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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 98/8

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

GLOBAL GAW STATION USHUAIA

ARGENTINA, NOVEMBER 1998

Submitted by

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WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

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1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone and Carbon Monoxide, at the global GAW Ushuaia, Argentina. Below, the findings, comments and recommendations are summarised:

Air Inlet System:
All teflon tubes were clean and free of dust and adequate for trace gas measurements in particular with regard to minimal loss of ozone.

Instrumentation:
Ozone Analysers:
The operation of an ozone analyser and a backup instrument (both UV method), considerably increases confidence in data quality concerning parallel measurements as well as data availability.

Carbon Monoxide Analyser:
The CO NDIR analyser (TEI 48) in use is, taking into account the measurement principle, in acceptable condition. However, for observations of long term a substantially more sensitive instrument would be necessary. Nevertheless, for the actual situation operating the TEI 48 analyser, parallel operation of two analysers would considerably increase confidence in the acquired data, moreover since no regular quality checks can be performed. But lack of necessary spare parts had forced the team to shutdown the second instrument.

Operation and Maintenance:
The appearance inside the station is clean and functional.
One of the main factors of quality assurance is to perform regular multipoint calibrations. Thus, the replacement of the reasonable priced CO standard (ppm) which had been used for standard addition is essential for a successful continuing of the CO measurements. Further should be guaranteed that the ozone calibrator of the SMN is regularly used for calibrating and thus verifying the ozone measurements made at the global GAW site Ushuaia.
However, as long as the necessary references are not available at the site it is recommended to change as little as possible at the working instruments. Any maintenance that could alter the performance should be avoided.

Data Handling:
The procedure of data treatment is rather working intensive and is composed of a lot of single working steps. It seems advisable to invest in either the actual system to make it more flexible or to get running the system provided by the INM, Spain. It is further suggested to contact other experts and discussing the chosen procedure of data filtering.

Documentation:
The documentation of the ozone and CO measurement meets the requirements of the guidelines for GAW stations.

Ozone Intercomparisons:
The ozone concentrations observed at Ushuaia (1998) usually ranged between 15 and 35 ppb (5- and 95-percentile of hourly mean values).
Both instruments clearly fulfil the assessment criteria as "good" over the tested range up to 100 ppb (figure 1). Fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instruments are in good condition.

Carbon Monoxide Intercomparisons:
On the one hand, the regression analysis result of the CO intercomparison shows a deviation of moderate 3 to 4% compared to the conventional true value but a high standard deviation of the residuals of 5ppb on the other (see fig. 3). This rather high standard deviation is due to the used

measurement technique since the instrument is operated at the edge of its sensitivity and detection limit (background pollution level of the site of Ushuaia ranges between 40 ppb to 70 ppb CO). Considering the quality objectives of the GAW programme, the analyser seems to be adequate for segregation of polluted against background air masses but insufficient for observations of long term trends. A substantially more sensitive instrument, like other comparable GAW sites on the southern hemisphere, i.e. Cape Point or Cape Grim, would be necessary to achieve that goal. The ambient air measurements of the station analyser and the EMPA transfer standard (Horiba 360 APMA) in parallel, agreed well.

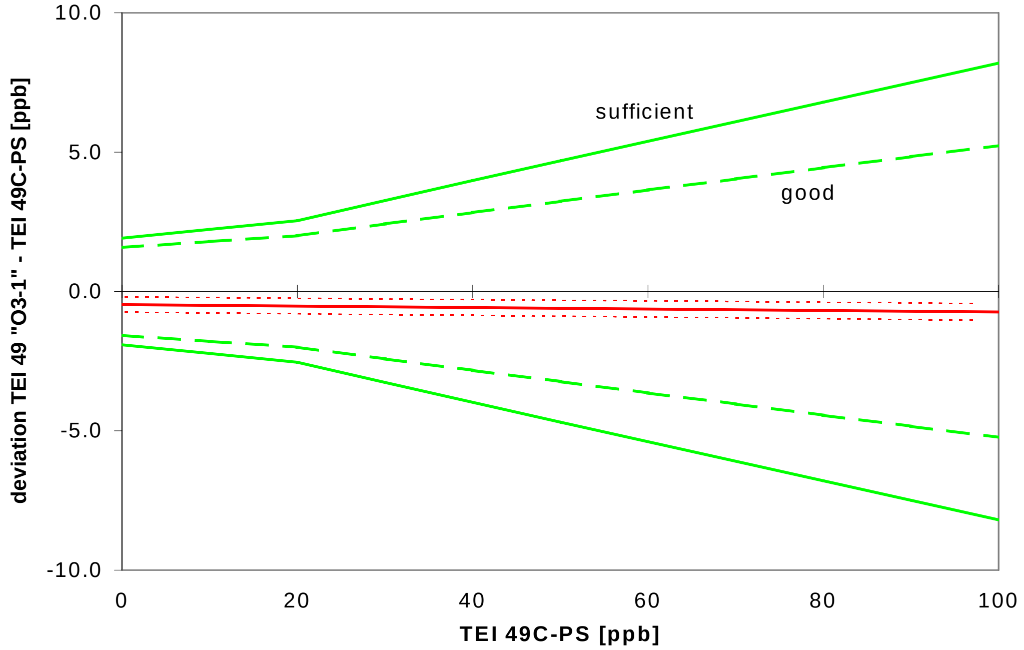

Figure 1: Intercomparison of instrument TEI 49 "O3-1" (linear regression, prediction interval 95%)

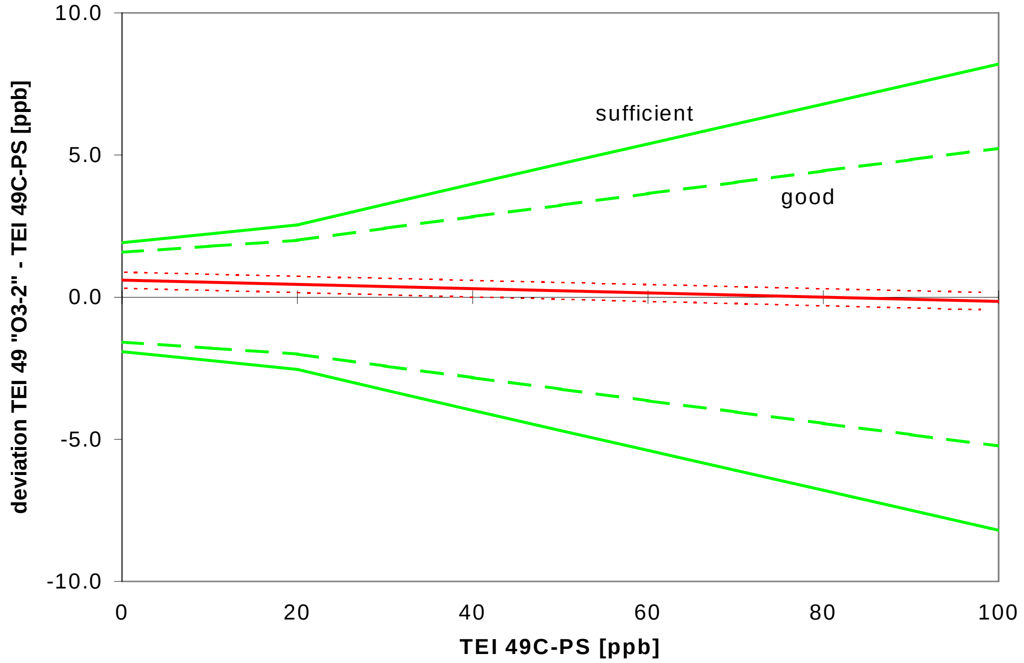

Figure 2: Intercomparison of instrument TEI 49 "O3-2" (linear regression, prediction interval 95%)

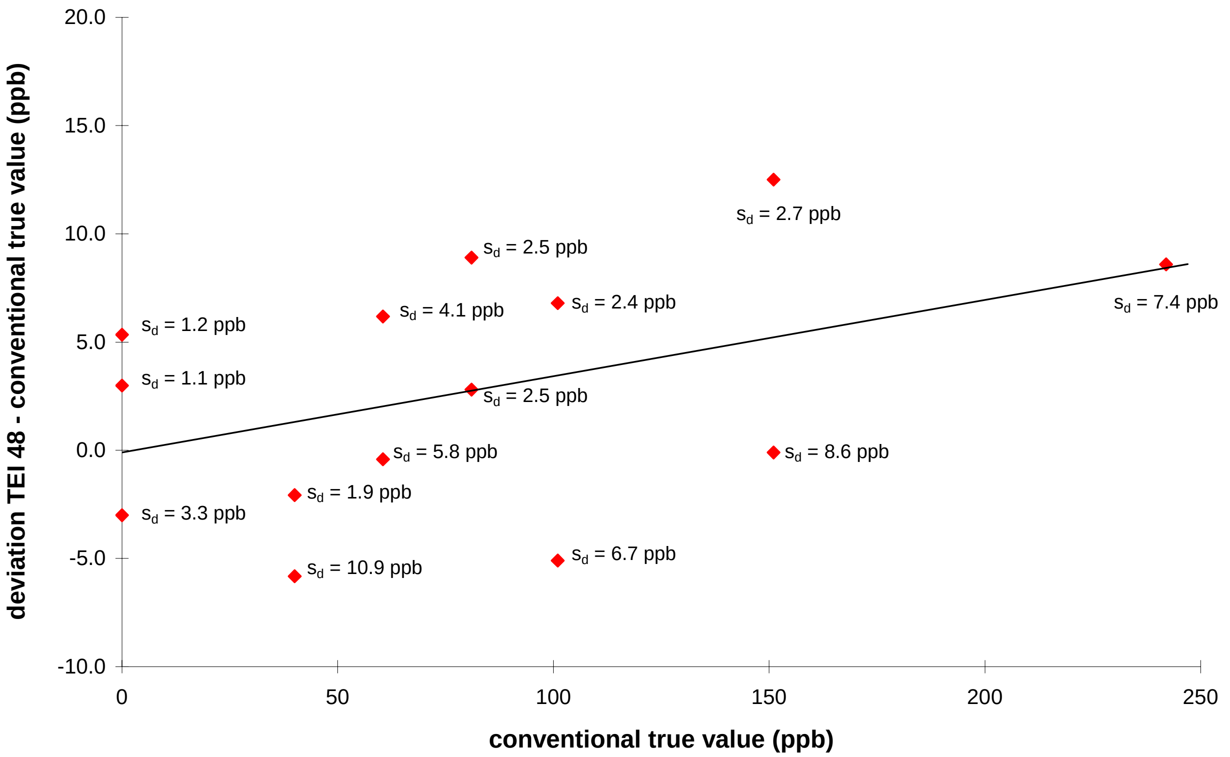

Figure 3: Intercomparison of the CO analyser TEI 48 "CO-2", linear regression line

Dübendorf, 2. July, 1999

EMPA, World Calibration Centre

Project engineer

Project manager

A. Herzog

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 and Carbon Monoxide. At the beginning of 1996 our work had started within the GAW programme with the parameter surface ozone. The activities were extended for carbon monoxide in the middle of the year 1997. The detailed goals and tasks of the WCC concerning surface ozone are described in the WMO-GAW report No. 104.

In agreement with the according personnel of SMN (Servicio Meteorologico National) and the Province Government of Terra del Fuego, a system and performance audit at the global GAW station Ushuaia, Argentina, was conducted. This station was established within the framework of GEF and is designated for long-term measurements of several chemical compounds and physical and meteorological parameters in the lower free troposphere.
The scope of the audit was confined to the tropospheric ozone and carbon monoxide measurements. The entire process, beginning with the inlet system and continuing up to the data processing, and also the supporting measures of quality assurance, were inspected during the audit. The audit concerning ozone 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. No Standard Operation Procedures (SOP) have been established for CO measurements by QA/SAC until now. For this reason the ozone SOP was adapted for carbon monoxide. The assessment criteria for the ozone intercomparison have been developed by EMPA-WCC and are based on WMO-GAW Report No. 97 (EMPA-WCC report 98/5 "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, September 1998, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The present audit report is submitted to the station manager, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

Previous audits:

- November 1994 by the QA / SAC for Europe and Africa, "Report on the performance and system audits at the GAW observatory in Ushuaia and at INQUIMAE in Buenos Aires, Argentina", L. Martini, F. Slemr and V. Mohnen
- June 1997 by the INM of Spain, (operators of the global GAW station Izaña), "System and Performance Audit for Surface Ozone at Pilar, La Quiaca and Asuncion SCO3P Stations and Ushuaia GAW Station", Juan Manuel Sancho, Emilio Cuevas

System and performance audits at global GAW stations will be regularly conducted on mutual arrangement.

