Global Atmosphere Watch
World Calibration Centre for Surface Ozone
WCC-O_3

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

REPORT

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE

GLOBAL GAW STATION CAPE POINT

SOUTH AFRICA, JANUARY 1997

Submitted by

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1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone at the global GAW station Cape Point, South Africa. Below, the findings, comments and recommendations are summarised:

Air Inlet System:

The teflon tubes of both inlet systems and the glass line inside the station were clean and free of dust. The new inlet system, concerning construction materials as well as residence time, is adequate for gas analysis and fulfils the recommendations about inlet systems of the WMO-GAW Report No. 97.
The extended investigations of the two air inlet systems are highly welcomed and it will be very interesting to see the results.

Instrumentation:

The measurement technique used is the UV-method which is the preferred method in the GAW programme.
The operation of two ozone analysers, as basic and backup instrument, in parallel considerably increases confidence in data quality. However, with the additional ozone instrument three sets of data are produced which is believed to cause more confusion than use. This since the analysers are in different good condition and the data that is submitted to the GAW data centre can only originate from one analyser. Therefore, after the experiments to investigate eventual differences between the former and the new air inlet are completed, we suggest operating again only two instruments. According to the age of the analysers and the intercomparison results the TEI 49 is recommended to be defined as the basic instrument and, after a complete overhaul, one of the Dasibi monitors as the backup instrument.

Data Handling:

The procedure of data treatment is well organised and clearly arranged spreadsheets result so that any recalculation can easily be traced back to the raw values. The reprocessing of the data is done on a regular monthly interval. In this manner detecting irregularities is possible early. Reviewing of the final data set by two persons is welcome, since this action increases the reliability of the data.
As already pointed out in a former audit report by the QA / SAC, a direct data transfer via modem is still not possible. Such data transfer would enable remote diagnosis of instrument malfunctions and by this a reduction of data loss.

Operation and Maintenance:

The appearance of the station is clean and functional.
One of the main factors of quality assurance is the regular intercomparison by multipoint calibration between the analysers and an ozone reference (transfer standard) that is traceable to the NIST. The purchase of such an instrument would certainly progress the entire measurements and is therefore very desirable.
It is noted that the advantage of maintenance on a case by case basis is 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.
Regarding the zero point problem with the Dasibi 1008RS analyser it is recommended to stop with the daily zero checks and carry out only regular manual checks. Replacement of the lamp drive heater control board, by a new designed board, could help to overcome the peculiar instrument characteristic.

Documentation:

The documentation of the ozone measurement meets all the requirements of the GAW guidelines.

However, a practice orientated SOP for maintenance and operation should be implemented as a preventive action to avoid loss of accumulated knowledge due to personnel changes.

Competence:

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

Instrument Intercomparisons:

The ozone concentrations observed at Cape Point (1995) usually ranged between 12 and 32 ppb (5- and 95-percentile of hourly mean values).

Dasibi PC

All the data of the long-term measurements of Cape point are based on the Dasibi 1008PC instrument which, considering the range relevant to the site, fulfils the assessment criteria as "good". For concentrations higher than 40 ppb it only partly satisfies them (figure 1). This is due to a relatively wide precision interval reflecting the large discrepancy of the three intercomparisons, in particular in the higher ppb range (see Fig. 9). This is an indication of the relative poor stability of the instrument.

Dasibi RS

This analyser has only backup purpose and the data has not been used for publications. This is noted since for this instrument the ozone values lower 35 ppb lie outside or in the "sufficient" range of the assessment criteria (figure 2). If further used without overhaul, adjustment of the instrument to the basic analyser is indicated.

TEI 49

The instrument clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 3). Small deviation among the three intercomparisons is the reason for a very narrow prediction interval for the analyser. The recently obtained instrument is in excellent condition and is recommended to be used as basic instrument (see Appendix IV).

Figure 1: Intercomparison of instrument Dasibi 1008PC

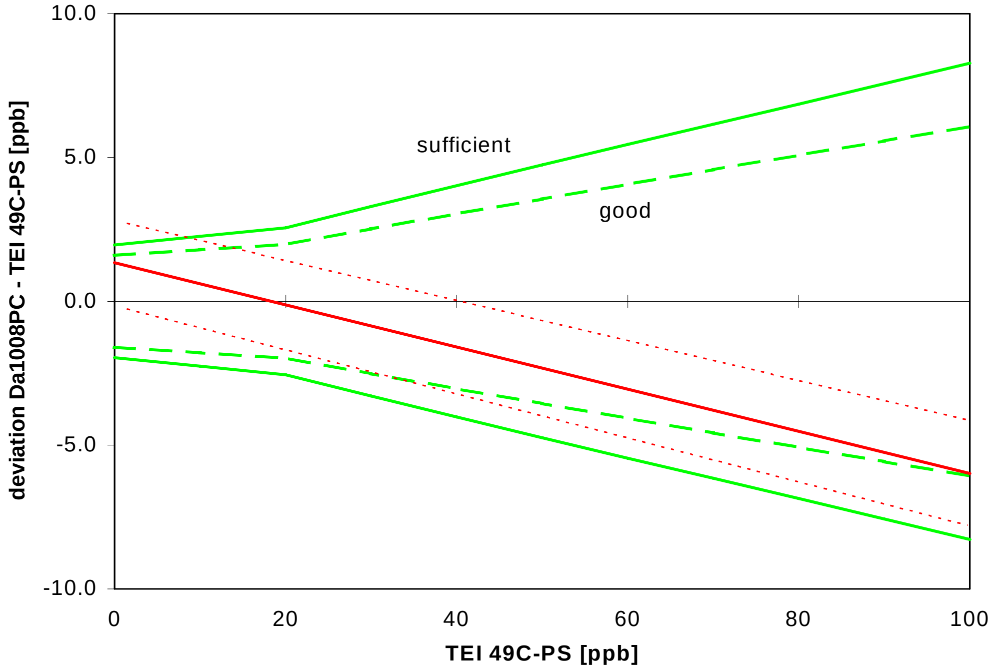

10.0
5.0
0.0
-5.0
-10.0
deviation Da1008PC - TEI 49C-PS [ppb]
sufficient
good
0
20
40
60
80
100
TEI 49C-PS [ppb]

Figure 2: Intercomparison of instrument Dasibi 1008RS

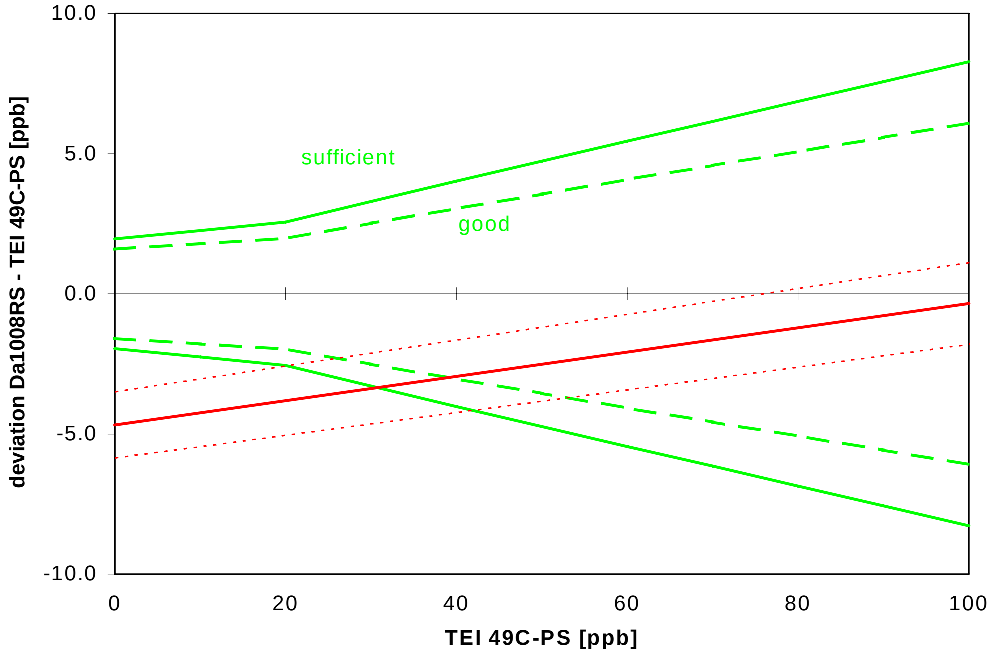
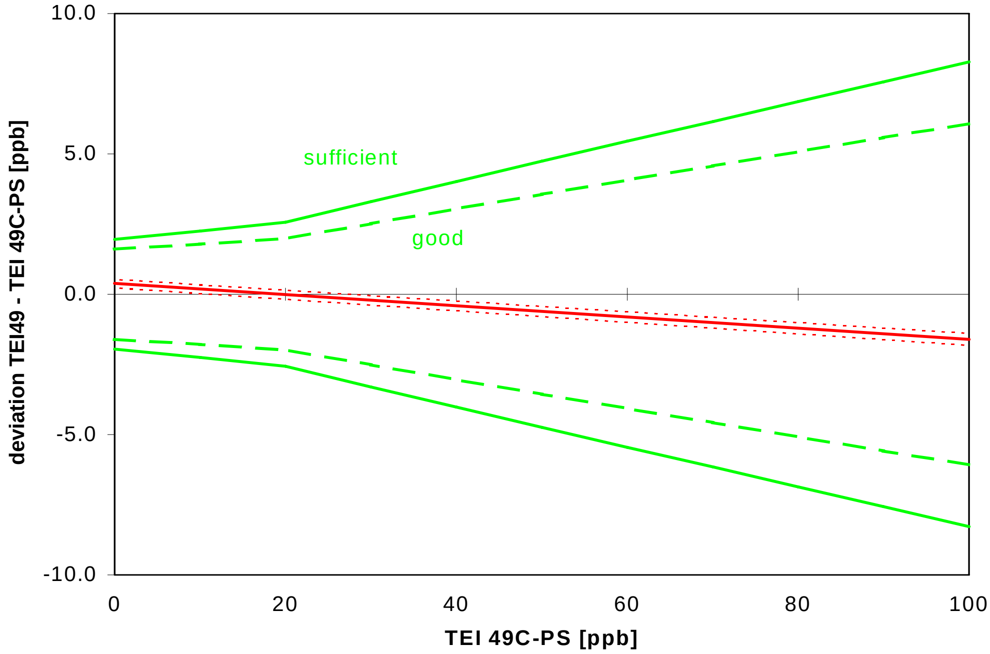


Figure 3: Intercomparison of instrument TEI 49



Dübendorf, 19. June 1997

EMPA Dübendorf, WCC-O_3

Project engineer

Project manager

A. Herzog 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 for Surface Ozone for Europe and Africa (WCC-O_3). At the beginning of 1996 our work started within the GAW programme. The detailed goals and tasks of the WCC-O_3 are described in WMO-GAW Report No. 104.

