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 Organisation

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE

GLOBAL GAW STATION PALLAS-SODANKYLÄ

FINLAND, JUNE 1997

Submitted by

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WMO World Calibration Centre for Surface Ozone for Europe and Africa

EMPA Dübendorf, Switzerland

Contents:

1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone, at the global GAW station Pallas-Sodankylä, Finland. Below, the findings, comments and recommendations are summarised:

Air Inlet System:

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

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 and is particularly important for this site since no daily zero checks are performed. As agreed with the operators the backup instrument needs to be replaced due to instrument failure.

Data Handling:

The procedure of data treatment is organised and clearly arranged. The reviewing of the data is done on a regular, mostly daily, interval so that irregularities can be detected early. Review of the final data set by two persons is welcome, since this increases the reliability of the data.

Operation and Maintenance:

The appearance of the station is clean and functional.
A continuing good co-operation with the Finnish Forest Research Institute, Metla, is seen as essential for succesfully maintaining this remote station of Pallas.
The schedule of preventive maintenance including quarterly multipoint calibrations is well established in order to improve the operation of the ozone analysers. However, it is recommended that the ozone levels applied during a calibration are shifted towards the relevant ozone concentration range of the site.
Although the station was only established in 1991, the sense of quality assurance is very well developed and implemented, i.e. by intercomparing the internal standard to an independent primary standard. This is certainly due to the experience at FMI of operating the national monitoring network for many years.

Documentation:

Because the station logbook contains information about all measurements it might be very time consuming to trace back specific events. It is therefore recommended to upgrade the necessary documentation in the FMI's interests and to note information and remarks more detailed.
Plans to digitise the logbooks in the way that the operators would fill in the information directly into a file on the PC and transfer it to FMI ultimately, were discussed and are seconded.

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 Pallas (1995) usually ranged between 22 and 50 ppb (5- and 95-percentile of hourly mean values).
The basic instrument clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 1). Small deviation among the three intercomparisons is the reason for a very narrow prediction interval for the analyser. The instrument is in good condition to be used as basic instrument.
For the backup analyser a circuit break on an electronic board was located which causes unstable signals and problems with a shifting offset so it needs to be replaced. Considering the range relevant of the site, the Dashibi 1008PC instrument does not fulfil the assessment criteria but this is, because of the mentioned instrument problems, of subordinate relevance (figure 2).

Figure 1: Intercomparison of instrument Dasibi 1008AH

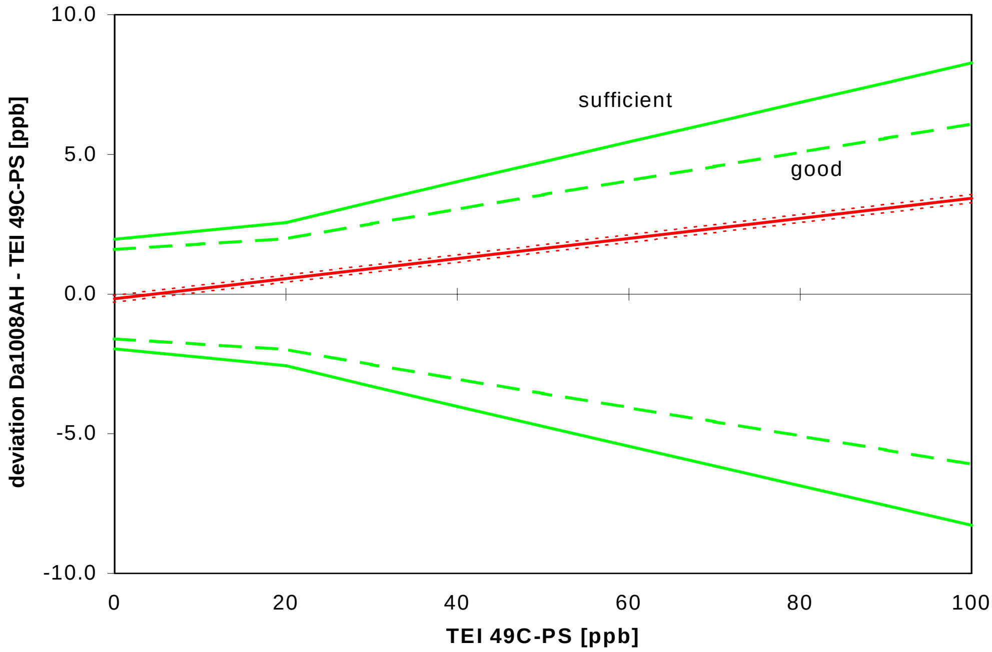
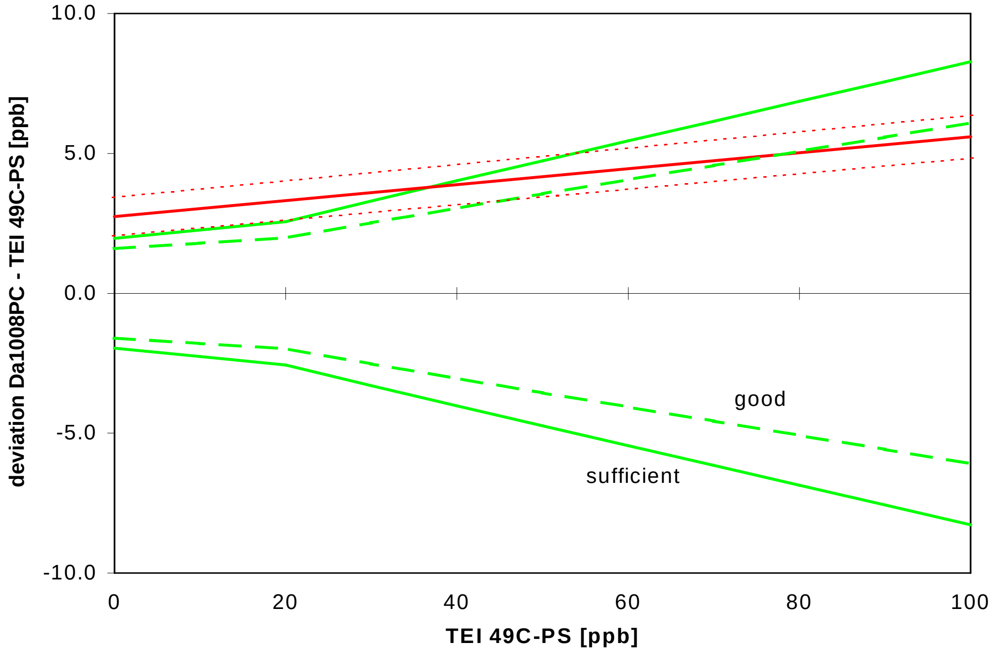


Figure 2: Intercomparison of instrument Dasibi 1008PC



Dübendorf, 29. July 1997

EMPA Dübendorf, WCC-O_3

Project engineer

Project manager

A. Herzog

Dr. B. Buchmann

Technical assistant: B. Schwarzenbach

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 tropospheric ozone measurements at the Air Quality Department of the Finnish Meteorological Institute (FMI) a system and performance audit at the global GAW station Pallas-Sodankylä was conducted. The station Pallas was established in September 1991 for long-term measurements of several chemical compounds and physical and meteorological parameters. Located in the boreal forest area in Finnish Lapland the remote site offers excellent opportunities for scientific research investigating the global climate.