3. Global GAW Site Ushuaia

3.1. Site Characteristics

The Ushuaia Station is located on the "Isla Grande de la Tierra del Fuego", Argentina (54° 50' S – 68° 18' W), roughly 10 km south-west of the city of Ushuaia.
The station is located in a coastal cliff at an altitude of 18 m a.s.l., on a remote sub-Antarctic marine coast. Steady winds blow prevailing from the clean air sector (SW) down the Beagle Channel. Tierra del Fuego and its adjacent oceanic area are under the westerlies influence. The ground in the vicinity around the station is covered with pasture and bush. The vegetation in the surrounding area (30 Km) is consisting mainly of *Notophagus'* forest.

The facilities at the site consist of the main building of 150 m^2, which provides space for offices, meeting rooms and laboratories. Attached to this building is the Dobson spectrophotometer (white cabinet). On the platform at the top of the roof, the air inlet and several radiation and meteorological equipment are mounted.
In addition to the main facility, a remote island sampling site with a 12 m tower called "Isla Redonda" is located on Beagle Channel (54° 51' S – 68° 28' W) and can be used for special projects.

Since two years, the new Ushuaia airport has opened in the near vicinity of the station. It is located about 300 m north-east of the site towards the city of Ushuaia. Air traffic is estimated to 5-10 flight movements per day. As already stated in the first audit report '94 (Martini, Slemr, Mohnen) there is some concern regarding a possible influence of the measurements, in particular when the airport should further develop.

Figure 4: Picture of the station Ushuaia

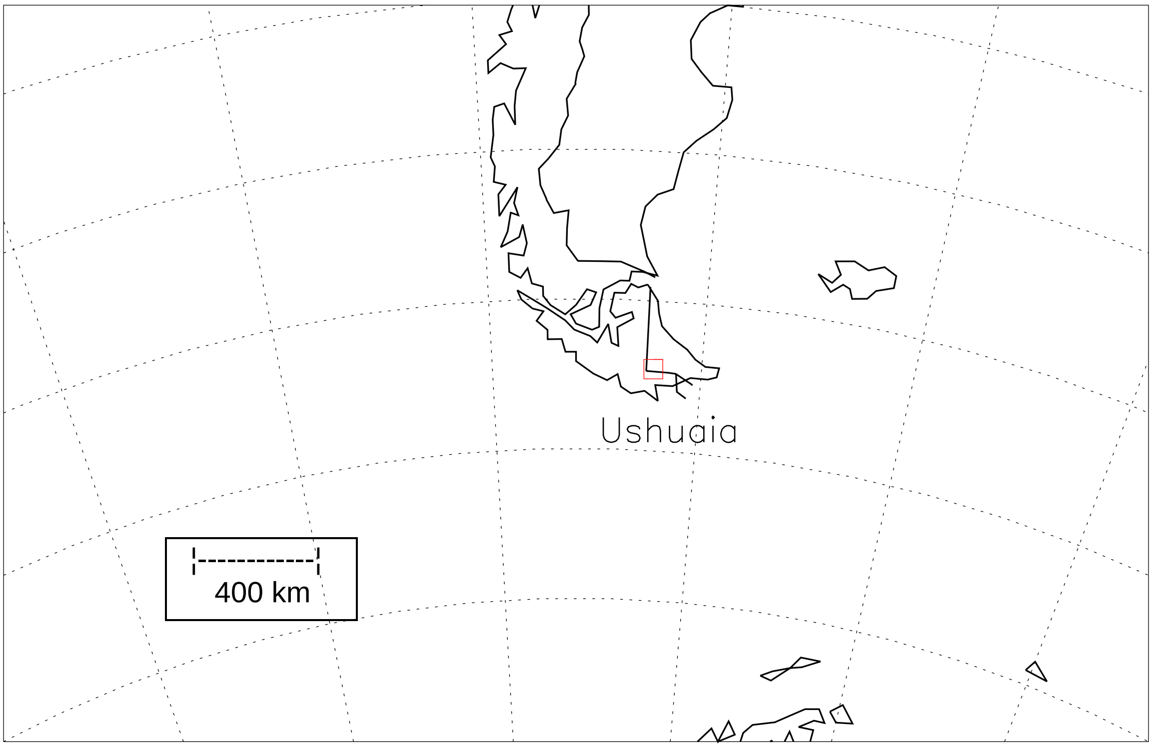

Figure 5: Map of the southern part of South America:

3.2. Operators

The main station is operating since September of 1994, under an agreement between the Servicio Meterorológico Nacional, that acts as lead agency, and the Government of Tierra del Fuego, with twinning expertise provided by Germany, Austria, Spain an the United States of America. The Servicio Meterorológico Nacional is part of the Argentinean Air Force. The structure of the station management at Ushuaia is shown in Table 1.

Table 1: Operators

Mr Osvaldo Barturen, Officer-in-charge, SMN	
Operators and Observers	
Servicio Meteorólogico Nacional (SMN)	Government of Tierra del Fuego
- Mr Gabriel Karamanian, Vice-chief - Mr Marcelo Rosa, Observer - Mr Adrian Silva, Observer - Ms Erica Picaluga	- Mr Sergio Luppo, (chemical engineer) responsible for CO - Mr Miguel Pereira, (chemical engineer) responsible for surface ozone - Ms Lilian Riebel, Technician (math. and geography degree) data management

Contact address at the global GAW station:

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3.3. Ozone Level

The site characteristics and the relevant surface ozone concentration range can be well defined by the frequency distribution. In figure 6 the frequency distribution of the values from the year 1998 is shown. The relevant ozone concentrations were calculated, ranging between 15 and 35 ppb according the 5 and 95 percentile values. Annual data capture 41.5 %.

Source of data: received from SMN

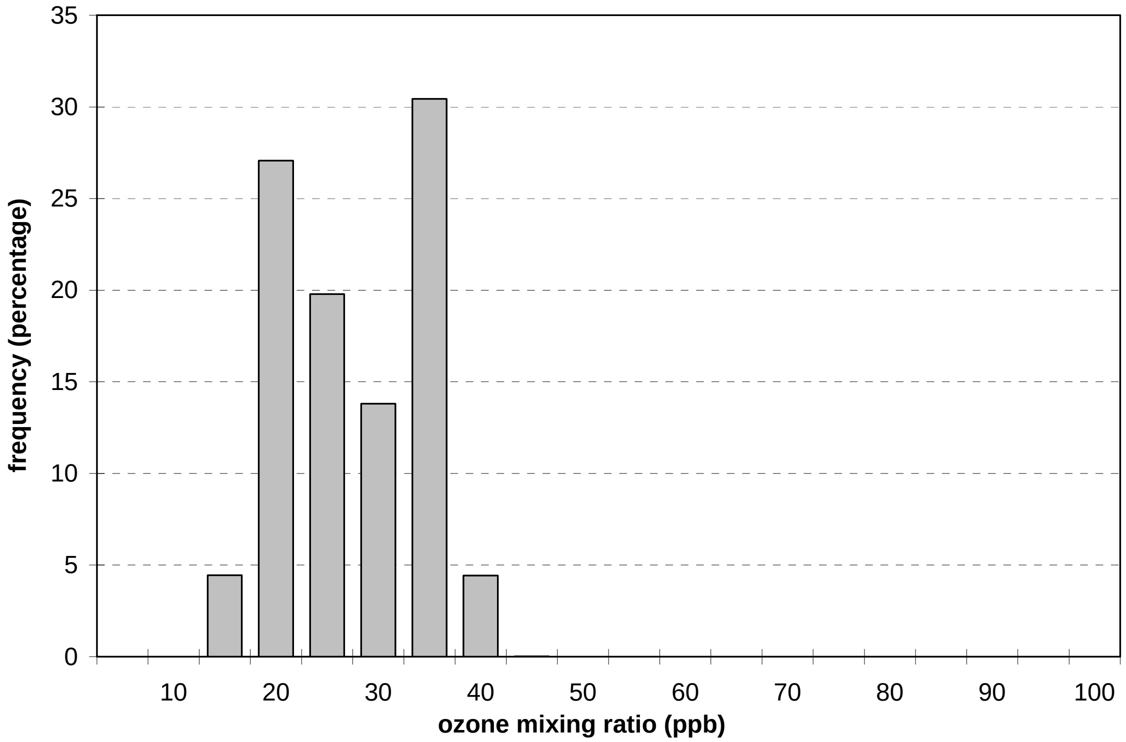

Figure 6: Frequency distribution of the values of the ozone mixing ratio (ppb) at the Ushuaia of the year 1998.

3.4. Carbon Monoxide Level

The relevant carbon monoxide concentration range can be well defined by the frequency distribution. In figure 7 the frequency distribution of the values from the year 1998 is shown. The relevant carbon monoxide concentrations were calculated, ranging between 37 and 66 ppb according the 5 and 95 percentile values. Annual data capture 41.6 %.

Source of data: received from SMN

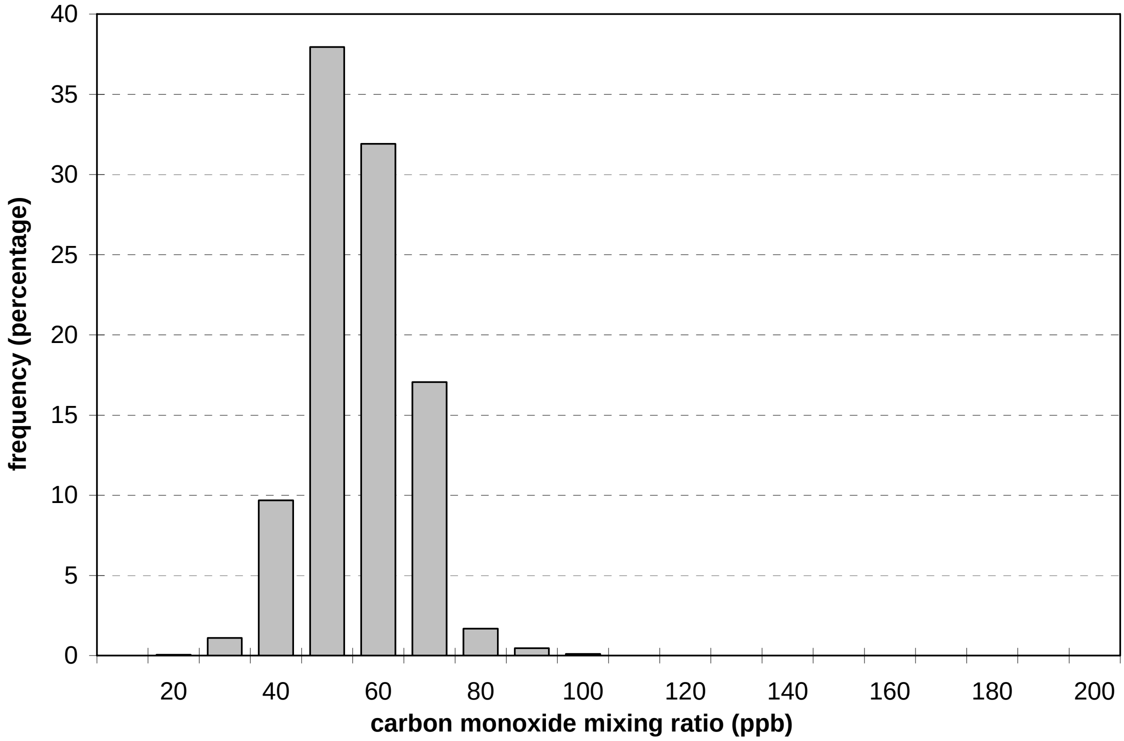

Figure 7: Frequency distribution of the values of the carbon monoxide mixing ratio (ppb) at the Ushuaia of the year 1998.

4. Measurement Technique (O_3 and CO)

4.1. Air Inlet System

Two separate inlet systems are installed for the ozone and CO measurements. Both inlets are located nearby, on top of the flat roof of the building, approximately 7m above the ground. An inverse funnel is used for each line as protection from rain and snow. Teflon tubes lead along the outside wall (south-west) down to the basement and through a cutting into the instrument room. The tubes on the outside are not heated. The ambient air is not dried (pre-treatment) before analysed.

Ozone: Downstream, the system consists of the funnel (PE), a 1.5 m, ½ " teflon tubing, a particle filter (teflon). The air is then split in two 6 m, ¼ " teflon tubing leading directly into each of the instruments. The air is sucked through the system by the instrument pumps (each 2 l/min). The residence time of the ambient air in the inlet line lies around 3 seconds.

CO: Downstream, the system consists of the funnel (PE), a 1.5 m, ½ " teflon tubing, a particle filter (teflon), a 6 m, ½ " teflon tubing which is leading directly into the instrument. The air is sucked through the system by the instrument pump (2 l/min). The residence time of the ambient air in the inlet line lies around 10 seconds, with just one instrument operating. Since the split for the additional analyser is right at the end of the line, a second instrument would half the residence time.