In agreement with the responsible persons in charge of surface ozone measurements at the Earth, Marine and Atmospheric Sciences Division (CSIR), South Africa, a system and performance audit at the global GAW station Cape Point was conducted. The station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters for background, clean air, conditions. Its location in the Southern Hemisphere, with only few stations, makes it additionally valuable for scientific research investigating the global climate south of the equator.

The scope of the audit, which took place from January 20 to 27 in 1997, was confined to the surface ozone 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 at Cape Point 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 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, 1996, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The last audit at Cape Point had been performed in October 1995 by the QA / SAC that is located at the Fraunhofer Institute for Atmospheric Environmental Research (report: "System Audit GAW Station Cape Point, Republic of South Africa", by Dr. F. Slemr, October 1995).

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

3. Global GAW Site Cape Point

3.1. Site Characteristics

The Cape Point station is located in a nature reserve at the southern end of the Cape Peninsula, South Africa, (coordinates: 34°21' S, 18°29' E). The monitoring station is exposed to the sea on top of a cliff 230 m a.s.l., about 60 km south from the city of Cape Town. Since the dominant wind direction is SE - S - SW, the station is subjected to maritime air from the South Atlantic most of the time.

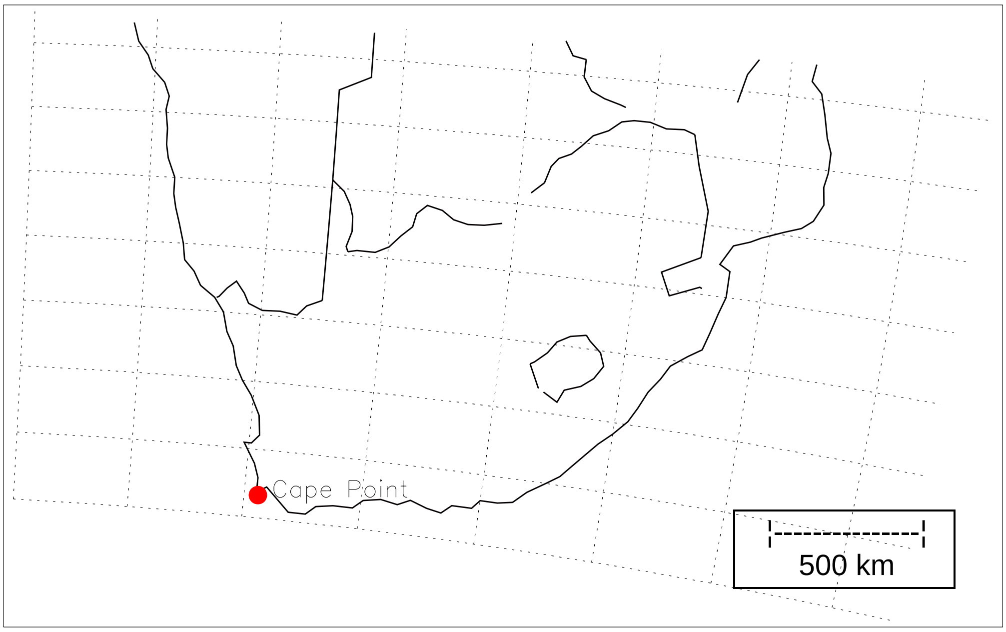
Due to its very special location on a peninsula extremity, the vicinity around Cape Point (sector larger than 300°) is primarily ocean and the only ground in the surrounding area consists of sparsely vegetated rock.

In 1995, the station moved from the two former lighthouse cottages to a newly built one story measurement station. The new location provides excellent space for present and future measurement activities and underlines the importance given to the site by the Government. It is situated adjoining the old station beneath the 30 m sampling tower and is built partially into the rock. The air inlet and several pieces of meteorological equipment are mounted on a platform at the top of the flat roof.

In the last few years the Cape Point area has developed into a major tourist attraction with hundreds of daily visitors from Cape Town arriving by cars and busses. About 400 m north of the station a large parking lot was built for the public traffic. From there, the station is approximately 150 m above and is reached by a funicular. Up to know, only a few Mini-busses and the station operators are permitted to travel up the steep drive to the station. Since the developing process will continue one should be aware that scientific interests need to be met in spite of increased tourism.

Figure 4: Picture of Cape Point:

Figure 5: Map of southern Africa:



3.2. Operators

The Atmospheric Trace Gas Research Station at Cape Point was set up in 1978 and is operated by the Earth Marine and Atmospheric Sciences Division of the CSIR in co-operation with the Fraunhofer Institute for Atmospheric Environmental Research (IFU). The CSIR provides the staff and founding to maintain the station while the IFU supplies much of the instrumentation and supporting material and assists the station operators in QA matters.

Mr E.-G. Brunke, who is in charge of the operation of the Atmospheric Trace Gas Research Station at Cape Point, directs a team of two co-workers. In March of this year, the group could be completed again with the addition of Mr Labuschagne. The structure of the station management at Cape Point is shown in Table 1.

As part of a restructuring at CSIR it is planned to shift the operational responsibility of the station to the South African Weather Bureau. The attachment to the new Department is still in progress and a satisfying solution of it for the future of the station is expected soon.

Table 1: Operators

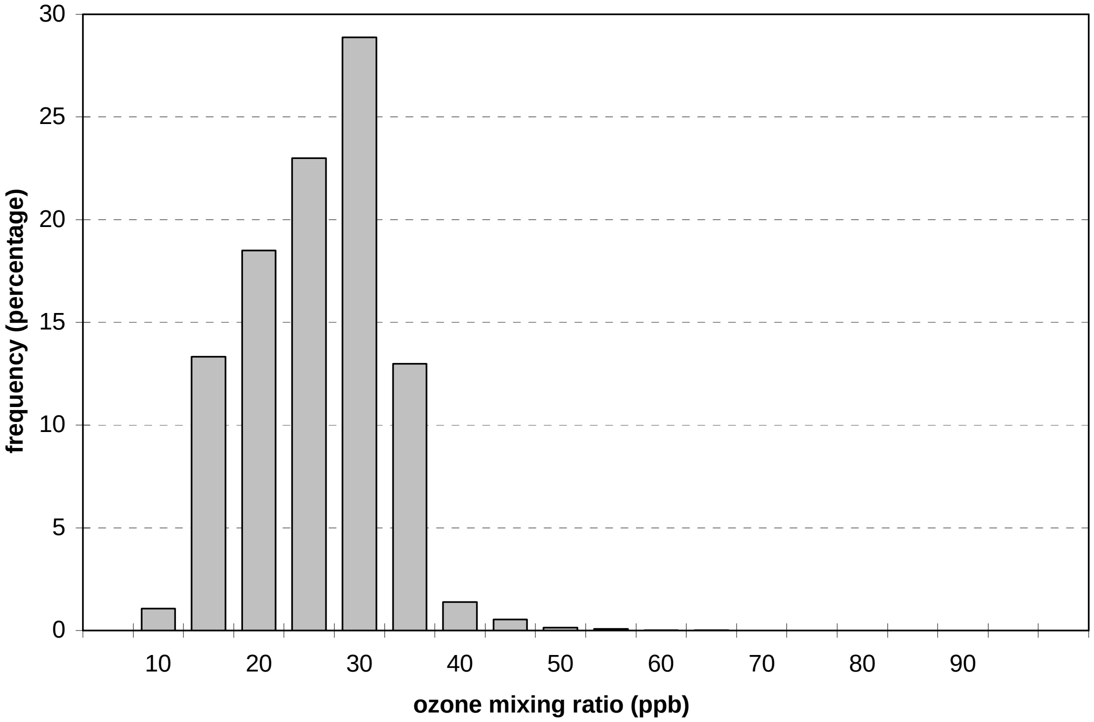
Mr Ernst-Guenther Brunke, Station director
Operators Mr Eugéne Mabille, Electronical engineer Mr Casper Labuschagne
External expert Dr H.E. Scheel, Fraunhofer Institute Garmisch-Partenkirchen (D) Scientific consultant

3.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well defined by the frequency distribution. In figure 6 the frequency distribution of the hourly mean values from the year 1995 is shown. The relevant ozone concentrations were calculated, ranging between 12 and 32 ppb according the 5 and 95 percentile values.

Source of data: received from Dr H.E. Scheel, April 1997

Figure 6: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Cape Point of the year 1995. Data capture higher 96 per cent



4. Measurement Technique

4.1. Air Inlet System

At the time of the audit two different air inlet systems were in operation that are described below:

Original air inlet system

The original air inlet system for the ozone measurements is located at the top of the 30 m high aluminum sampling tower. The tower itself is mounted adjacent to the flat roof of the laboratory building. Thus the air sample has to pass through about a 43 m long 1/4" PFA tubing before reaching the analysers. The ambient air (6 l per minute) is drawn by means of a Metal Bellow pump (model 41) to minimise the pressure drop in the inlet tubing and to increase the flow rate. Then, the sample pumps of the analysers, downstream, are being used to draw ambient air through the last 50 cm of teflon tube (ambient pressure) according to the instrument's specified internal flows. The inlet part of the system on the mast consists of an inverse teflon bucket, stacked on the teflon tube, shielding the system from rain. The instruments are further protected from dust and particles with a teflon inlet filter. The total residence time of the ambient air to the instruments is about 10 seconds. The operators have tested the Metal Bellow pump repeatedly for ozone losses but could not prove it. The used pump is disassembled every two months and cleaned by washing its parts in alcohol. Connected to this intake system are the two Dasibi instruments 1008PC and 1008RS.