The scope of the audit, which took place from June 23 to 26 in 1997, was confined to the tropospheric ozone measurements which is also the reason why the other site, Sodankylä, of the combined global GAW station Pallas-Sodankylä was not part of the audit. 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 Pallas 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 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.

System and performance audits at global GAW stations will be regularly conducted on mutual arrangement every 12 to 18 month.

3. Global GAW Site Pallas

3.1. Site Characteristics

The global GAW station Pallas-Sodankylä constitutes of the two sites Pallas and Sodankylä with a one another complementing measurement programme. Radionuclides, ozone soundings, climatological and other meteorological measurements and upper-air soundings are performed at the Sodankylä observatory (coordinates: 67°22' N, 26°39' E), while tropospheric air composition and related boundary layer meteorological measurements are conducted at Pallas. The audit was confined to the activities at Pallas.

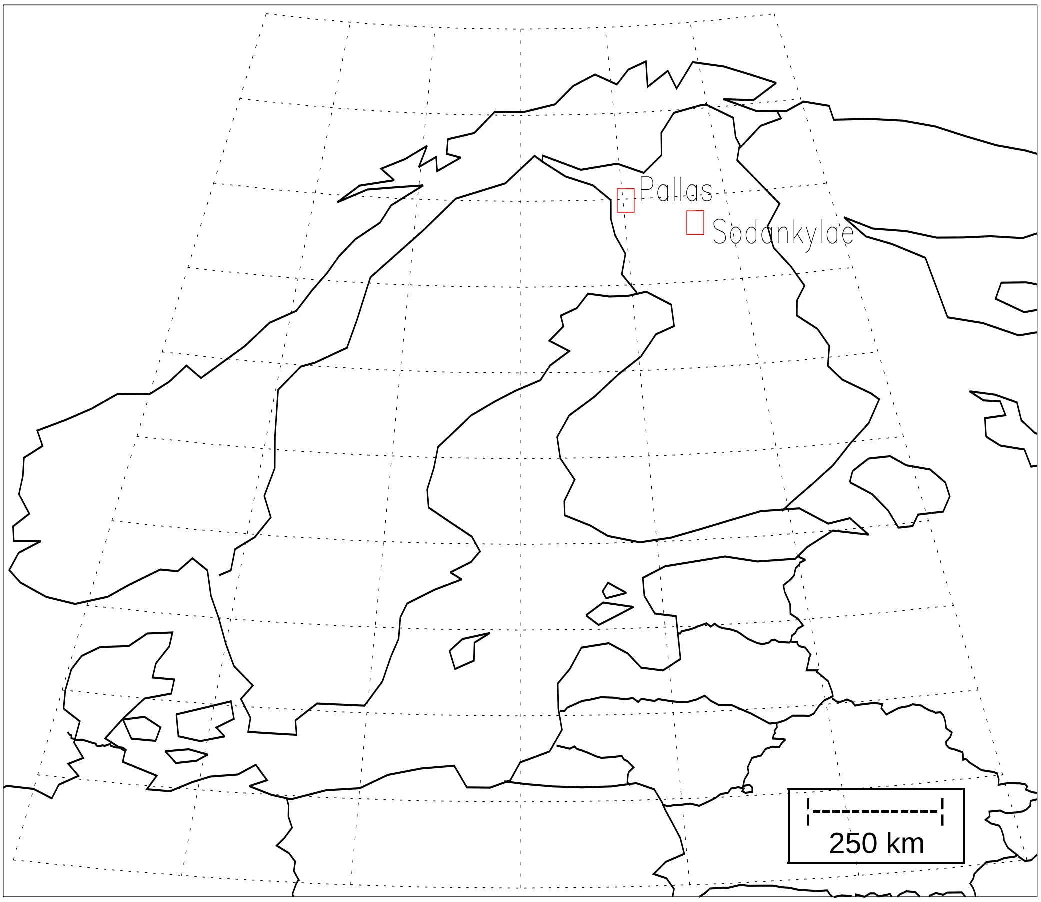
The Pallas station is located in the Finnish National Park Pallas-Ounastunturi, in the boreal zone (coordinates: 67°58' N, 24°07' E). The monitoring station is on top of the Sammaltunturi fell, at an altitude of 560 m. a. s. l., and over 300 m above the surrounding area. The local wind field at the site is dominated by south-westerly winds.

The National Park covers 50'000 hectares consisting of 22'000 hectares of timberline forests, 10'000 hectares of open wetlands, and 18'000 hectares of open fell tundra. The vegetation on the fell where the station is located is sparse.

About 2 km westerly of the station an unsealed road which is closed to public traffic branches off from the main road between Muonio and Rattama. It leads nearby the site from where after another 20 min hike the wooden constructed building is reached (figure 3). Because the road is closed to public traffic, only 2 cars a week (maintenance) pass the vicinity.

Figure 3: Picture of the station Pallas:

Figure 4: Map of the Scandinavian Countries:



3.2. Operators

The station at Pallas was established in September 1991, and in 1994, together with the Sodankylä Meteorological Observatory, Pallas was adopted as part of the GAW programme. It is operated by the Finnish Meteorological Institute and is maintained in co-operation with the Finnish Forest Research Institute (Metla), which is managing the maintenance of the Pallas-Ounastunturi National Park.

The group of Dr Y. Viisanen, research manager of the section Air Quality Research, is in charge of the operation of the GAW Station at Pallas. The structure of the station management at Pallas is shown in Table 1.

During the entire audit procedure Dr Viisanen, Mr Lättilä and Mr Hatakka of FMI were present.