Comment

All teflon tubes were clean and free of dust and adequate for trace gas measurements in particular with regard to minimal loss of ozone.

4.2. Instrumentation

Both, ozone and CO instruments are installed on movable benches in a room (average temperature around 20°C) with no air-condition. The outdoor temperatures at Ushuaia are moderate the whole year round, thus, even without air-conditioning the variation of the indoor temperature might be acceptable. The analysers are protected from direct sunlight.

Until the middle of 1997, ultrapure air from gas cylinders was used as zero air (the cylinders are empty and no spare could be purchased). On the occasion of the last audit (operators of the global GAW station Izaña, Spain), the auditor had supplied the station Ushuaia with a zero air unit for ozone, consisting of an air compressor, a silica gel and a charcoal cartridge and a particle filter.

Instrumental details for the ozone and carbon monoxide analyser on site are listed in table 2 and 3, respectively.

4.2.1. Ozone Analysers

Table 2: Field instruments, ozone

type	TEI 49 #47306-278 "O3-1"	TEI 49 #47312-278 "O3-2"
method	UV absorption	UV absorption

usage	basic instrument	backup instrument
at Ushuaia	since September 1994	since November 1994
range	0-100 ppb	0-100 ppb
analog output	0-10 V	0-10 V
Instrument specials	internal ozone generator	

Comment

The operation of an ozone analyser and a backup instrument (both UV method), considerably increases confidence in data quality concerning parallel measurements as well as data availability.

4.2.2. Carbon Monoxide Analyser

Originally, the station had been equipped with a second (backup) CO analyser. Because of a lack of necessary spare parts the operating team was forced to switch off one of the instruments. Today, only one instrument is running, the other instrument is shutdown.

Table 3: Field instrument, carbon monoxide

type	TEI 48, internal code "B" #47169-278
method	NDIR / GFC
usage	basic instrument
at Ushuaia	since November 1994
range	0-1000 ppb
analog output	0-10 V
zero trap	Degussa Type E221 P/D 0.5% at 180°C

In general, two different principles of measuring carbon monoxide can be distinguished and are in practical use at several global GAW stations:

- method: NDIR / GFC, continuous monitoring
- method: GC / HgO, discreet

Distinct characteristics and capabilities of current instruments are discussed in WMO-GAW Report No. 98, WMO meeting of experts on global CO measurements.

The monitoring analysers of the type that is in use at present, show a continuous drift for the zero point potentiometer which makes a frequent zeroing of the system necessary. Thus, ambient air and zero is measured alternatingly in a seven-minutes / three-minutes interval. Valve switching directs the ambient air stream either straight into the analyser or through the CO trap.

Comment

The CO NDIR analyser (TEI 48) in use is, taking into account the measurement principle, in acceptable condition. However, for observations of long term a substantially more sensitive instrument would be necessary. Nevertheless, for the actual situation operating the TEI 48 analyser, parallel operation of two analysers would considerably increase confidence in the acquired data, moreover since no regular quality checks can be performed. But lack of necessary spare parts had forced the team to shutdown the second instrument.

4.3. Operation and Maintenance

On a regular working day, the person in charge inspects the measurements for a quick check of general operation of the analysers. Exchange of the teflon filters on the flat roof platform to protect the instrument inlets, is made every 2 to 3 weeks. In periods with very strong wind conditions the filters are replaced more often due to expected accumulation of aerosols from the sea. The charcoal cartridge of the ozone zero air supply on site is not replaced, while the silica gel is regenerated on demand. The Degussa CO catalyst for producing CO free air has not been replaced either, nor exists a possibility to check the catalyst efficiency. In a monthly interval, for both ozone and CO, the flow through the cells, lamp intensity and temperatures are checked and noted in the logbook. Preventive maintenance of the ozone and carbon monoxide instruments is not performed unless indicated by analyser malfunction. However, an exception are the ozone measurement cells, which have been cleaned every two years. Manual zero and span checks (20 ppb and 95 ppb, each) are made monthly with the ozone analysers using the internal ozone generators. The zero values are used for recalculating the final data set. In the case of CO, due to the lack of an independent CO free source and because the former CO standard cylinder (ppm) is empty, there is no zero or span check performed since around two years. Originally, once a day, a known amount of this high concentrated and relatively cheap CO standard was automatically added to the ambient air in the inlet line (standard addition).

Ozone calibration: No ozone calibrator available at the site. The only calibration ever carried out were the ones during the three audits between 1994 and 1998.

CO calibration: From the time on when the mentioned standard addition proceeding stopped, the only check was an annual calibration using five certified gas cylinders which had been received from the carbon cycle group of the CMDL / NOAA. The standards range from 50, 100, 150, 200 to 300 ppb, respectively, and thus have to be used undiluted. The consumption of such a costly intensive standard for a calibration is high (in the order of a litre per minute) so saving air was the reason why the calibration was not performed more regularly. However, the instrument was checked and maintained intensively by Dr E. Scheel at IFU, in Garmisch in summer 1996. Since that time the continuous measurements and the CMDL flask sample results agreed very well.

Comment

The appearance inside the station is clean and functional. One of the main factors of quality assurance is to perform regular multipoint calibrations. Thus, the replacement of the reasonable priced CO standard (ppm) which had been used for standard addition, is essential for a successful continuing of the CO measurements. For the zero check of the CO measurements, the zero trap from the instrument which was shutdown could be used to verify the unit in use.

Further should be guaranteed that the ozone calibrator of the SMN is regularly used for calibrating and thus verifying the ozone measurements made at the global GAW site Ushuaia.

However, as long as the necessary references are not available at the site it is recommended to change as little as possible at the working instruments. Any maintenance that could alter the performance should be avoided.

4.4. Data Handling

A data acquisition facility is installed at the site consisting of a 12-bit AD converter and a self-made Qbasic acquisition software. The data acquisition calculates one-minute averages (from 10s running averages) and stores the data in a file of the following structure: Day-Month-Year, value of ozone equipment O3-1 mV, value of ozone equipment O3-2 mV, value of CO equipment CO-2 mV. Adjustment of parameters, e.g. averaging intervals or offsets, requires programming capability and can not be carried out by the station personnel. A new acquisition system provided to the station by the INM of Spain in 1997, is not in operation anymore. The software would be more flexible and more user friendly but stops acquisition around midnight without any reason. Thus, switching back to the former system became necessary.

The data validation procedure is split up into two parts and is carried out monthly. In a first step, the person who is responsible for data management reprocesses the one-minute raw data doing offset correction, zero-point-drift calculation, and application of filter functions.
- For the ozone data the appropriate artificial zero offset (average between two monthly determined zero values) is subtracted first.
- The CO raw data set can be devided in 10 minute cycles consisting of a "invalid" one-minute value (flushing), six-minutes of span values, another "invalid" one-minute value (flushing) and two-minutes of zero. The signal intensity (mV) between the zero and the span stands in direct relation to ppb. The subtracted zero signal consists of the average between the zero values acquired before and after the span.

Than, a filter function is applied to both data to achieve a baseline condition data set. This is done taking only data from the very narrow wind sector 220° to 270° which is considered as clean air sector. Additionally, the extracted data has to fulfil the criteria to be acquired under strong wind conditions, defined as wind speed > 5 m/s. With this quite restrictive procedure only about 40 % of the totla data is defined as valid data.

In a second step, the person in charge of the CO and ozone measurements removes invalid data, i.e. calibration data or zero check values. The acquired ozone data of the two instruments is compared with each other by regarding differences. CO is used for a consistency check of the ozone data and vice versa; controlled on plots.

To date, only a daily average value for ozone and CO is calculated and reported to SMN. The data is not submitted to the World Data Centres, yet.

Comment

The procedure of data treatment is rather working intensive and is composed of a lot of single working steps. It seems advisable to invest in either the actual system to make it more flexible or to get running the system provided by the INM, Spain. It is further suggested to discusse the issue of data filtering with other experts in order of re-evaluating the chosen procedure.

4.5. Documentation

Within the GAW guidelines a documentation of the work is required. During the audit the documentation was reviewed for availability and usefulness.
The main information is written down in a bound logbook, for both the ozone and the CO measurements, which is a combination of instrument-, station- and maintenance logbook. The logbook was kept up-to-date and contained all necessary information about maintenance, changes, events and special investigations. Data plots and graphs are stored in a separate file.

Comment

The documentation of the ozone and CO measurement meets the requirements of the guidelines for GAW stations.

4.6. Competence

All persons associated with the operation of the examined parameters are highly motivated and experts in their fields. The operators are well familiar with the techniques and problems connected with ozone and CO measurements.

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the WCC transfer standard (detailed description see Appendix Ozone II) was hooked up to power for warming up over night (deviation to the GAW report No. 97 in which only one hour of warm-up time is required). In the morning, before the intercomparison was started the transfer standard, the PFA tubing connections to the instrument and the instrument itself were conditioned with about 200 ppb ozone for 20 min. During the 1. and 2. December, three comparison runs between the field instruments and the WCC transfer standard were performed. In the meantime the inlet system and the instrument maintenance were inspected and discussed. Table 4 shows the experimental details and figure 8 the experimental set up of the audit. In general, no modifications of the ozone analysers which could have influenced the measurements were made for the intercomparisons.

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 WCC calibration laboratory at EMPA. The results are shown in the Appendix Ozone III.

Table 4: Experimental details, ozone

auditor, WCC	A. Herzog
reference:	WCC: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49 #-47306-278 "O3-1" TEI 49 #-47312-278 "O3-2"
ozone source:	WCC: TEI 49C-PS, internal generator
zero air supply:	WCC: silicagel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm
data acquisition system:	WCC: 16 channel ADC circuit board, software
surrounding conditions:	p: 995 hPa $\pm$ 2 hPa and T_{indoor}: approx. 23°C
pressure transducers reading:	TEI 49C-PS: 995 hPa TEI 49 "O3-1": 995 hPa TEI 49 "O3-2": 991 hPa
concentration range:	0 - 100 ppb
number of concentrations:	5 + zero air at beginning and end
approx. concentration levels:	15 / 35 / 55 / 75 / 95 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes

number of runs:	2 x on 1. December 1 x on 2. December
connection between instruments:	approx. 1.2 meter of 1/4" PFA tubing

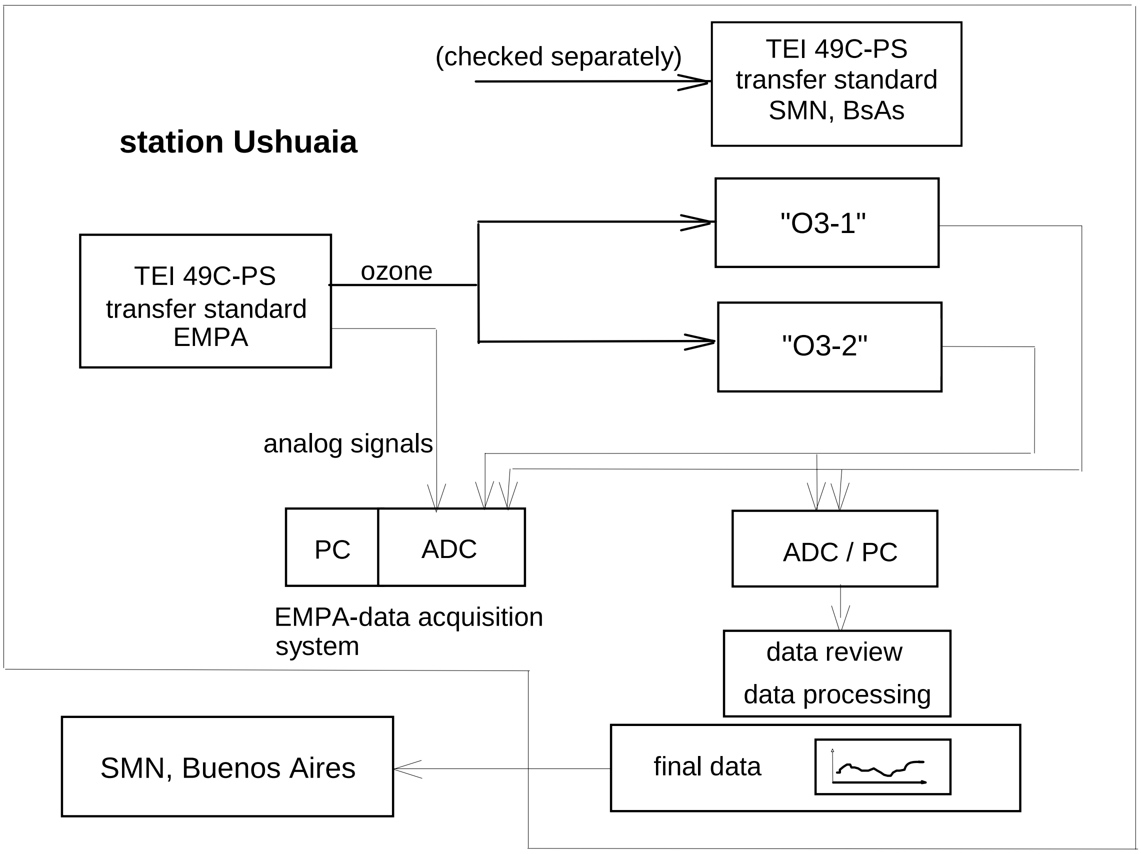

Figure 8: Experimental set up, ozone

The WCC acquisition system, which was used for the audit, consists of a 16 channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of all the instruments involved the data was collected by the data acquisition system of the WCC. In advance, it was checked that the readings of the two acquisition systems were equal at zero (ozone) and at 200 ppb ozone. For data interpretation the WCC data is used.