New air inlet system

In November 1996 a new air inlet system was taken in use. It is mounted on the flat roof of the laboratory tower. The inlet part of the system on the flat roof consists of an inverse stainless steel bucket shielding the system from rain and is stacked on a stainless steel tube (100 mm i.d., 4.3 m long) that surrounds an internal SCHOTT glass tube (50 mm o.d.). The glass tube leads straight through a hole in the ceiling into the laboratory building connected to a SCHOTT glass manifold indoors (80 mm i.d., 40 cm 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., 1.5 m long) branches off from the glass manifold leading to the ozone analyser that is a TEI 49. The sample pump of the analyser is being used to draw ambient air through this teflon tube according to the instrument's specified internal flow. The instrument is further protected from dust and particles with a teflon inlet filter. The total residence time of the ambient air, through the inlet line to the instrument, is about 2 seconds.

The described system with the long tubing leading up to the top of the tower was chosen initially, in 1978, to avoid any contamination from generators, which were located adjacent to the mast. However, the long tube and the Metal Bellow pump was repeatedly subject to critics and lead to the conclusion of the last audit report, performed by the QA / SAC in 1995, that the system has to be modified since it is not consistent with the WMO-GAW Report No. 97. The audit report was submitted to the WMO ("System Audit GAW Station Cape Point, Republic of South Africa", by Dr. F. Slemr, October 1995).

In 1992, Cape Point was connected to the national electricity grid thereby making a short, fast air intake system possible. This was, however, first implemented in November 1996, because the new laboratory building was in the process of being built in the mean time.

It is planned to substitute the original 30 m mast system by the new short inlet line. But first, the operators have made systematic cross checks to compare data obtained from the 4 m inlet system with those from the 30 m mast aiming to make a potential "back correction" to the historical data set possible. This exercise is still ongoing.

Comment

The teflon tubes of both inlet systems and the glass line inside the station were clean and free of dust. The new inlet system, concerning construction materials as well as residence time, is adequate for gas analysis and fulfils the recommendations about inlet systems of the WMO-GAW Report No. 97.

The extended investigations of the two air inlet systems are highly welcomed and it will be very interesting to see the results.

4.2. Instrumentation

The instruments are installed in racks in a room that is equipped with air condition. Nevertheless, a temperature raise of about 4°C on a sunny hot day was observed. The analysers are protected from direct sunlight.

The instrumentation used for measuring ozone at Cape Point during the audit is shown in table 2 below.

The ozone analyser Dasibi 1008PC is the basic instrument since 1985 and is supported by the present backup instrument since 1991. To investigate the potential difference between the new and the original inlet line a TEI 49 was obtained from IFU and connected to the new inlet line in parallel to the two Dasibis.

Table 2: Field instruments

type	Dasibi 1008PC#4243	Dasibi 1008RS #4840	TEI 49 #51594-288
method	UV absorption	UV absorption	UV absorption
usage	basic instrument	backup instrument	new air intake investigation
at Cape Point	since 1985	since 1991	since August 1996
range	0-1000 ppb	0-1000 ppb	0-1000 ppb
analog output	0-1 V	0-10 V	0-10 V
electronic offset	0 (units)	0 (units)	56
electronic coeff.	308 (absorption coeff.)	307 (absorption coeff.)	507
instruments specials	- at original air inlet	- at original air inlet - connected to an external ozone generator	- at new air inlet - internal ozone generator

The zero air unit, used for the backup instrument, consists of an external charcoal cartridge (approx. 1 litre volume), a pump followed by a stabilisation canister and a particulate filter. It is used to generate the zero air for the daily zero checks. These are automatically triggered at midnight by an IFU constructed unit that is including also an ozone generator.

For the TEI 49 another zero air unit consisting of an oil-free-compressor, molecular sieve and charcoal is used in combination with the internal TEI ozone generator to perform the daily zero and span checks (50 ppb).

Comment

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

The operation of two ozone analysers, as basic and backup instrument, in parallel considerably increases confidence in data quality. However, with the additional ozone instrument three sets of data are produced which is believed to cause more confusion than use. This since the analysers are in different good condition and the data that is submitted to the GAW data centre can only originate from one analyser. Therefore, after the experiments to investigate eventual differences between the former and the new air inlet are completed, we suggest operating again only two instruments. According to the age of the analysers and the intercomparison results the TEI 49 is recommended to be defined as the basic instrument and, after a complete overhaul, one of the Dasibi monitors as the backup instrument.

4.3. Data Handling

The data acquisition facility is installed at the site in the same room as the ozone analysers. It consists of several ADC circuit boards (one for each instrument) to store the data on the computer. Every month the data is reprocessed and recalculated in a spreadsheet file containing the data from all the ozone analysers. For details about data treatment factors see chapter 5.2.
Then the invalid values (according logbook), i.e. data from manual calibration or daily zero / span checks or analytically invalid data, are manually removed from the database. The validated data is averaged to the hourly mean values. Analytically invalid data is evaluated, beside the logbook information, by means of parameters like wind speed, CO or CFC's (Note: the purpose is not to achieve a baseline condition data set). The data are stored on the PC and a magnetic media. Once a year they are then sent to the external expert at IFU and are reviewed again.

The raw data on the acquisition system consist of digits (according ADC board, 12-bit) which have to be converted into ppb by applying a formula (span and offset). For the Dasibi 1008PC instrument the operators checked the corresponding ADC board for linearity and on grounds of the results a formerly used factor replaced the actually (January 1997) used one (ppb = (digits / 0.4475) - 1.5 ppb). The used transforming formula of digits to ppb has been for the Dasibi 1008RS: ppb = digits / 4 + 0.0 ppb, and for the TEI 49: ppb = (digits / 4.10467) - 4.9 ppb.

Comment

The procedure of data treatment is well organised and clearly arranged spreadsheets result so that any recalculation can easily be traced back to the raw values. The reprocessing of the data is done on a regular monthly interval. In this manner detecting irregularities is possible early. Reviewing of the final data set by two persons is welcome, since this action increases the reliability of the data.

As already pointed out in a former audit report by the QA / SAC, a direct data transfer via modem is still not possible. Such data transfer would enable remote diagnosis of instrument malfunctions and by this a reduction of data loss.

4.4. Operation and Maintenance

Preventive maintenance of the instruments includes adjustment of the pressure transducers and exchanging of the teflon inlet filters, and is performed on a case by case basis (every 2-6 month). Around once a year the instrument glass cells are cleaned.

For the backup instrument (Dasibi 1008RS) an automatic zero check at midnight is triggered with an IFU constructed unit including an ozone generator. The check is intended to have only confirming character and data is not used to correct the zero point of the Dasibi. However, the obtained zero-check data has been unreliable and could not have been used in practice.

Automatic zero and span checks are made as a daily check of the TEI 49 analyser. At midnight, a span check (50 ppb) is made for about 15 minutes as a routine check of the ozone analyser. These data are not used for correcting the ambient air measurement values because the precision and stability of ozone generators would be generally too poor to be used for calibration purposes. At the same time, a zero check is performed for an hour. The data is used later for the calculation of O_3 mixing ratios.

Regular multipoint calibrations of the analysers can not be carried out, because there is no ozone calibrator for reference that is traceable to the NIST, at Cape Point. The only accuracy checks therefore are calibrations against the standard of CSIR Pretoria, every few years, and long-term parallel measurement of ambient air between the field instruments.

Comment

The appearance of the station is clean and functional.

One of the main factors of quality assurance is the regular intercomparison by multipoint calibration between the analysers and an ozone reference (transfer standard) that is traceable to the NIST. The purchase of such an instrument would certainly progress the entire measurements and is therefore very desirable.

It is noted that the advantage of maintenance on a case by case basis is 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.

Regarding the zero point problem with the Dasibi 1008RS analyser it is recommended to stop with the daily zero checks and carry out only regular manual checks. Replacement of the lamp drive heater control board, by a new designed board, could help to overcome the peculiar instrument characteristic.

4.5. Documentation

Within the GAW guidelines for documentation, the transparency of and the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness. At Cape Point, a separate, bound logbook is attached to each instrument and is a combination of instrument-, station- and maintenance logbook. The logbook was easy accessible at the site and contained all necessary information about maintenance, changes, events and special investigations. A station specific system operating procedure (SOP) for maintenance was not available.

Comment

The documentation of the ozone measurement meets all the requirements of the GAW guidelines. However, a practice orientated SOP for maintenance and operation should be implemented as a preventive action to avoid loss of accumulated knowledge due to personnel changes.

4.6. Competence

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

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix I) was hooked up to power for warming up over the weekend in deviation to the GAW report No. 97 which recommends only one hour of warm-up time (warm-up over night is recommended). Every morning, before a calibration was started the transfer standard, the PFA tubing connections to the instruments and the instruments themselves were conditioned with about 200 ppb ozone for 20 to 30 min. During four days, the comparison runs between the field instruments and the EMPA transfer standard were performed. In the meantime the inlet system and the station's documentation were inspected. Table 3 shows the experimental details and figure 7 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 data 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 the field instruments and of the transfer standard the data was collected, at the beginning, by both data acquisition systems (EMPA and CSIR) and showed a negligible discrepancy. For data interpretation the EMPA data is used. Finally, the observed results were discussed in an informal review with the persons 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 II.

