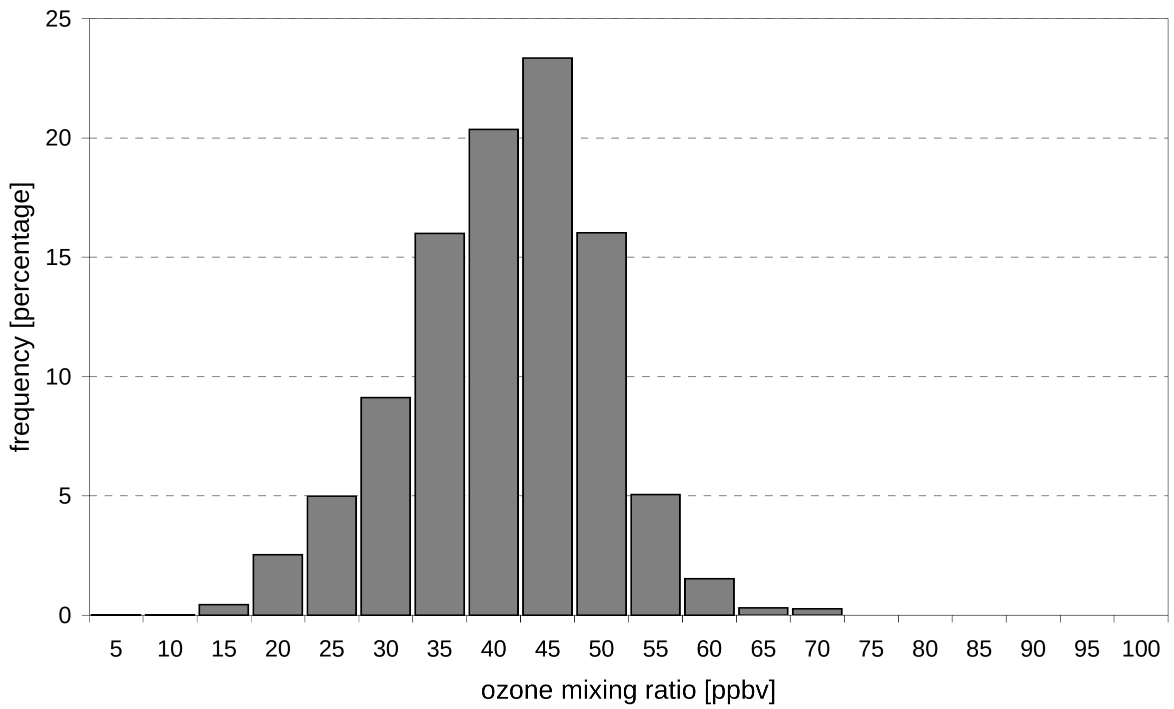

Figure 21: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Punta del Hidalgo of the year 1997. Availability of data: 86%.

8. Measurement Technique at Punta del Hidalgo

8.1. Air Inlet System

The air inlet system for the ozone measurement is mounted on top of the lighthouse. The inlet part of the system on the flat roof is 3 m high and about 60 m above ground and consists of an inverse PVC bucket, stacked on a stainless steel tube, shielding the system from rain. The sampling line is a 4 m long PFA tube leading directly from the ozone analyser to the end of the stainless steel tube. The total residence time of the ambient air through in the inlet line is less than 2 seconds.

Comment

The Teflon tube and the rain protection at the inlet were clean and free of dust. The inlet system, concerning construction materials as well as residence time, is adequate for ozone analysis. The inlet system was not checked against ozone loss during the audit. However, due to the materials used and the short residence time, no considerable loss of ozone is expected.

8.2. Instrumentation

The instrument is installed in a non air-conditioned room on the top of the Punta del Hidalgo lighthouse. Air-conditioning of the station is not a really important matter at the present time, since the room temperature is expected to remain constant at this location. However, if Punta del Hidalgo becomes a site with a more extensive measurement program in the future, air-conditioned should be considered.

At Punta del Hidalgo, a Dasibi 1008-AH is used for ozone measurements. The instrument details are shown in Table 12. Calibrations of the instrument are performed every 3 months at Izaña. For this purpose, the instrument is transported to the Izaña Observatory. For details of the calibrator see Appendix I.