5.2. Results

The results comprise three intercomparisons between the two field instruments TEI 49 "O3-1" and "O3-2" and the WCC transfer standard TEI 49C-PS, carried out on 1. / 2. December, 1998.

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

Furthermore, the diagrams show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard. The results of the three runs are then summarised to the mean regression equation and presented in a graph with the assessment criteria for GAW field instruments (Figures 13 and 14).

Table 5: 1. Intercomparison, ozone

No.	**transfer standard**		**TE 49 "O3-1"**				**TE 49 "O3-2"**			
	TE 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	0.6	0.44	0.2	0.36	-0.4		1.3	0.14	0.7	
2	30.0	0.17	29.6	0.31	-0.5	-1.6%	30.5	0.17	0.5	1.7%
3	10.2	0.15	9.8	0.31	-0.4	-4.0%	10.8	0.24	0.6	5.9%
4	40.0	0.14	39.6	0.25	-0.5	-1.2%	40.5	0.22	0.4	1.0%
5	20.2	0.14	19.7	0.29	-0.5	-2.3%	20.6	0.23	0.4	1.9%
6	90.0	0.12	89.3	0.22	-0.7	-0.8%	89.9	0.12	-0.1	-0.1%
7	0.5	0.12	0.1	0.27	-0.4		1.1	0.13	0.6	

Table 6: 2. Intercomparison, ozone

No.	**transfer standard**		**TE 49 "O3-1"**				**TE 49 "O3-2"**			
	TE 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	0.5	0.12	0.1	0.27	-0.4		1.1	0.13	0.6	
2	40.0	0.17	39.3	0.27	-0.7	-1.7%	40.4	0.19	0.4	1.0%
3	20.1	0.15	19.7	0.27	-0.4	-2.2%	20.6	0.23	0.5	2.5%
4	10.2	0.20	9.7	0.30	-0.5	-4.7%	10.5	0.23	0.3	3.3%
5	90.0	0.13	89.4	0.29	-0.6	-0.6%	89.8	0.20	-0.2	-0.2%
6	30.1	0.12	29.5	0.23	-0.6	-1.9%	30.3	0.17	0.2	0.6%
7	0.4	0.11	-0.1	0.22	-0.5		1.1	0.34	0.7	

Table 7: 3. Intercomparison, ozone

No.	**transfer standard**		**TE 49 "O3-1"**				**TE 49 "O3-2"**			
	TE 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	0.5	0.17	0.1	0.29	-0.3		1.3	0.21	0.8	
2	39.8	0.16	39.1	0.25	-0.7	-1.7%	40.0	0.18	0.2	0.4%
3	29.9	0.17	29.2	0.28	-0.7	-2.3%	30.2	0.17	0.3	0.9%
4	89.9	0.23	89.1	0.35	-0.8	-0.8%	89.9	0.30	0.0	0.1%
5	20.1	0.21	19.3	0.31	-0.7	-3.7%	20.5	0.18	0.4	1.9%
6	10.2	0.28	9.4	0.25	-0.8	-7.5%	10.4	0.19	0.3	2.5%
7	0.4	0.13	0.0	0.29	-0.4		1.0	0.11	0.6	

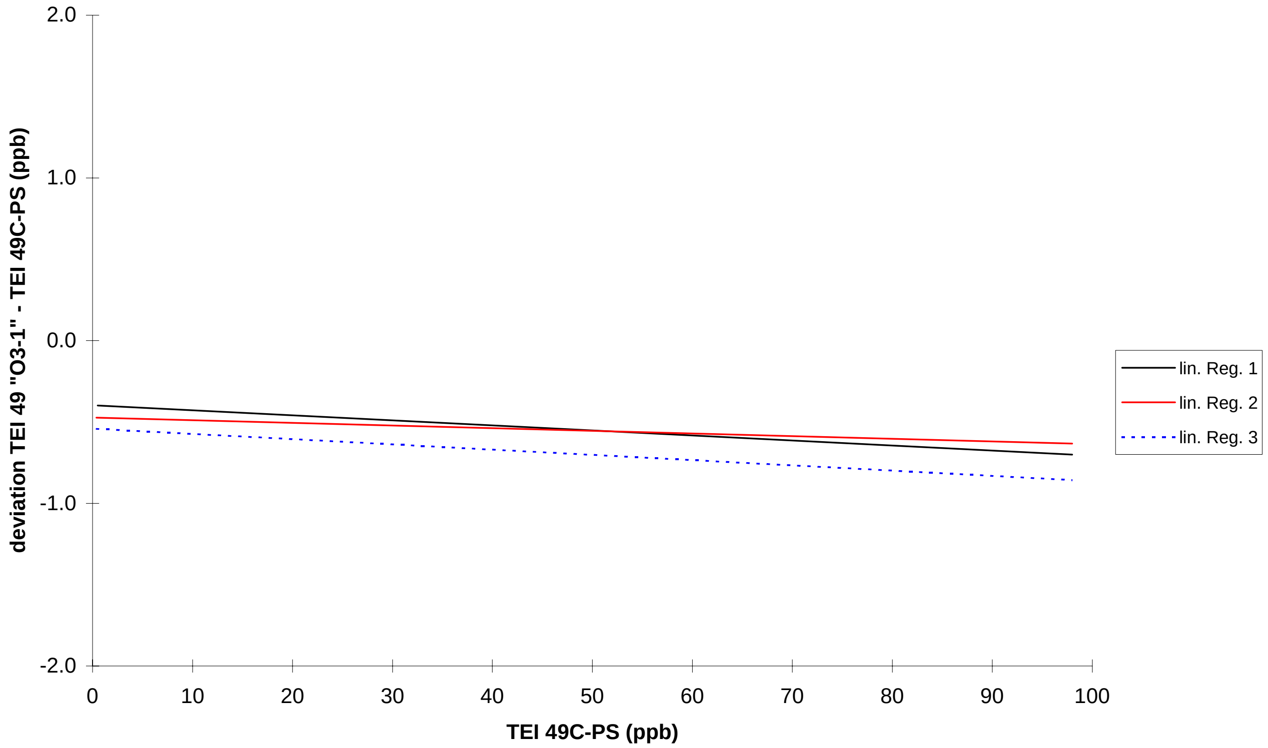

Figure 9: Individual linear regressions of ozone intercomparisons, TEI 49 "O3-1"

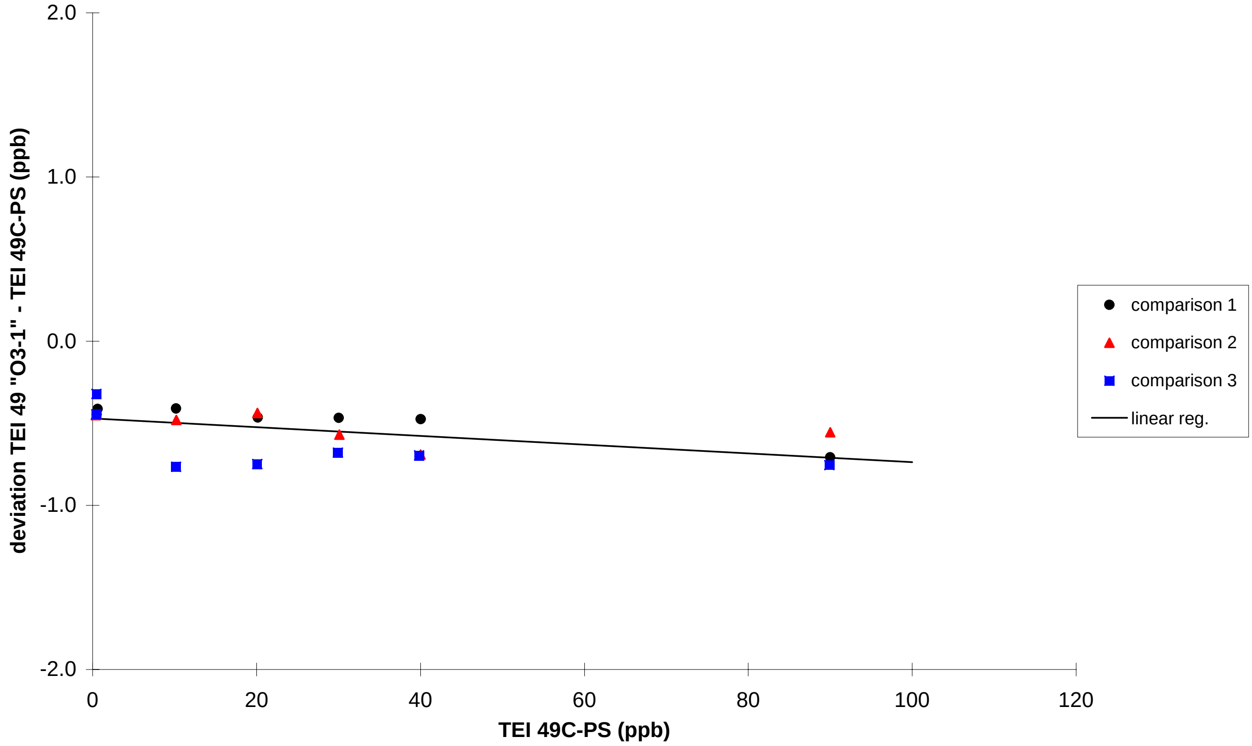

Figure 10: Mean linear regression of ozone intercomparisons, TEI 49 "O3-1"

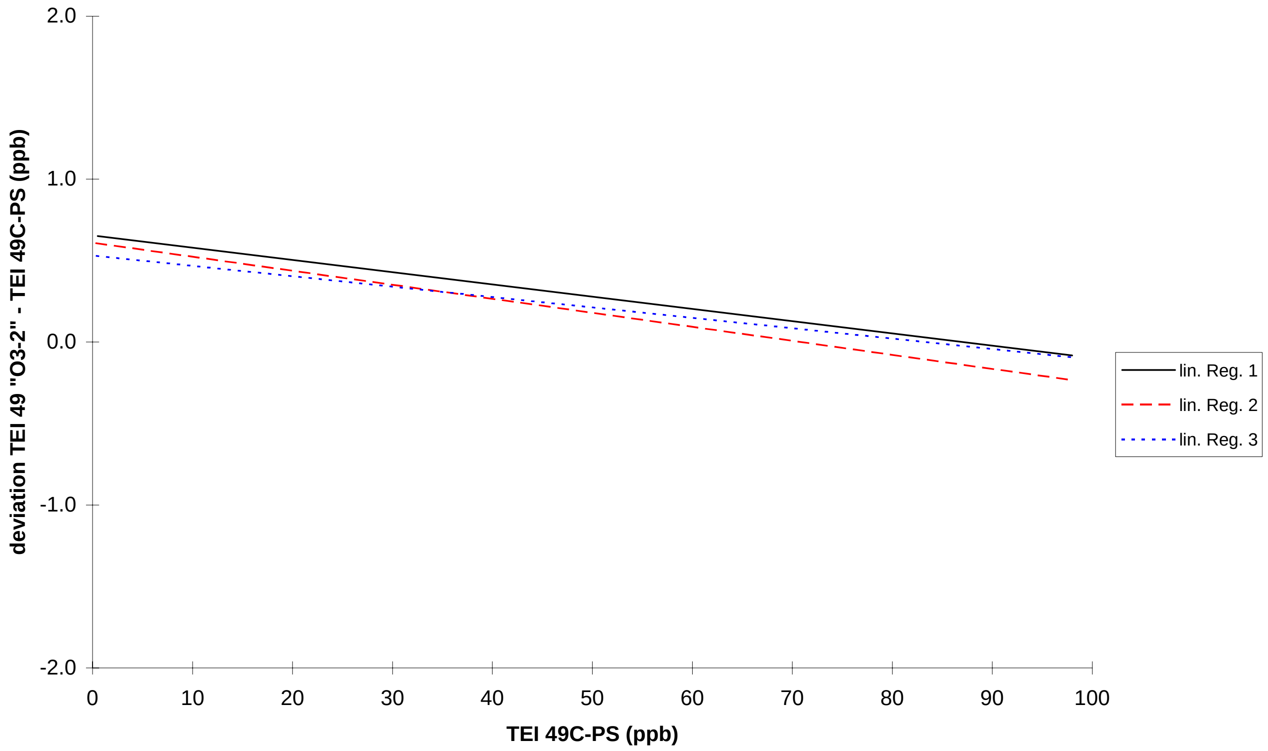

Figure 11: Individual linear regressions of ozone intercomparisons, TEI 49 "O3-2"