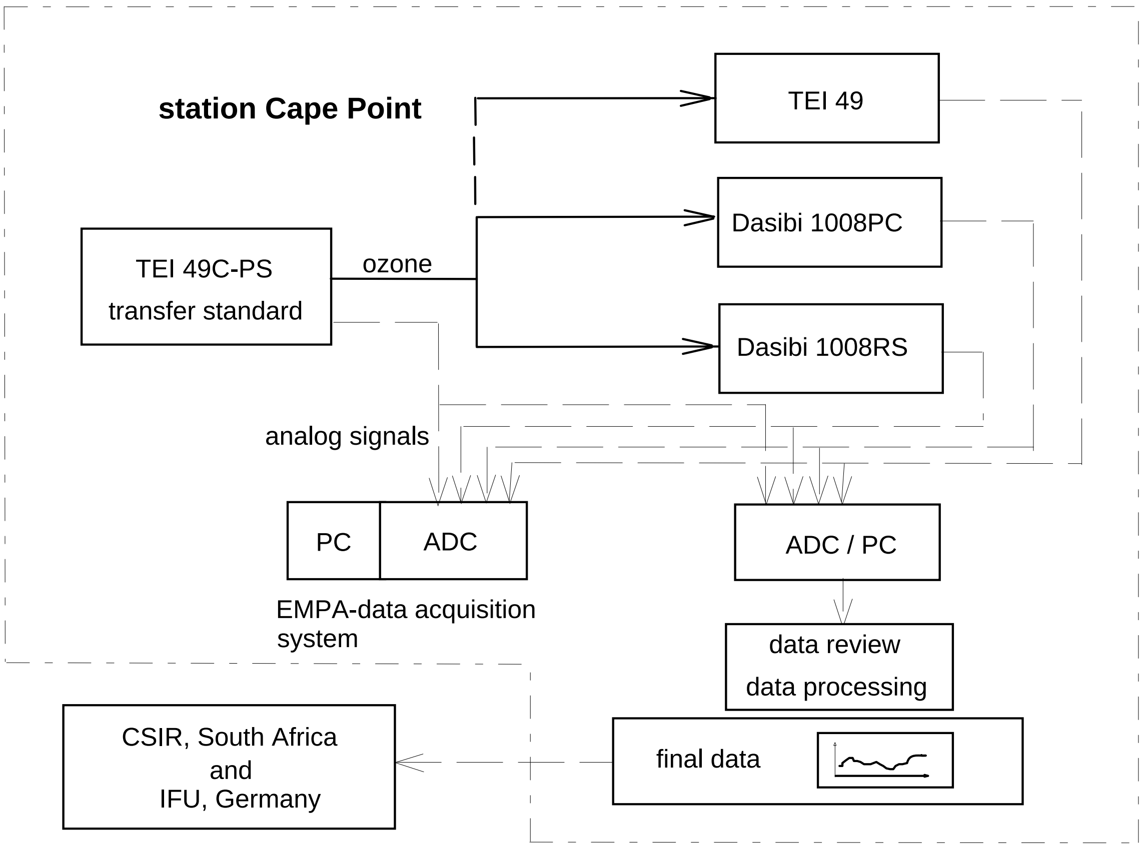
Table 3: Experimental details

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	Dasibi 1008PC #4243 Dasibi 1008RS #4840 TEI 49 #51594-288
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 systems:	EMPA: 16 channel ADC circuit board, software CSIR: IFU made system called IDAS, each instrument has its own ADC board
pressure transducers reading:	reference*: 991 hPa TEI 49C-PS: 990 hPa Dasibi 1008PC: 993 hPa, Dasibi 1008RS: 993 hPa, TEI 49: 991 hPa
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end

approx. concentration levels: sequence of concentration:	10 / 20 / 30 / 50 / 90 ppb random
averaging interval per concentration:	10 minutes
number of runs:	1 x January 20, 1997 (Dasibis) 2 x, January 21, 1997 (Dasibis) 3 x, January 22, 1997 (TEI 49) 2 x, January 23, 1997 (Dasibis)
connection between instruments:	about 1 meter of 1/4" PFA tubing

* pressure transducer reference: Thommen, certified absolute pressure manometer

Figure 7: Experimental set up



In principal the results of the intercomparison, i.e. deviations between the ozone analysers, should be confirmed by ambient air measurements. This was made with ambient air measurement values of the period from 15.-18. March when all three instruments were connected to the new air inlet system.

5.2. Results

The results comprise three runs of the intercomparisons between the three field instruments Dasibi 1008PC, Dasibi 1008RS and TEI 49 and the transfer standard TEI 49C-PS, carried out on January 21 - 23, 1997.

In the following tables the resulting mean values of each ozone concentration and the standard deviations (s_d) of 20 x 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 the field instruments compared to the EMPA transfer standard. The results of the runs are then summarised to the mean regression equation and presented with the assessment criteria for GAW field instruments (Figure 14, 15 and 16).
After two runs comparing the two Dasibi instruments to the transfer standard a loose tubing connection was noticed and fixed. When the data, after the third run, was analysed a marked deviation between the first two runs and the third one could be seen. Therefore, another two runs were carried out in addition which confirmed the findings. So the calculated regression equation for the two Dasibi analysers is based on the runs three to five, while the first two runs are neglected.
The data used for the evaluation were recorded by the EMPA data acquisition system. This raw data was treated according the usual station specific procedure:

Dasibi 1008PC	no formula applied
Dasibi 1008RS	applying a factor 1.05 (from intercalibration with IFU)
TEI 49:	minus determined offset 4.9 ppb (monthly mean from daily zero checks)

In tables 4 to 9 the recalculated data are listed.

Table 4: 3. Intercomparison, Dasibi field instruments

No.	transfer standard		Dasibi 1008PC				Dasibi 1008RS			
	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	0.3	0.13	1.7	0.34	1.4		-5.16	0.42	-5.1	
2	49.7	0.10	46.2	0.35	-3.6	-7.1%	47.11	0.66	-4.9	-9.8%
3	19.8	0.11	19.2	0.42	-0.6	-3.3%	15.79	0.92	-4.8	-24.0%
4	89.8	0.16	82.5	0.47	-7.3	-8.1%	89.17	0.42	-4.9	-5.4%
5	29.8	0.13	28.6	0.61	-1.2	-4.2%	27.38	0.50	-3.8	-12.7%
6	9.9	0.14	10.2	0.44	0.4	3.8%	5.72	0.40	-4.4	-44.5%
7	0.2	0.18	1.7	0.47	1.5		-4.81	0.68	-4.8	

Table 5: 4. Intercomparison, Dasibi field instruments

No.	transfer standard		Dasibi 1008PC				Dasibi 1008RS			
	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	0.7	0.22	1.6	0.19	0.9		-4.61	0.00	-5.0	
2	29.8	0.12	29.3	0.68	-0.5	-1.8%	27.56	0.35	-3.6	-12.0%
3	59.8	0.14	58.2	0.46	-1.6	-2.6%	58.7	0.34	-3.9	-6.5%
4	10.0	0.10	11.0	0.40	1.0	9.6%	5.66	0.22	-4.6	-46.0%
5	89.7	0.15	85.6	0.10	-4.2	-4.6%	88.84	0.35	-5.1	-5.7%
6	19.9	0.06	20.4	0.36	0.4	2.1%	16.44	0.41	-4.3	-21.5%
7	0.5	0.32	1.9	0.56	1.4		-4.63	0.32	-4.9	

Table 6: 5. Intercomparison, Dasibi field instruments

No.	transfer standard		Dasibi 1008PC				Dasibi 1008RS			
	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	0.7	0.22	1.6	0.19	0.9		-4.61	0.00	-5.0	
2	49.8	0.12	47.9	0.44	-1.9	-3.9%	47.27	0.66	-4.8	-9.6%
3	29.9	0.11	29.5	0.56	-0.4	-1.2%	26.3	0.83	-4.8	-16.2%
4	89.8	0.14	85.0	0.51	-4.9	-5.4%	87.50	0.37	-6.5	-7.2%
5	10.2	0.16	10.7	0.55	0.6	5.7%	6.15	0.50	-4.3	-42.4%
6	19.8	0.10	19.4	0.43	-0.4	-1.9%	17.02	0.40	-3.6	-18.1%

7	0.5	0.13	1.8	0.33	1.4		-4.12	0.62	-4.4	

Table 7: 1. Intercomparison, Thermo Environmental (TEI) field instrument

No.	transfer standard		TEI 49			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.3	0.11	0.9	0.24	0.6	
2	19.7	0.22	20.0	0.20	0.3	1.6%
3	89.6	0.13	88.1	0.22	-1.5	-1.7%
4	30.0	0.23	29.6	0.23	-0.4	-1.4%
5	10.0	0.11	9.9	0.23	-0.1	-0.7%
6	49.7	0.19	48.9	0.22	-0.8	-1.6%
7	0.3	0.13	0.9	0.21	0.6	

Table 8: 2. Intercomparison, Thermo Environmental field instrument

No.	transfer standard		TEI 49			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.3	0.08	0.9	0.14	0.6	
2	89.8	0.19	88.5	0.33	-1.3	-1.4%
3	30.0	0.17	29.8	0.35	-0.2	-0.8%
4	50.0	0.19	49.3	0.12	-0.7	-1.3%
5	10.2	0.15	9.8	0.25	-0.4	-3.5%
6	20.1	0.16	20.1	0.20	0.0	0.0%
7	0.4	0.08	0.8		0.4	

Table 9: 3. Intercomparison, Thermo Environmental field instrument

No.	transfer standard		TEI 49			
	TEI 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.4	0.10	0.8	0.27	0.5	
2	89.8	0.10	88.6	0.27	-1.1	-1.3%
3	20.0	0.10	19.9	0.12	0.0	-0.2%
4	49.8	0.08	49.2	0.31	-0.6	-1.2%

5	19.9	0.13	19.9	0.18	0.0	-0.2%
6	9.9	0.09	9.8	0.14	-0.1	-0.6%
7	0.4	0.11	0.9	0.10	0.5	

Figure 8: Individual linear regressions of intercomparisons 3 to 5, Dasibi 1008PC