Table 1: Operators

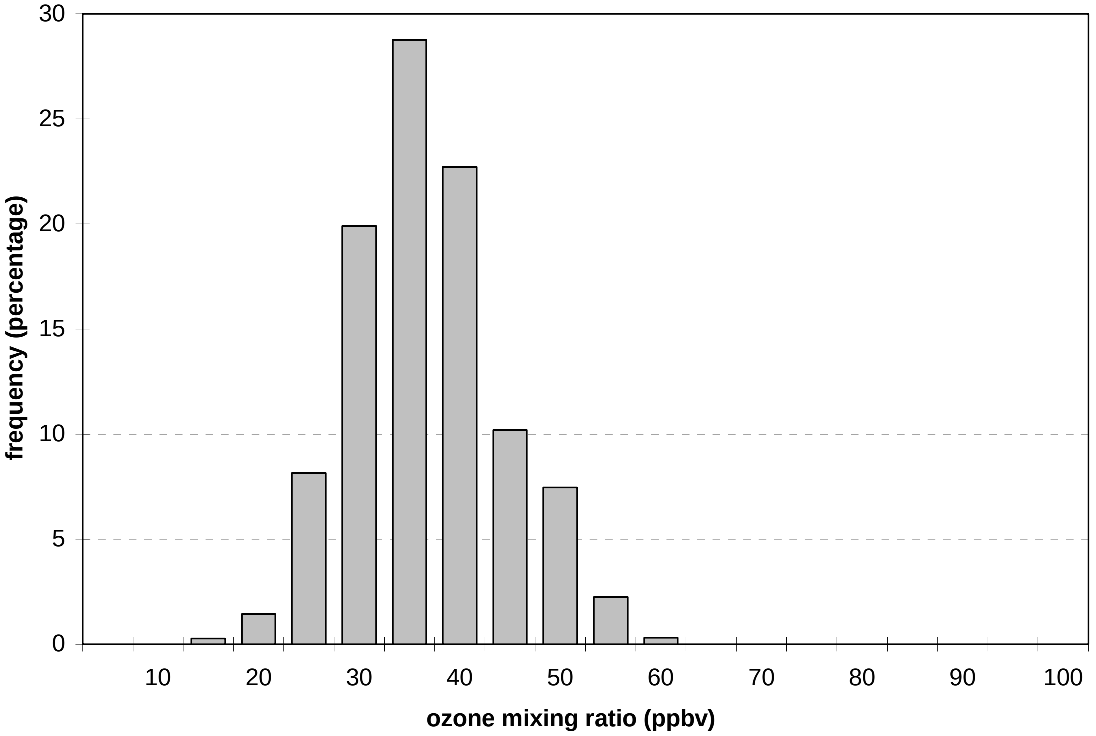
Dr Yrjö Viisanen, Co-ordinator (Physics PhD)
Operators Mr Heikki Lättilä, (Chemist graduate), surface ozone specialist, final data reviewer Mr Timo Anttila, (Technician), maintenance Mr Juha Hatakka, (Chemist graduate), aerosol and radioactivity measurements Ms Sisko Laurila, Data review Mr Timo Virtanen, (Engineer), data acquisition
Calibration laboratory at FMI Mr Jari Walden, (Physics graduate), Quality control for tropospheric ozone Mr Timo Koskinen, (Chemist graduate), Operating the standard for ozone Mr Tapio Poutianen, Data base management

3.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well defined by the frequency distribution. In figure 5 the frequency distribution of the hourly mean values from the year 1995 is shown. The relevant ozone concentrations were calculated, ranging between 22 and 50 ppb according the 5 and 95 percentile values.

Source of data: received from Dr Y. Viisanen, June 1997

Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Pallas of the year 1995. Data capture 98 per cent.


30
25
20
15
10
5
0
frequency (percentage)
10
20
30
40
50
60
70
80
90
100
ozone mixing ratio (ppbv)

4. Measurement Technique

4.1. Air Inlet System

The air inlet system for the ozone measurements is mounted at the side of the measuring station. The inlet part of the system is 1 m above the roof and about 5 m above the ground and consists of a 300 x 200 mm H-shaped tubing construction (56 mm i.d.), stacked on the stainless steel inlet line, shielding the system from rain and snow. It is warmed-up to between 30 and 40 °C using a special heating tape wrapped around the inlet part. The sampling line is a 11 m long, 56 mm i.d. stainless steel tube leading directly through a hole in the side-wall into the measuring cabin. It is continuously flushed at 150 m^3 per hour with ambient air and the part that is inside the station is insulated with insulation material to avoid condensation. The high flow in the line causes a low pressure of about 20 mbar. For the ozone measurements, PFA teflon tubes (4 mm i.d., 1.5 m long) branch off from the stainless steel manifold leading to the ozone analysers. An external vacuum pump is being used to draw ambient air (2 l / min) through these teflon tubes according to the instrument's specified internal flows. The vent of the sampling manifold is lead through a tunnel about 50 m away from the station in NE direction (usually lee side).The analysers are 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 instruments, lies around 2 seconds.

Comment

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

4.2. Instrumentation

The instruments are installed on a bench in a temperature controlled room where the daily variations are rather small with 2-3 °C and seasonal variations with maximum low of 15 °C in winter up to 25 °C in summer. It is planned to improve the temperature control this winter.

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

The ozone analyser Dasibi 1008AH is the basic instrument since October 1995 and is supported by the present backup instrument since November 1996. However, as already suspected by the operators according the results of the last calibration, it was confirmed that the backup analyser, although only recently purchased, has an instrument failure.

Table 2: Field instruments

type	Dasibi 1008AH #5454	Dasibi 1008PC #6605
method	UV absorption	UV absorption
usage	basic instrument	backup instrument
at Pallas range	since October 1995 0-1000 ppb	since November 1996 0-1000 ppb
analog output	0-1 V	0-1 V
electronic offset	4 (units)	4 (units)
electronic coeff.	302 (absorption coeff.)	305 (absorption coeff.)
last calibration by FMI	5. June '97	5. June '97
instruments specials		internal ozone generator

A zero air unit was not available on site since no daily (or regular) zero checks are performed. For the quarterly calibrations at the station a zero air unit is carried with consisting of a charcoal cartridge and a particulate filter.

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 and is particularly important for this site since no daily zero checks are performed. As agreed with the operators the backup instrument needs to be replaced due to instrument failure.

4.3. Data Handling

An FMI constructed data acquisition facility is installed at the site next to the ozone analysers. It consists of an ADC circuit board and a PC to store the one-minute actual point concentration from where this data is automatically daily transferred via a modem connection to the FMI. Data processing is prepared at FMI and consists of a daily or alternate day visual inspection of graph plots of the raw data. The invalid values, i.e. data from manual calibration, are manually flagged as invalid data but are not removed from the database. Further, concentration values lower 0 and higher 200 ppb are automatically flagged as invalid. Based on the results of the quarterly calibrations a global recalculation of the acquired data is made. Deviations up to 5 percent are accepted and are not considered for recalculating the dataset. While deviations higher 5 percent need to be verified by the next calibration three month later to cause recalculation of the data.
The checked data are from time to time reviewed by a second person. In addition to the final one-minute dataset an hourly mean value dataset is created.

The raw data in ppb units is automatically converted on site in μg/m³ unit by applying the factor x 1.995 (corresponding to 1013 mbar and 20 °C). Only the converted values are stored in μg/m³ on the computer.

Comment

The procedure of data treatment is organised and clearly arranged. The reviewing of the data is done on a regular, mostly daily, interval so that irregularities can be detected early. Review of the final data set by two persons is welcome, since this increases the reliability of the data.