Table 12: Field instrument at Punta del Hidalgo

Type	Dasibi 1008-AH #4283
Method	UV absorption
Range	0-1000 ppb (0-1 V)
Analog output	0-100 mV amplified to 0-10 V
Electronic offset	5 units (corresponding ppb)
Electronic coefficient	308 (absorption coeff.)

The zero air unit consists of an activated charcoal cartridge (approx. 1 litre volume) and a particulate filter. It is used to determine the analyser's zero offset.

A zero check is performed manually about every two weeks. The data of twelve one-minute zero means is stored in a separate file.

Comment

The measurement technique used is the UV-method which is the preferred method in the GAW programme.

8.3. Operation and Maintenance

Preventive maintenance of the instruments incorporates adjustment of the pressure transducers and cleaning of the instruments glass cell, and is performed on a case by case basis (every 2-6 month). At the time of audit no reference pressure was available at the site. However, meteorological measurements are planned for the near future. The instruments are protected with a dust inlet filter. The filter is changed every month. There is a detailed checklist available at the site, and the instrument checks including a zero check are performed every two weeks.

The data of the zero checks is stored in a separate file and is used later for data reprocessing and correcting the ambient air measurement values. Three to four times a year, a multipoint calibration using the TEI 49C-PS #56085-306 is performed at Izaña and the applied ozone levels are 0 / 10 / 30 / 45 / 60 / 90 ppb.

8.4. Data Handling

The person who is responsible for the instrument operation is also in charge of data reviewing and processing.

The same data acquisition system as at Izaña is used (see section 4.1.4.). The only difference is that zero checks are performed manually. Since the station is only in operation since a few weeks, the data reviewing was not audited.

8.5. Documentation

Within the GAW guidelines for documentation, the transparency as well as the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness. The station logbook was found at the site. It contained all necessary information listed chronologically.

9. Intercomparison of Ozone Instruments (Hidalgo)

9.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix II) was hooked up to power for warming up over the weekend in deviation from the GAW Report No. 97 which recommends only one hour of warm-up. During this stabilisation time the standard and the PFA tubing connections to the instruments were conditioned with 200 ppb ozone for 10 minutes. Two comparison runs between the field instrument (analyser) and the WCC transfer standard were performed. In the meantime the inlet system and the station documentation were inspected. Table 13 shows the experimental details of the audit. In general, no modifications of the ozone analyser which could influence the measurements were made for the intercomparisons.

The EMPA acquisition system, which was used for the audit, consisted of a 16-channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instrument and of the transfer standard the data was collected by both data acquisition systems (EMPA and INM) and showed no discrepancy. For data interpretation the EMPA data was used. Finally, the observed results were discussed in an informal review with the person involved.

The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in the Appendix III.

Table 13: Experimental details

audit team:	C. Zellweger, A. Herzog
reference:	WCC: TEI 49C-PS #62026-333 transfer standard
field instruments:	Dasibi 1008-AH #4283
ozone source:	EMPA: TEI 49C-PS, internal generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	EMPA: 16-channel ADC circuit board, software
pressure transducers reading:	TEI 49C-PS (EMPA): 1018 hPa Dasibi 1008-AH: 998 hPa, adjusted to 1018 hPa
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	10 / 20 / 30 / 50 / 85 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	2 x on June 12, 2000
connection between instruments:	about 1.5 meter of 1/4" PFA tubing

9.2. Results

The results comprise the two runs of the intercomparison between the field instrument Dasibi 1008-AH and the EMPA transfer standard TEI 49C-PS, carried out on June 12, 2000.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Tables 14 and 15. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 19 and 20 show the results of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The results of the two runs are then summarised to the mean regression equation and presented in a graph with the assessment criteria for GAW field instruments (Figure 24).

The data used for the evaluation were recorded by the EMPA data acquisition system. This raw data was treated according the usual station method. Corresponding to this procedure the zero offset was determined by a zero check. The resulting offset was subtracted from the data of the intercomparison. Tables 14 and 15 show the recalculated data.