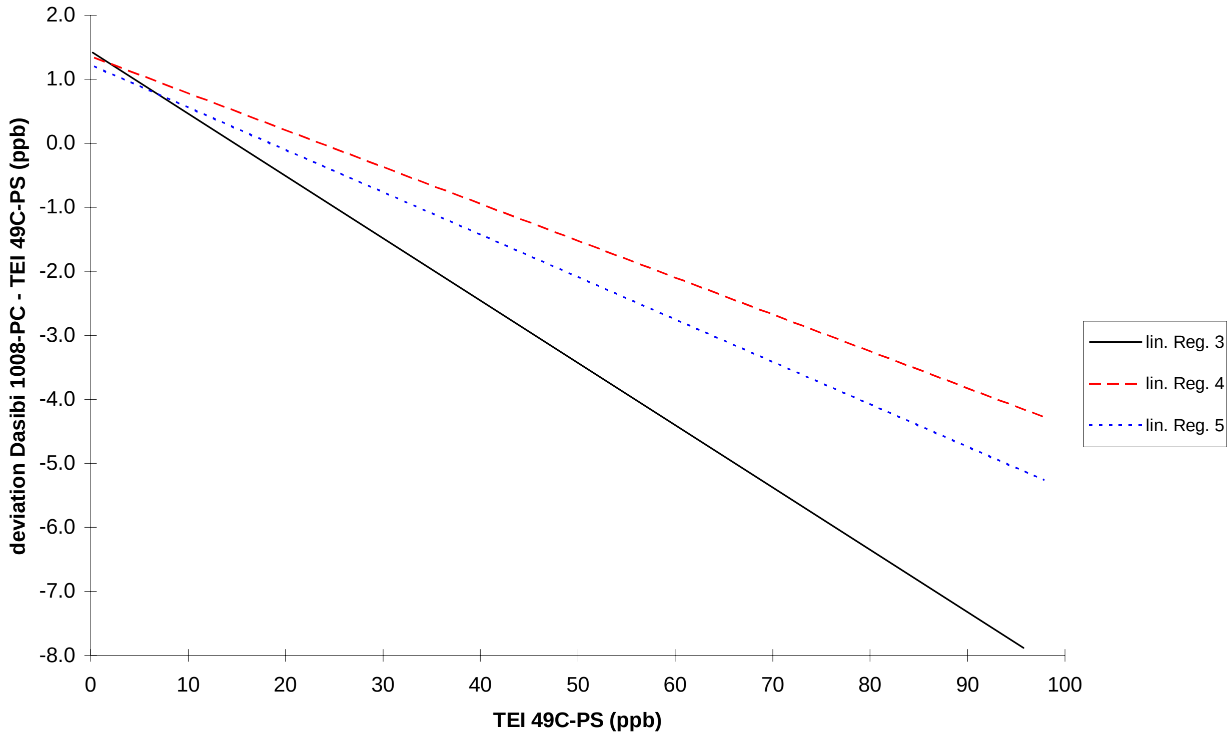


Figure 9: Mean linear regression of intercomparisons 3 to 5, Dasibi 1008PC

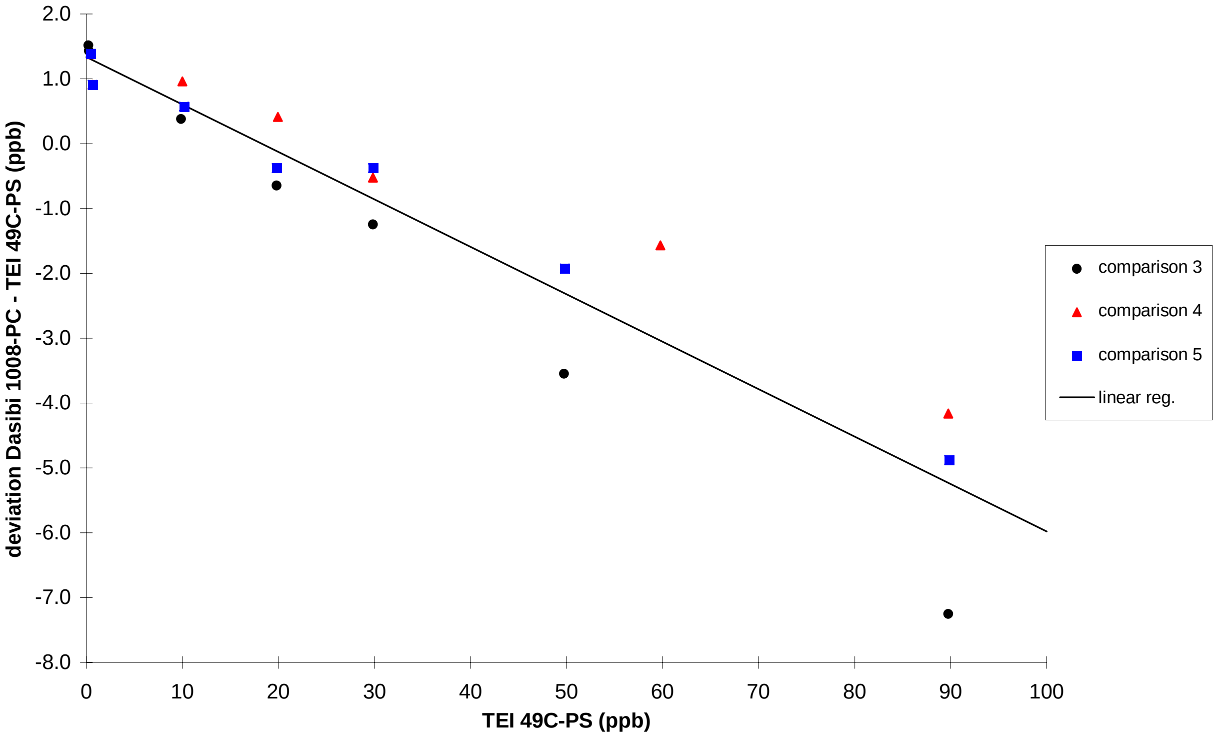

2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
deviation Dasibi 1008-PC - TEI 49C-PS (ppb)
0
10
20
30
40
50
60
70
80
90
100
TEI 49C-PS (ppb)
comparison 3
comparison 4
comparison 5
linear reg.

Figure 10: Individual linear regressions of intercomparisons 3 to 5, Dasibi 1008RS