4.4. Operation and Maintenance

Considering the remote location of Pallas and the distance to the FMI in Helsinki an extensive instrument maintenance which requires experienced staff can only carried out four times a year. During such a station visit the operators are following a quarterly or annually schedule of preventive maintenance works. It incorporates multipoint calibration, exchange of the inlet filter and checking of the pressure transducer every three month, cleaning of the instruments glass cells and testing the scrubber performance once a year. The UV-lamp or the scrubber are replaced if necessary.

The Pallas station is maintained in co-operation with the Finnish Forest Research Institute (Metla) that is a few kilometres away the station. Twice a week a person of Metla does some primary maintenance, i.e looking after the building, getting an overview if anything is working well or filling in basic information in the monitor's logbook.

The precision of the instruments can be controlled by the long-term parallel measurement of ambient air although no daily (or regular) zero or span checks are performed. Quarterly multipoint calibrations of the analysers are carried out using a transfer standard. The applied ozone levels are 0 / 45 / 80 / 120 / 160 / 200 ppb. The transfer standard used for this multipoint calibrations, Dasibi 1008PC #5455, is annually calibrated with the NIST Standard Reference Photometer #11 of the Stockholm University. In the week after the audit it was supplementary intercompared with the EMPA transfer standard TEI 49C-PS #54509-300.
In addition, there is a calibration laboratory at FMI operating a similar standard as the one used as transfer standard in the network. Regular intercomparisons are planned.

The backup instrument at Pallas contains an ozone generator which would make it suitable to produce ozone. However, this facility is not in use and is also not planned to.

Comment

The appearance of the station is clean and functional.

A continuing good co-operation with the Finnish Forest Research Institute, Metla, is seen as essential for succesfully maintaining this remote station of Pallas.

The schedule of preventive maintenance including quarterly multipoint calibrations is well established in order to improve the operation of the ozone analysers. However, it is recommended that the ozone levels applied during a calibration are shifted towards the relevant ozone concentration range of the site.

Although the station was only established in 1991, the sense of quality assurance is very well developed and implemented, i.e. by intercomparing the internal standard to an independent primary standard. This is certainly due to the experience at FMI of operating the national monitoring network for many years.

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. The station logbook contained the necessary information about maintenance, changes, events and special investigations listed chronologically in a bound book. During the biweekly maintenance by the Metla staff a questionnaire-like single sheet is filled in containing analyser specific data. These sheets are stored in the monitor's maintenance logbook file and a copy is sent to FMI.

Comment

Because the station logbook contains information about all measurements it might be very time consuming to trace back specific events. It is therefore recommended to upgrade the necessary documentation in the FMI's interests and to note information and remarks more detailed.

Plans to digitise the logbooks in the way that the operators would fill in the information directly into a file on the PC and transfer it to FMI ultimately, were discussed and are seconded.

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 night in deviation to the GAW report No. 97 which recommends only one hour of warm-up time. In the morning, before the intercomparison runs were started the transfer standard, the PFA tubing connections to the instruments and the instruments itself were conditioned with about 200 ppb ozone for 20 to 30 min. On 24 June, the comparison runs between the field instruments and the EMPA transfer standard were performed. In the meantime and on the following days the inlet system, the station's documentation and the data reprocessing were inspected and discussed. Table 3 shows the experimental details and figure 6 the experimental set up of the audit. In general, no modifications of the ozone analysers which could influence the measurements were made for the intercomparisons.

The EMPA acquisition system, which was used for the audit, 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 by both data acquisition systems (EMPA and FMI). In advance, the readings of two acquisition systems were compared at zero (ozone) and at 200 ppb ozone and, accordingly to equalise them, a very slight adjustment (offset of 0.2 and 0.4 ppb) of the EMPA system to the one at the station was made. 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.

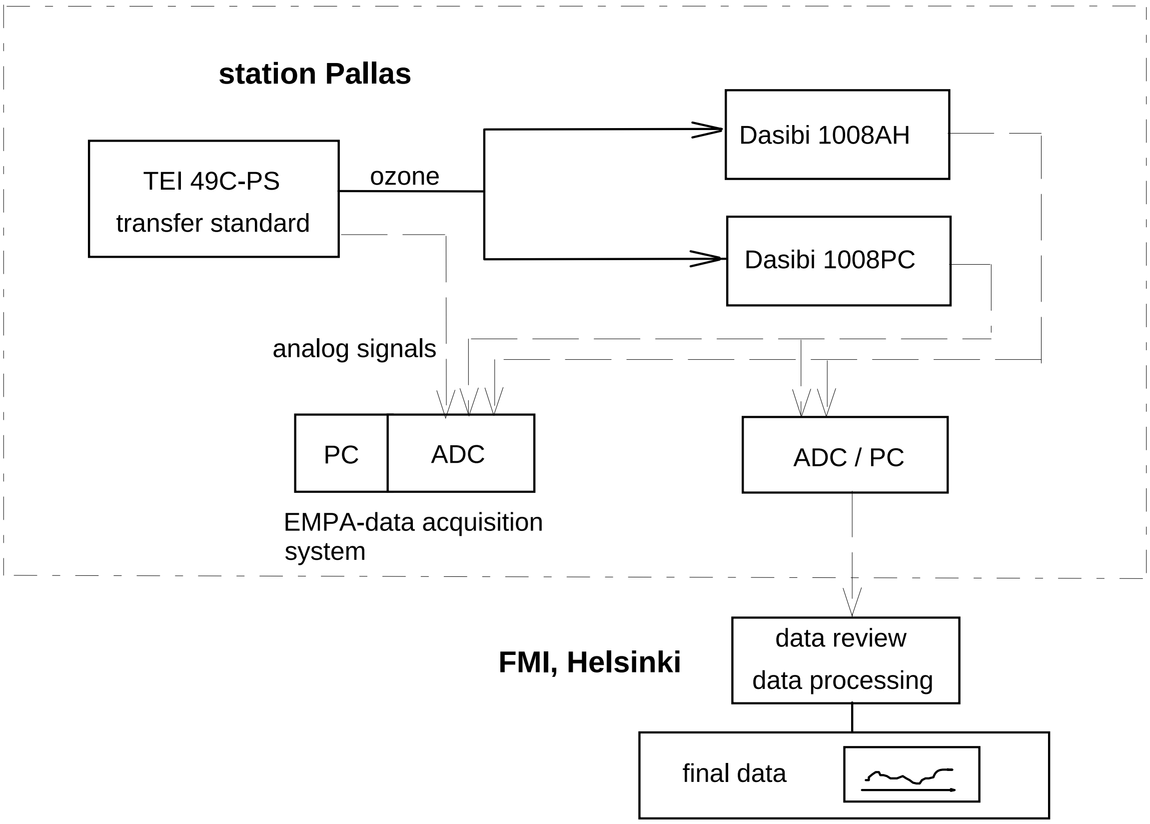
Table 3: Experimental details

audit-team, EMPA	B. Schwarzenbach, A. Herzog
reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	Dasibi 1008AH #5454 Dasibi 1008PC #6605
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
pressure transducers reading:	reference: 933 hPa TEI 49C-PS: 932 hPa Dasibi 1008AH: 899 hPa, Dasibi 1008PC: 929 hPa
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end

approx. concentration levels:	15 / 30 / 45 / 60 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x June 24, 1997
connection between instruments:	about 1 meter of 1/4" PFA tubing

* pressure transducer reference: station pressure manometer

Figure 6: Experimental set up



5.2. Results

The results comprise three runs of the intercomparisons between the two field instruments Dasibi 1008AH and Dasibi 1008PC and the transfer standard TEI 49C-PS, carried out on June 24, 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 three runs are then summarised to the mean regression equation and presented with the assessment criteria for GAW field instruments (Figure 11, 12).