Table 14: 1. Intercomparison, field instrument

No.	**transfer standard**		**Dasibi 1008-AH**			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.1	0.13	0.0	0.27	-0.1	
2	29.8	0.14	28.4	0.58	-1.4	-4.8%
3	49.9	0.07	48.0	0.68	-1.9	-3.9%
4	10.0	0.13	9.4	0.52	-0.6	-6.5%
5	19.8	0.22	19.5	0.49	-0.3	-1.5%
6	84.8	0.12	81.8	0.47	-3.0	-3.5%
7	0.1	0.12	1.2	0.52	1.2	

Table 15: 2. Intercomparison, field instrument

No.	**transfer standard**		**Dasibi 1008-AH**			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.1	0.12	1.2	0.52	1.2	
2	49.9	0.12	48.5	0.28	-1.3	-2.7%
3	10.1	0.16	10.7	0.73	0.7	6.5%
4	29.8	0.12	29.4	0.54	-0.3	-1.2%
5	84.8	0.14	81.1	0.39	-3.7	-4.4%
6	20.1	0.15	19.0	0.63	-1.1	-5.3%
7	0.1	0.10	0.7	0.58	0.5	

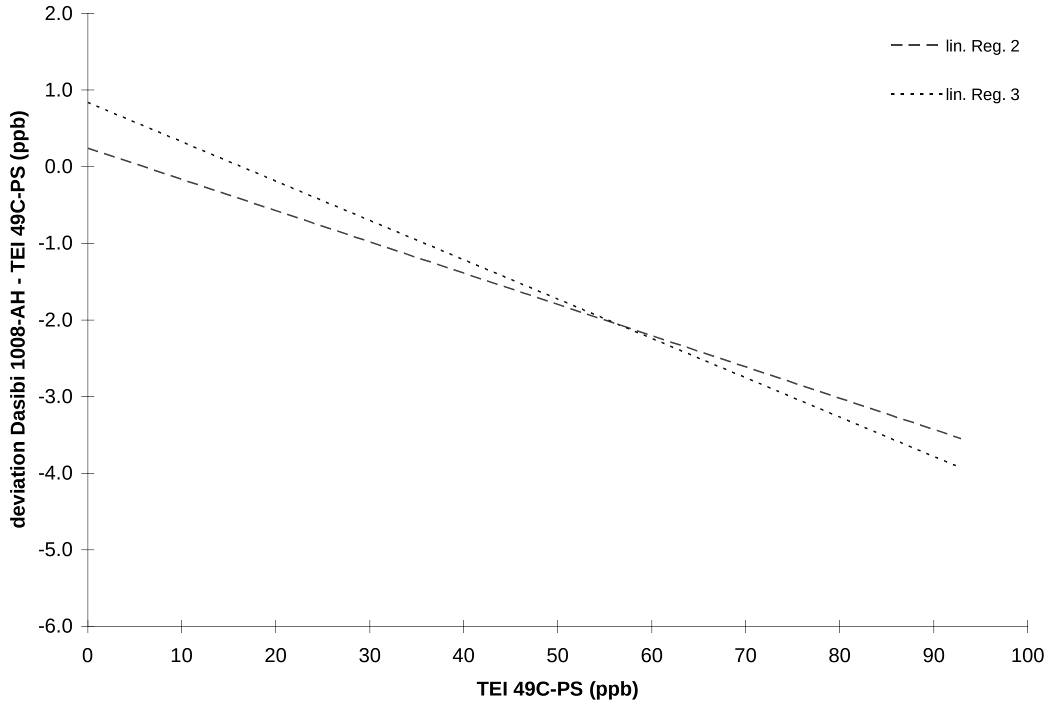

Figure 22: Individual linear regressions of intercomparisons 1 and 2, Dasibi 1008-AH