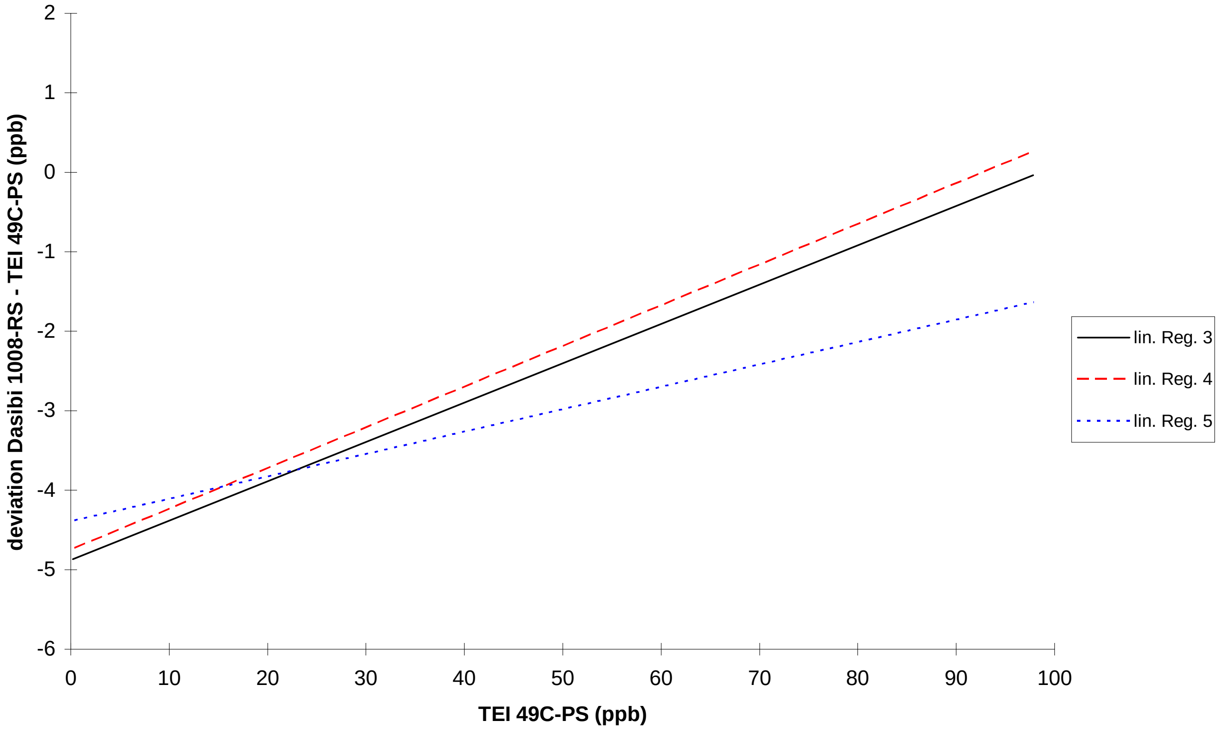


Figure 11: Mean linear regression of intercomparisons 3 to 5, Dasibi 1008RS

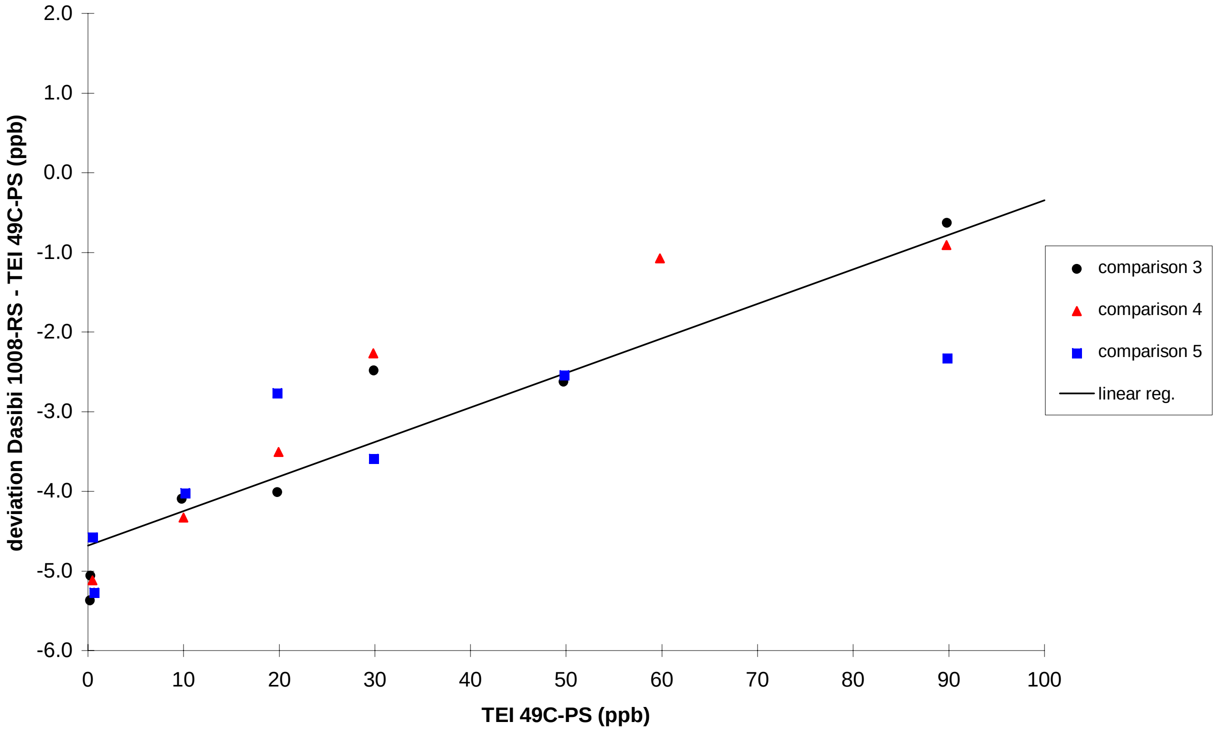


Figure 12: Individual linear regressions of intercomparisons 1 to 3, TEI 49

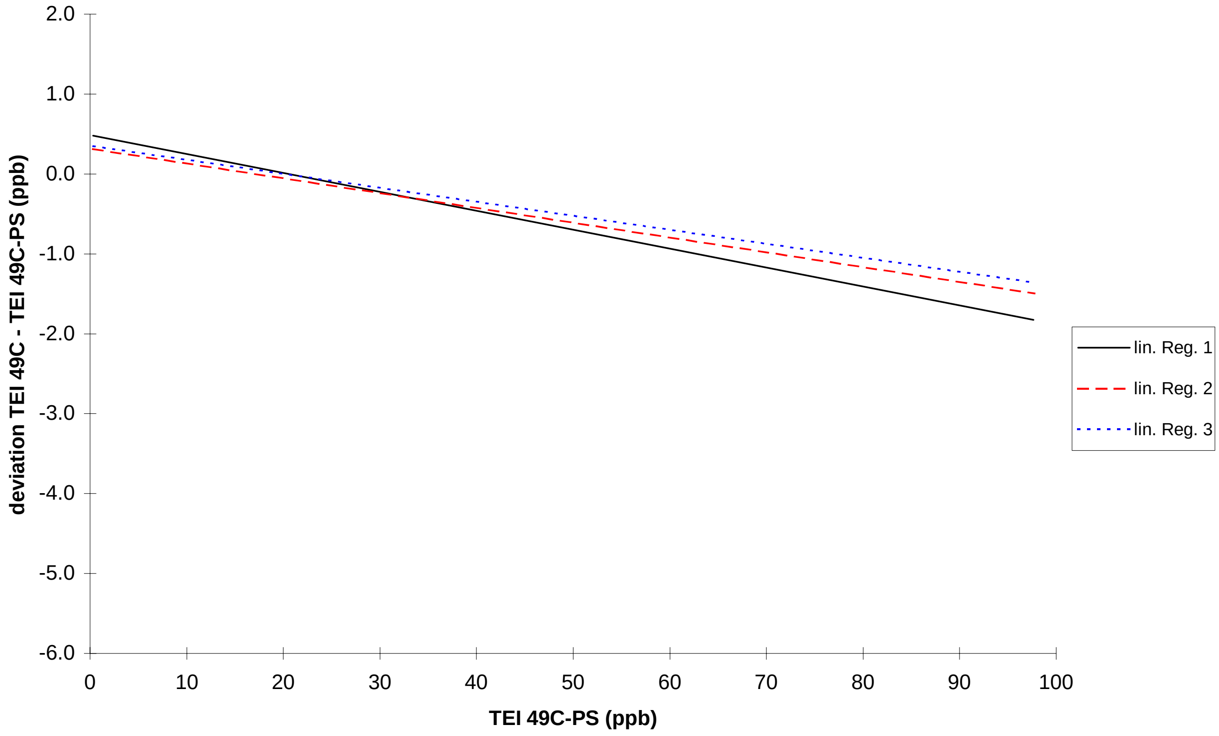
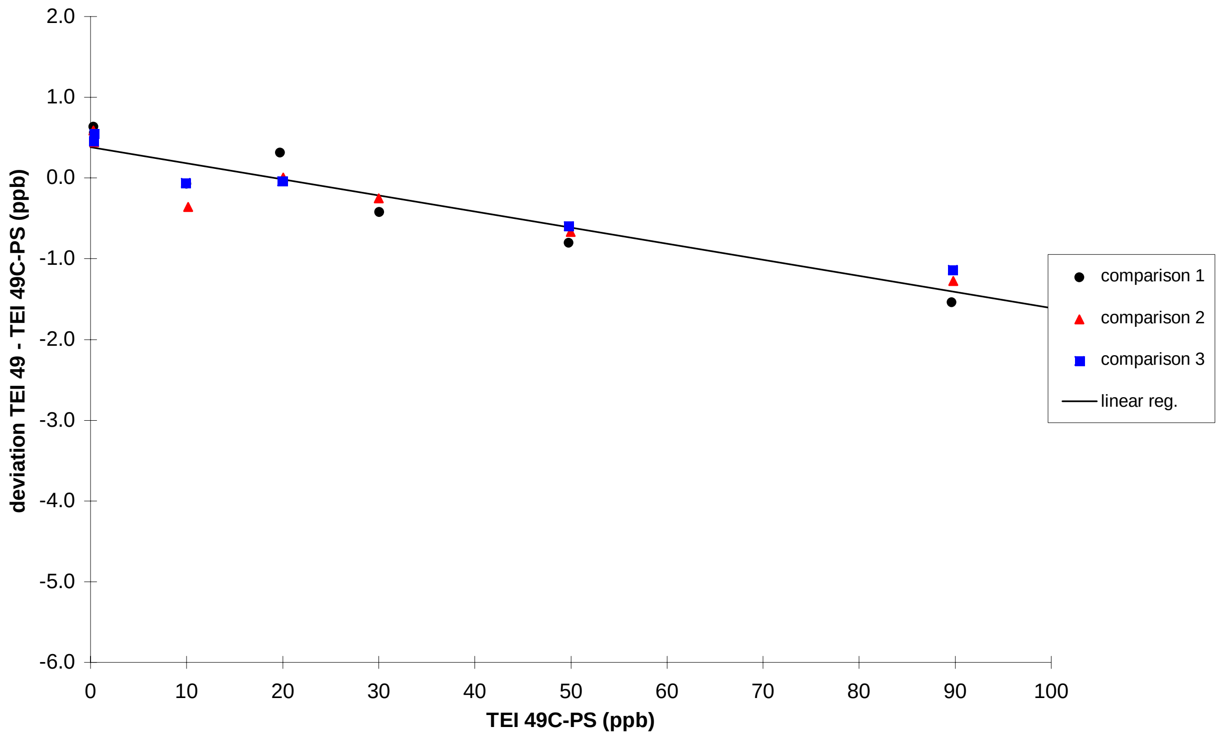


Figure 13: Mean linear regression of intercomparisons 1 to 3, TEI 49



From the intercomparisons of the Dasibi 1008PC #4243, the Dasibi 1008RS #4840 and the TEI 49 #51594-288 field instruments with the TEI 49C-PS transfer standard from EMPA the resulting linear regressions (for the range of 0-100 ppb ozone) are:

-Dasibi 1008PC:

Dasibi 1008PC = 0.927 x TEI 49C-PS + 1.34 ppb

Dasibi 1008PC = O_3 mixing ratio in ppb, determined for Dasibi 1008RS #4243

TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0055	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.23	(f = 3)
	- residuals in ppb	0.25	(f = 19)

-Dasibi 1008RS:

Dasibi 1008RS = 1.043 x TEI 49C-PS - 4.68 ppb

Dasibi 1008RS = O_3 mixing ratio in ppb, determined for Dasibi 1008RS #4840

TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0048	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.20	(f = 3)
	- residuals in ppb	0.54	(f = 19)

-TEI 49:

TEI 49 = 0.980 x TEI 49C-PS + 0.38 ppb

TEI 49 = O_3 mixing ratio in ppb, determined for TEI 49 #51594-288

TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0016	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.07	(f = 3)
	- residuals in ppb	0.20	(f = 19)