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 1008AH no factor applied
- Dasibi 1008PC no factor applied

In table 4 to 6 the recalculated data are listed.

Table 4: 1. Intercomparison, Dasibi field instruments

No.	**transfer standard**		**Dasibi 1008AH**				**Dasibi 1008PC**			
	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	0.1	0.12	0.0	0.24	0.0		2.3	0.64	2.2	
2	30.1	0.11	31.3	0.03	1.2	4.0%	32.9	1.07	2.8	9.3%
3	90.1	0.16	93.3	0.44	3.1	3.5%	96.3	1.05	6.2	6.8%
4	45.2	0.14	46.9	0.22	1.7	3.8%	49.3	0.86	4.1	9.1%
5	60.2	0.20	62.4	0.18	2.3	3.8%	64.5	1.11	4.3	7.2%
6	15.3	0.11	15.6	0.20	0.4	2.4%	19.1	0.73	3.8	24.9%
7	0.1	0.11	-0.1	0.30	-0.2		3.7	0.86	3.6	

Table 5: 2. Intercomparison, Dasibi field instruments

No.	**transfer standard**		**Dasibi 1008AH**				**Dasibi 1008PC**			
	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	0.0	0.16	-0.1	0.24	-0.2		2.6	0.89	2.5	
2	60.1	0.14	62.1	0.41	2.0	3.3%	64.2	0.45	4.1	6.8%
3	30.1	0.17	31.1	0.23	1.1	3.6%	33.4	0.69	3.4	11.2%
4	15.2	0.17	15.5	0.07	0.3	1.8%	17.7	0.66	2.5	16.7%
5	90.1	0.13	92.9	0.28	2.8	3.1%	94.8	0.56	4.6	5.1%
6	45.2	0.18	46.8	0.29	1.5	3.4%	48.6	0.50	3.4	7.5%
7	0.1	0.09	-0.3	0.14	-0.4		2.8	0.47	2.7	

Table 6: 3. Intercomparison, Dasibi field instruments

No.	**transfer standard**		**Dasibi 1008AH**				**Dasibi 1008PC**			
	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	0.1	0.14	-0.1	0.33	-0.2		3.5	0.75	3.5	
2	15.2	0.15	15.4	0.05	0.3	1.9%	19.0	0.79	3.9	25.5%
3	60.1	0.13	61.9	0.42	1.7	2.9%	64.7	0.85	4.6	7.6%
4	45.1	0.18	46.5	0.40	1.4	3.2%	49.4	0.79	4.3	9.6%
5	90.1	0.15	93.0	0.41	3.0	3.3%	95.8	0.98	5.7	6.3%
6	30.2	0.18	31.3	0.21	1.1	3.8%	34.0	0.54	3.8	12.7%

7	0.1	0.14	-0.3	0.17	-0.4		2.2	0.60	2.2	

Figure 7: Individual linear regressions of intercomparisons 1 to 3, Dasibi 1008AH