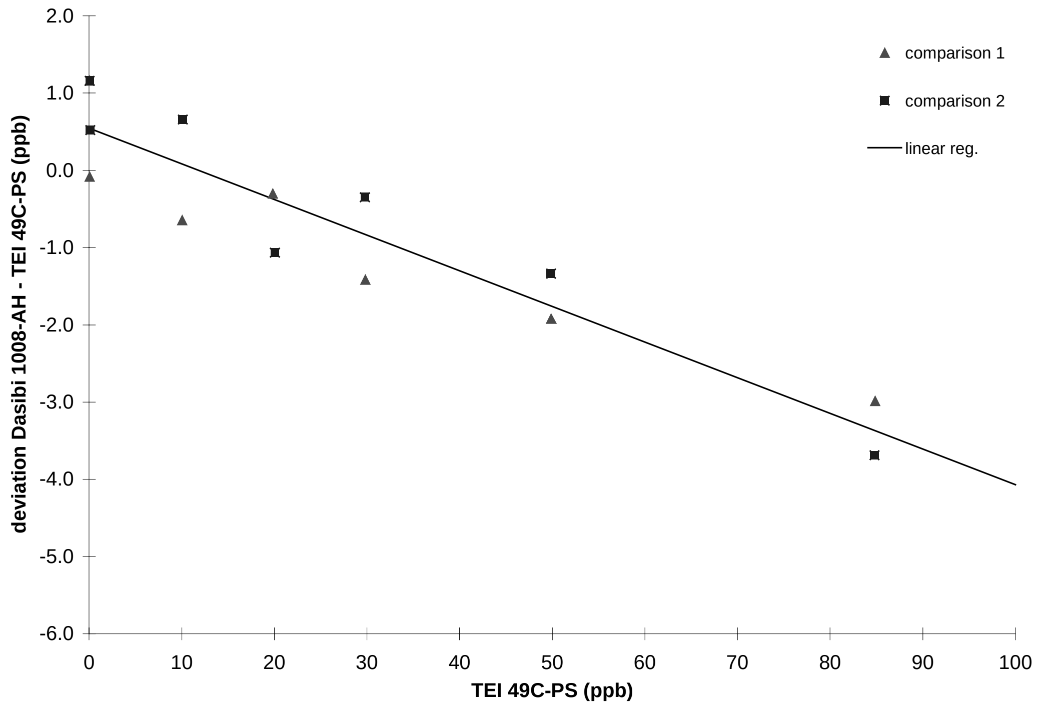

Figure 23: Mean linear regression of intercomparisons 1 and 2, Dasibi 1008-AH

From the intercomparisons of the TEI 49C #62900-337 and the Dasibi 1008-AH #4283 field instruments with the TEI 49C-PS transfer standard, from EMPA, the resulting linear regression (for the range of 0-100 ppb ozone) are:

<u>-Dasibi 1008-AH:</u>

$$\text{Dasibi 1008-AH} = 0.954 \times \text{TEI 49C-PS} + 0.55 \text{ ppb}$$

Dasibi 1008-AH = O_3 mixing ratio in ppb, determined for Dasibi 1008-AH #4283

TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #62026-333

Standard deviation of:	- slope s_m	0.0051	(f = 2) f=degree of freedom
	- offset S_b in ppb	0.20	(f = 2)
	- residuals in ppb	0.52	(f = 12)