Figure 14: Intercomparison of instrument Dasibi 1008PC

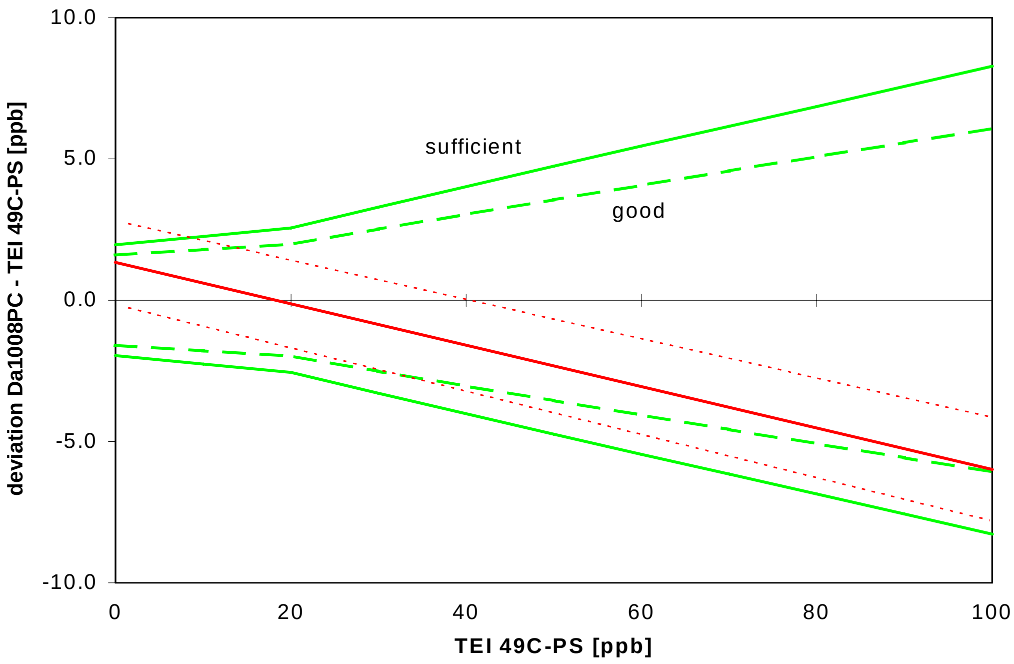


Figure 15: Intercomparison of instrument Dasibi 1008RS

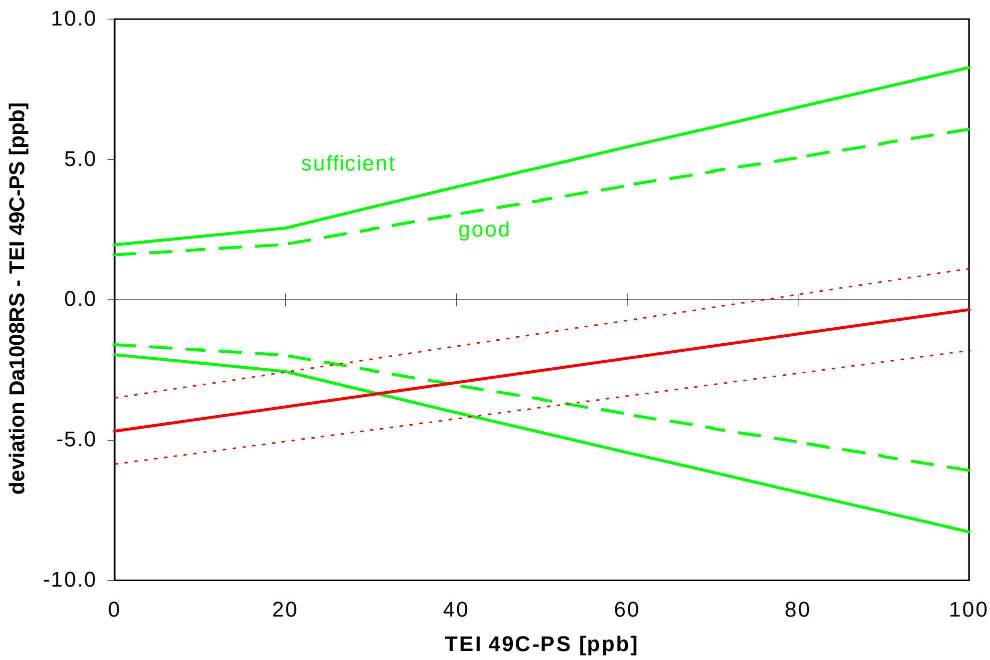
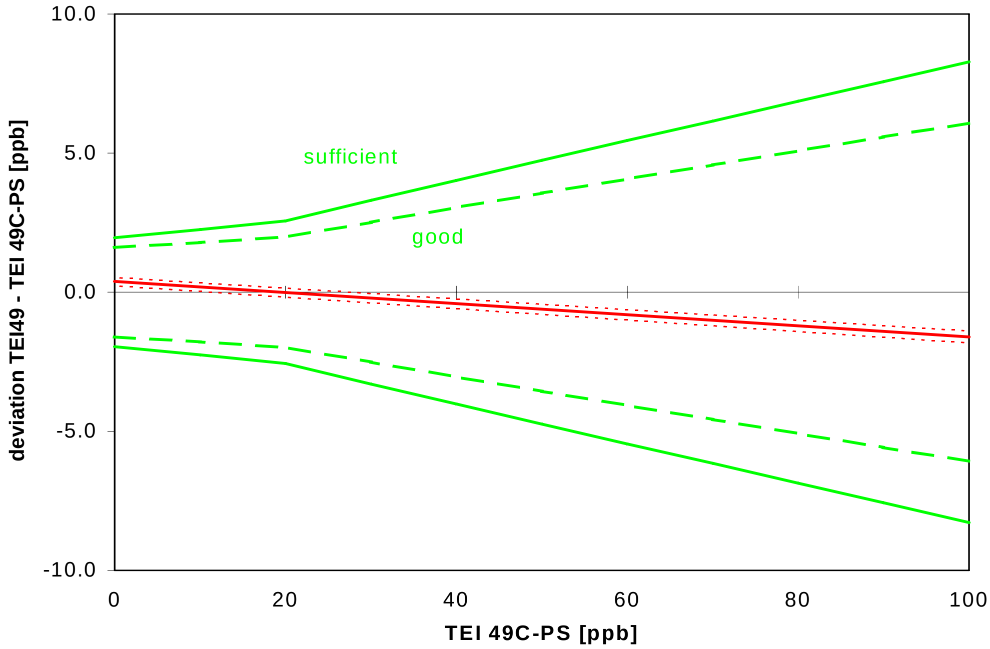


Figure 16: Intercomparison of instrument TEI 49



Comment

In figures 9, 11 and 13 of the linear regressions no clear trend could be observed during the day when the intercomparison took place.

The ozone concentrations observed at Cape Point (1995) usually ranged between 12 and 32 ppb (5- and 95-percentile of hourly mean values).

Dasibi PC
All the data of the long-term measurements of Cape point are based on the Dasibi 1008PC instrument which, considering the range relevant to the site, fulfils the assessment criteria as "good". For concentrations higher than 40 ppb it only partly satisfies them (figure 1). This is due to a relatively wide precision interval reflecting the large discrepancy of the three intercomparisons, in particular in the higher ppb range (see Fig. 9). This is an indication of the relative poor stability of the instrument.

Dasibi RS
This analyser has only backup purpose and the data has not been used for publications. This is noted since for this instrument the ozone values lower 35 ppb lie outside or in the "sufficient" range of the assessment criteria (figure 15). If further used without overhaul adjustment of the instrument to the basic analyser is indicated.

TEI 49
The instrument clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 16). Small deviation among the three intercomparisons is the reason for a very narrow prediction interval for the analyser. The recently obtained instrument is in excellent condition and is recommended to be used as basic instrument (see Appendix IV).

The discrepancy in the findings comparing ambient air data and the intercomparison results using dry zero air were rather small (see Appendix III). Despite the circumstance of applying air with a different humidity and matrix the results could not give raise to question the method of the intercomparison in general. Nevertheless, since the humidity dependency of ozone analysers is known but not very well investigated some effort should be made to close this lack of information.

Appendix

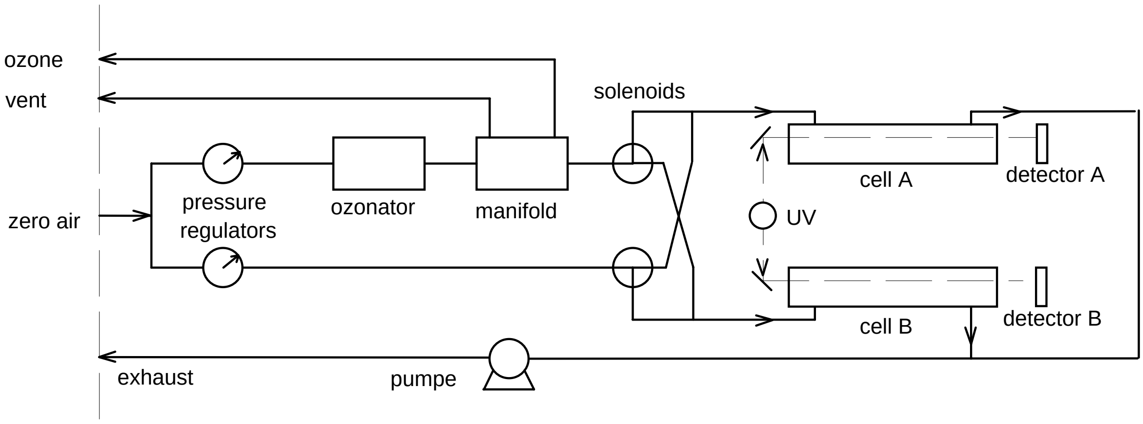
I EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The 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 17. 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 17: Flow schematic of TEI 49C-PS



II Stability of the Transfer Standard TEI 49C-PS

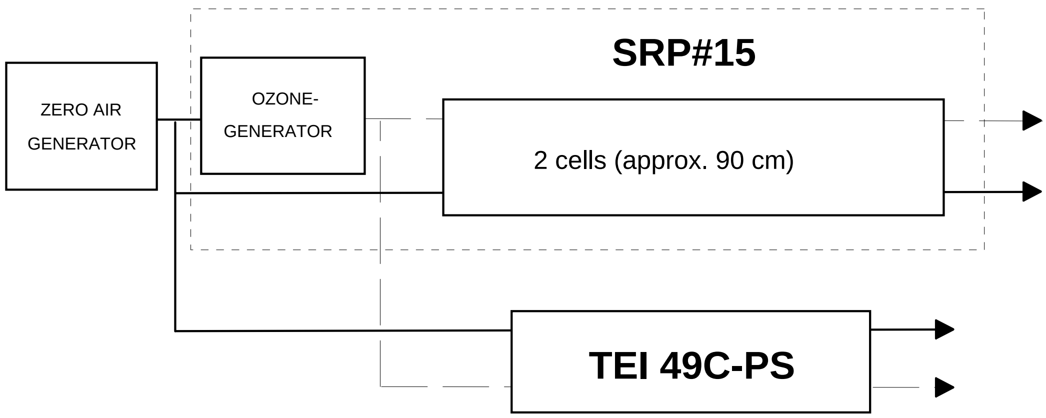
To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 10 and Figure 18.