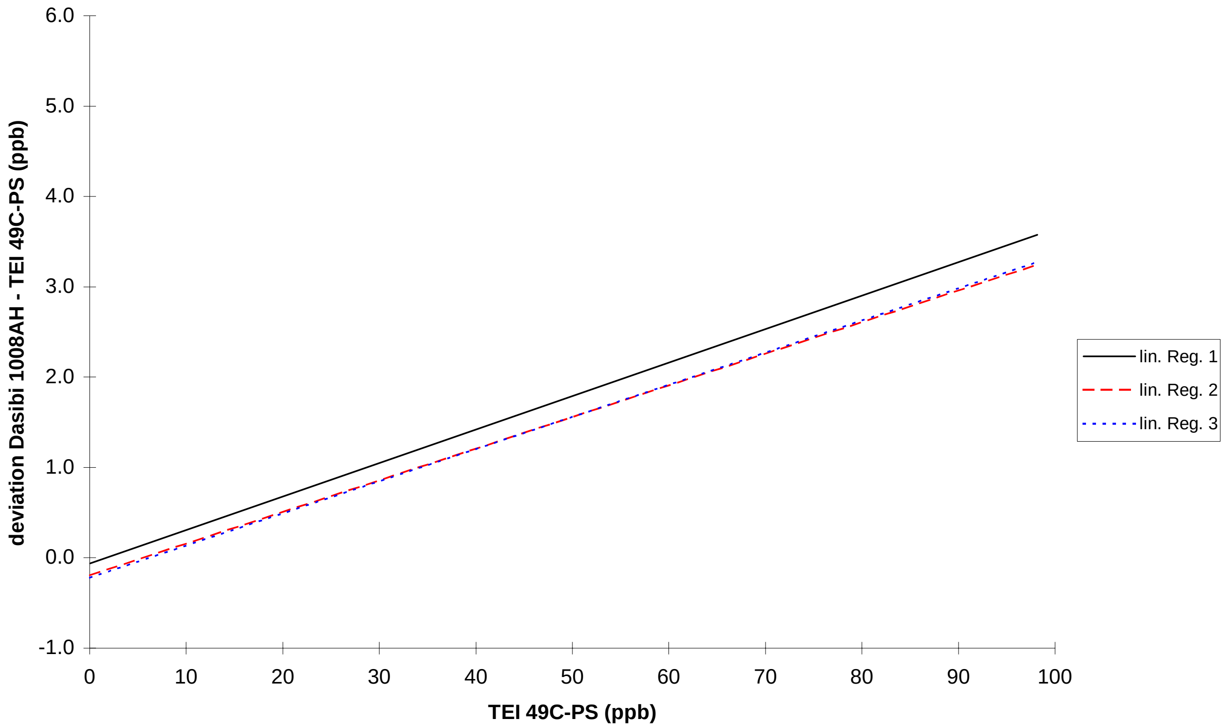


Figure 8: Mean linear regression of intercomparisons 1 to 3, Dasibi 1008AH

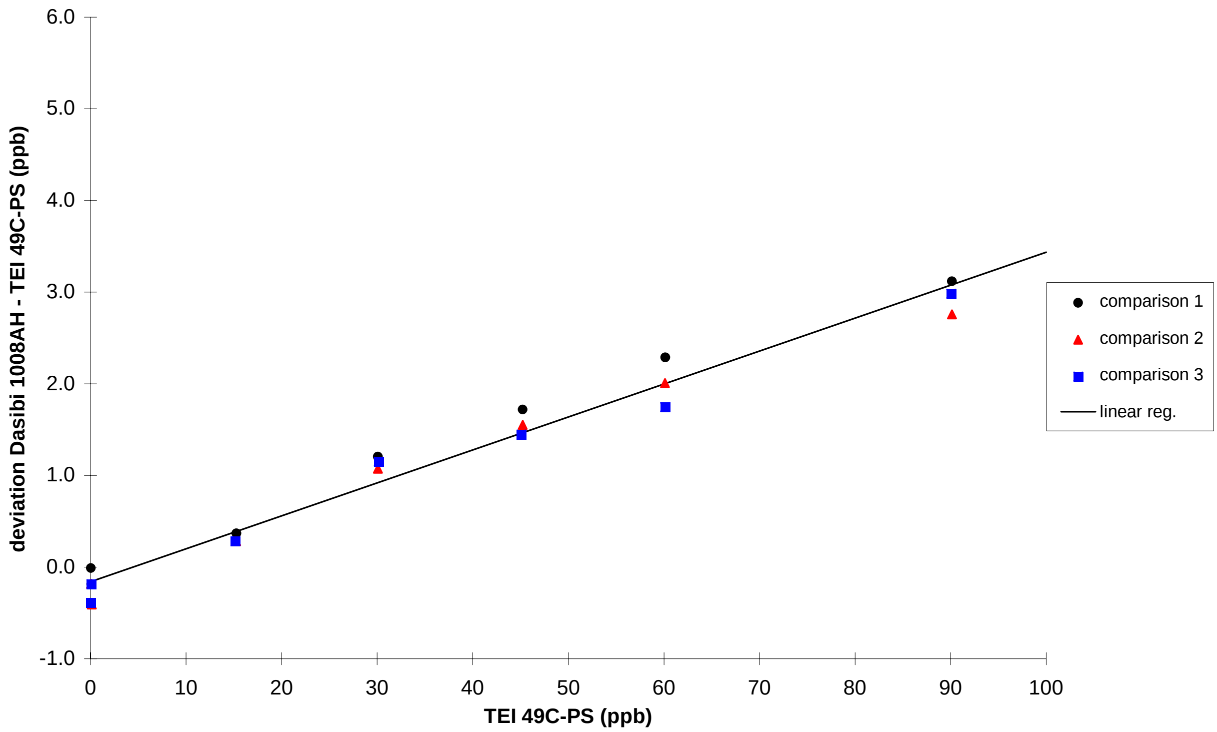


Figure 9: Individual linear regressions of intercomparisons 1 to 3, Dasibi 1008PC

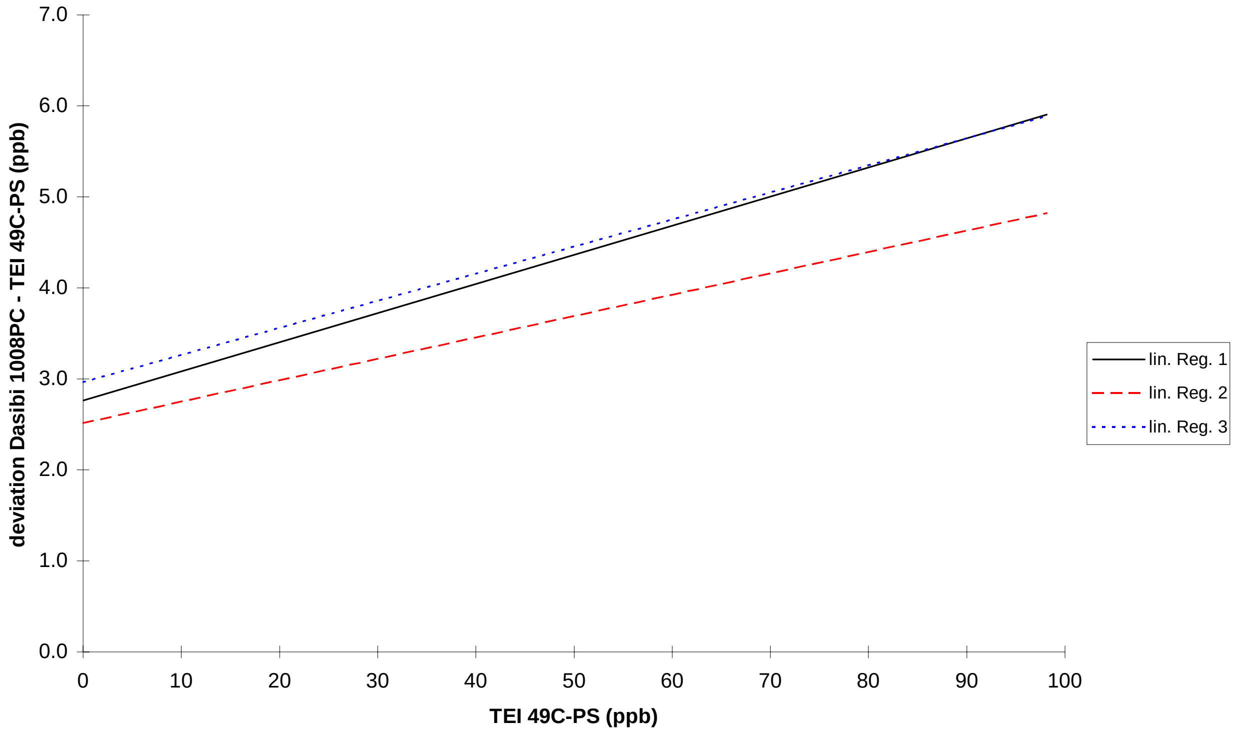
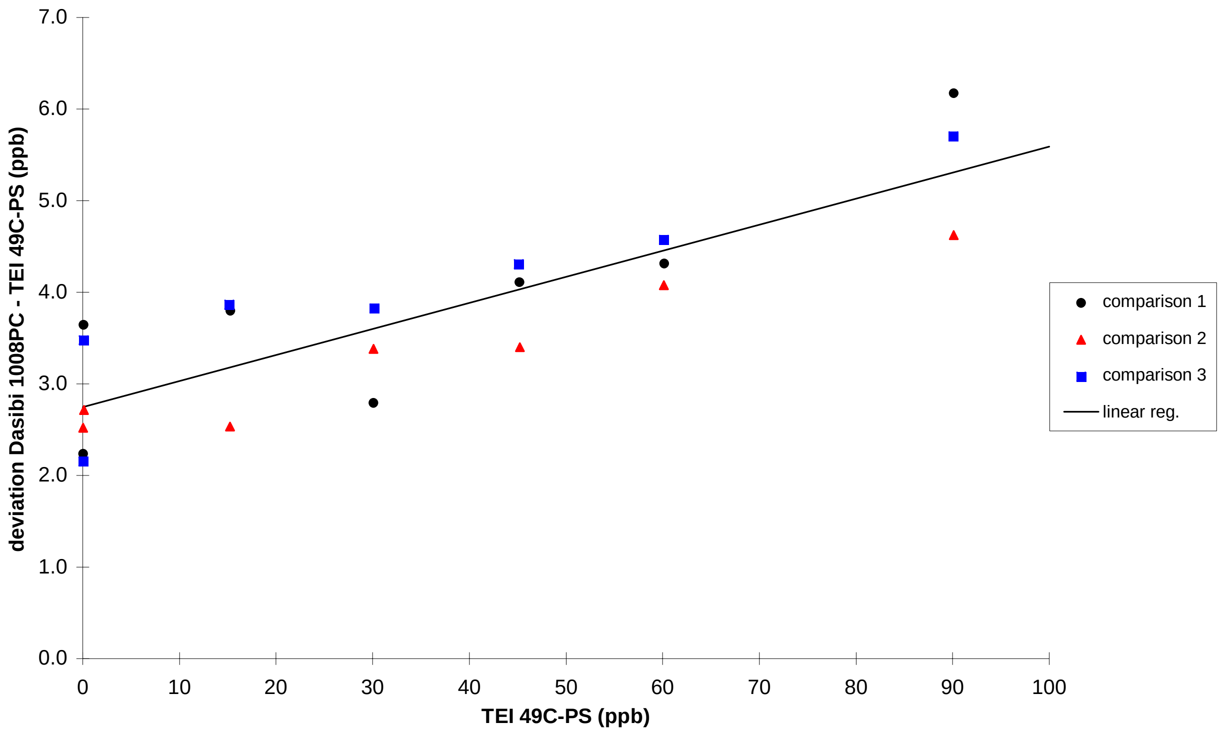