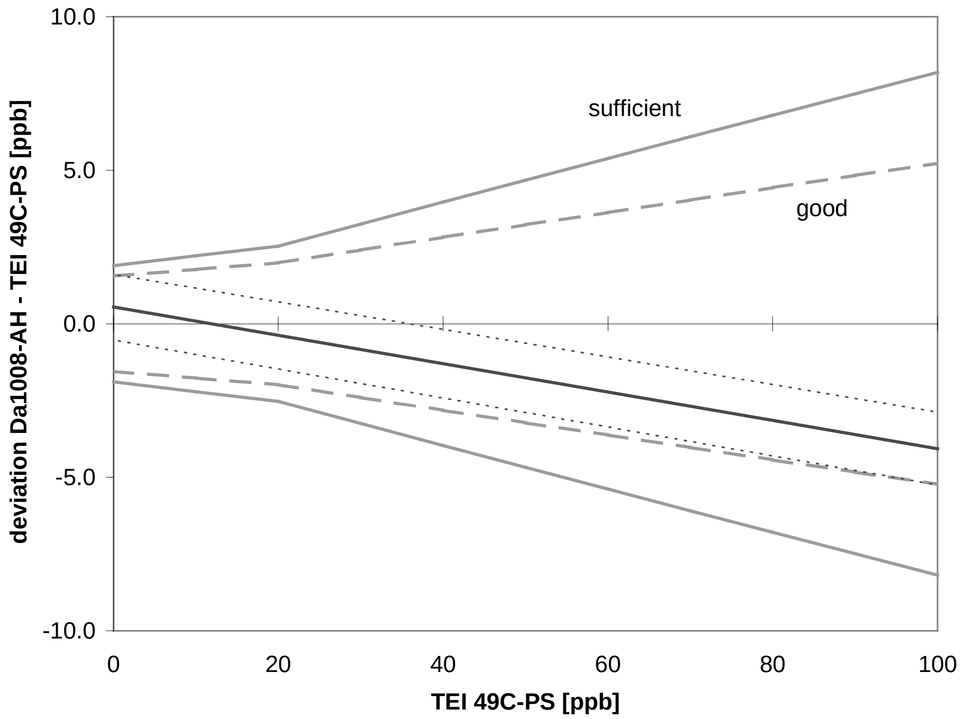

Figure 24: Intercomparison of instrument Dasibi 1008-AH

Comment

Ozone measurements started recently at Punta del Hidalgo. The Dasibi 1008-AH fulfils the assessment criteria as "good" over the tested range up to 100 ppb (see Figure 24).

Recommendation

Punta del Hidalgo serves as a local measurement site additionally compromising the ozone measurements of Izaña. It has not yet reached the state of continuos routine operation, but future activities are planned at the site.

The recommendation of the WCC can be summarised as follows:

The Dasibi 1008-AH fulfils the assessment criteria as "good" over the tested range up to 100 ppb. However, an adjustment of the calibration factors should be considered. Calibrations of the instrument are planned to take place at Izaña, three or four times a year. The WCC suggest that at least one calibration per year is performed at Punta del Hidalgo. However, this is not a very critical matter, because an informal comparison of the calibration results conducted at Izaña by INM showed good agreement with the calibration performed by the WCC.

If the ozone measurement at Punta del Hidalgo will become operational, the following action should be taken:

1) Start with the measurement of meteorological parameters. This will be necessary for the data interpretation. These measurements are already planned for the near future.

2) A reference pressure should be available at the site.

Appendix

I Calibrator TEI 49C-PS #306 of the Izaña Observatory

In April 1997, an ozone calibrator of the type TEI 49C-PS had been purchased for the Izaña Observatory and is used for regular calibration of the analysers on site as well as for conducting ozone audits within the SCO_3P Project and the GAW Programme in South America.

In the course of the intercomparisons of the ozone analysers at Izaña, an intercomparison of the ozone calibrator, TEI 49C-PS #306, was additionally performed. In principal, the experimental procedure was the same as for the analysers described in chapter 5.1. Details of the calibrator are listed in Table 17. The results are shown below in table 18 to 20. This calibrator was calibrated last time by the WCC in February 1998 during the audit procedure

Table 16: Experimental details

reference:	EMPA: TEI 49C-PS #62026-333 transfer standard
station calibrator:	INM: TEI 49C-PS #56085-306 transfer standard
ozone source:	EMPA: TEI 49C-PS, internal generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	EMPA: 16 channel ADC circuit board, software
pressure transducers reading:	TEI 49C-PS (EMPA): 769.8 hPa TEI 49C-PS (INM): 778.2 hPa, for the intercomparison adjusted to 769.8 hPa
concentration range	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 130 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on June 8, 2000
connection between instruments:	about 1.0 meter of 1/4" PFA tubing, ozone connected to station calibrator between manifold and solenoid valve

It should be noted that the pressure transducer of the INM transfer standard had to be adjusted from 778.2 hPa to 769.8 hPa or by about 1.1 %. Increasing the pressure reading of the sensor has an indirect proportional effect on the ozone reading.

Table 17: Ozone calibrator at global GAW station Izaña

type	TEI 49C-PS #306
method	UV absorption
at Izaña	since April 1997
range	0-200 ppb
analog output	0-10 V
electronic offset	- 1 ppb, artificial electronic offset
calibration coefficient	1.000

Table 18: 1. Intercomparison, TEI 49C-PS #306

No.	**TEI 49C-PS (EMPA)**		**TEI 49C-PS #306**			
	conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.3	0.17	0.1	0.15	-0.2	
2	130.0	0.16	129.7	0.19	-0.3	-0.2%
3	89.9	0.18	89.7	0.23	-0.3	-0.3%
4	29.8	0.15	29.9	0.23	0.1	0.3%
5	190.1	0.15	189.9	0.24	-0.1	-0.1%
6	59.9	0.14	59.9	0.24	0.0	-0.1%
7	0.3	0.14	0.3	0.14	-0.1	