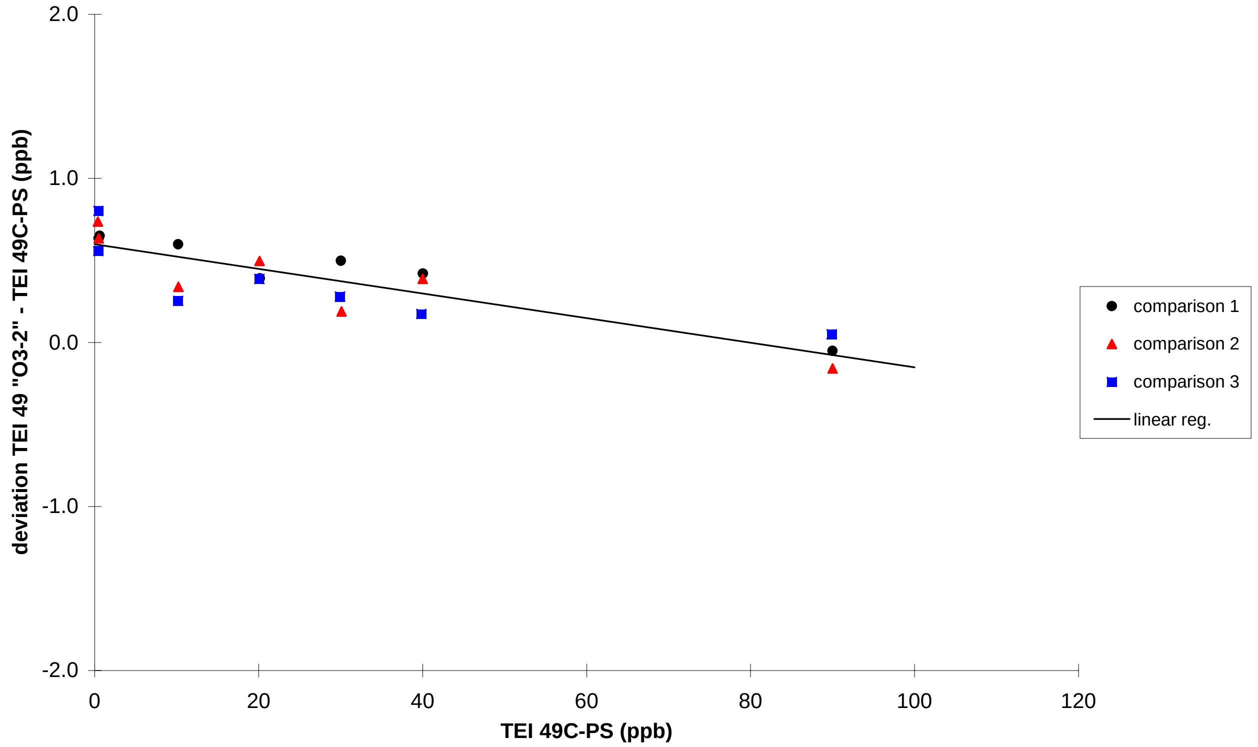

Figure 12: Mean linear regression of ozone intercomparisons, TEI 49 "O3-2"

From the comparisons of the two TEI 49 field instruments with the WCC transfer standard the resulting linear regression equations (valid for the range of 0-100 ppb ozone) are:

TEI 49 "O3-1"

TEI 49 "O3-1" = 0.997 x TEI 49C-PS - 0.5 ppb

TEI 49 "O3-1" = O_3 mixing ratio in ppb, determined for TEI 49 #47306-278
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0009	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.03	(f = 3)
	- residuals in ppb	0.09	(f = 19)

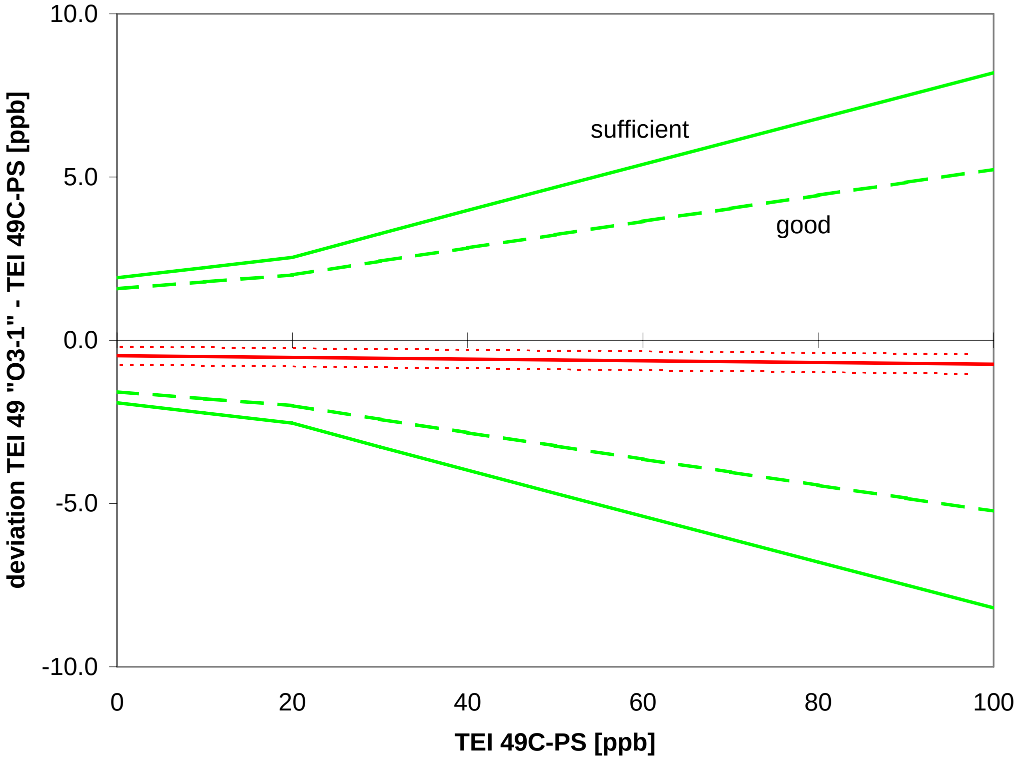

Figure 13: Intercomparison of ozone instrument TEI 49 "O3-1" (linear regression with prediction interval 95%)

TEI 49 "O3-2"

TEI 49 "O3-2" = 0.992 x TEI 49C-PS + 0.6 ppb

TEI 49 "O3-2" = O_3 mixing ratio in ppb, determined for TEI 49 #47312-278
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0010	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.04	(f = 3)
	- residuals in ppb	0.11	(f = 19)

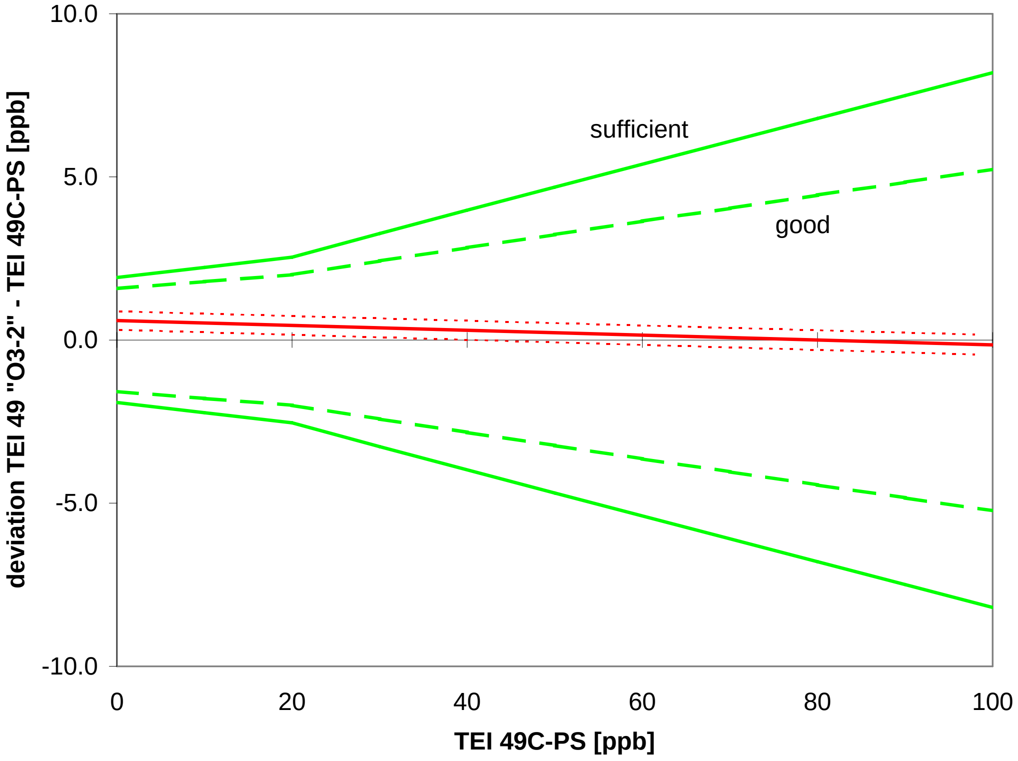

Figure 14: Intercomparison of ozone instrument TEI 49 "O3-2" (linear regression with prediction interval 95%)

Comment

In the linear regressions of the instruments (figures 9 and 11), no trend as a function of time could be observed during the intercomparison.

The ozone concentrations observed at the Ushuaia (1997) usually ranged between 15 and 35 ppb (5- and 95-percentile of hourly mean values).

Both instruments clearly fulfil the assessment criteria as "good" over the tested range up to 100 ppb (figures 13 / 14). Fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instruments are in good condition.

6. Intercomparison of CO Instrument

6.1. Experimental Procedure

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

At the site the MGM diluter (see Appendix Carbon Monoxide III) was hooked up to power for warming up and for stabilisation for several hours. The calibration gas (NMI reference gas) was stored at the site over night before the audit measurements were started. At the end of the stabilisation time the whole dilution system including PFA tubing was flushed with 350 ppb CO for 20 minutes. Between 2. and 4. December, the intercomparison was made with the field instrument TEI 48 "CO-2" . Different concentration levels between 40 and 240 ppb were applied (figure 15). Table 8 shows the experimental details and figure 16 the experimental set up of the CO performance audit. In general, no modification of the carbon monoxide analyser was made for the intercomparison. The signal of the field instrument was acquired by the WCC data acquisition system. During the audit WCC zero air (synthetic air + Sofnocat) was used. The station zero air was tested and there was no significant difference between the site zero air and the WCC zero air, as can be seen in the results of the zero values (No. 1, 7, 13, in table 13). The CO trap efficiency was checked by comparing the zero values when the CO trap is flushed with either with air containing 240 ppb of CO or CO free air. No significant difference was detected pointing to still good efficiency of the Degussa zero trap in use.

Finally, the observed results were discussed in an informal review with the person involved.

The audit procedure included a direct intercomparison of the MGM diluter transfer standard with the Califlow (Standard Reference) before and after the audit in the calibration laboratory at (see Appendix CO, MGM Diluter). The NMI-Reference Gas (Transfer Standard) is traceable to NIST and the CMDL Laboratory Standard Gases.