Figure 10: Mean linear regression of intercomparisons 1 to 3, Dasibi 1008PC



From the intercomparisons of the Dasibi 1008AH #5454 the Dasibi 1008PC #6605 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 1008AH:

Dasibi 1008AH = 1.036 x TEI 49C-PS - 0.16 ppb

Dasibi 1008AH = O_3 mixing ratio in ppb, determined for Dasibi 1008AH #5454

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

Standard deviation of:	- slope s_m	0.0013	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.06	(f = 3)
	- residuals in ppb	0.14	(f = 19)

-Dasibi 1008PC:

Dasibi 1008PC = 1.028 x TEI 49C-PS + 2.75 ppb

Dasibi 1008PC = O_3 mixing ratio in ppb, determined for Dasibi 1008PC #6605

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

Standard deviation of:	- slope s_m	0.0040	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.18	(f = 3)
	- residuals in ppb	0.27	(f = 19)

Figure 11: Intercomparison of instrument Dasibi 1008AH

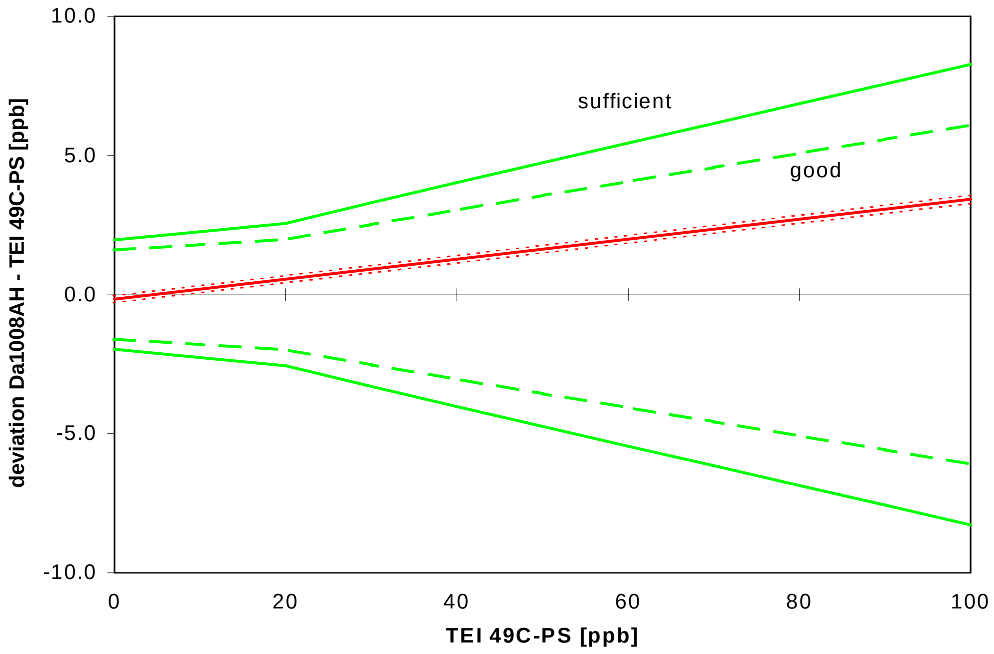
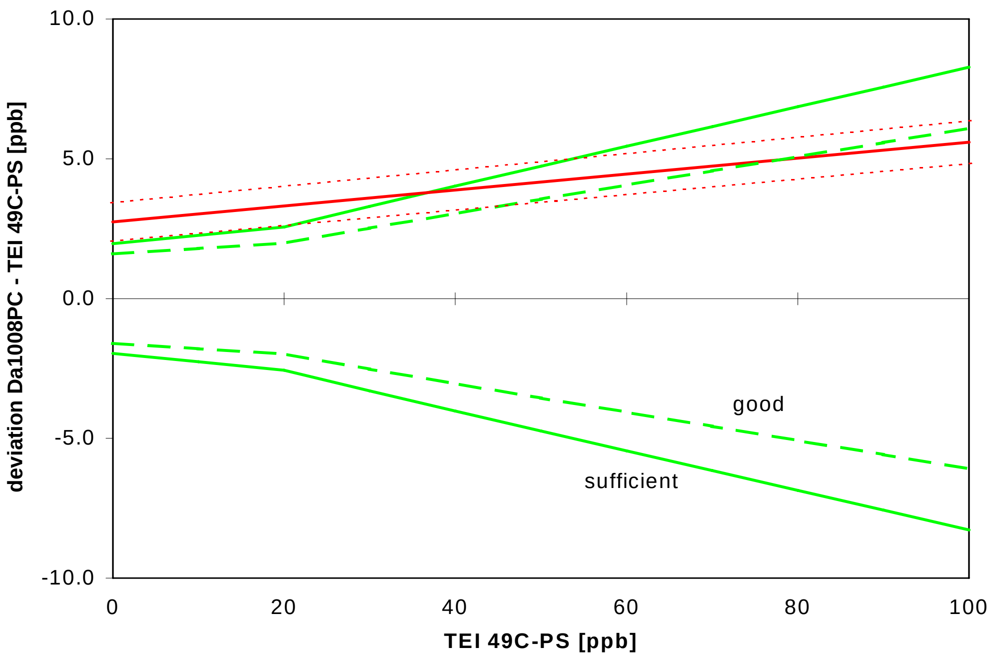


Figure 12: Intercomparison of instrument Dasibi 1008PC



Comment

In figures 7, 9 of the linear regressions no clear trend could be observed during the day when the intercomparisons took place. Such a drift could indicate insufficient warm up time (stability) or pollution in the measurement cell of the instrument.