Table 19: 2. Intercomparison, TEI 49C-PS #306

No.	**TEI 49C-PS (EMPA)**		**TEI 49C-PS #306**			
	conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.4	0.17	0.3	0.20	-0.1	
2	59.9	0.17	59.9	0.17	0.0	0.1%
3	30.1	0.18	30.1	0.20	0.0	-0.1%
4	129.9	0.29	129.9	0.47	0.0	0.0%
5	90.2	0.30	90.3	0.21	0.1	0.1%
6	190.1	0.20	190.2	0.26	0.2	0.1%
7	0.5	0.15	0.3	0.24	-0.2	

Table 20: 3. Intercomparison, TEI 49C-PS #306

No.	TEI 49C-PS (EMPA) conc. ppb	S_d ppb	TEI 49C-PS #306 conc. ppb	S_d ppb	deviation from reference ppb	deviation from reference %
1	0.4	0.15	0.2	0.18	-0.2	
2	89.9	0.14	90.0	0.22	0.1	0.1%
3	30.1	0.12	30.1	0.16	0.0	-0.1%
4	130.0	0.17	130.1	0.26	0.0	0.0%
5	60.2	0.23	60.2	0.32	0.0	0.0%
6	190.0	0.11	190.4	0.24	0.5	0.2%
7	0.5	0.14	0.3	0.16	-0.2	

From the intercomparisons of the TEI 49C-PS #306 ozone calibrator with the TEI 49C-PS transfer standard from EMPA the resulting linear regression (for the range of 0-200 ppb ozone) is:

calibrator Izaña = 1.001 x TEI 49C-PS (EMPA) - 0.1 ppb

calibrator Izaña = O_3 mixing ratio in ppb, determined for TEI 49C-PS #306
TEI 49C-PS (EMPA) = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:
- slope s_m 0.0005 (f = 3) f=degree of freedom
- offset S_b in ppb 0.05 (f = 3)
- residuals in ppb 0.16 (f = 19)

Comment

After the audit in February 1998 an adjustment of the calibration factors was suggested by the WCC. This adjustment was obviously successful done by the station operators. The deviation of the INM to WCC transfer standard was now 0.1% for the slope (1998: 1.2%) with an offset of -0.1 ppb (1998: -0.8 ppb). Therefore no further action is necessary.

II EMPA Transfer Standard TEI 49C-PS

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

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 25. One gas stream flows through a pressure regulator to the reference solenoid valve to become the reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

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

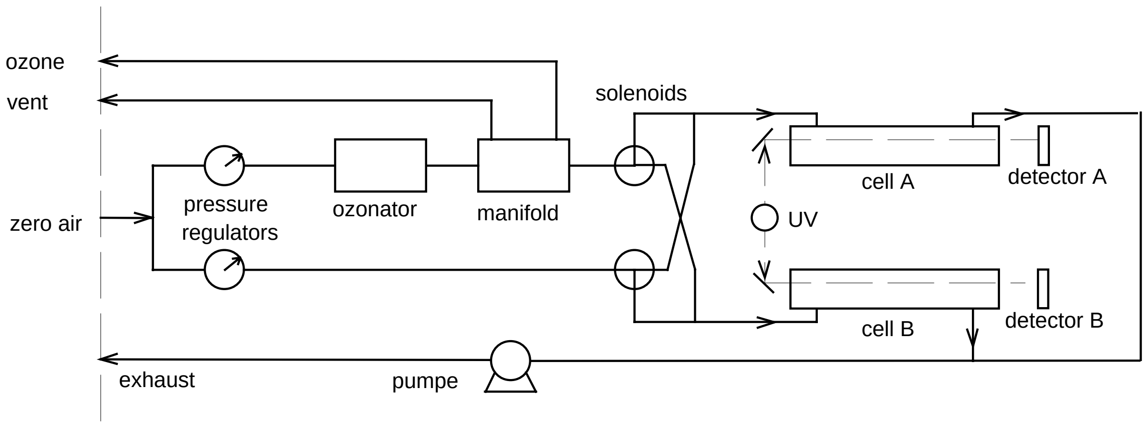

Figure 25: Flow schematic of TEI 49C-PS

III Stability of the Transfer Standard TEI 49C-PS

To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #62026-333 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this intercomparison at the EMPA calibration laboratory are summarised in Table 21 and Figure 26.

Table 21: Intercomparison procedure SRP - TEI 49C-PS

pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 125 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurised air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP’s internal generator
data acquisition system:	SRP’s ADC and acquisition

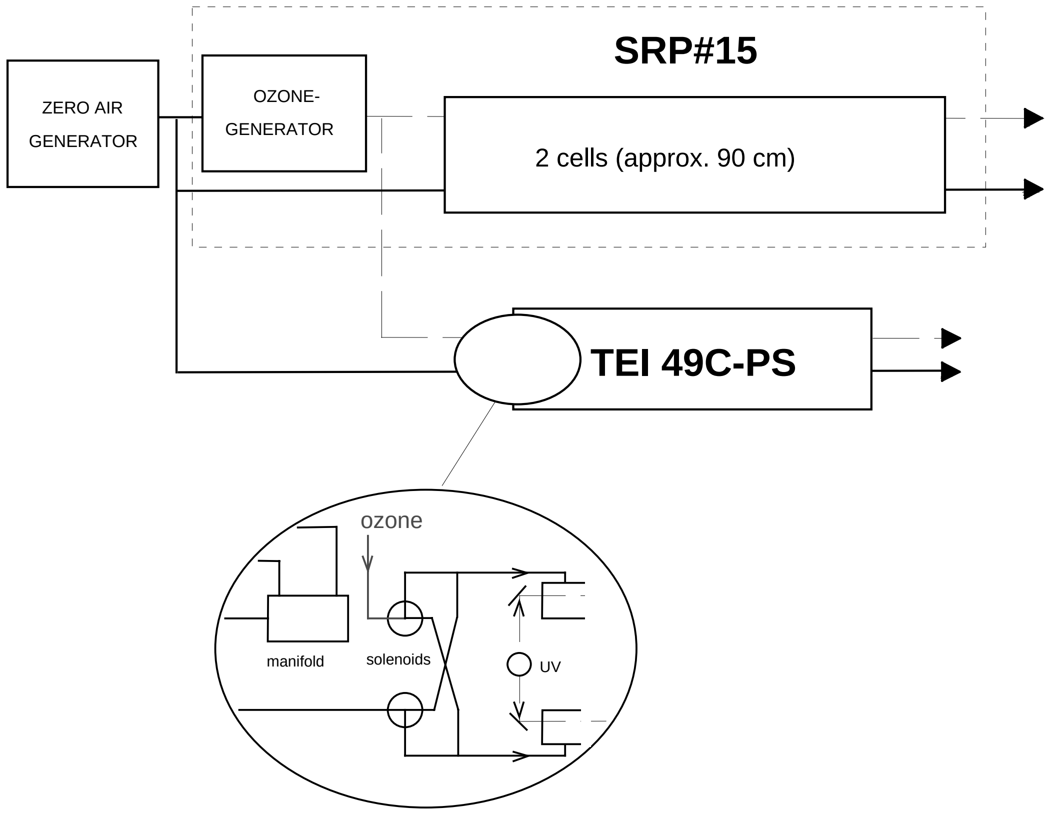

Figure 26: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the WCC-O_3 (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to approximately ±(1 ppb + 0.5%).

Figures 27 and 28 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. The results show that the EMPA transfer standard fulfilled the recommended criteria for the period of the audit, including transportation.