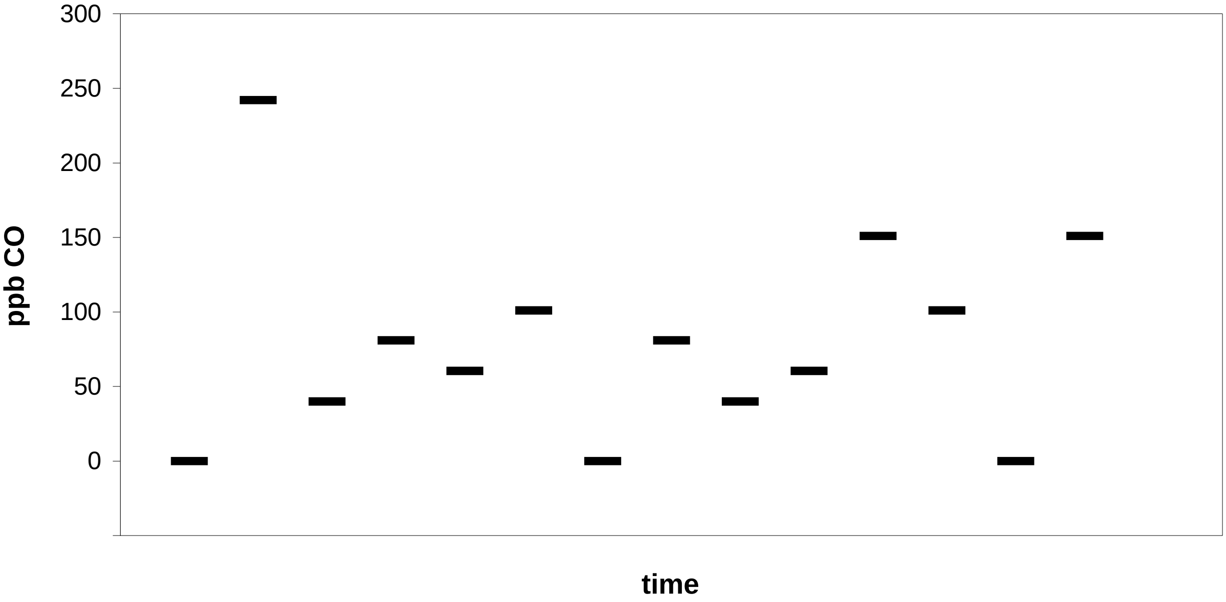

Figure 15: Sequence of concentrations during audit, CO

Table 8: Experimental details, carbon monoxide

auditor, WCC	A. Herzog
reference:	Transfer standards: MGM diluter, NMI Reference Gas
field instrument:	TEI 48 #47169-278, "CO-2"
zero air supply:	WCC: synthetic air + Sofnocat station: ambient air + Degussa Type E221 P/D 0.5% at 180°C
data acquisition system:	WCC: 16 channel ADC circuit board, software
surrounding conditions:	p: 995 hPa ± 2 hPa and T_{indoor}: approx. 23°C
instrument range:	0 – 1000 ppb
number of concentrations:	6 + zero air of station and WCC
approx. concentration levels:	40 / 60 / 80 / 100 / 150 / 240 ppb
sequence of concentration:	see figure 14
averaging interval per concentration:	30 minutes
measuring cycle	1 minute flush - 6 minutes measurement-mode 1 minute flush - 2 minutes zero-mode
connection to instrument:	less than 3 meter of 1/4" PFA tubing

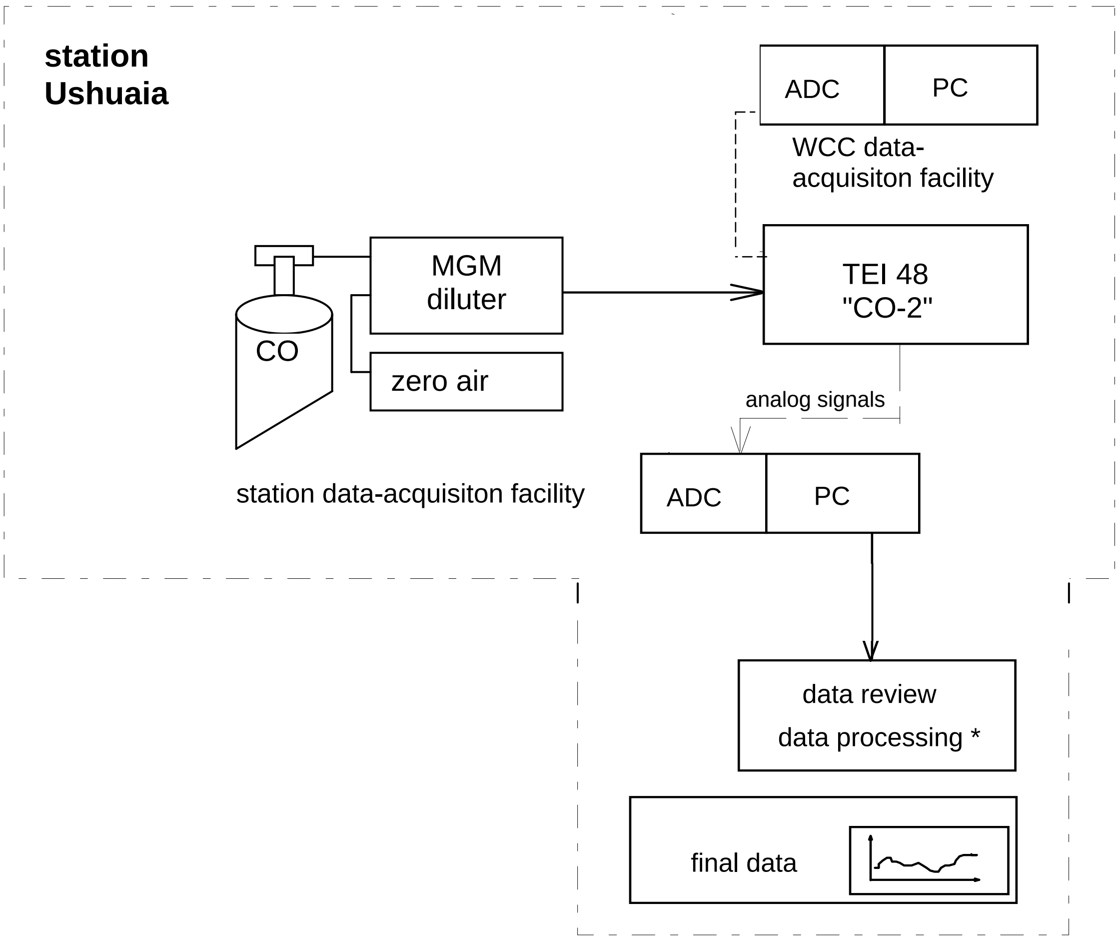

Figure 16: Experimental set up, carbon monoxide

6.2. Results

The results consist of 14 measurements between the field instrument TEI 48 "CO-2" and the WCC transfer standard carried out between 2. and 4. December, 1998.
In the following table the resulting mean values of each carbon monoxide concentration and the standard deviations of a 30-minute interval with 3 measuring cycles (1 minute flush - 6 minutes measurement mode - 1 minute flush - 2 minutes zero mode) are presented. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and in %. Further figure 17 shows the results of the linear regression analysis of the field instrument compared to the WCC transfer standard.

Table 9: Intercomparisons, CO

No.	**transfer standard**	**TEI 48 "CO-2"**			
	MGM conc. ppb	conc. ppb	s_d ppb	deviation from reference ppb	%
1	0.0	3.0	1.1	3.0	
2	242.0	250.6	7.4	8.6	3.5
3	40.0	37.9	1.9	-2.1	-5.2
4	81.0	83.8	2.5	2.8	3.5
5	60.5	60.1	5.8	-0.4	-0.7
6	101.0	95.9	6.7	-5.1	-5.0
7	0.0	-3.0	3.3	-3.0	
8	81.0	89.9	2.5	8.9	11.0
9	40.0	34.2	10.9	-5.8	-14.5
10	60.5	66.7	4.1	6.2	10.2
11	151.0	150.9	8.6	-0.1	-0.1
12	101.0	107.8	2.4	6.8	6.7
13	0.0	5.3	1.2	5.3	
14	151.0	163.5	2.7	12.5	8.3

The summary of the CO comparisons (valid for the CO range 0 - 250 ppb) of the TEI 48 CO analyser with the WCC transfer standards is the following linear regression line:

TEI 48 "CO-2" = 1.035 x TS – 0.1 ppb

TEI 48 "CO-2" = CO mixing ratio in ppb, determined for TEI 48 #47169-278
TS = CO mixing ratio in ppb, produced by the Transfer standards (MGM diluter + NMI Reference gas) and related to the Standard References at the EMPA-WCC (Califlow, CMDL + NIST gases).

Standard deviation of:	- slope s_m	0.02	(f = 1) f=degree of freedom
	- offset S_b in ppb	2.2	(f = 1)
	- residuals in ppb	5.3	(f = 12)

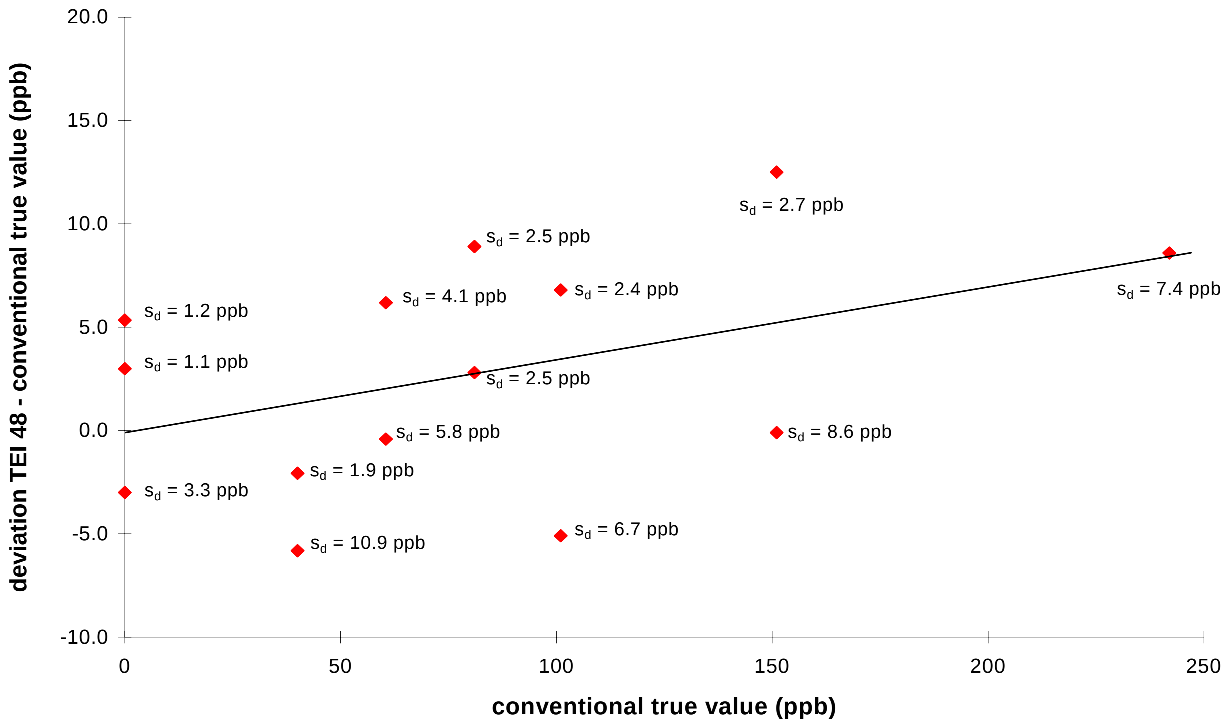

Figure 17: Absolute differences between the TEI 48 "CO-2" analyser and the transfer standard, linear regression line, s_d of three cycle averages (6 min span / 2 min zero)

Figure 18 shows the relative differences (%) between TEI 48 "CO-2" and the transfer standard. The total uncertainty of the transfer standard (red whiskers in figure 18) has been calculated for the whole audit procedure. Most of the uncertainty is caused by the uncertainties of the Reference gases.