Table 10: Intercomparison procedure SRP - TEI 49C-PS

pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 250 ppb
number of concentrations:	6 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 120 / 150 / 240 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	2 before and 2 after audit
zero air supply:	Pressurised air - activated charcoal - zero air generator (AADCO)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

Figure 18: 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 ±(1 ppb + 0.7%).

Figures 19 and 20 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the results show that the EMPA transfer standard fulfilled the recommended criterias for the period of the audit, including transportation.

Figure 19: Transfer standard before audit

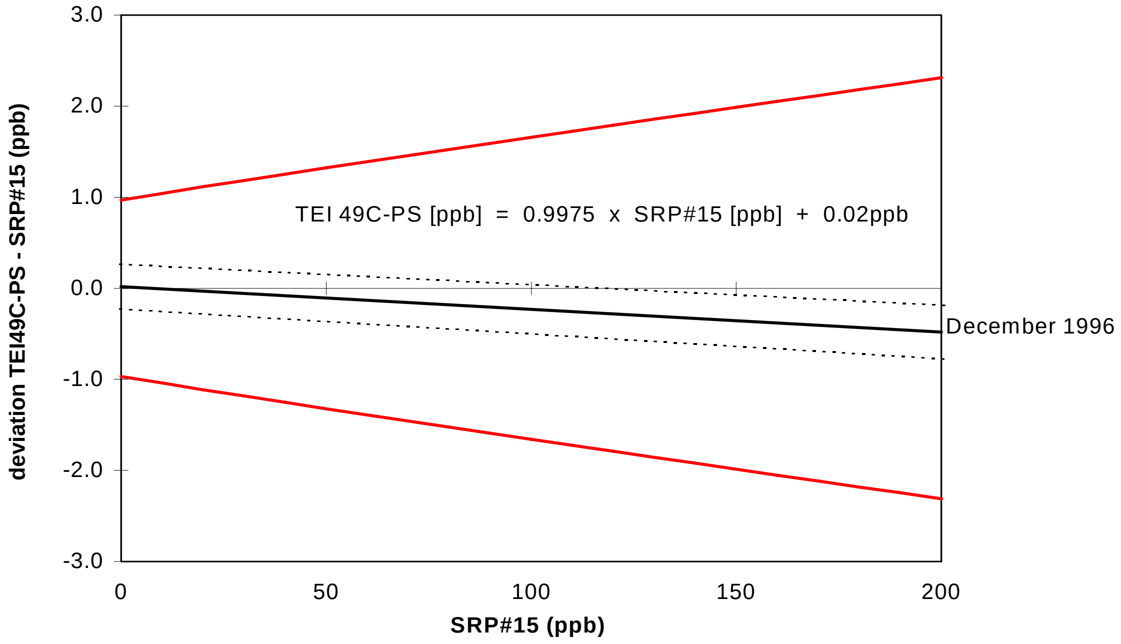
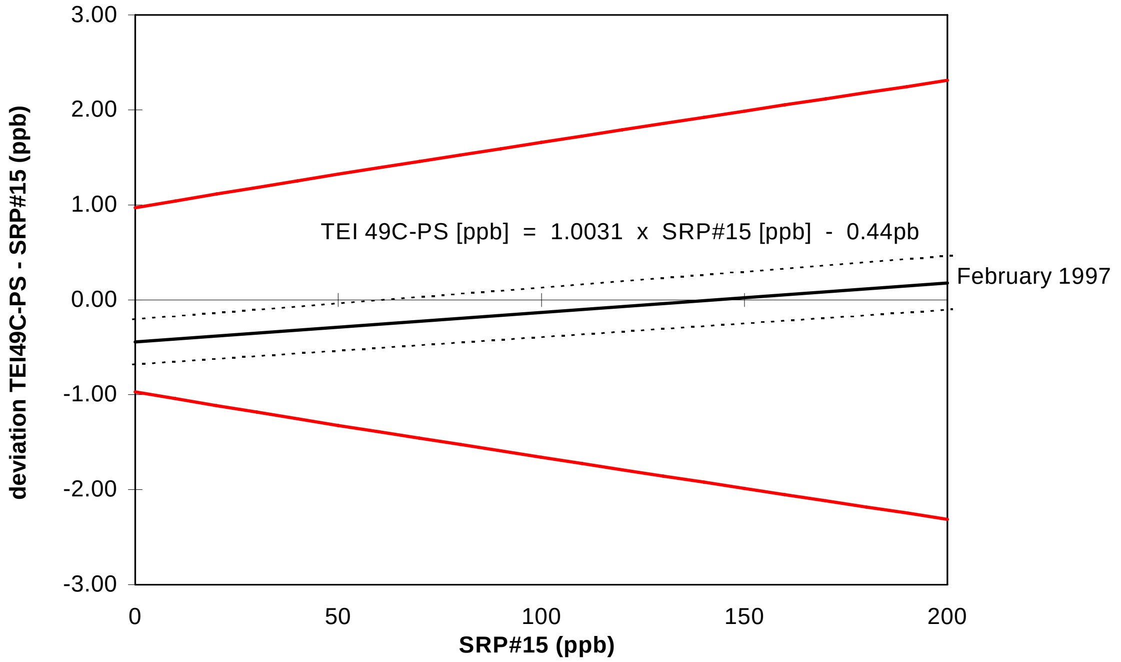


Figure 20: Transfer standard after audit

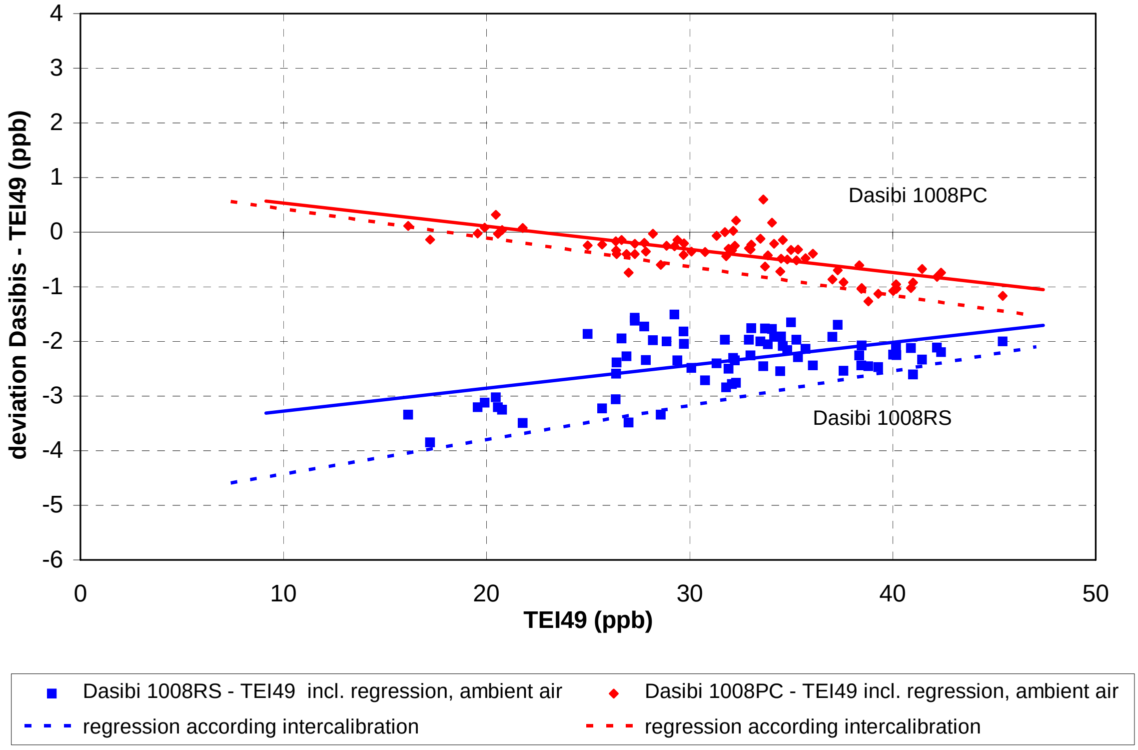


III Cross-checking Intercomparison Results with Ambient Air Data

For figure 21, the hourly mean values of all three analysers (15. - 18. March 1997) connected to the new air inlet system and the results of the intercomparison measurements (WCC-EMPA) were used. Plotted are the deviations of the Dasibi analysers and the TEI 49 versus the TEI 49 including the regression (solid lines). The dotted lines mark the theoretical regressions corresponding the results of the intercomparisons.

By rating the results in the figure below it has to be taken into account that several assumptions were made and that they therefore can only have orienting character. So was the TEI 49 chosen as "reference" and it was assumed that all the instruments are in the same condition as during the intercomparison two weeks before. Further should the relatively large prediction interval of the Dasibi analysers (approximately +/- 1.5 ppb) be considered.

Figure 21: Cross-checking intercomparison results with ambient air data



IV Changes after the Audit

Additionally confirmed through the very good results of the intercomparison measurements the operators designated the newly obtained TEI 49 analyser as the basic instrument, dated back to the beginning of this year (1997). It replaced thereby the Dasibi 1008PC, of which the long-term measurements of Cape Point originated, with regard to its age and the decreasing stability. The quality of the long-term measurements at Cape Point therefore can continue on a reliable analytical basis.