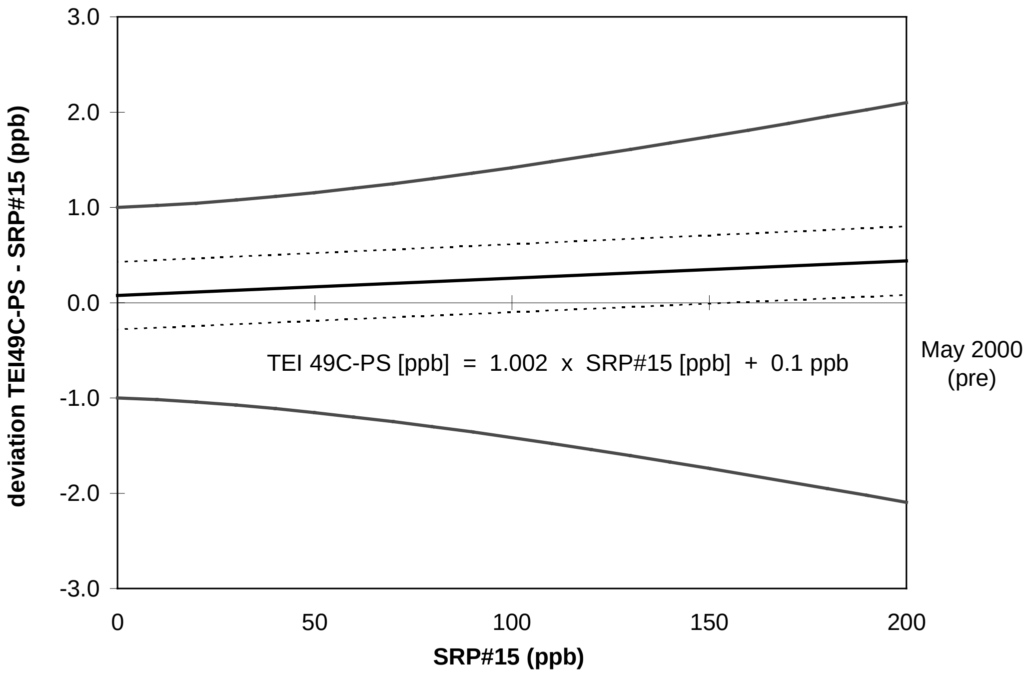

Figure 27: Transfer standard before audit

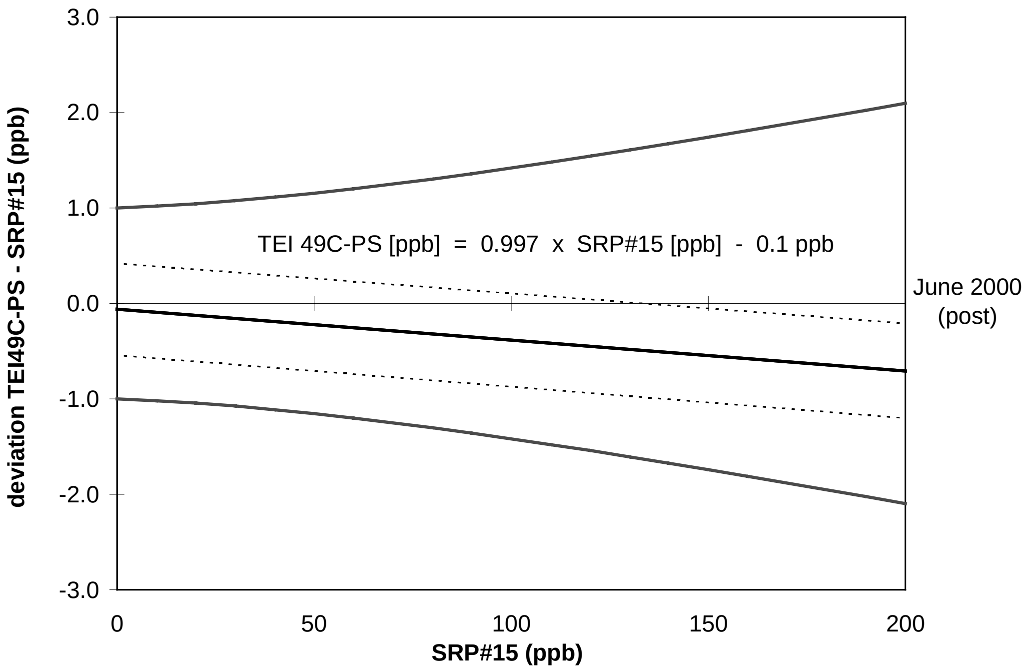

Figure 28: Transfer standard after audit

IV WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference within the GAW programme. The standards used at the WCC are listed in Table 22:

Table 22: CO Standards at the WCC

Standard (Gas Cylinders)	CO	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 nmole/mole	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 nmole/mole	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 nmole/mole	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 nmole/mole	CA02859
WCC Transfer Standard (6 l cylinder)	58.9 ± 1.5 nmole/mole	FF31496
WCC Transfer Standard (6 l cylinder)	98.4 ± 1.0 nmole/mole	FA01469
WCC Transfer Standard (6 l cylinder)	150.0 ± 1.5 nmole/mole	FF30491
WCC Transfer Standard (6 l cylinder)	205.4 ± 2.0 nmole/mole	FA01467

The absolute accuracy of the NOAA/CMDL CO scale has not yet been rigorously determined. This scale will be probably revised in the near future.

The listed WCC transfer standards were checked against the CMDL laboratory standards.