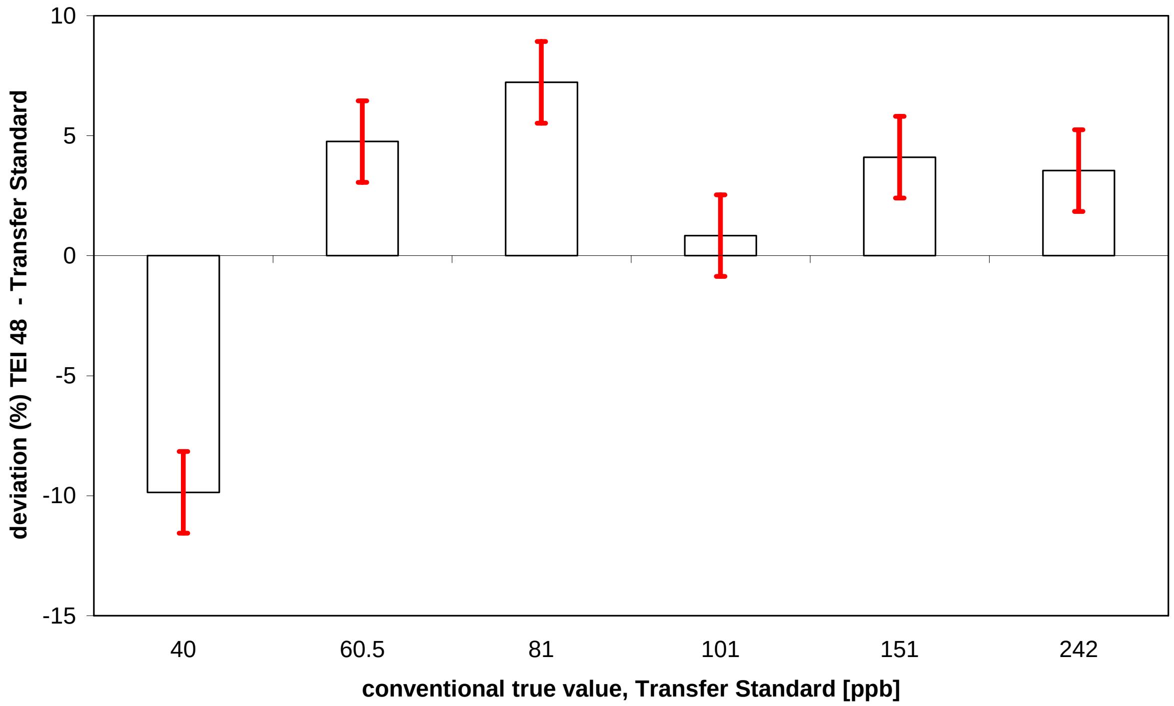

Figure 18: Differences (%) between the TEI 48 "CO-2" and the transfer standard (the red whiskers show the total uncertainty for the whole audit procedure)

During the night of 2. – 3. December 1998, an ambient air intercomparison between the field instrument TEI 48 "CO-2" and the transfer standard Horiba 360 APMA (EMPA-WCC) was carried out. In figures 19, the 10 minutes mean values of the results of the two instruments are shown. Interesting in the graph below is the episode during 2 a.m. and 6 a.m. when the wind had shifted from south-west (clean air) to north-east direction, representing air coming from the city of Ushuaia and the airport.

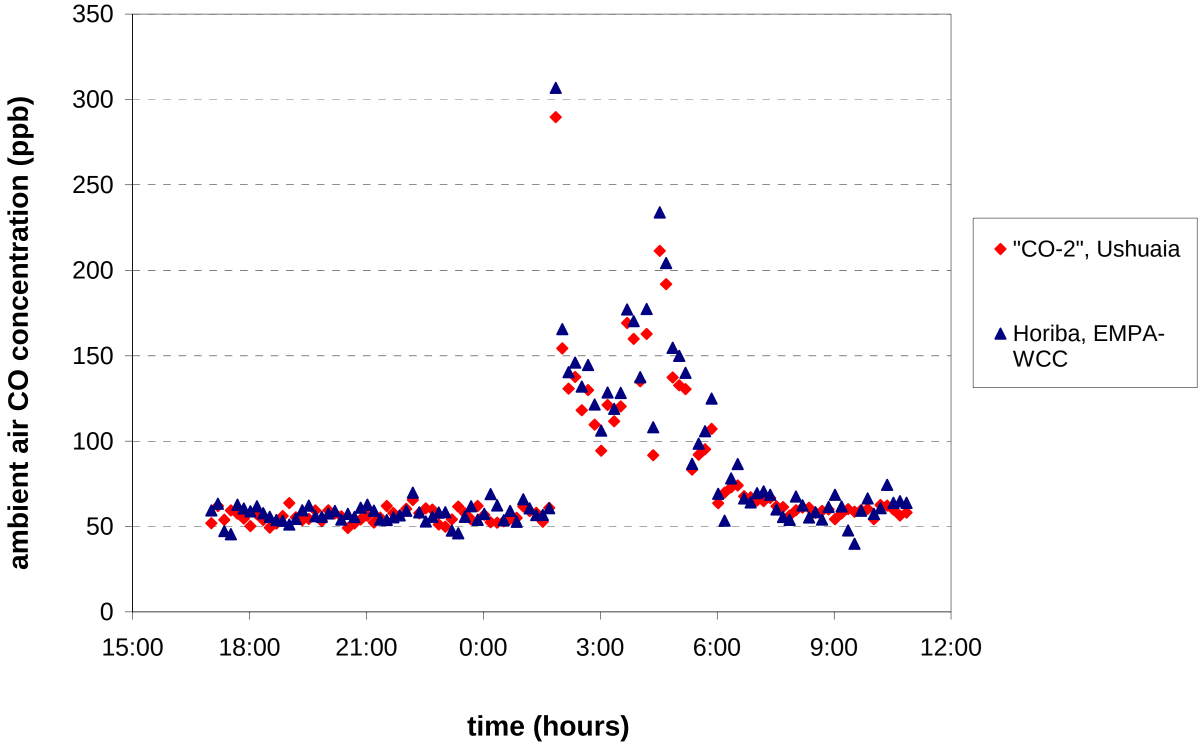

Figure 19: Ambient air concentrations measured with the field instrument TEI 48 "CO-2" and the transfer standard Horiba 360 APMA (EMPA-WCC) during the night of 2. – 3. December, 1998. Showed values are 10 minutes averages

Comment

On the one hand, the regression analysis result of the CO intercomparison shows an overall moderate deviation of 3 to 4% compared to the conventional true value but a high standard deviation of the residuals in the order of 5ppb on the other (see fig. 17). This rather high standard deviation is due to the used measurement technique since the instrument is operated at the edge of its sensitivity and detection limit (background pollution level of the site of Ushuaia ranges between 37 ppb to 66 ppb CO). Considering the quality objectives of the GAW programme, the analyser seems to be adequate for segregation of polluted against background air masses but insufficient for observations of long term trends. A substantially more sensitive instrument, like other comparable GAW sites on the southern hemisphere, i.e. Cape Point or Cape Grim, would be necessary to achieve that goal.

The ambient air measurements of the station analyser and the EMPA transfer standard (Horiba 360 APMA) in parallel, agreed well.

Appendix Ozone

I Calibrator TEI 49C-PS #56084-306 of the SMN, Argentina

In addition to the intercomparisons of the actual ozone analysers at Ushuaia, an intercomparison of the ozone calibrator TEI 49C-PS #56084-306 of the SMN was performed. The calibrator is usually located at the SMN in Buenos Aires and was originally purchased for the WMO project the "southern cone ozone project (SCO3P)". During this audit by the WCC-EMPA the mentioned calibrator was carried to Ushuaia for calibration purposes. The experimental procedure was exactly the same as for the other analysers and is described in chapter 5.1. Some technical data is listed in table 10. In June '97, the operators of the global GAW station Izaña, Spain, had determined a deviation of about 3 % in a comparison between their calibrator and the one from SMN. Due to these results a pre-run was carried out which again showed a similar deviation. Thus, the background (intercept) and the coefficient (slope) of the SMN ozone calibrator was changed accordingly (see table 9). The results of the intercomparison are shown below in table 12 and 13.

Table 10: Experimental details, SMN calibrator

Reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
Station calibrator:	SNM: TEI 49C-PS #56084-306 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): 993 hPa TEI 49C-PS (SNM): 993 hPa
Concentration range	0 - 100 ppb
Number of concentrations:	5 + zero air at start and end
Approx. concentration levels:	20 / 35 / 55 / 75 / 95 ppb
Sequence of concentration:	random
Averaging interval per concentration:	10 minutes
Number of runs:	1 x pre-run on 4. Dec. '98 2 runs (4. and 7. Dec. '98)
Connection between instruments:	about 1.0 meter of 1/4" PFA tubing, ozone connected to station calibrator between manifold and solenoid valve

Table 11: Ozone calibrator of the SMN, Argentina

Type	TEI 49C-PS #306
Method	UV absorption
at Ushuaia	for calibration purpose
Range	0-200 ppb
analog output	0-10 V
Electronic offset	changed from 0.0 ppb to 1.5 ppb (according pre-run)
Calibration coefficient	changed from 1.000 to 1.021 (according pre-run)

Table 12: 1. 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	%
1	0.7	0.15	0.4	0.08	-0.2	
2	54.6	1.40	54.8	0.23	0.2	0.3%
3	34.7	0.72	34.9	0.13	0.2	0.5%
4	20.0	0.09	20.0	0.14	0.0	0.0%
5	74.9	0.11	74.9	0.23	-0.1	-0.1%
6	95.0	0.23	94.9	0.26	-0.1	-0.1%
7	0.6	0.12	0.7	0.12	0.1	

Table 13: 2. 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	%
1	0.6	0.45	0.8	0.11	0.2	
2	74.9	0.18	75.1	0.13	0.2	0.2%
3	35.0	0.16	35.0	0.17	0.1	0.2%
4	20.1	0.22	20.3	0.09	0.2	1.0%
5	54.9	0.18	55.1	0.19	0.2	0.4%
6	95.1	0.24	95.5	0.27	0.5	0.5%
7	0.5	0.27	0.7	0.10	0.2	

The resulting linear regression (valid for the range of 0-100 ppb ozone) out of two runs between the TEI 49C-PS #306 ozone calibrator of the SMN and the TEI 49C-PS transfer standard from EMPA is:

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

calibrator SMN = O_3 mixing ratio in ppb, determined for TEI 49C-PS #56084-306
TEI 49C-PS (EMPA) = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0014	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.07	(f = 3)
	- residuals in ppb	0.10	(f = 19)

Comment

As mentioned, the instrument was originally purchased for the SCO_3Project and will be used for the planned ozone calibration centre in Buenos Aires. However, it would be very desirable to leave the calibrator at the Ushuaia GAW station until the centre in Buenos Aires has established.
After the adjustment of the ozone calibrator of the SMN, the instrument is traceable to the ozone reference at EMPA. The calibrator has been rarely used and is in good condition.

II WCC 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 degree to which the UV light is absorbed 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 20. 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 and manifold 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.

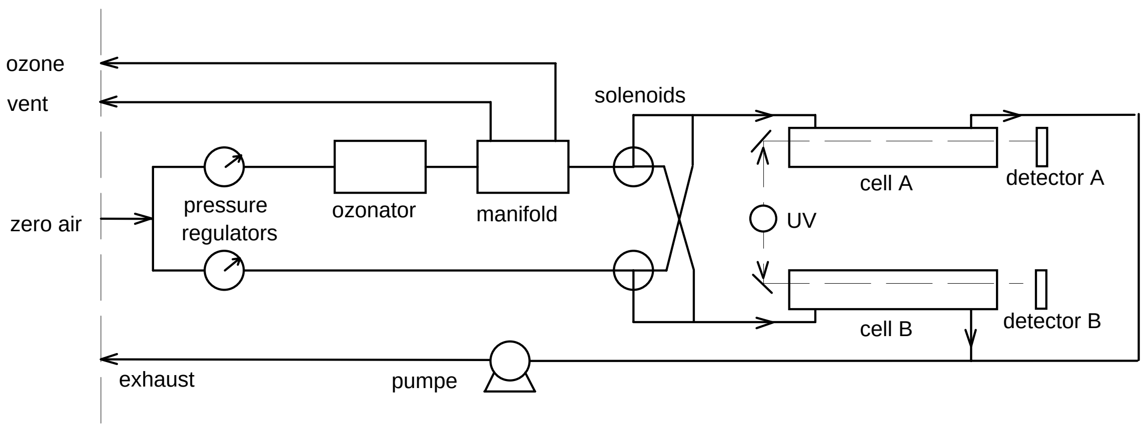

Figure 20: Flow schematic of TEI 49C-PS

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 #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at the EMPA-WCC are summarised in Table 14 and Figure 21.

Table 14: Intercomparison procedure SRP - TEI 49C-PS

pressure transducer:	span check (calibrated barometer)
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 125 / 185 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

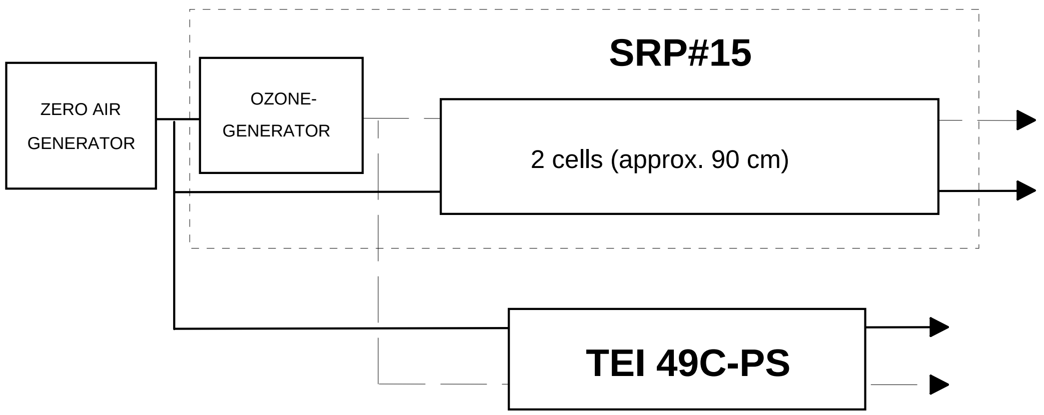

Figure 21: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). The assessment criteria for the transfer standard of the WCC-O_3 (TEI 49C-PS) are defined to ± (1 ppb + 0.6%), taking the uncertainty of the SRP into account.