The ozone concentrations observed at Pallas (1995) usually ranged between 22 and 50 ppb (5- and 95-percentile of hourly mean values).

The basic instrument clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 1). Small deviation among the three intercomparisons is the reason for a very narrow prediction interval for the analyser. The instrument is in good condition to be used as basic instrument.

For the backup analyser a circuit break on an electronic board was located which causes unstable signals and problems with a shifting offset so it needs to be replaced. Considering the range relevant of the site, the Dashibi 1008PC instrument does not fulfil the assessment criteria but this is, because of the mentioned instrument problems, of subordinate relevance (figure 2).

Appendix

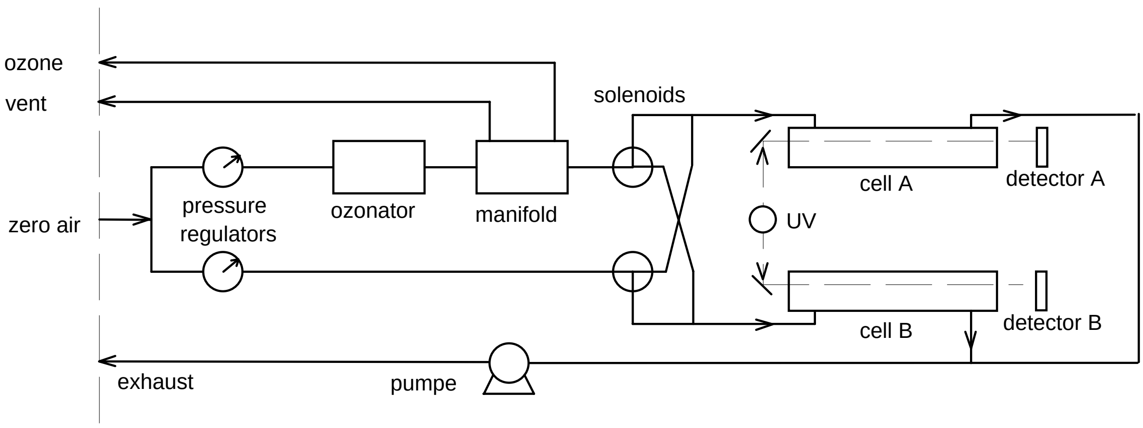
I EMPA Transfer Standard TEI 49C-PS

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 13. 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 13: Flow schematic of TEI 49C-PS



II Stability of the Transfer Standard TEI 49C-PS

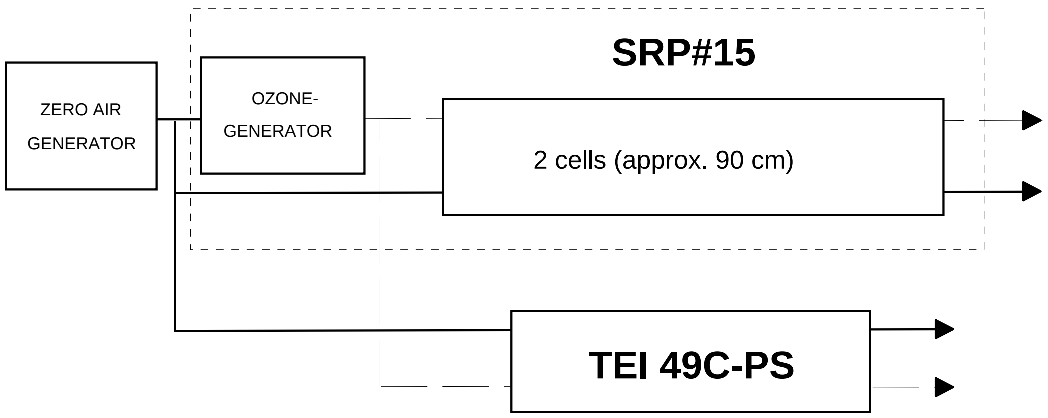
To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 7 and Figure 14.

Table 7: 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 / 185 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 4 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 14: 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 15 and 16 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 15: Transfer standard before audit

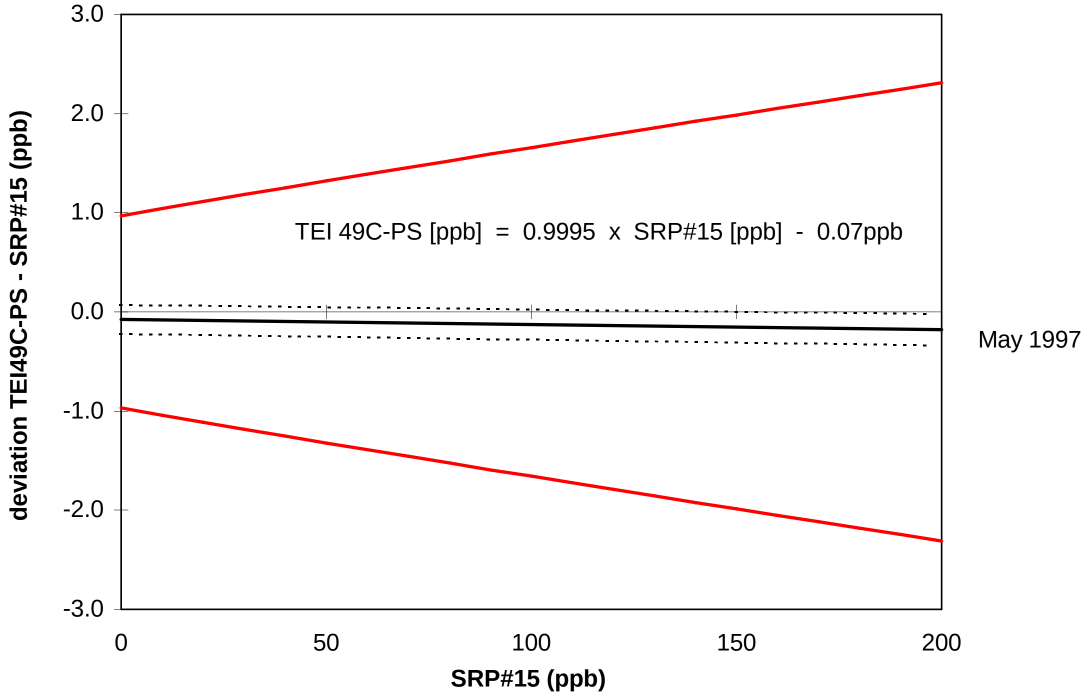


Figure 16: Transfer standard after audit