Figures 22 and 23 show the resulting linear regression and the corresponding 95% prediction interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the linear regression and the prediction interval remain within the recommended tolerance.

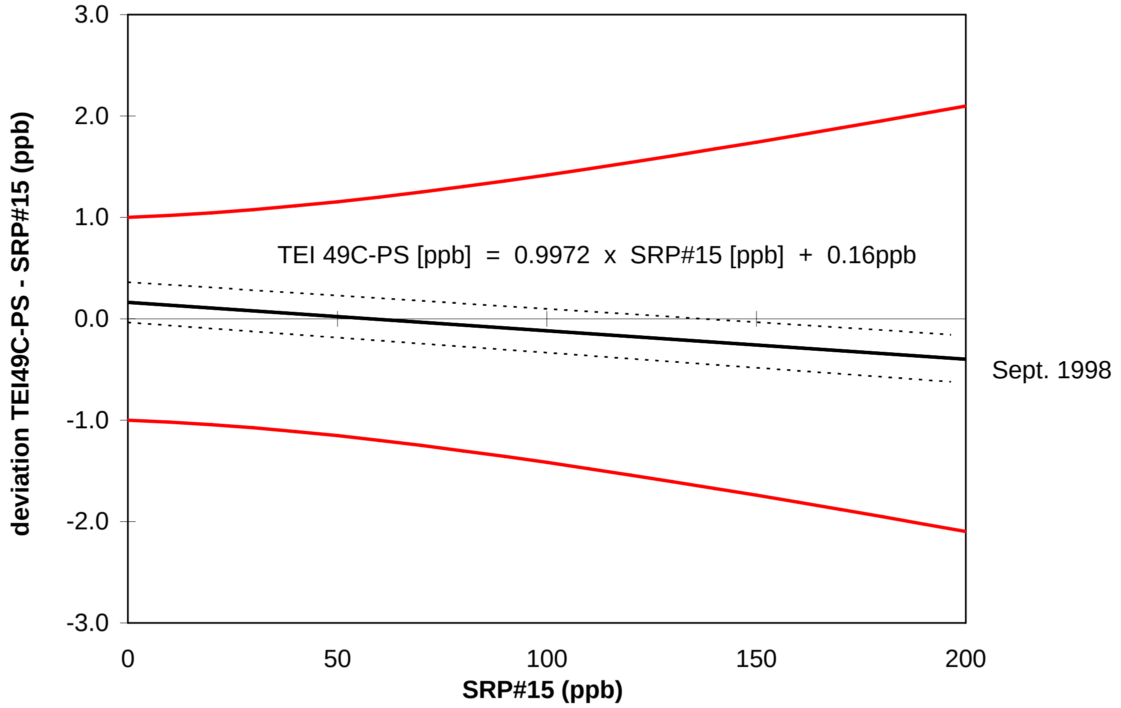

Figure 22: Transfer standard (O_3) before audit

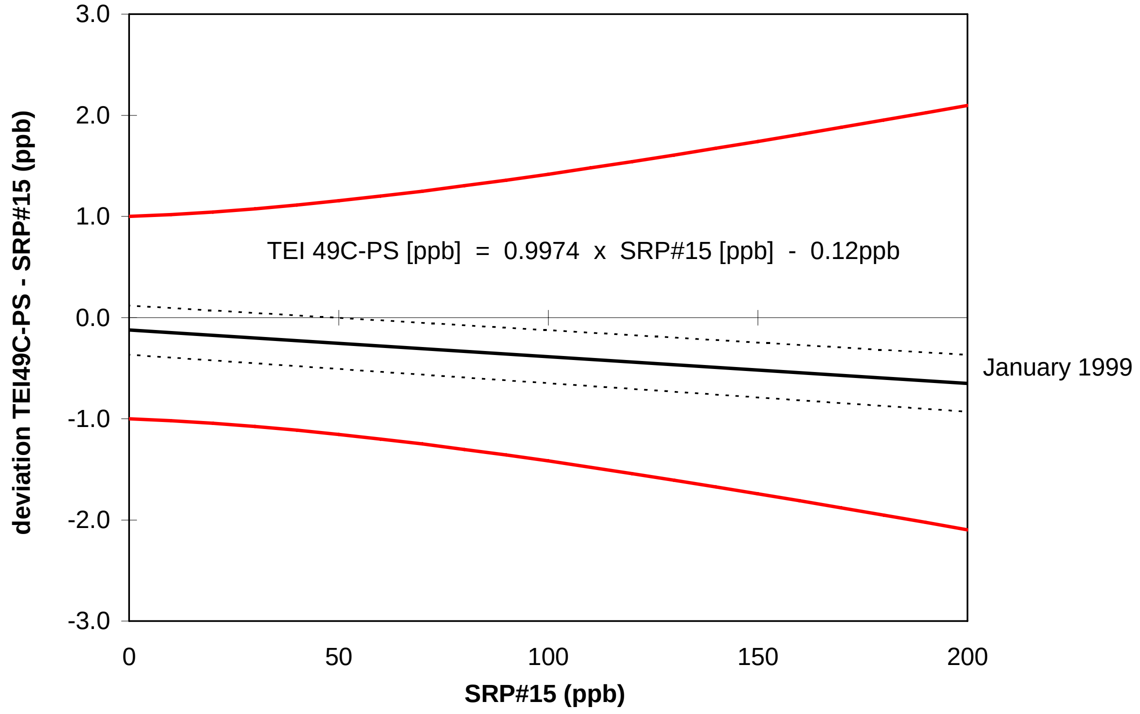

Figure 23: Transfer standard (O_3) after audit

Appendix Carbon Monoxide

I. Traceability Chain

Since no Standard Operation Procedure (SOP) for CO measurements has been established yet, the available SOP for ozone was adopted accordingly. In figure 24 the traceability chain for the carbon monoxide, used by the WCC-CO is shown.

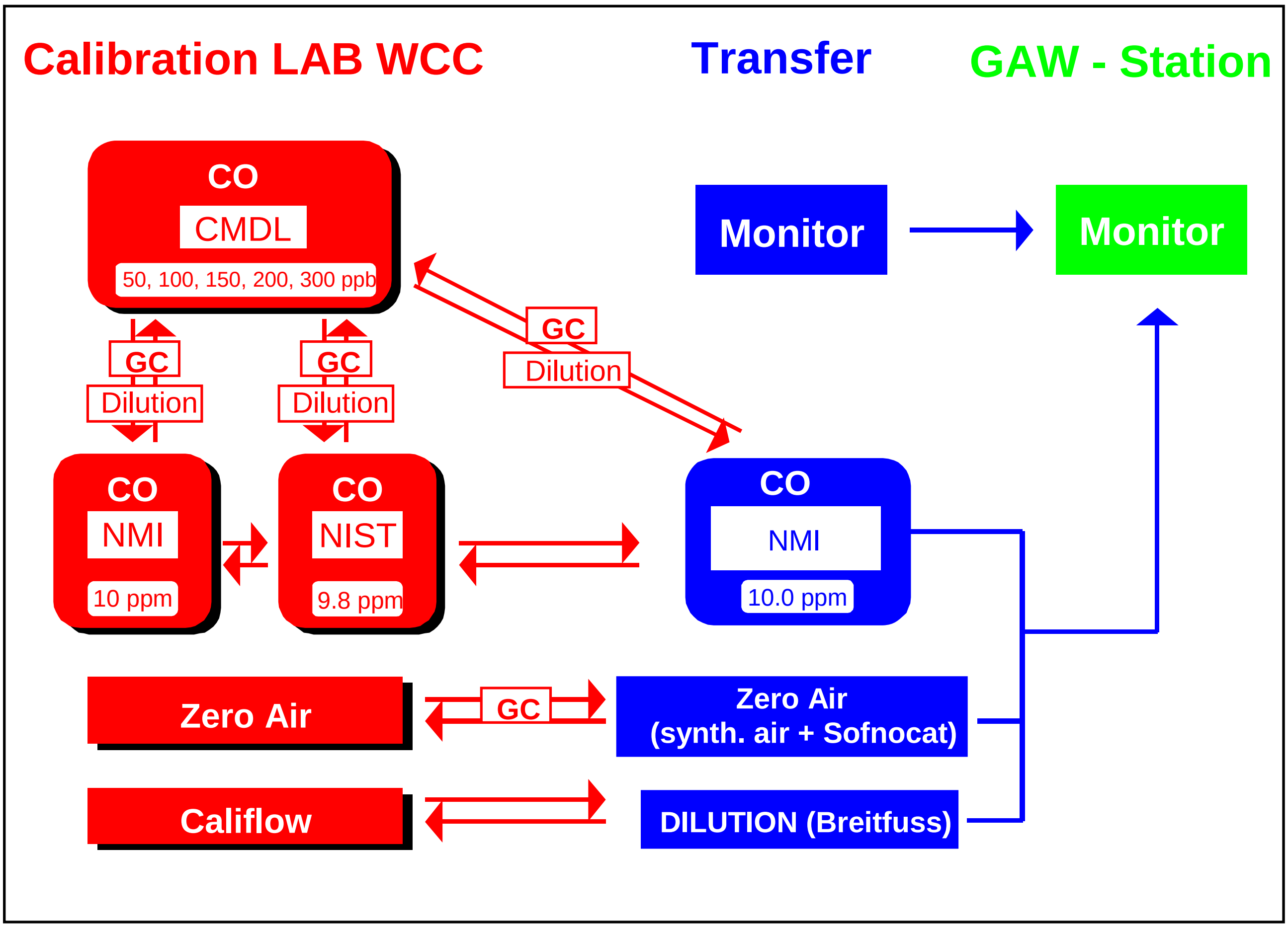

Figure 24: Traceability-Chain for the carbon monoxide

II. WCC CO Standards

Laboratory Gas Standards

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 is the designated reference for measurements of atmospheric CO within the WMO-GAW programme.

At the WCC we use the following standards:

Table 15: CO-Standards at the WCC

Standard	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
CMDL Laboratory Standard (")	287.5 ± 8.6 nmole/mole	CA02854

NIST Reference Standard	9.8 ± 0.05 μmol/mol	CLM006694
NMI Reference Standard	10.01 ± 0.04 μmol/mol	316511

The absolute accuracy of the NOAA/CMDL CO scale which is probably accurate to within 3%, is based on the uncertainties of the gravimetric and analytical procedures, and comparisons to the NIST CO scale (Kitzis D.R., NOAA/CMDL Carbon Cycle Group calibration laboratory, 1998, Personal Communication).
The listed μmol/mol standards from NIST and NMI are checked against the CMDL standards by using dynamic dilution and analysis on an RGA-3 system.

CALIFLOW (MKS, USA)

Califlow is a high accuracy Primary Standard, designed for accurate and efficient measurement of gas flow rates. Gas flow rates are measured by collecting a volume of gas under a piston, with a frictionless seal, which moves inside precision-bore borosilicate glass tube. The unit automatically places this volume measurement on a precision time base to establish flow rate. The Primary Standard Califlow shows these capabilities: traceable to National Institute of Standards and Technology (NIST, USA, high accuracy of 0.2% of reading and wide range calibration up to 50 l/min.

III. WCC Transfer Standards

NMI-Calibration Gas (Nederlands Meetinstituut, Netherlands)

The CO mixing ratios in ppb for the intercomparison were given by the NMI-Reference gas (10.01 ± 0.04 ppm) and the settings of the MGM diluter. The NMI standard was related to the NIST standard (National Institute of Standards and Technology, USA) and the mixing ratios, used during the intercomparison were related to the NOAA/CMDL (National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory) reference scale.

MGM Diluter (Breitfuss, Germany)

The MGM diluter (S/N 2262/97/1) consists of two thermal mass flow controllers (BRONKHORST HI TEC, Serial number 9720369 and B), a mixing chamber and electronics to produce the different mixing ratios. To exclude errors which might occur through transportation of the diluter its Mass Flow Controllers (MFC) were compared to the Califlow (Primary Standard) before and after the field audit. The deviation of the MFCs were around 1% and taken into account for calculating the mixing ratio. The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision).